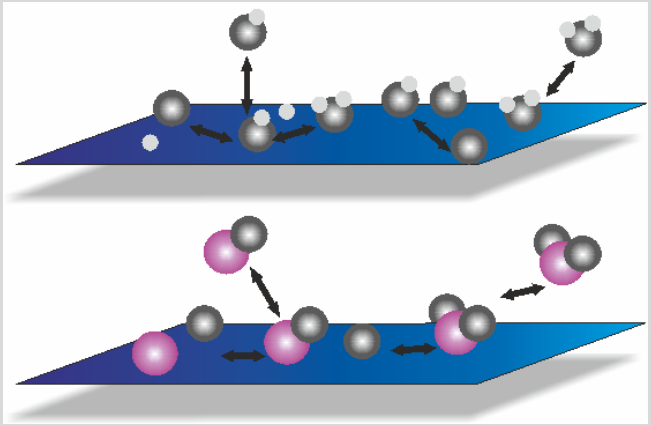
Microkinetic models for exhaust-gas after-treatment

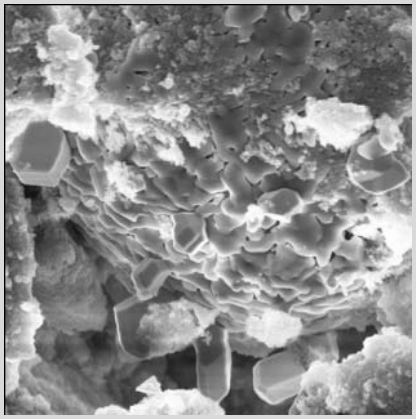
Olaf Deutschmann, Karlsruhe Institute of Technology (KIT)

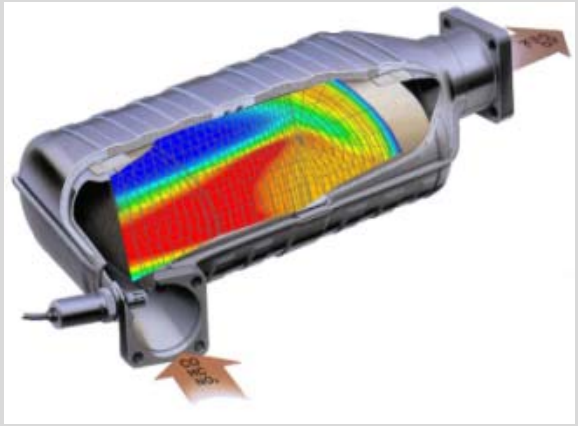
CLEERS 2015

Institute for Chemical Technology and Polymer Chemistry (ITCP)

Institute for Catalysis Research and Technology (IKFT)







THE CHALLENGE

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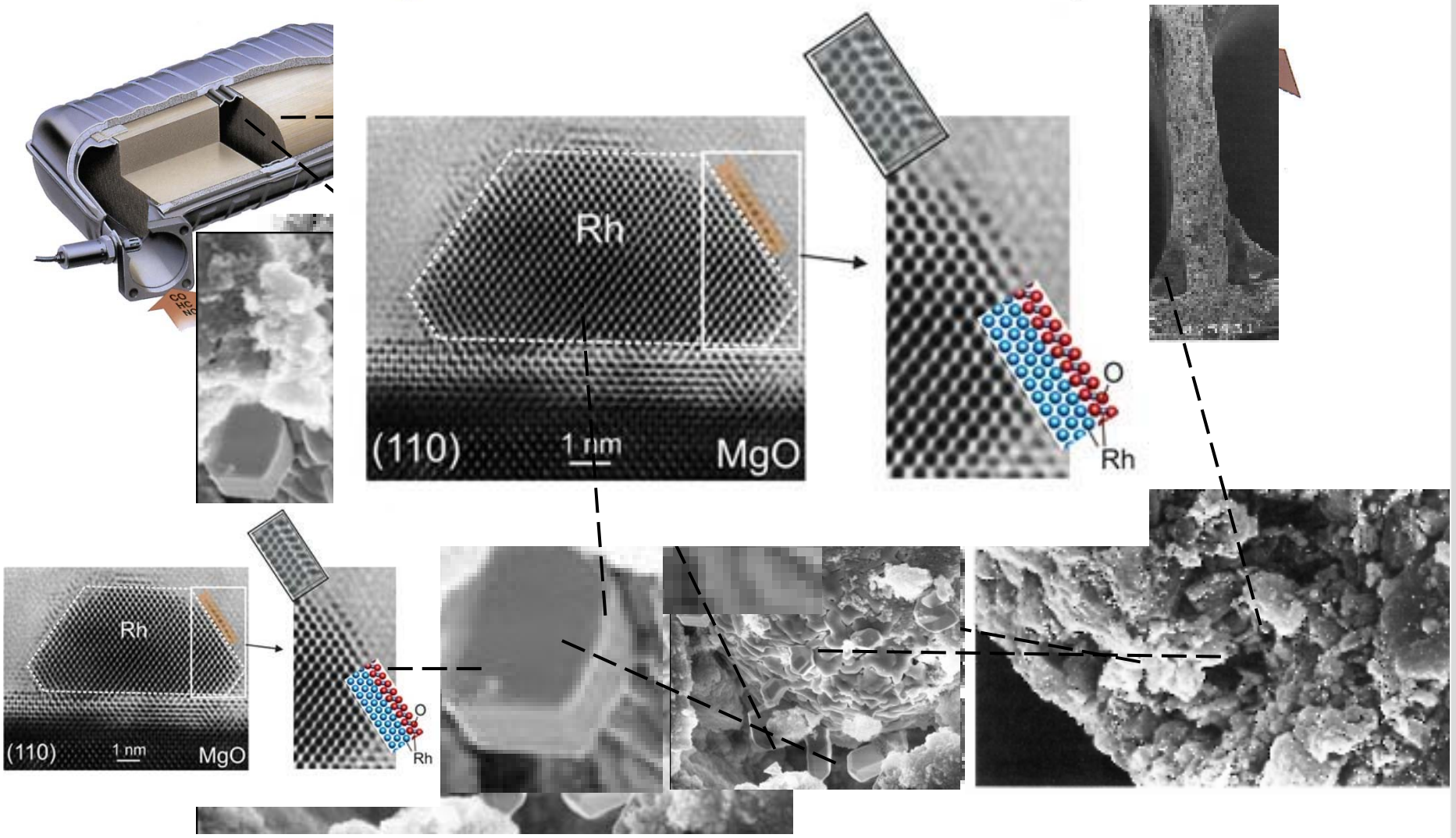
Catalytic converter:
Physics and chemistry on many scales



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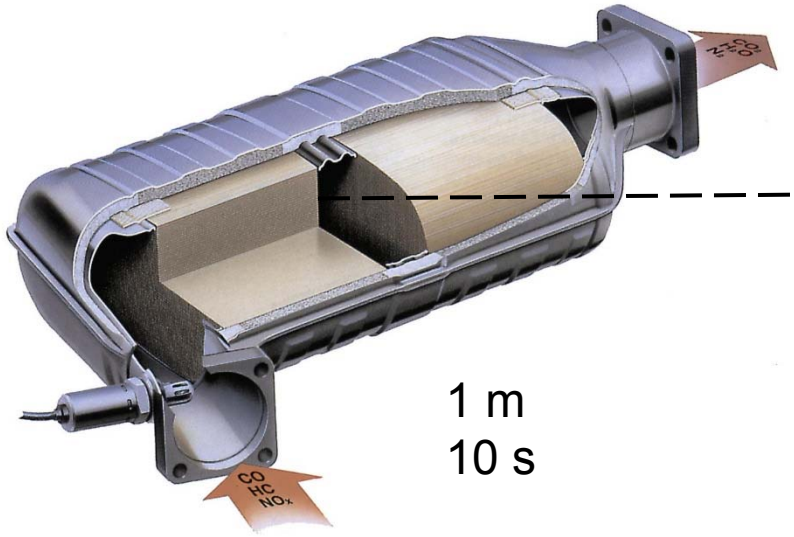
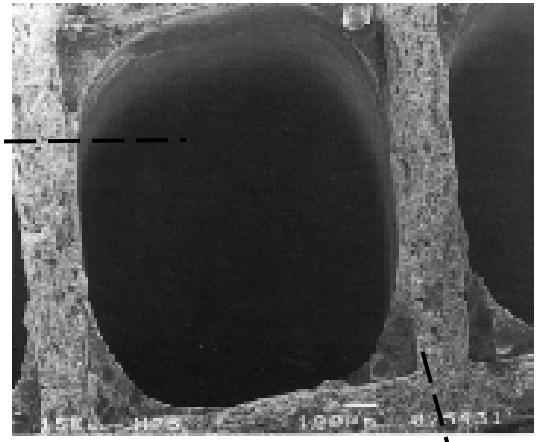
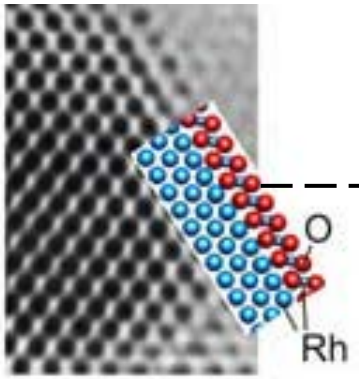
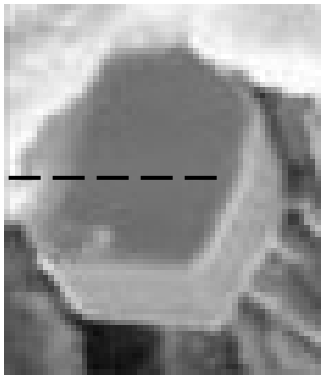
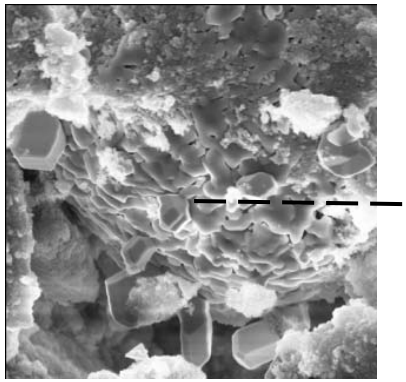
Catalytic converter: Physics and chemistry on many scales

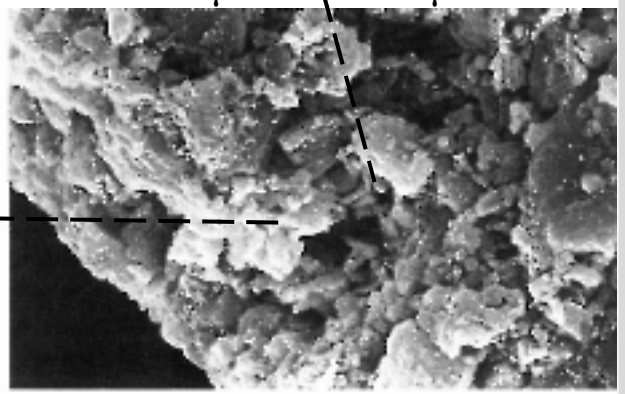












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THE DREAM

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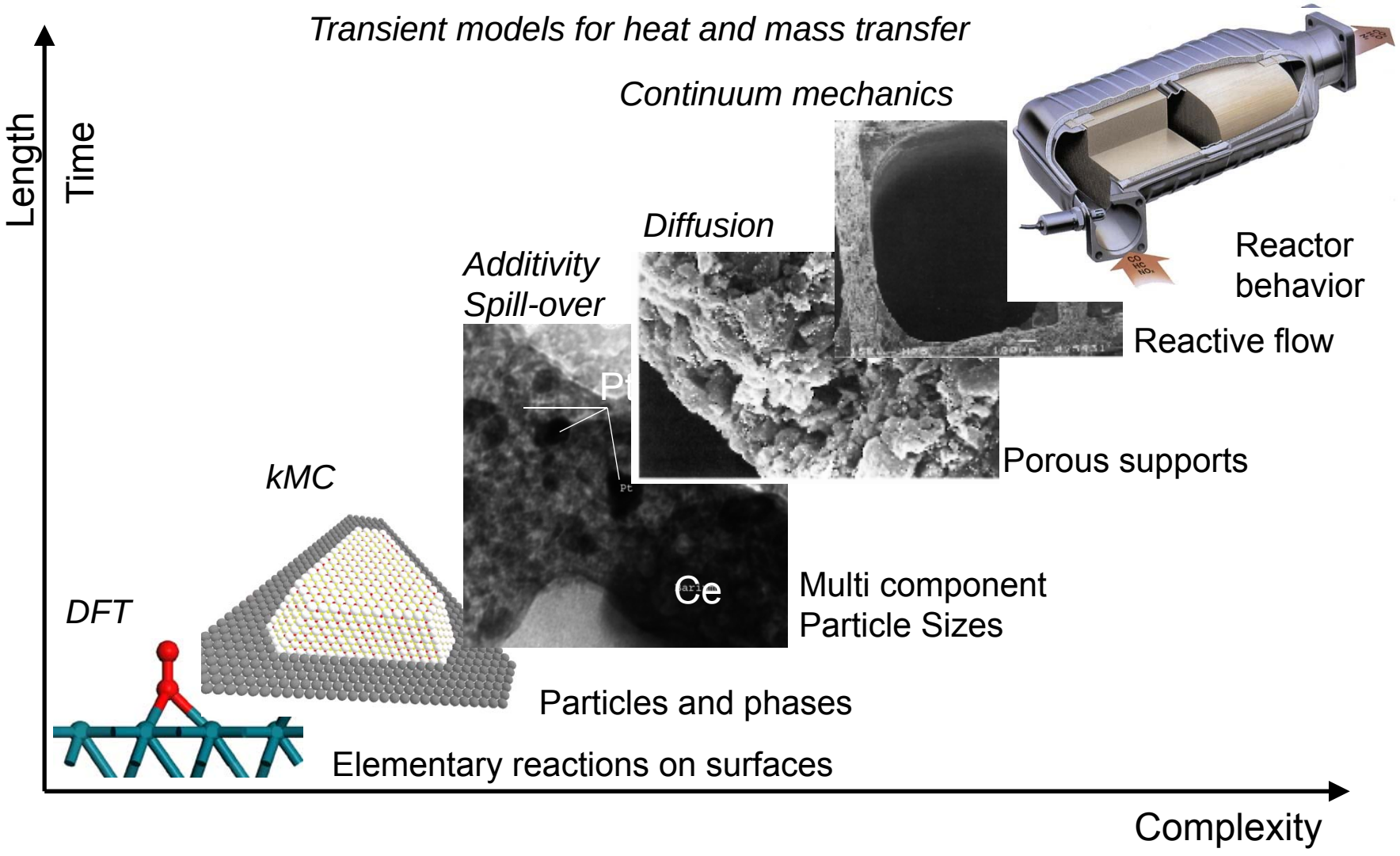
Simulation of catalytic reactors by multi-scale modeling: Information flux over the time and length scales



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THE REALITY

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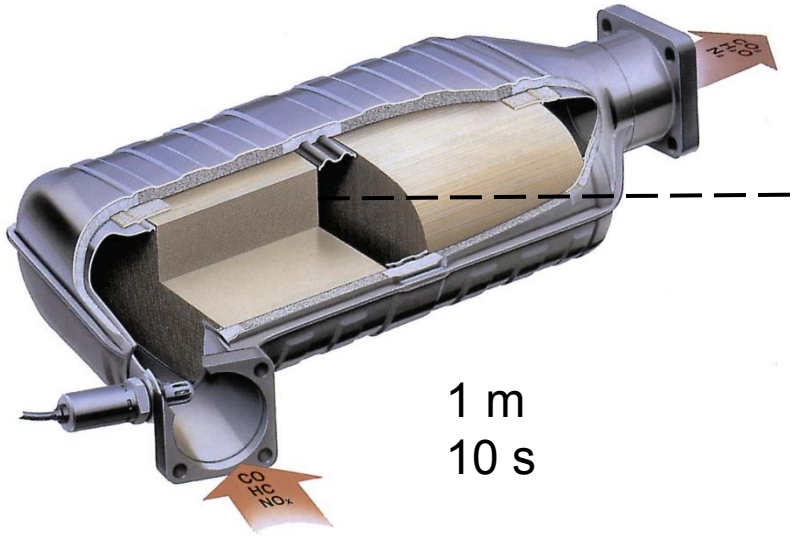
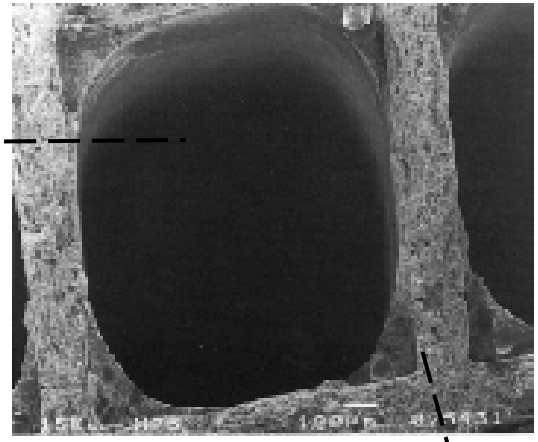
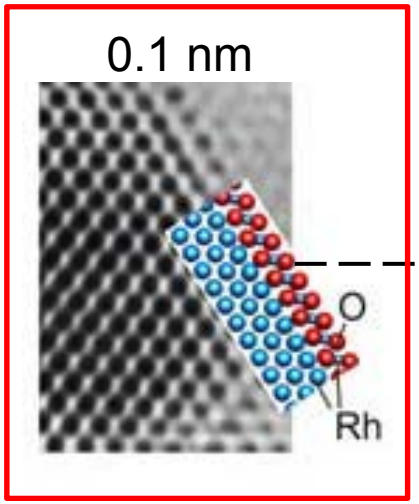
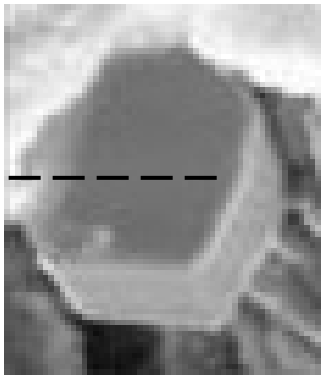
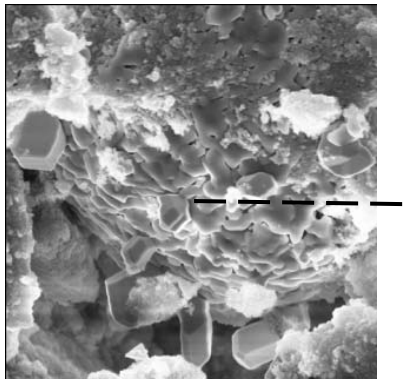
Catalytic converter: Physics and chemistry on many scales

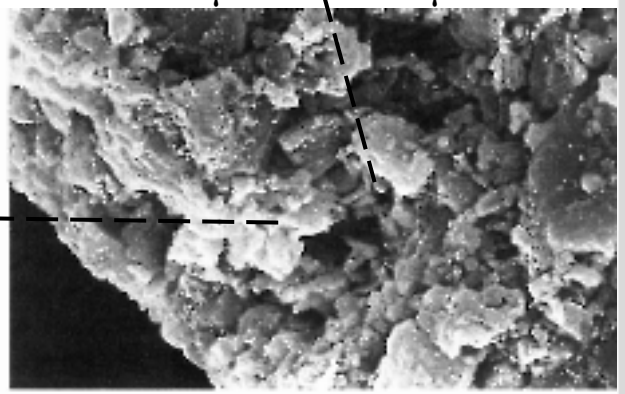












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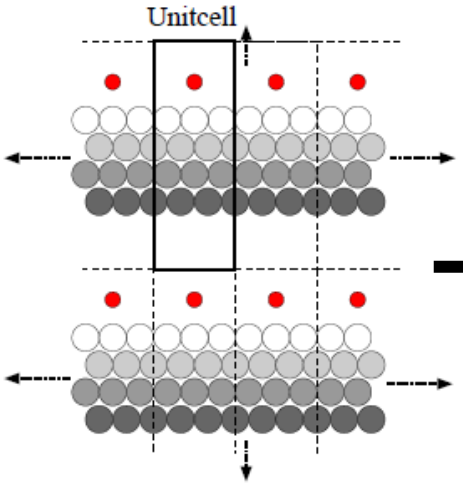
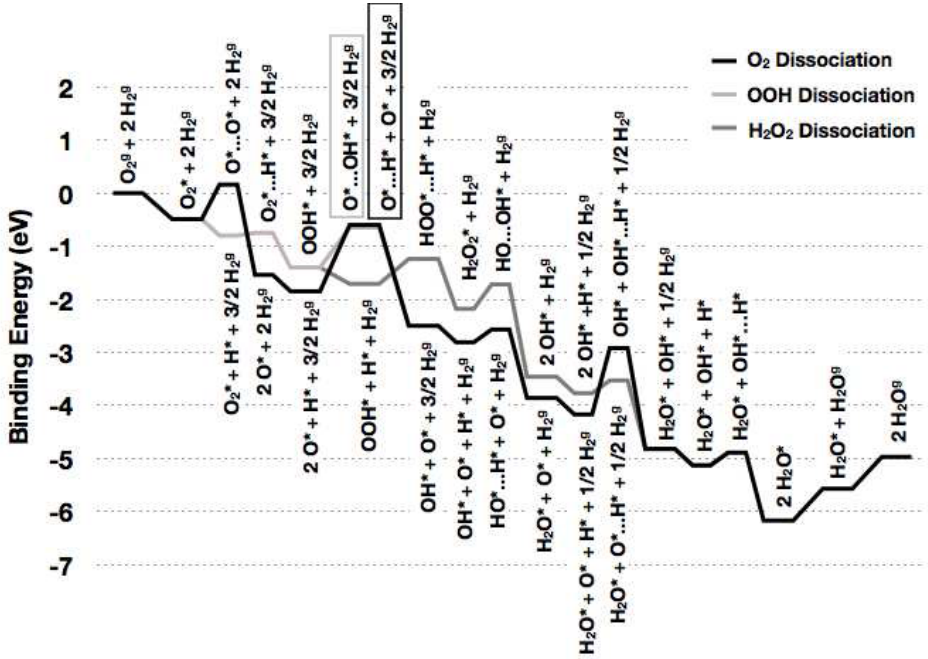
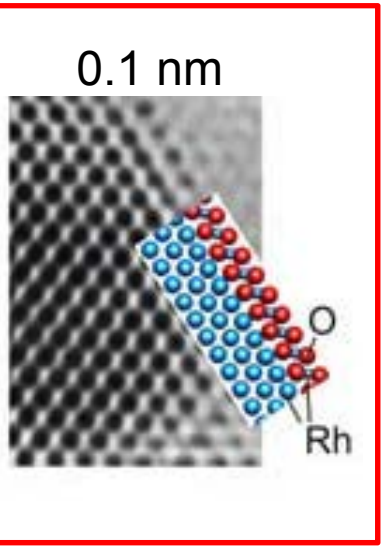
Density Functional Theory (DFT):
Understanding catalysis on a molecular level





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



- **Energy barriers**
- **Understanding reaction paths**
- **Pre-screening of catalysts**

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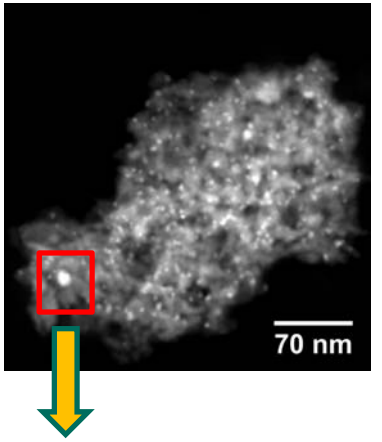
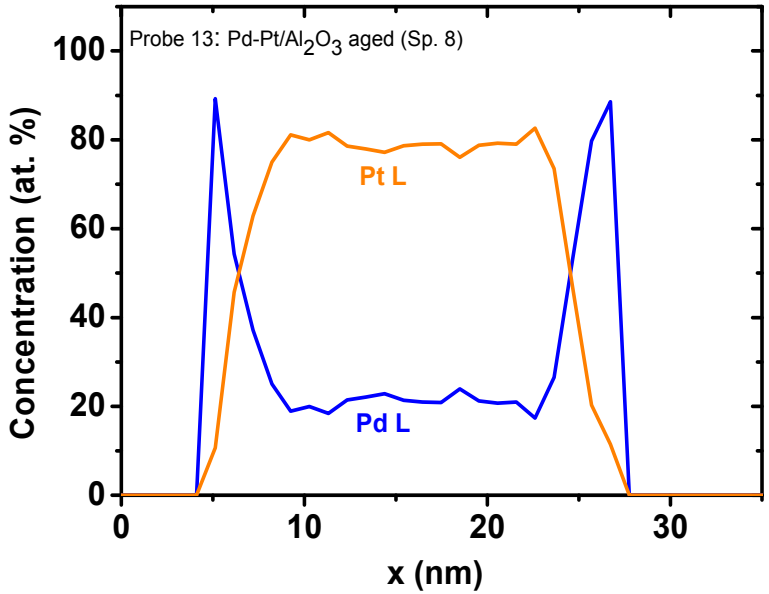
Institute for Chemical Technology and Polymer Chemistry

Aging of Pd/Pt catalyst for CH_4 total oxidation: Characterization by TEM and EDX

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

- **Total Pd/Pt loading 5:1**
- **Most particles d < 5 nm**
  - Homogenous alloy ($Pd_{100}Pt_0$ - $Pd_{89\pm5}Pt_{11\pm2}$)
- **Some particles d ≅ 10 nm**
  - Homogenous Alloy, higher Pt-content
- **Few large particles d > 30 nm**
  - Homogenous alloy
  - High Pt content
  - Formation of core-shell structure after 100 h, 1000 ppm CH_4, 10% O_2





A. T. Gremminger, H. W. Pereira de Carvalho, R. Popescu, J.-D. Grunwaldt, O. Deutschmann. Catalysis Today (2015) DOI 10.1016/j.cattod.2015.01.034

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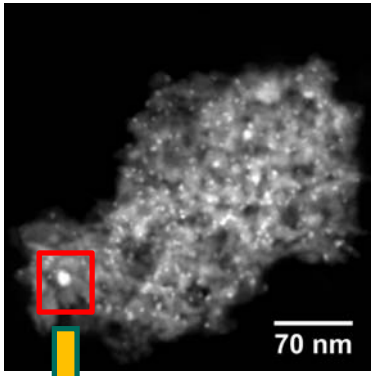
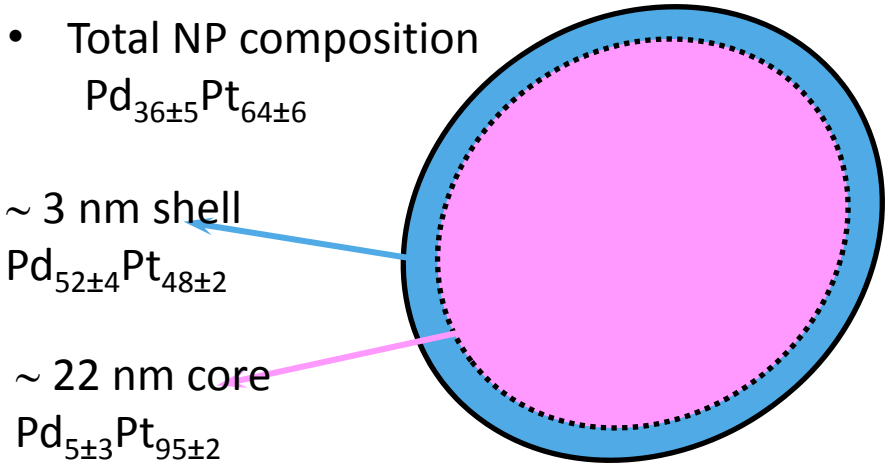


- Total NP composition $Pd_{36\pm5}Pt_{64\pm6}$



A. T. Gremminger, H. W. Pereira de Carvalho, R. Popescu, J.-D. Grunwaldt, O. Deutschmann. Catalysis Today (2015) DOI 10.1016/j.cattod.2015.01.034

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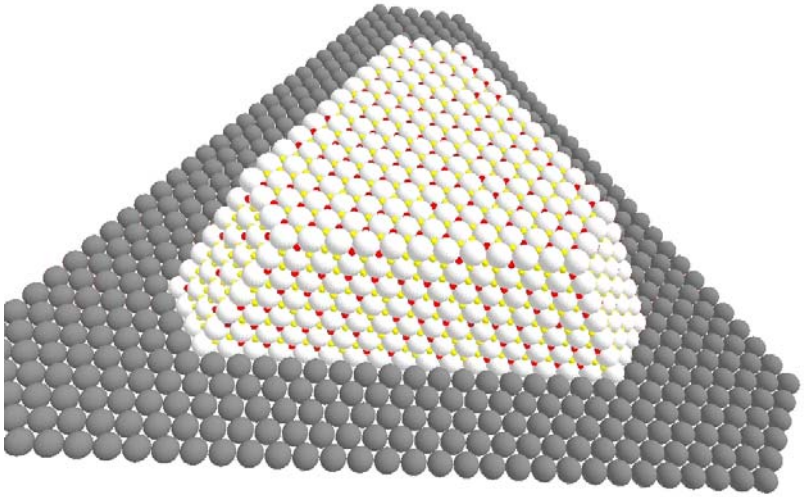
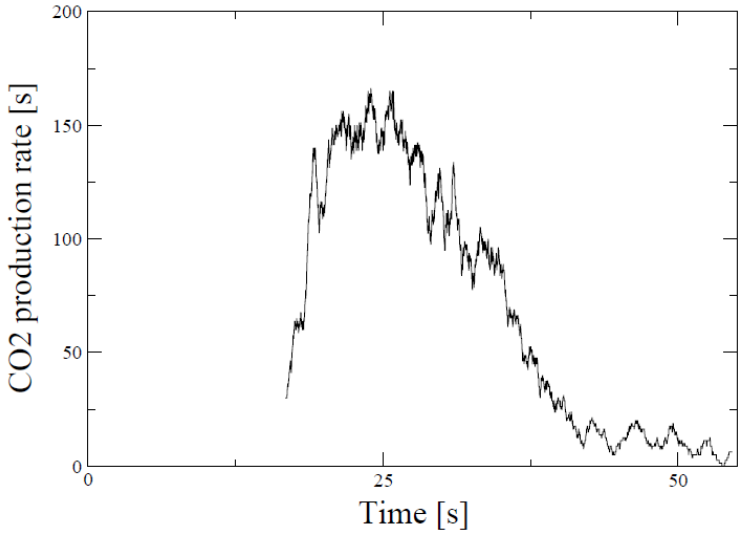
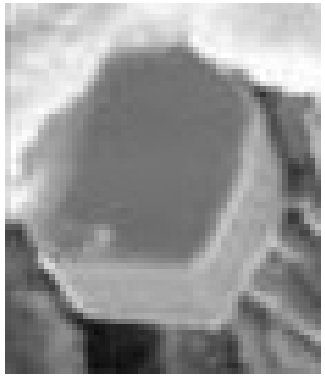
Kinetic Monte Carlo Simulation of surface reactions and diffusion on catalytic particles: CO oxidation on Pt/Al_2O_3





1-100 nm



- **Coverage 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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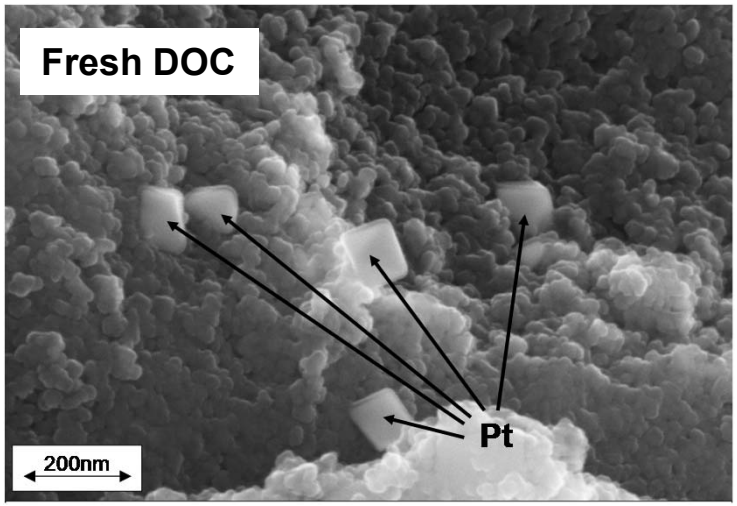
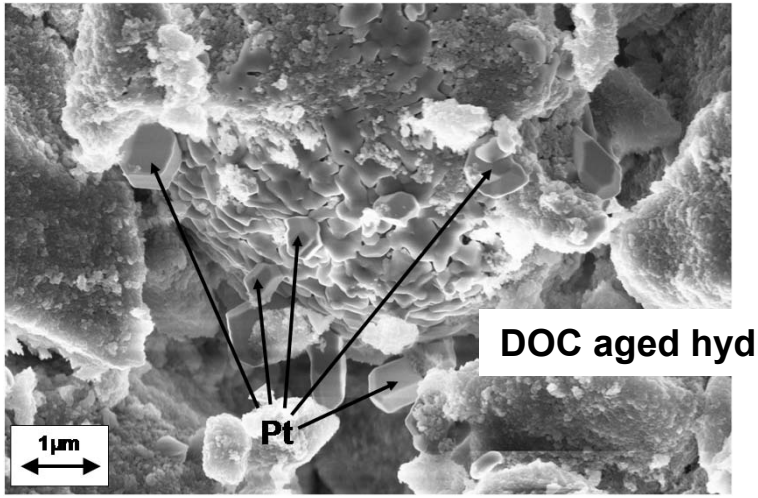
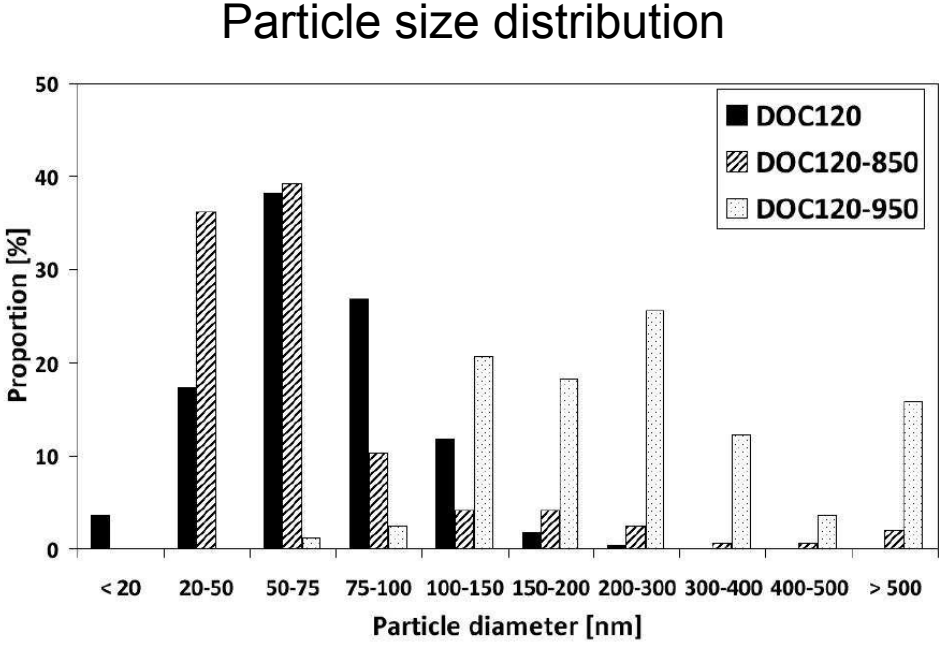
Effect of thermal aging on particle size distribution in DOC





DOC aged hydrothermally aging at 950°C



W. Boll, S. Tischer, O. Deutschmann, Ind. & Eng. Chem. Res. 49 (2010) 10303

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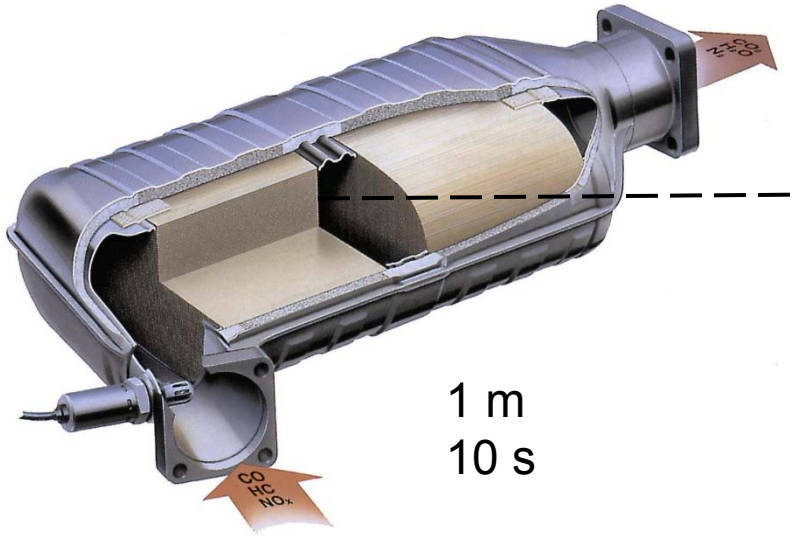
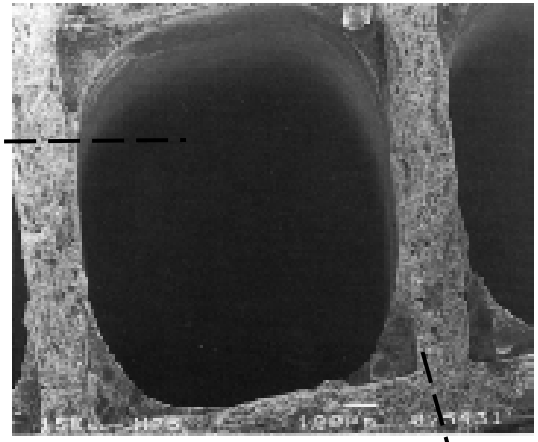
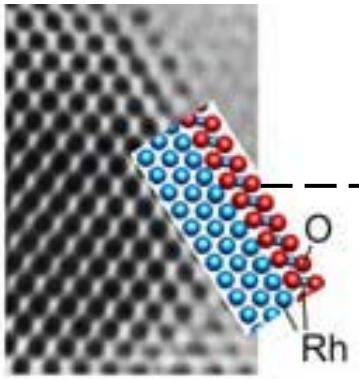
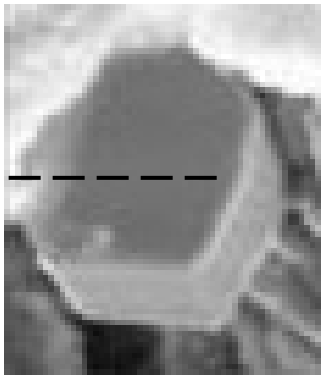
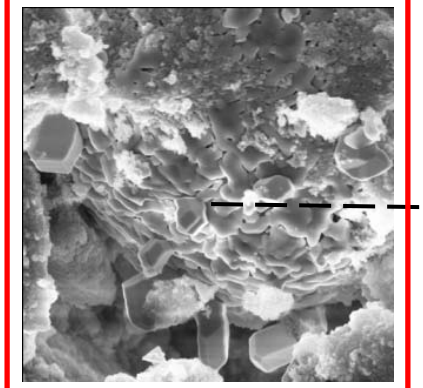
Catalytic converter:
Physics and chemistry on many scales

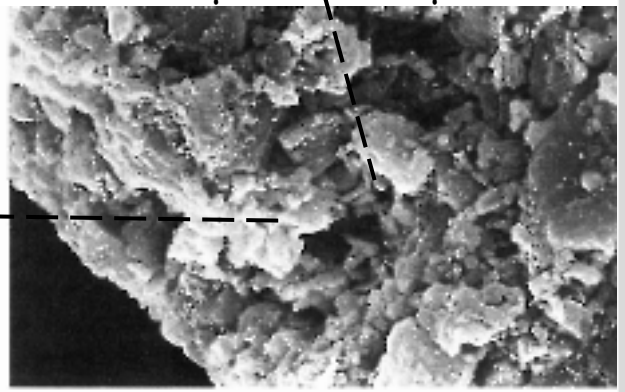












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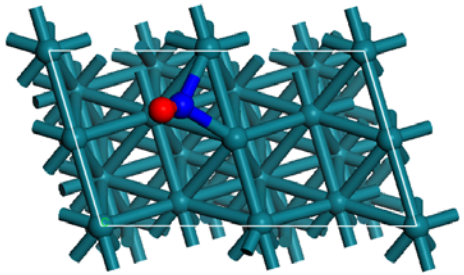
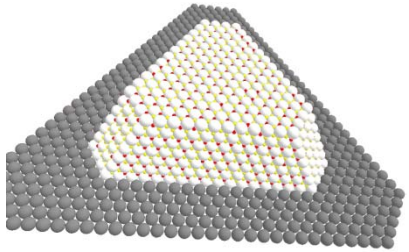
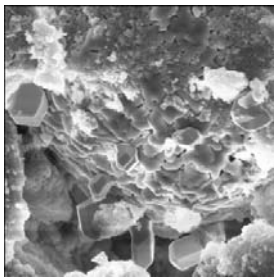
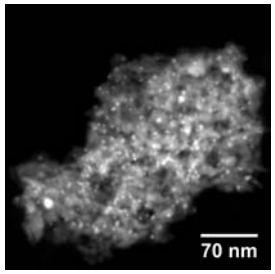
Modeling heterogeneous reactions: Concept of rate equations (mean-field approximation)

Surface coverage

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

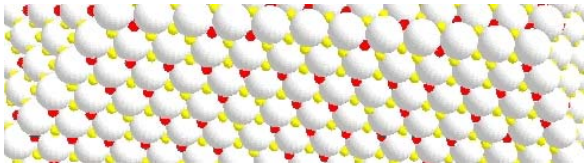
Surface reaction rate

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

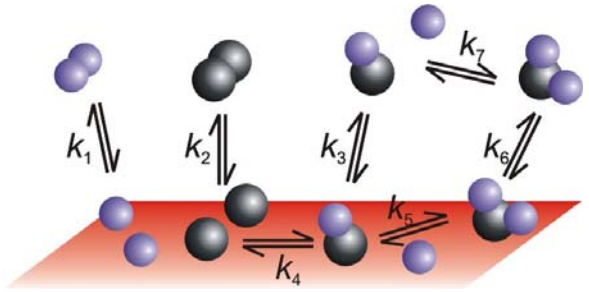
Rate expression

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

Γ = microscopic site density



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



O. Deutschmann. in Handbook of Heterogeneous Catalysis, 2nd Ed.,, G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp (eds.), p. 1811, Wiley-VCH, 2008

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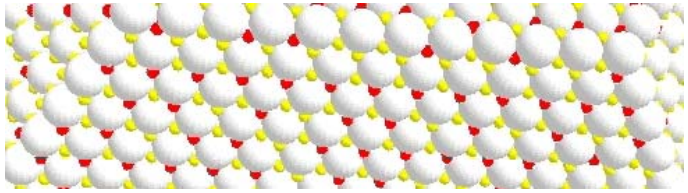
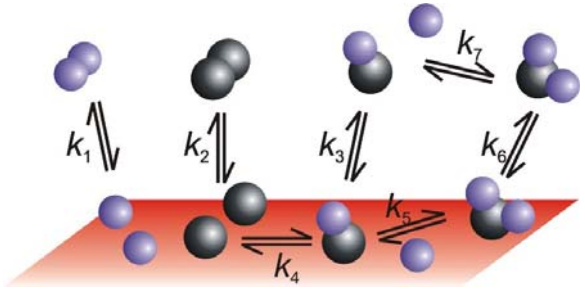
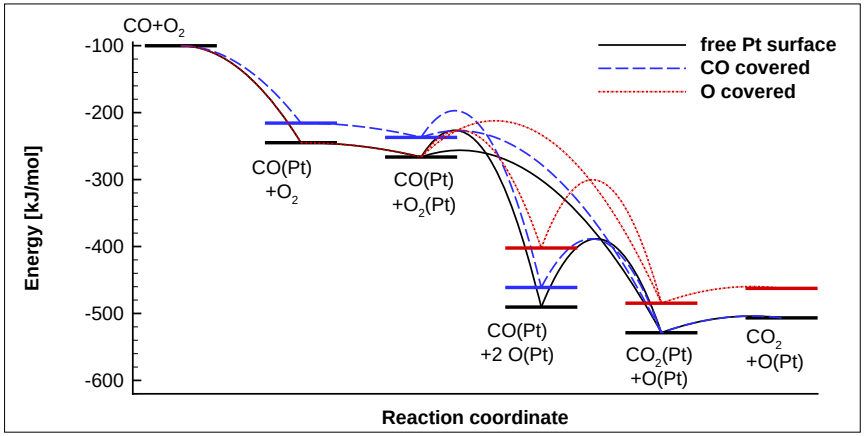
Surface reaction kinetics of CO oxidation on Pt/Al_2O_3 DOC: Mean field approximation







Reaction			A [mol, cm, s] / S^0	β	E_a $\left[\frac{kJ}{mol}\right]$
$O_2 + (Pt)$	$\longrightarrow$	$O_2(Pt)$	5.000×10^{-2}	0.000	0.00
$O_2(Pt)$	$\longrightarrow$	$O_2 + (Pt)$	5.243×10^{11}	−0.069	19.573
$O_2(Pt) + (Pt)$	$\longrightarrow$	$O(Pt) + O(Pt)$	8.325×10^{18}	0.000	39.933
$O(Pt) + O(Pt)$	$\longrightarrow$	$O_2(Pt) + (Pt)$	4.444×10^{21}	0.000	264.067
					$-88.2 \times \Theta_O$
$CO + (Pt)$	$\longrightarrow$	$CO(Pt)$	8.400×10^{-1}	0.000	0.000
$CO(Pt)$	$\longrightarrow$	$CO + (Pt)$	7.635×10^{12}	−0.139	143.145
					$-29.3 \times \Theta_{CO}$
$CO_2 + (Pt)$	$\longrightarrow$	$CO_2(Pt)$	3.193×10^{-3}	−0.035	2.686
$CO_2(Pt)$	$\longrightarrow$	$CO_2 + (Pt)$	1.894×10^{10}	0.139	21.855
$CO(Pt) + O_2(Pt)$	$\longrightarrow$	$CO_2(Pt) + O(Pt)$	4.124×10^{18}	0.069	9.494
					$+44.1 \times \Theta_O$
$CO_2(Pt) + O(Pt)$	$\longrightarrow$	$CO(Pt) + O_2(Pt)$	2.910×10^{23}	−0.069	272.506
					$+29.3 \times \Theta_{CO}$
$CO(Pt) + O(Pt)$	$\longrightarrow$	$CO_2(Pt) + (Pt)$	4.764×10^{18}	0.069	101.361
					$-29.3 \times \Theta_{CO}$
$CO_2(Pt) + (Pt)$	$\longrightarrow$	$CO(Pt) + O(Pt)$	6.297×10^{20}	−0.069	140.239
					$+44.1 \times \Theta_O$

D. Chan, S. Tischer, J. Heck, C. Diehm, O. Deutschmann. Applied Catalysis B: Environmental 156–157 (2014) 153.

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Proposed surface reaction mechanism for Pt/Rh-based three-way catalysts: 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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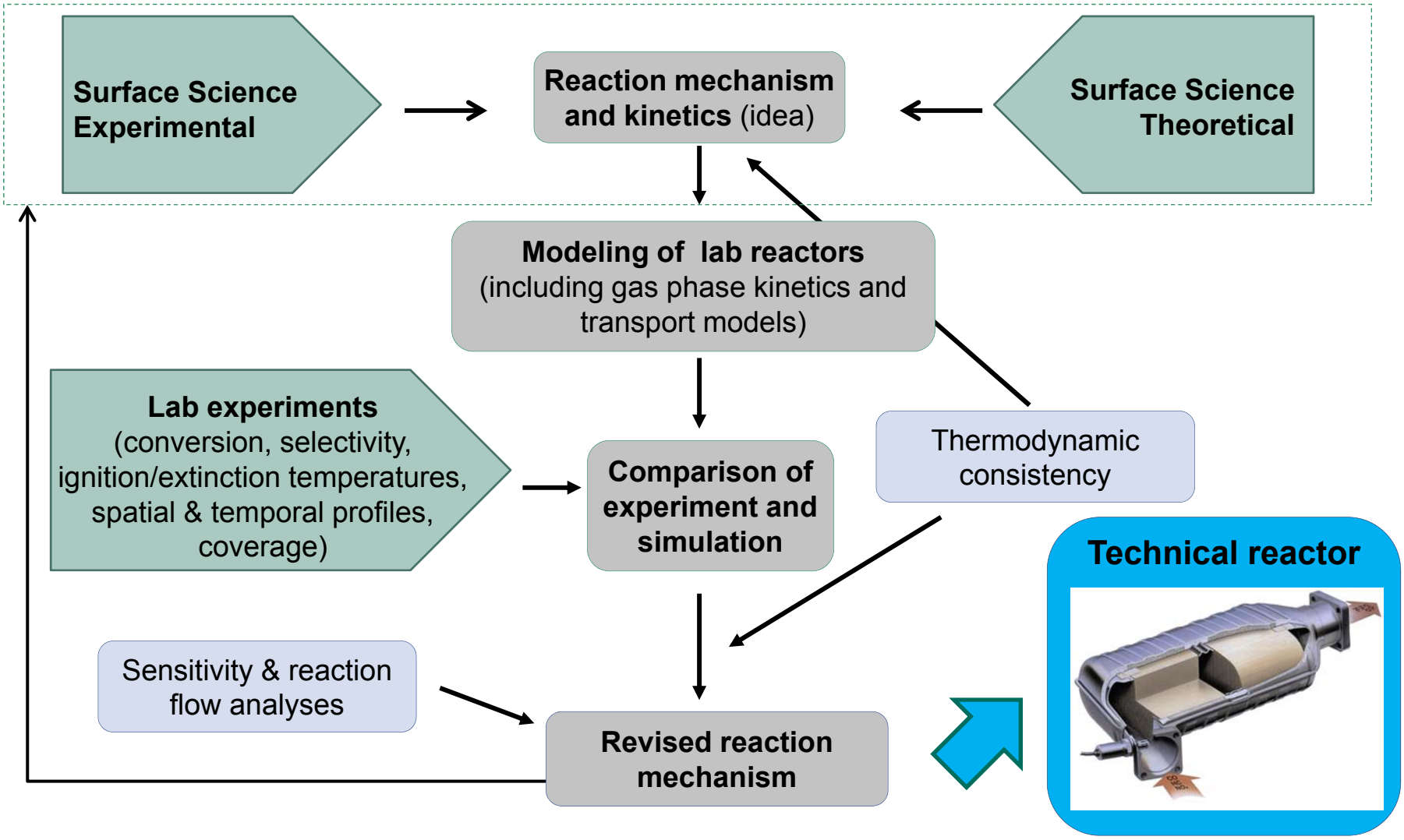
Development of micro kinetic models for simulations of catalytic reactors



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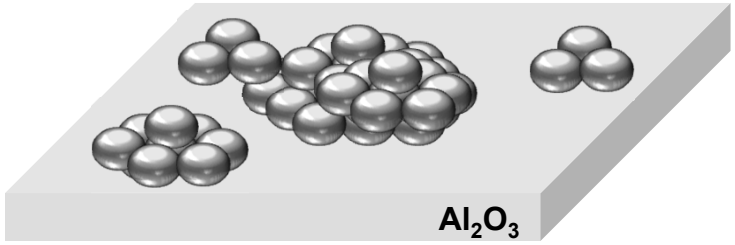
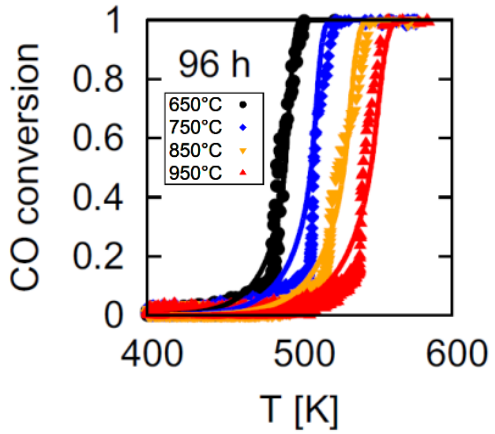
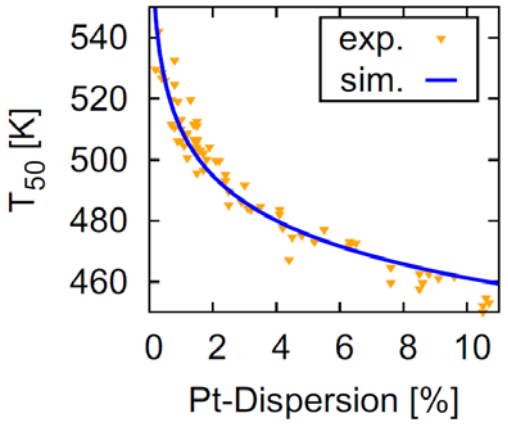
Modeling catalyst loading and dispersion: Variation of dispersion in a DOC due to aging

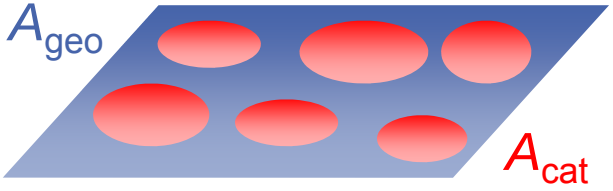


Pt particle sintering





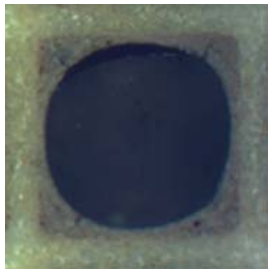
D. Chan, S. Tischer, J. Heck, C. Diehm, O. Deutschmann. Applied Catalysis B: Env. 156–157 (2014) 153.

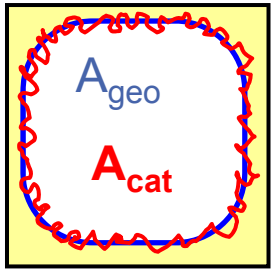


Surface reaction rate is proportional to the catalytic surface area A_{cat} determined by CO-chemisorption

Scaling factor:

$$F_{cat/geo} = \frac{A_{cat}}{A_{geo}} = D \cdot \frac{m_{cat}}{M_{cat} \cdot \Gamma_{cat} \cdot A_{geo}}$$





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

C. Karakaya, O. Deutschmann. Appl. Catal. A: Gen. 445-446 (2012) 221

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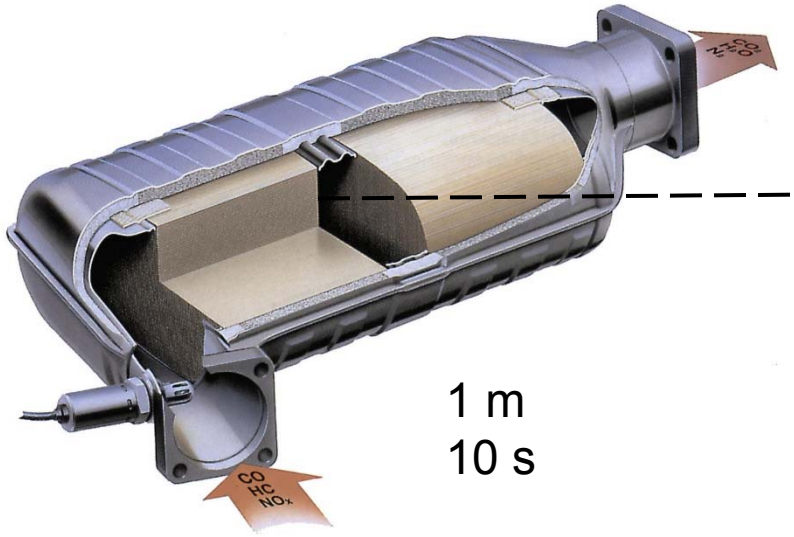
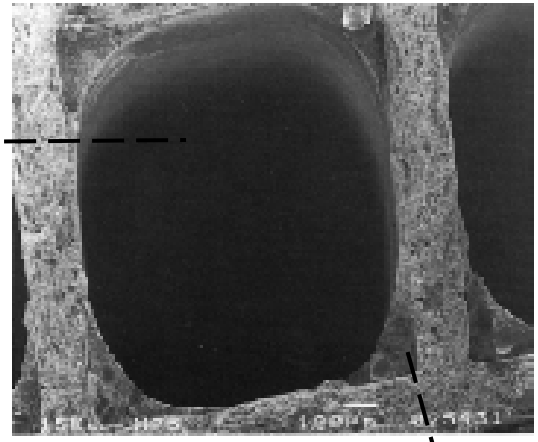
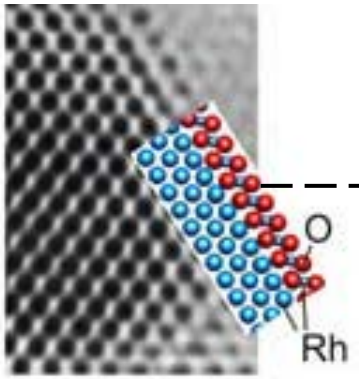
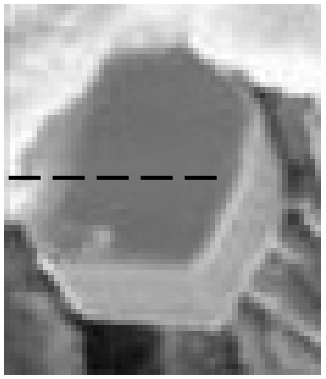
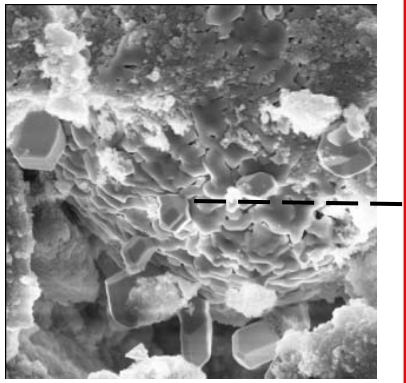
Multi-scale modeling:
From 10^{-10} m and 10^{-13} s to 1m and 10 s

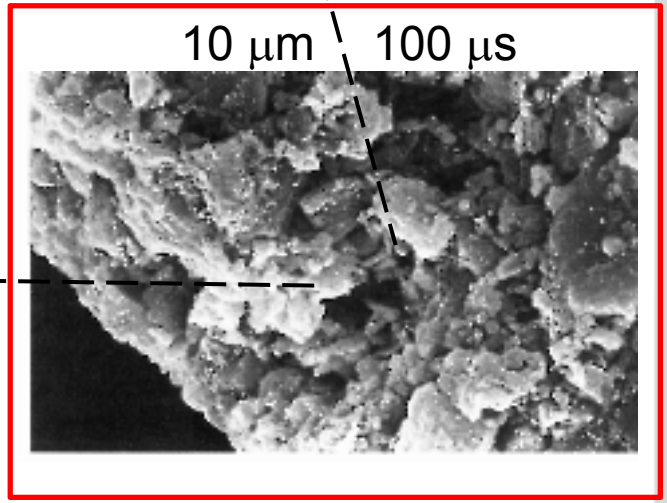












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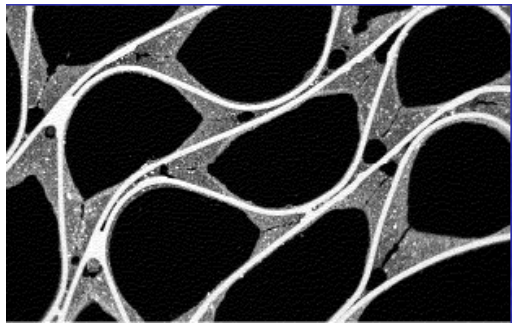
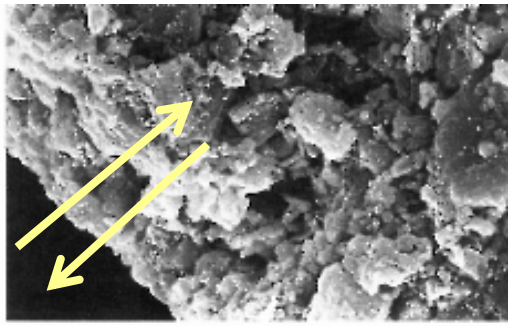
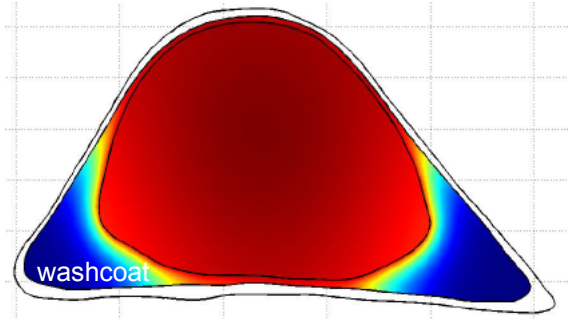
Coupling of surface reaction rate and flow field - Modeling internal transport limitation of reaction rate







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

Simple model: effectiveness factor

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

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

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

Reaction-diffusion equations

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

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

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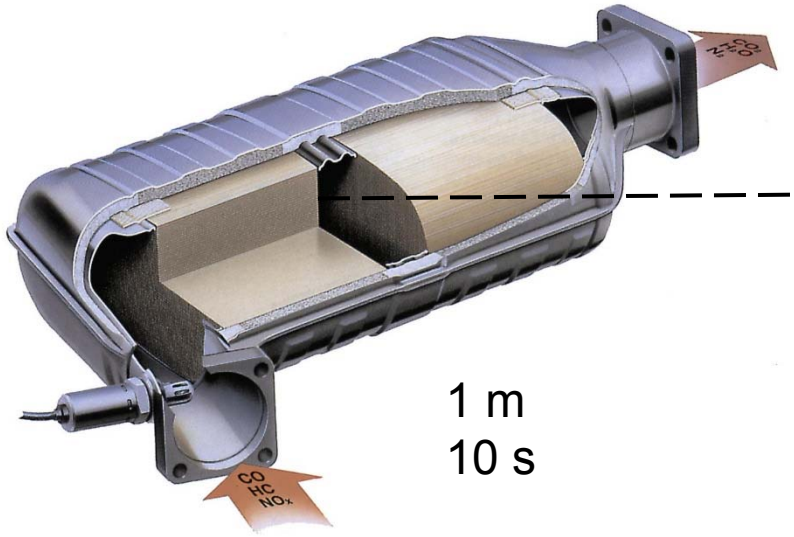
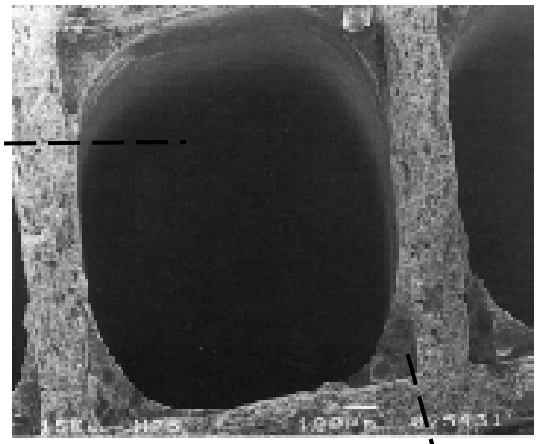
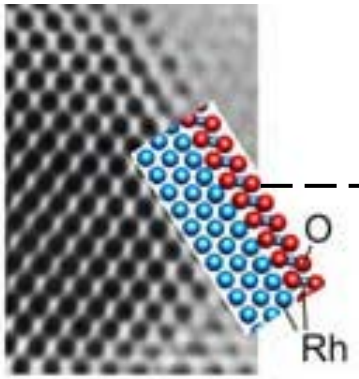
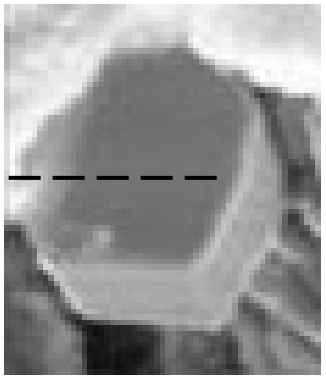
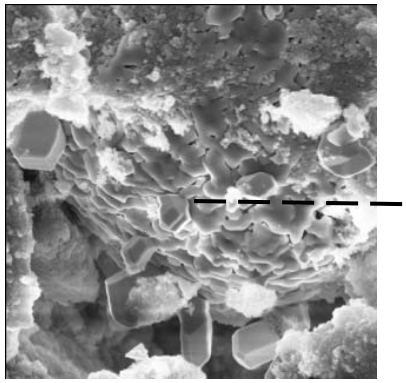
Multi-scale modeling:
From 10^{-10} m and 10^{-13} s to 1m and 10 s

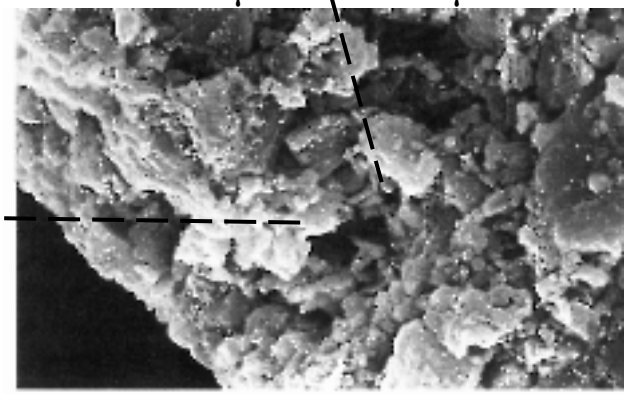












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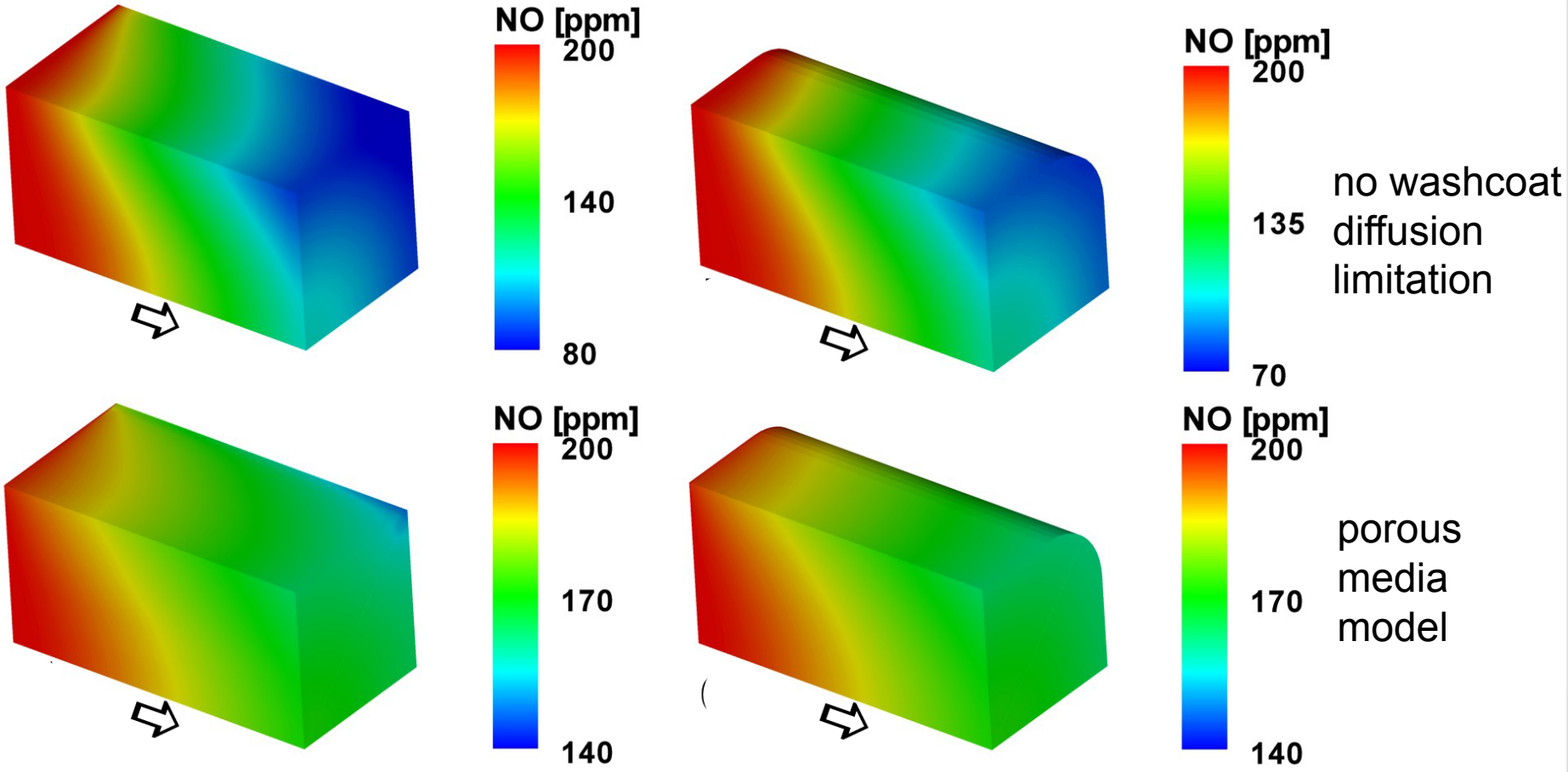
Impact of models for channel shape and washcoat diffusion on NO profiles in a DOC



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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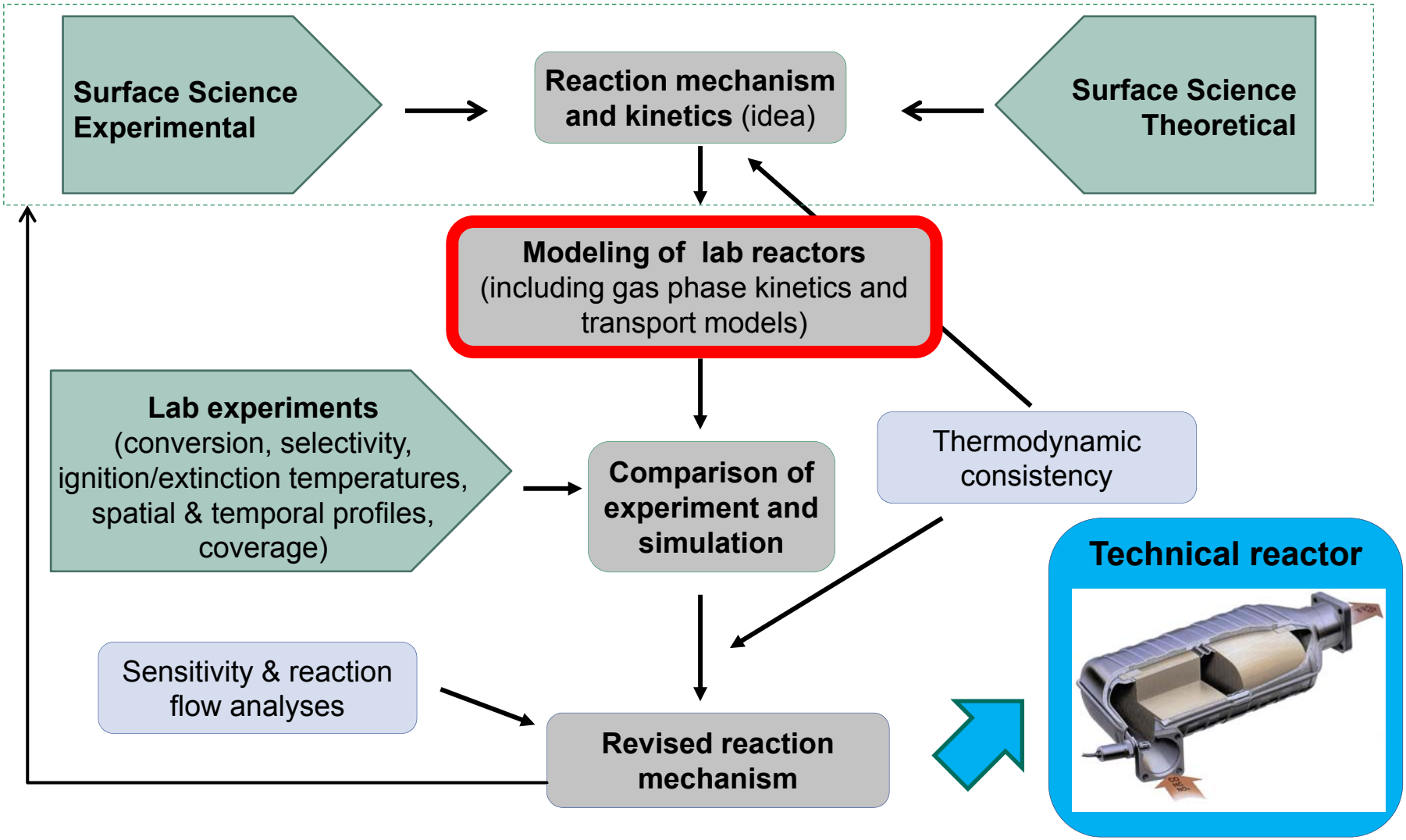
Development of micro kinetic models for simulations of catalytic reactors



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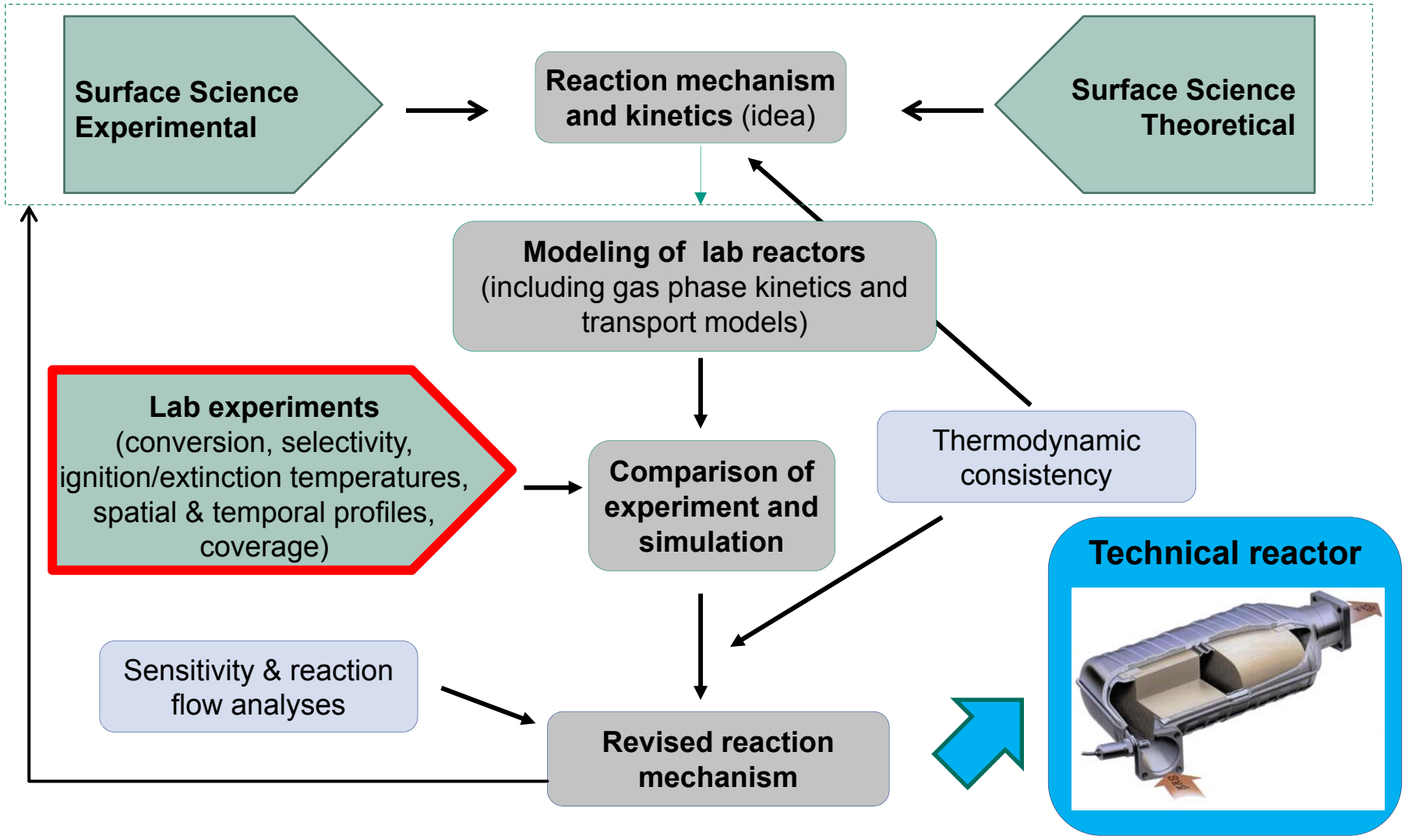
Development of micro kinetic models for simulations of catalytic reactors



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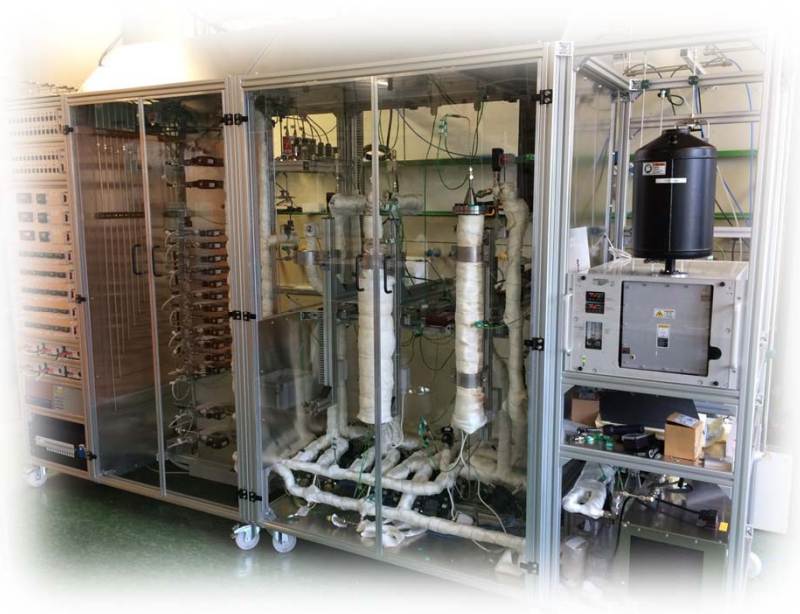
Lab test benches in the Exhaust-Gas Center Karlsruhe: High-Pressure setup



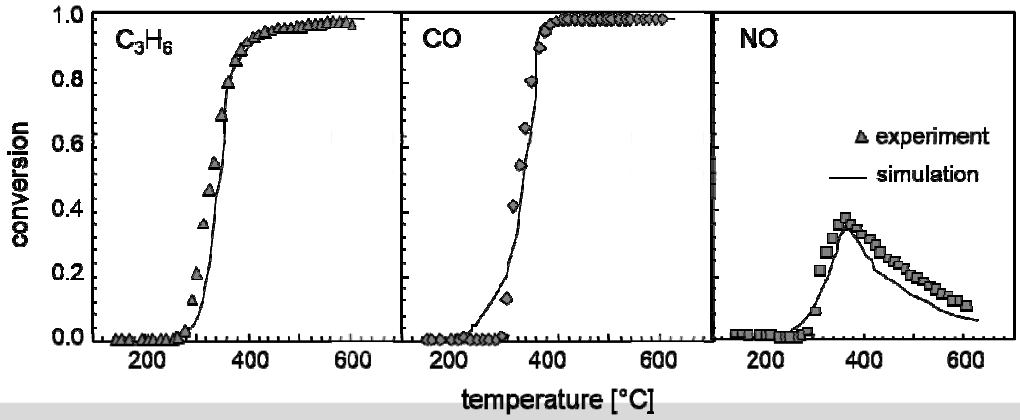
Tests of catalyst coated honeycombs

(d = 2.54 cm, length < 6cm)

Labview automatic controlled measurements

Coated pipes, reactor and analytics – for sulfur

Gases:	NO, NO_2, H_2O, CO…
Temperature:	RT – 700°C
Pressure:	1- 5 bar
Flow:	10 - 70 slpm
Gas analytics:	FTIR, (MS)



www.abgaszentrum-karlsruhe.de

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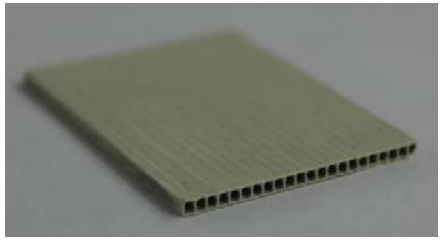
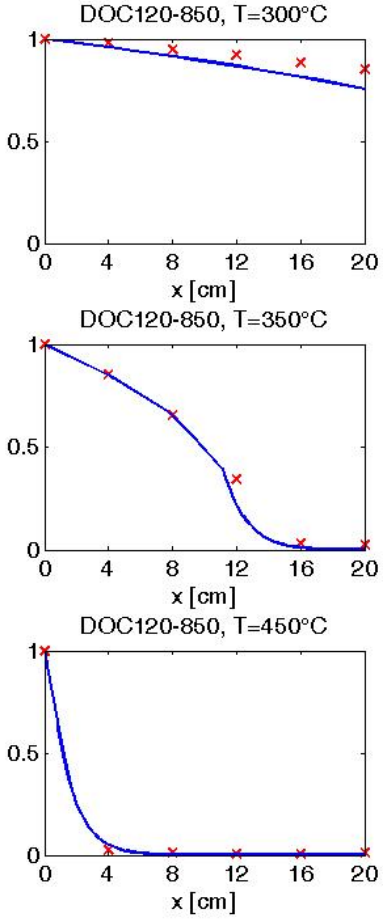
Isothermal flat bed reactor: Spatially and time-resolved exhaust-gas composition in catalyst channel



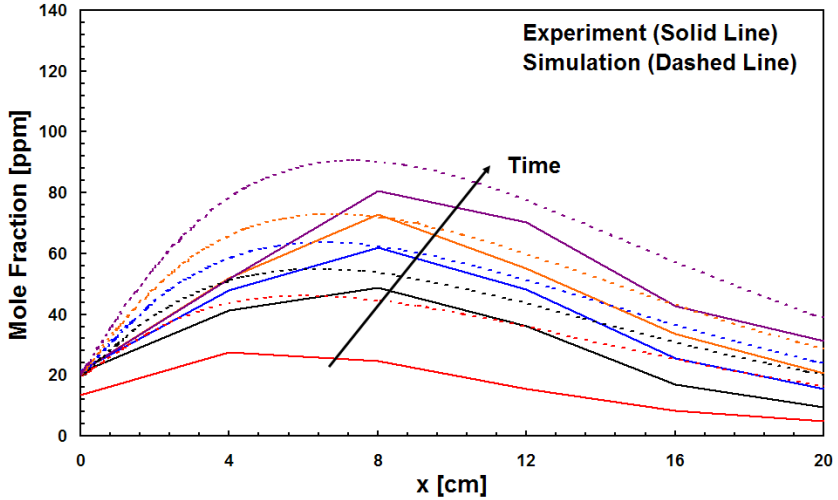
G. Eigenberger et al.

CO profile in DOC



V. Schmeißer, J. Perez, U. Tuttlies, G. Eigenberger, Top. Catal. 42 (2007) 15

NO_2 profile in NSC during storage



J. Koop, O. Deutschmann. SAE 2007-01-1142.
J. Koop, O. Deutschmann. Appl. Catal.B: Env. 91 (2009) 47

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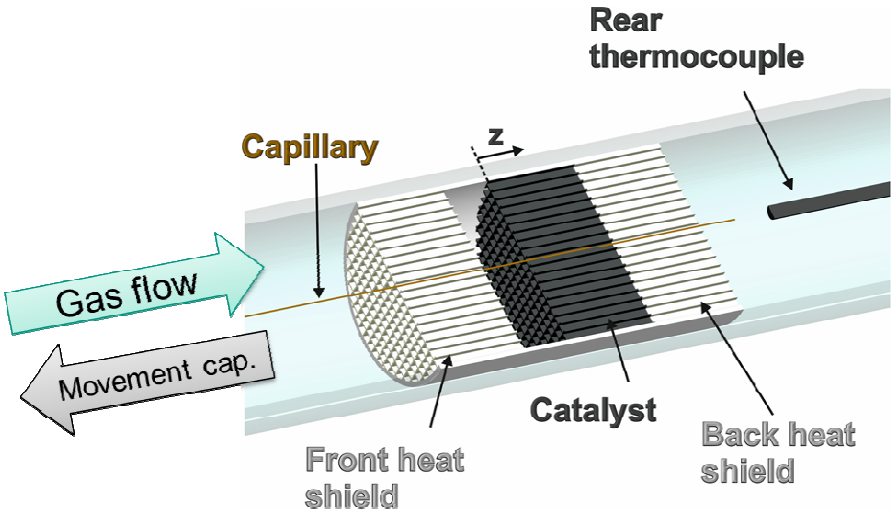
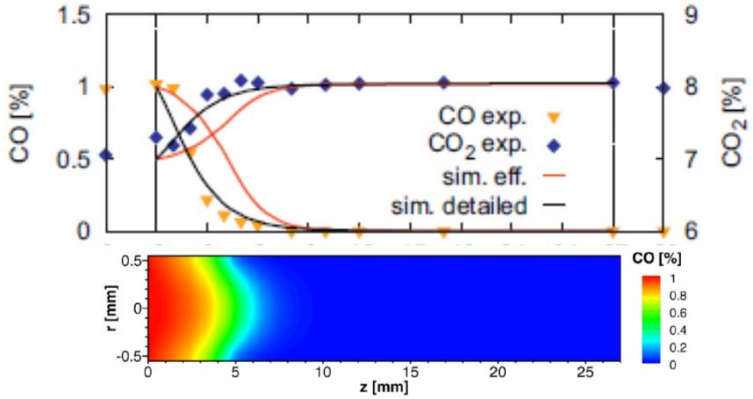
Lab test bench SpaciPro: Invasive in-situ technique for axially resolved profiles





D. Chan, S. Tischer, J. Heck, C. Diehm, O. Deutschmann. Applied Catalysis B: Environmental 156–157 (2014) 153.

Tests of catalytically coated honeycombs (d = 2 - 2,54 cm, length ~ 5 cm)

Axially resolved profiles of species concentration, gas-phase and surface temperatures (resolution: 0.25 mm)

Gases:	Gaseous and liquid HCs, CO, CO_2, NH_3, NO, NO_2, O_2, Air, N_2, H_2, H_2O
Temperature:	RT – 1000°C
Pressure:	1 atm
Flow:	0.5 - 5 slpm
Gas analytics:	FT- IR, MS, GC

G. Fisher et al., 2006
R. Horn, N. J. Degenstein, K. A. Williams, L. D. Schmidt, Catal. Lett. 110 (2006) 169.
J. Sá, D.L. Abreu Fernandes, F. Aiouache, A. Goguet, C. Hardacre, D. Lundie, W. Naeem, W.P. Partridge, C. Stere, Analyst 135 (2010) 2260.
A. Donazzi, D. Livio, M. Maestri, A. Beretta, G. Groppi, E. Tronconi, P. Forzatti, Angew. Chem. Int. Ed. 50 (2011) 3943.
D. Livio, C. Diehm, A. Donazzi, A. Beretta, G. Groppi, O. Deutschmann, Appl. Catal. A 467 (2013) 530.

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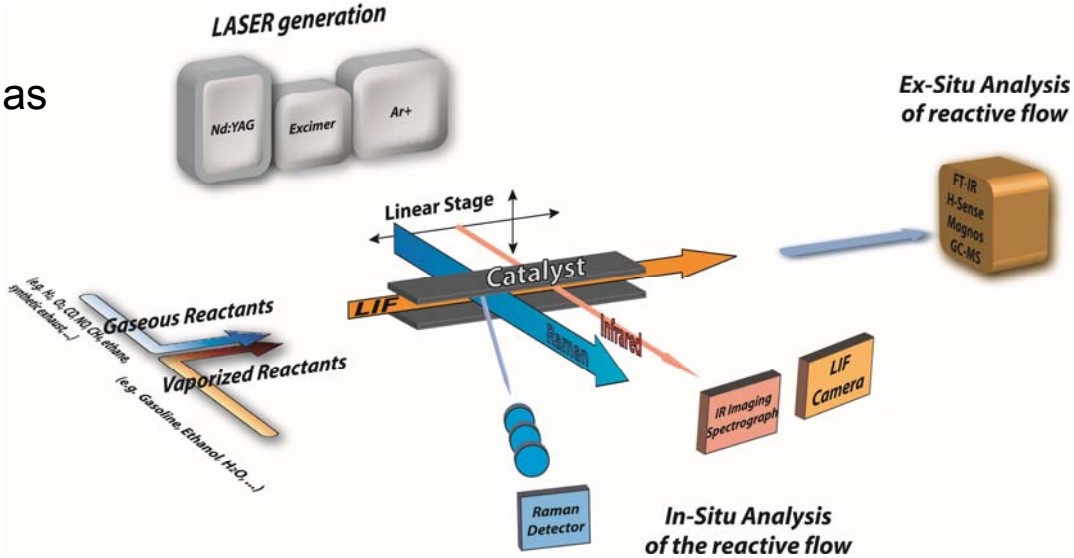
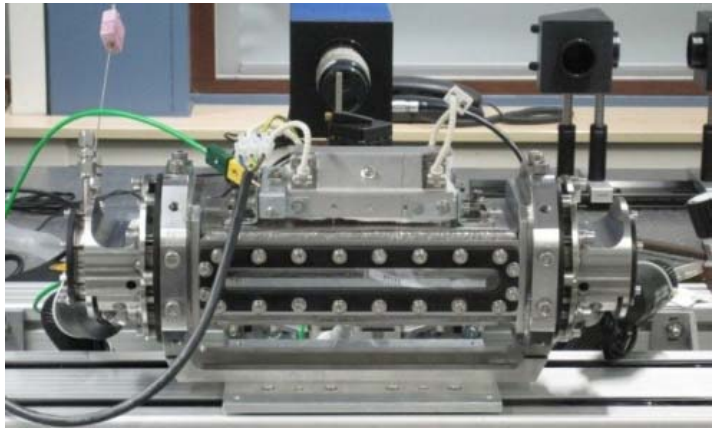
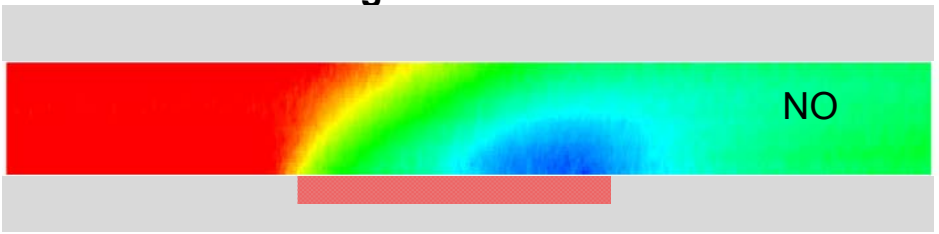
Lab test bench CATHLEN: Optical diagnostics of catalytic reactors

Non-invasive 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, Angew. Chem. Intl. Ed. 54 (2015) 2653.

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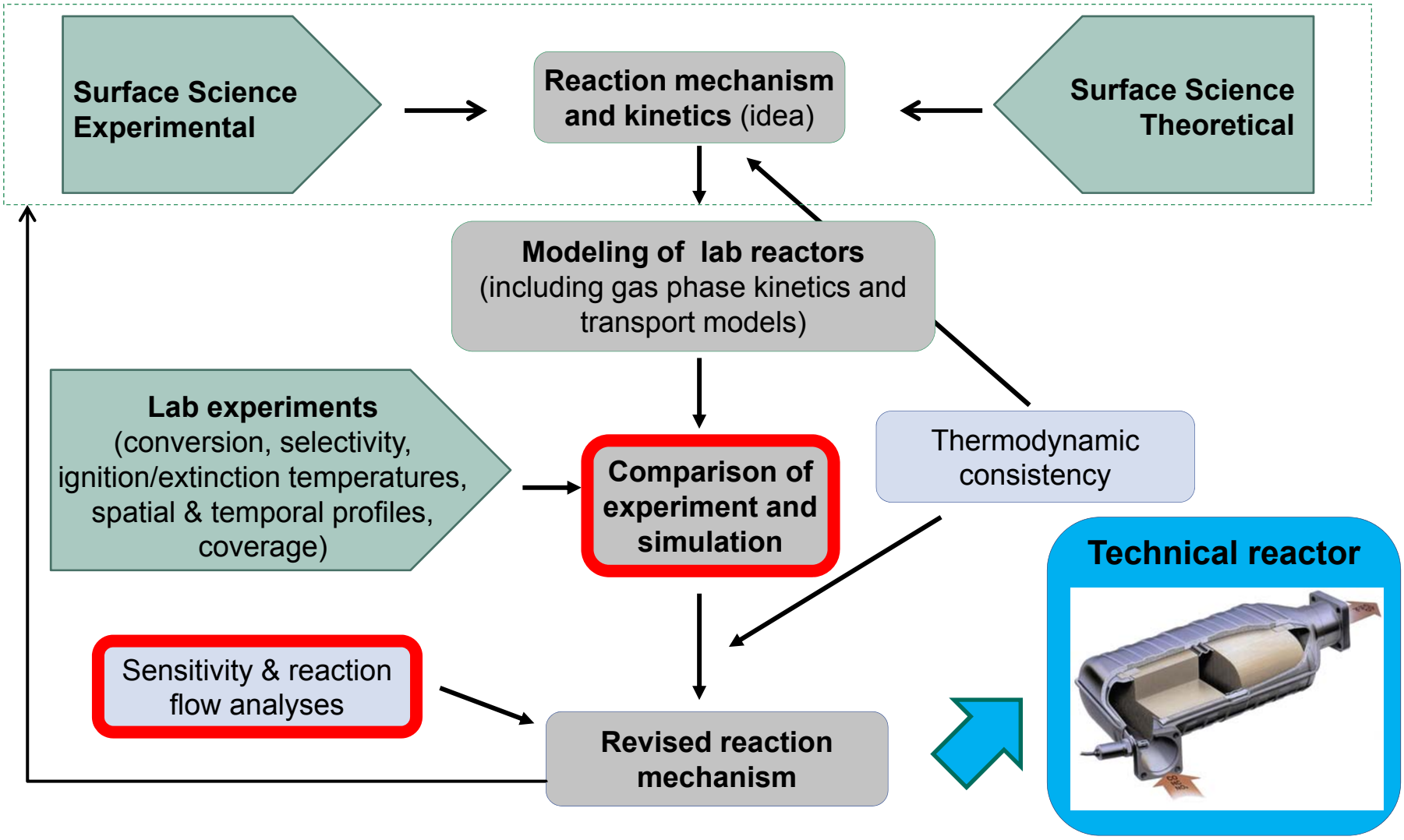
Institute for Chemical Technology and Polymer Chemistry

Development of micro kinetic models for simulations of catalytic reactors



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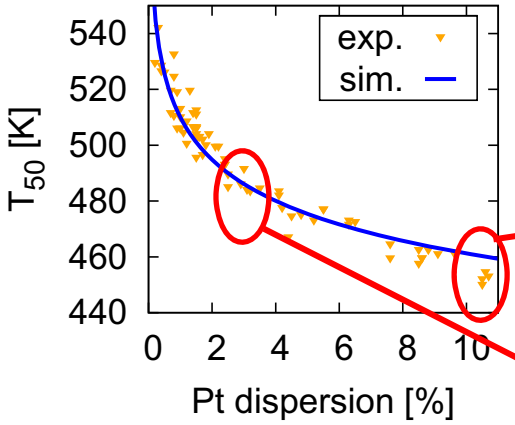
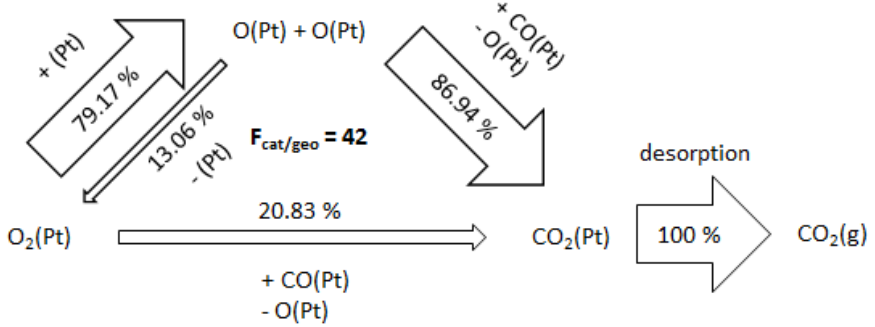
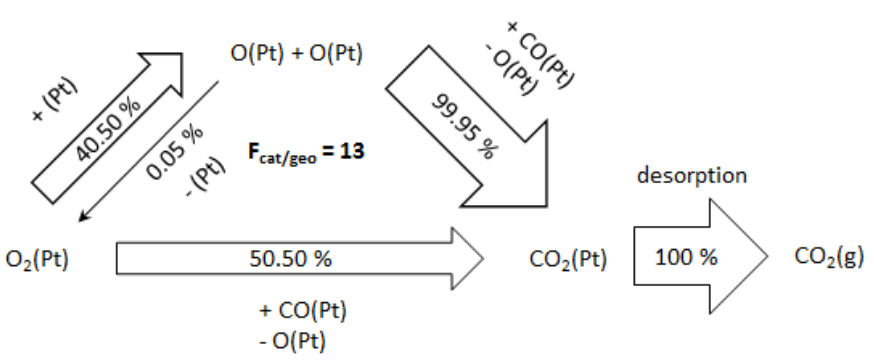
Effect of catalyst loading on conversion of CO in DOC
Reaction flow analysis





Reaction			A [mol, cm, s] / S^0	β	E_a $\left[\frac{kJ}{mol}\right]$
O_2 + (Pt)	⟶	O_2(Pt)	5.000×10^{-2}	0.000	0.00
O_2(Pt)	⟶	O_2 + (Pt)	5.243×10^{11}	−0.069	19.573
O_2(Pt) + (Pt)	⟶	O(Pt) + O(Pt)	8.325×10^{18}	0.000	39.933
O(Pt) + O(Pt)	⟶	O_2(Pt) + (Pt)	4.444×10^{21}	0.000	264.067
					$-88.2 \times \Theta_O$
CO + (Pt)	⟶	CO(Pt)	8.400×10^{-1}	0.000	0.000
CO(Pt)	⟶	CO + (Pt)	7.635×10^{12}	−0.139	143.145
					$-29.3 \times \Theta_{CO}$
CO_2 + (Pt)	⟶	CO_2(Pt)	3.193×10^{-3}	−0.035	2.686
CO_2(Pt)	⟶	CO_2 + (Pt)	1.894×10^{10}	0.139	21.855
CO(Pt) + O_2(Pt)	⟶	CO_2(Pt) + O(Pt)	4.124×10^{18}	0.069	9.494
					$+44.1 \times \Theta_O$
CO_2(Pt) + O(Pt)	⟶	CO(Pt) + O_2(Pt)	2.910×10^{23}	−0.069	272.506
					$+29.3 \times \Theta_{CO}$
CO(Pt) + O(Pt)	⟶	CO_2(Pt) + (Pt)	4.764×10^{18}	0.069	101.361
					$-29.3 \times \Theta_{CO}$
CO_2(Pt) + (Pt)	⟶	CO(Pt) + O(Pt)	6.297×10^{20}	−0.069	140.239
					$+44.1 \times \Theta_O$



D. Chan, S. Tischer, J. Heck, C. Diehm, O. Deutschmann. Applied Catalysis B: Environmental 156–157 (2014) 153.

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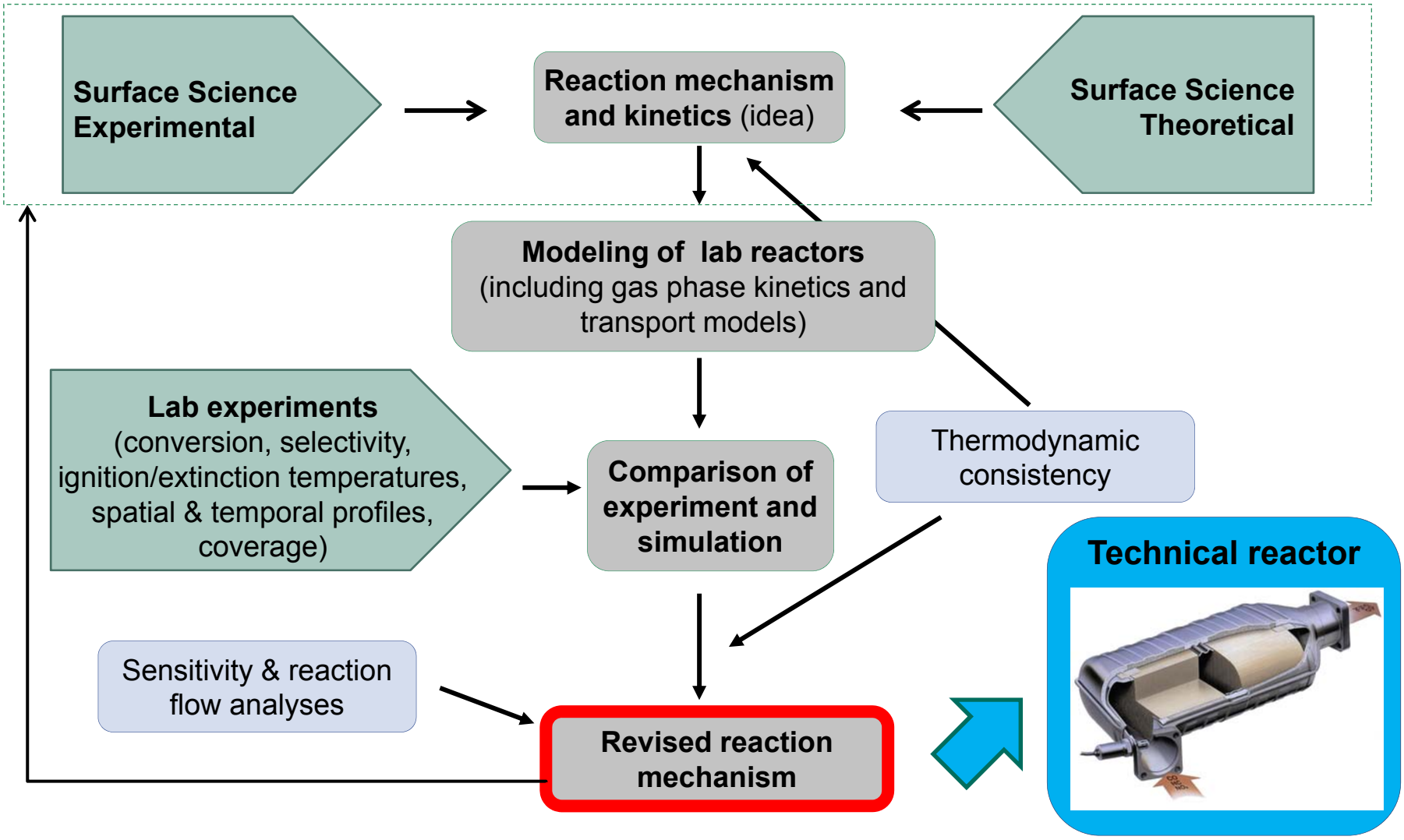
Development of micro kinetic models for simulations of catalytic reactors



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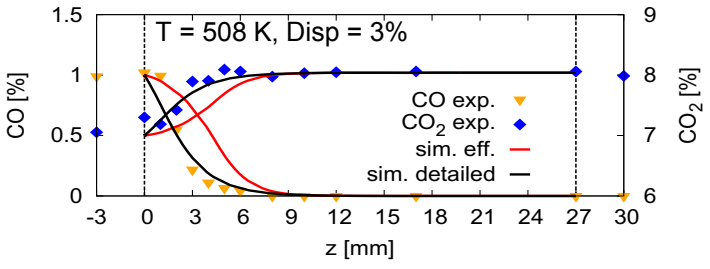
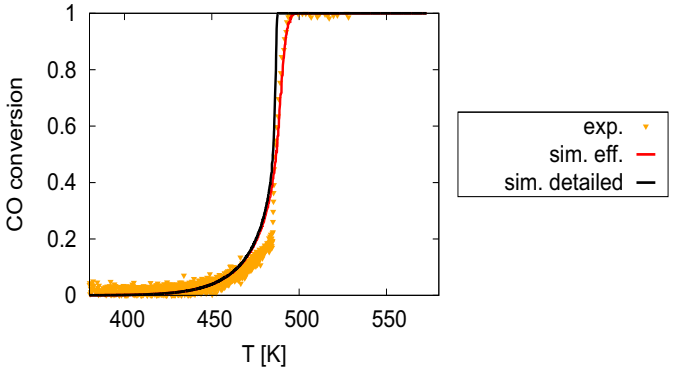
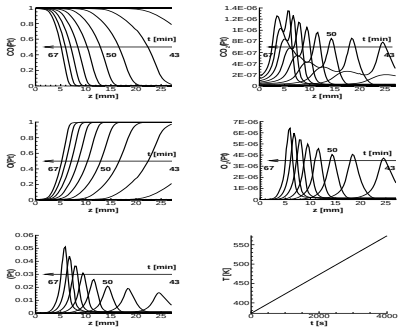
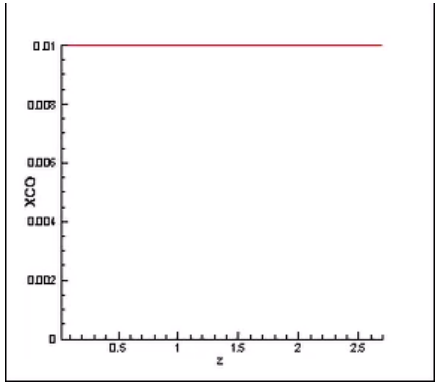
Transient simulation of lab light-off experiment: Temporal variation of axial profiles during light-off



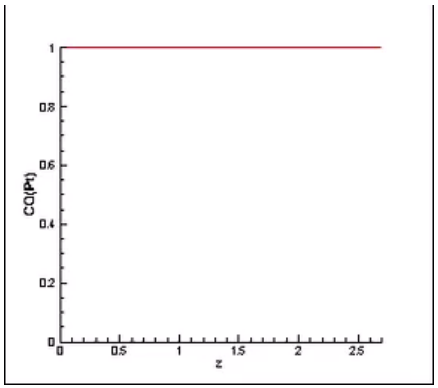


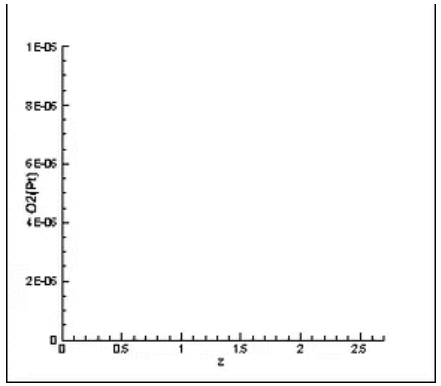


CO

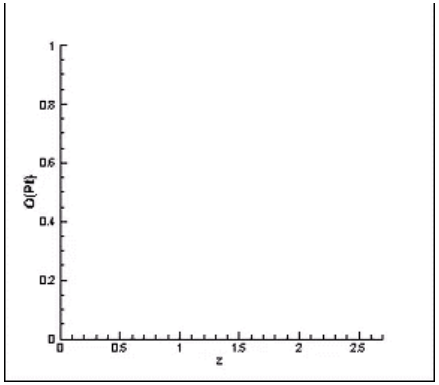


CO(Pt)





O_2(Pt)



O (Pt)

D. Chan, S. Tischer, J. Heck, C. Diehm, O. Deutschmann. Applied Catalysis B: Environmental 156–157 (2014) 153.

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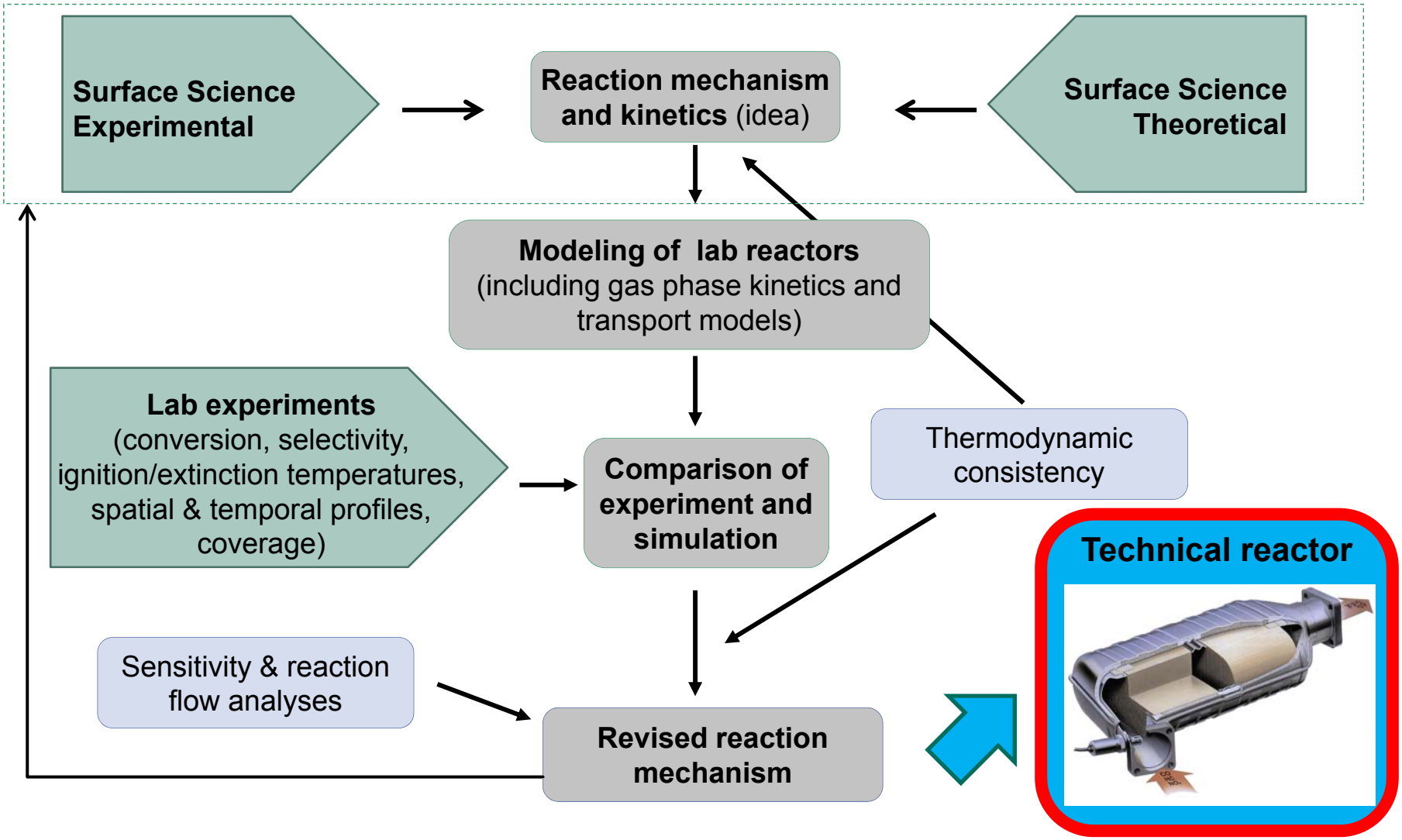

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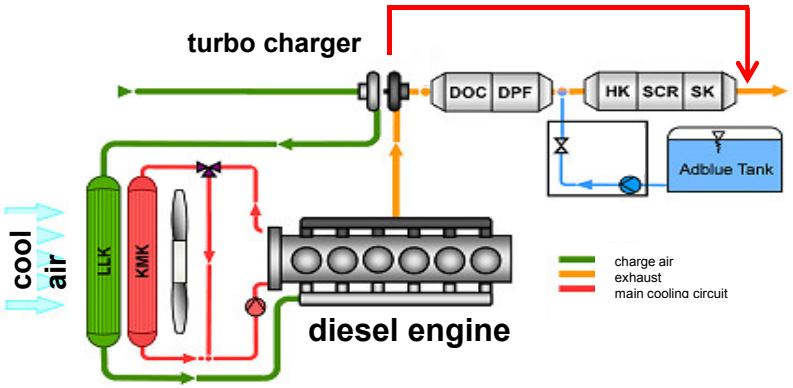
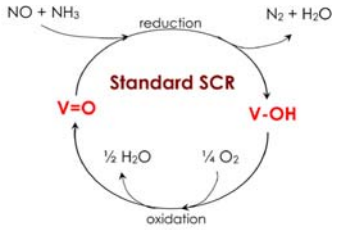
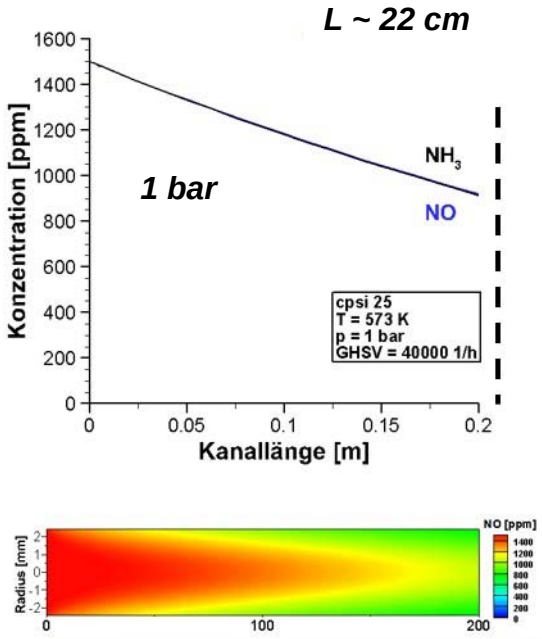
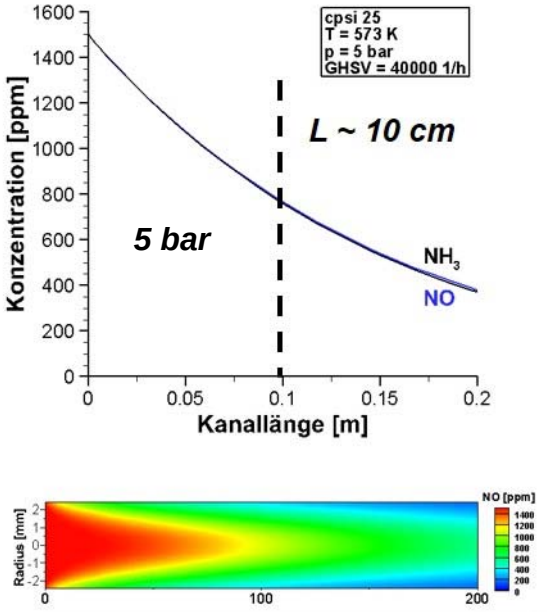
Pre-turbo SCR for large diesel engines: Effect of high pressure and temperature on conversion





E. Tronconi, I. Nova, C. Ciardelli, D. Chatterjee, M. Weibel; J. Catal. 245 (2007) 1.
I. Nova, C. Ciardelli, E. Tronconi, D. Chatterjee, M. Weibel; (2009), AIChE J.55, 6, 1514-1529





At constant mass flow:

Residence time ~ pressure
Diffusion ~ 1/pressure

C. Hauck, O. Deutschmann, 2014

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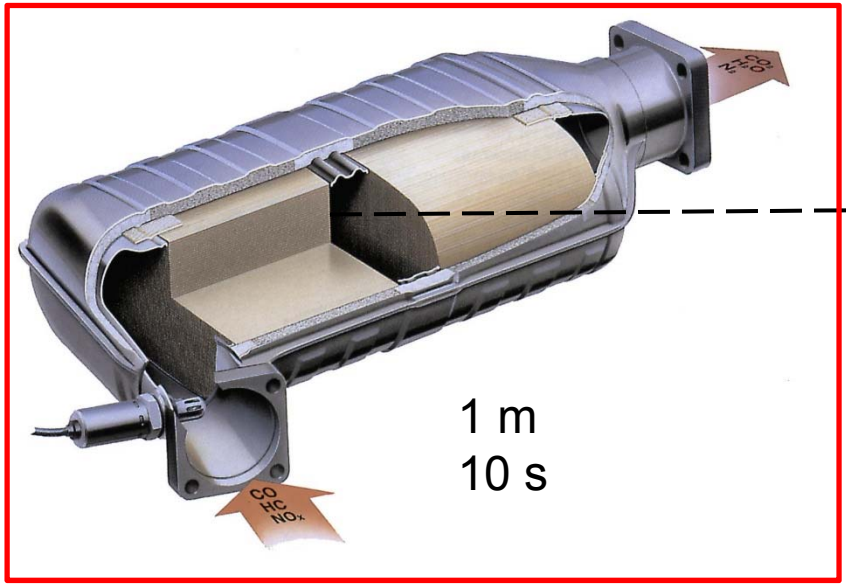
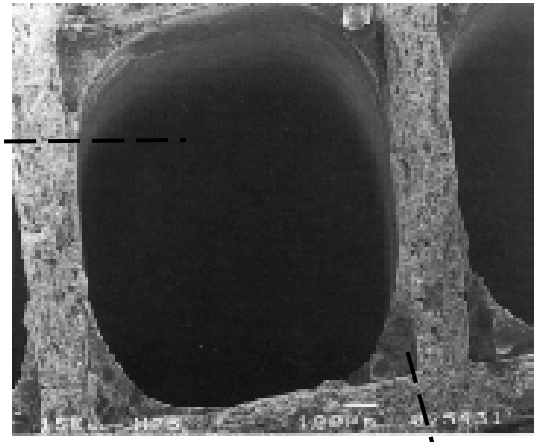
Institute for Chemical Technology and Polymer Chemistry

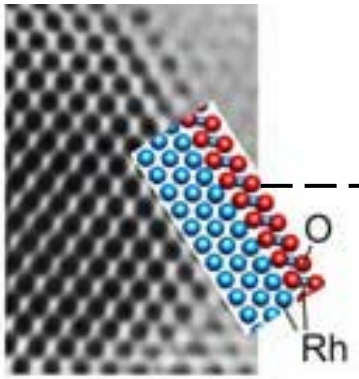
Multi-scale modeling:
From 10^{-10} m and 10^{-13} s to 1m and 10 s



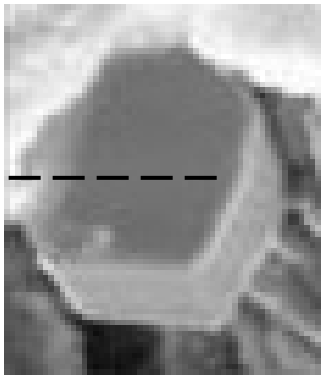


1 mm
10 ms

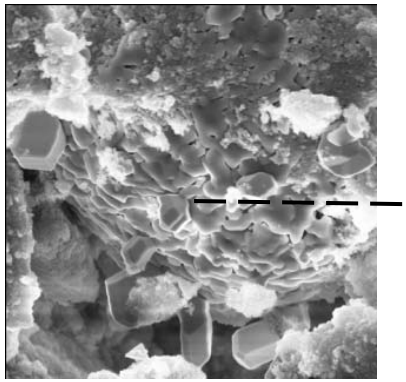
0.1 nm



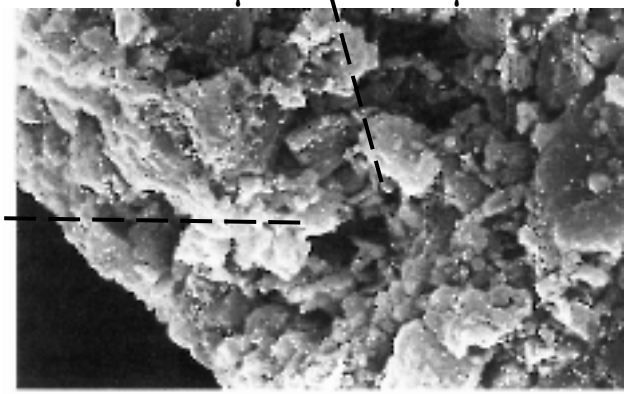
1 nm



10 nm



10 μm 100 μs



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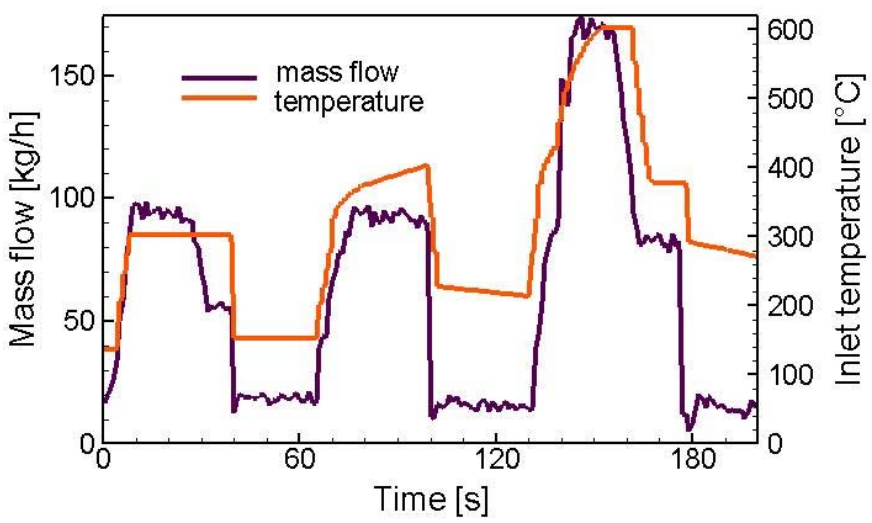
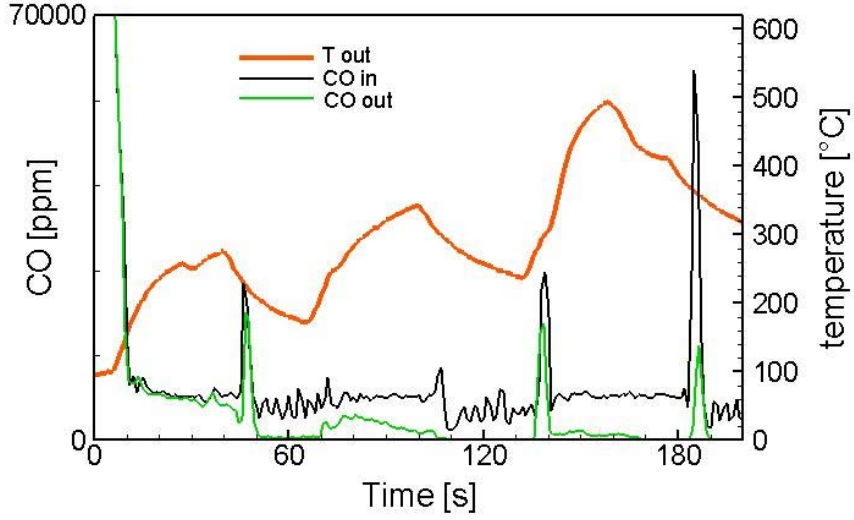
Simulation at real driving conditions is very challenging: Continuous variation of all inlet variables





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

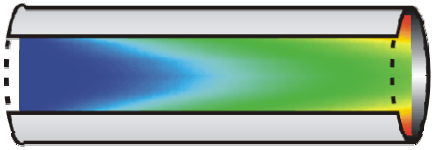
temperature profile
at the wall

heat source term

time scale ~ 1 s
residence time < 100 ms

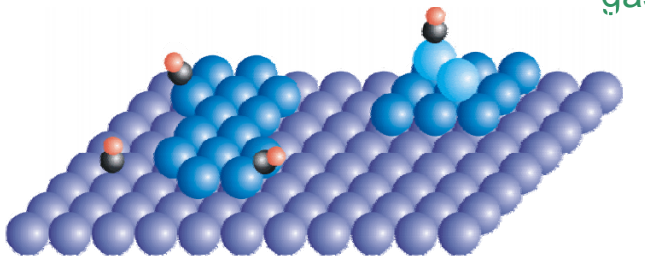
CHANNEL or PLUG

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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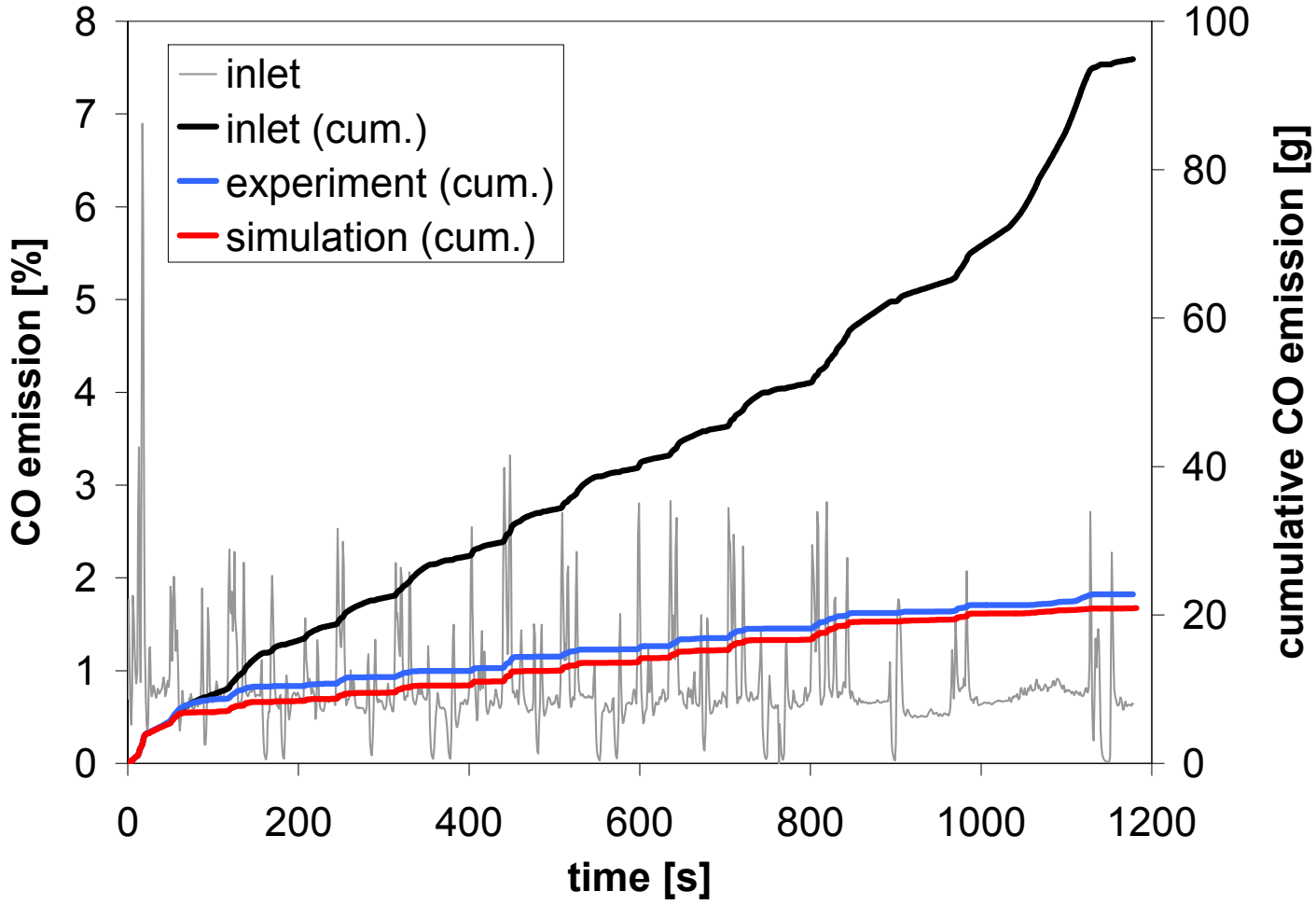
Institute for Chemical Technology and Polymer Chemistry

Cumulative CO emission in MEVG cycle: Experiment vs. simulation



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

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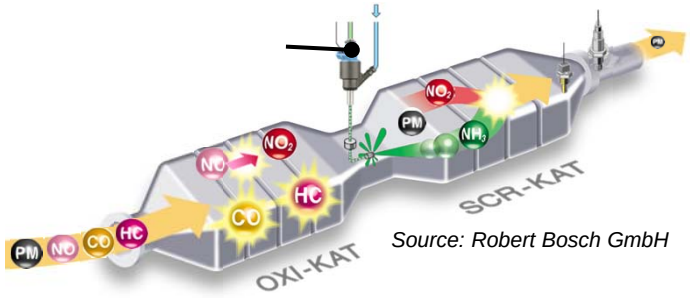
Selective catalytic reduction (SCR) of NO_x emissions by urea solution: Processes between injection and catalyst

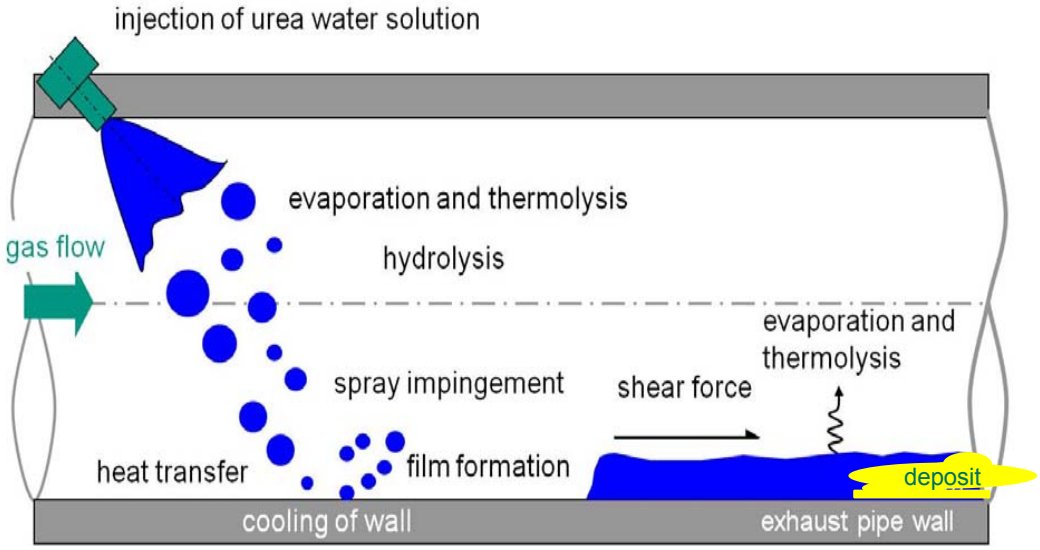


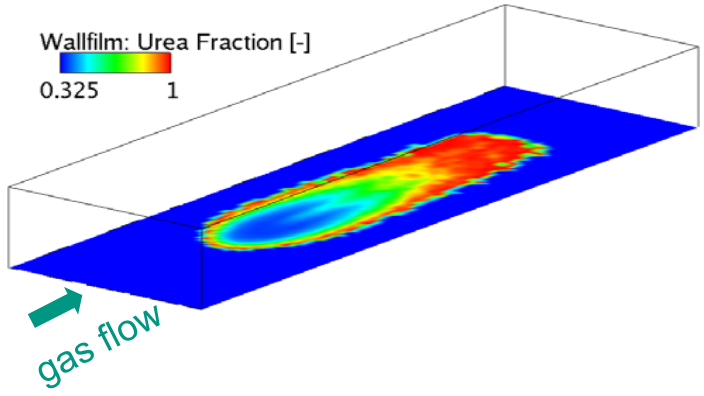
Source: Robert Bosch GmbH

$(NH_2)_2CO\ (l) \Rightarrow NH_3\ (g) + HNCO\ (g)$

$HNCO\ (g) + H_2O\ (g) \Rightarrow NH_3\ (g) + CO_2\ (g)$

$2\ NH_3 + NO + NO_2 \rightarrow 2\ N_2 + 3\ H_2O$





F. Birkhold, U. Meingast, P. Wassermann, O. Deutschmann. SAE Technical paper 2006-01-0643, SAE 2006 Trans. J. of Fuels and Lubricants (2006), 252
F. Birkhold, U. Meingast, P. Wassermann, O. Deutschmann. Appl. Catal. B: Environmental 70 (2007) 119-127

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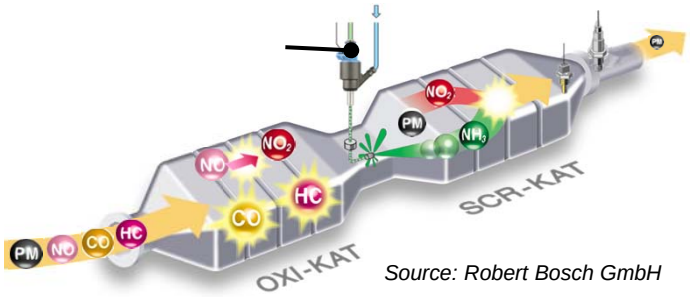
Modeling of deposit formation in Urea-SCR: Understanding the reaction mechanism



Source: Robert Bosch GmbH

	Reaction	γ_j	A	E_A (kJ/mol)
I	$CYA_{(s)} \rightarrow 3HNCO_{(g)}$	0	1.001×10^3 mol/s	118.42
II	$biuret_{(m)} \rightarrow urea_{(m)} + HNCO_{(l)}$	1	1.107×10^{20} 1/s	208.23
III	$urea_{(m)} + HNCO_{(l)} \rightarrow biuret_{(m)}$	1 / 1	3.517×10^{11} ml/mol s	75.45
IV	$urea_{(m)} \rightarrow HNCO_{(l)} + NH_{3(g)}$	0.3	2.000×10^4 $mol^{0.7}/ml^{0.7}$ s	74.00
V	$2biuret_{(m)} \rightarrow ammelide_{(s)} + HNCO_{(l)} + NH_{3(g)} + H_2O_{(g)}$	2	3.637×10^{26} 1/s	257.76
VI	$biuret_{(m)} + HNCO_{(g)} \rightarrow CYA_{(s)} + NH_{3(g)}$	1 / 1	9.397×10^{20} ml/mol s	158.68
VII	$biuret_{(m)} + HNCO_{(g)} \rightarrow triuret_{(s)}$	1 / 1	1.091×10^{15} ml/mol s	116.97
VIII	$triuret_{(s)} \rightarrow CYA_{(s)} + NH_{3(g)}$	1	1.238×10^{18} 1/s	194.94
IX	$urea_{(m)} + 2HNCO_{(l)} \rightarrow ammelide_{(s)} + H_2O_{(g)}$	1 / 2	1.274×10^{20} ml^2/mol^2 s^2	110.40
X	$biuret_{(m)} \rightarrow biuret_{(matrix)}$	1	8.193×10^{26} 1/s	271.50
XI	$biuret_{(matrix)} \rightarrow biuret_{(m)}$	1	3.162×10^{09} 1/s	122.00
XII	$biuret_{(matrix)} \rightarrow 2HNCO_{(g)} + NH_{3(g)}$	1	5.626×10^{24} 1/s	266.38
XIII	$urea_{(s)} \rightarrow urea_{(m)}$	1	$1.000 \times 10^{15} \cdot T^{1.5}$ 1/s	160.00
XIV	$ammelide_{(s)} \rightarrow ammelide_{(g)}$	1	1.000×10^{14} ml/mol s	201.67
XV	$HNCO_{(l)} \rightarrow HNCO_{(g)}$	Herz–Knudsen-equation (Huthwelker and Peter, 1996)		

W. Brack, B. Heine, F. Birkhold, M. Kruse, G. Schoch, S. Tischer, O. Deutschmann. Chem. Eng. Sci. 106 (2014)1–8.

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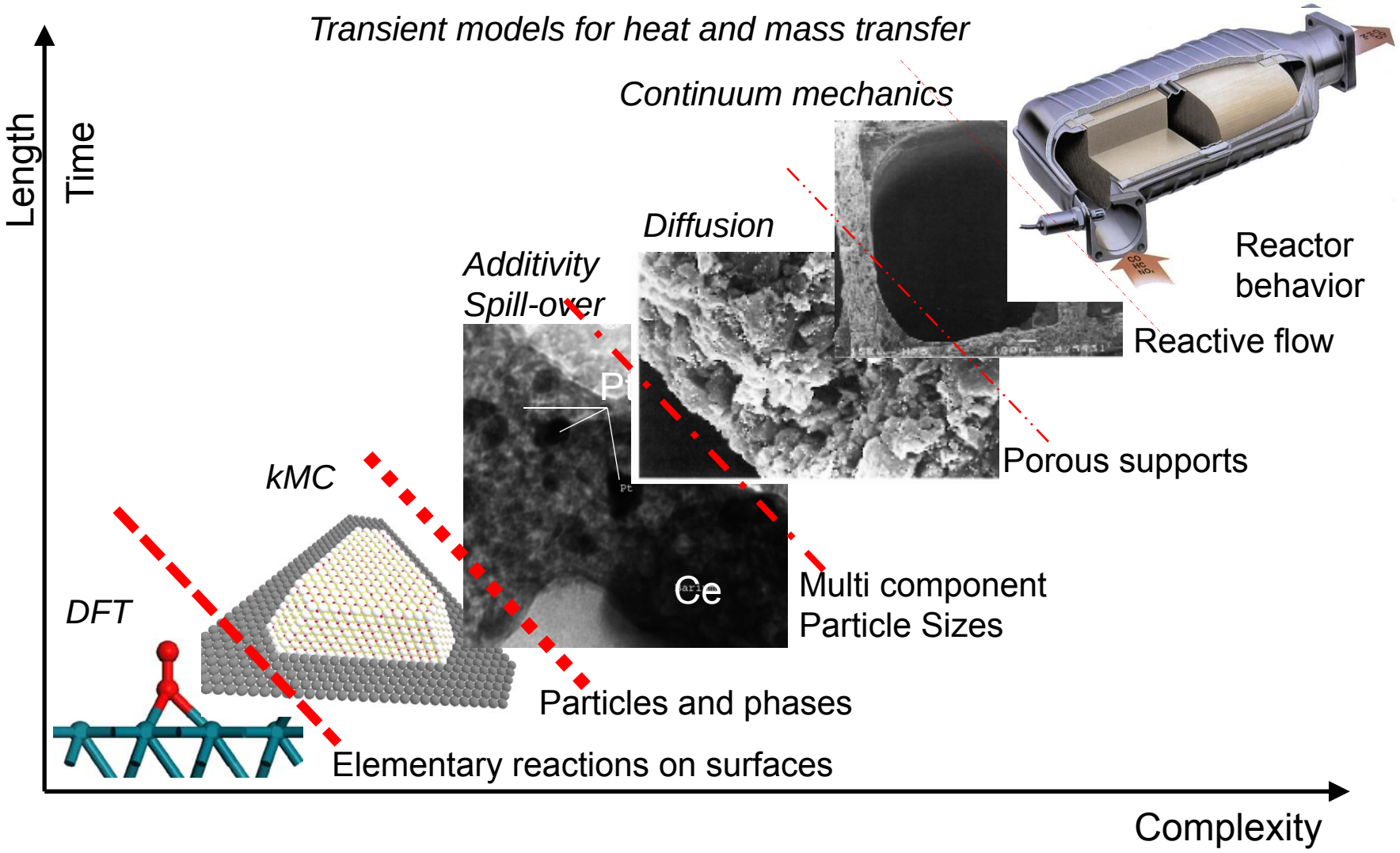
Simulation of catalytic converters from first principles: Dream or nightmare?



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4th International Symposium on Modeling of Exhaust-Gas After-Treatment

MODEGAT IV

Abstract due May 15

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Thank you!

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