Catalytic Combustion: State of the art and modeling needs

OLAF DEUTSCHMANN
Interdisciplinary Center for Scientific Computing (IWR), Heidelberg University
Im Neuenheimer Feld 368, D-69120 Heidelberg,
Phone: (+49)-6221-54 8886, Fax: (+49)-6221-54 8884
deutschmann@iwr.uni-heidelberg.de
http://reaflow.iwr.uni-heidelberg.de/~dmann

- Flow field simulation

- Catalyst materials and reaction kinetics

Catalytic combustion: Wide variety of applications, mainly driven by environmental concerns

Stationary gas turbine

XONON Combustor
Catalytica Combustion Systems, Inc.

VOC removal

Catabrun, Taikisha Ltd.
www.taikisha.co.jp (15/6/2000)

Portable radiant heater

Catalyst SystemTechnologies, Har Hotzvim, Israel

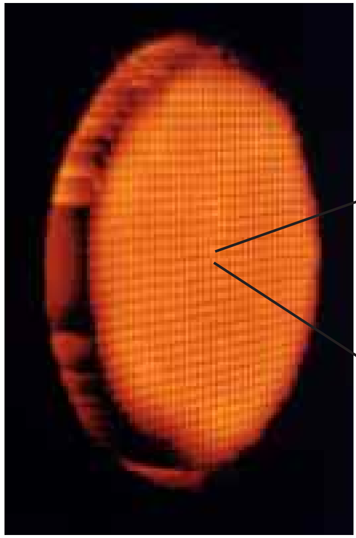
Domestic gas stove

Interpid II, L&S Fireplace Shoppe,
www.lsfireplace.com (15/6/2000)

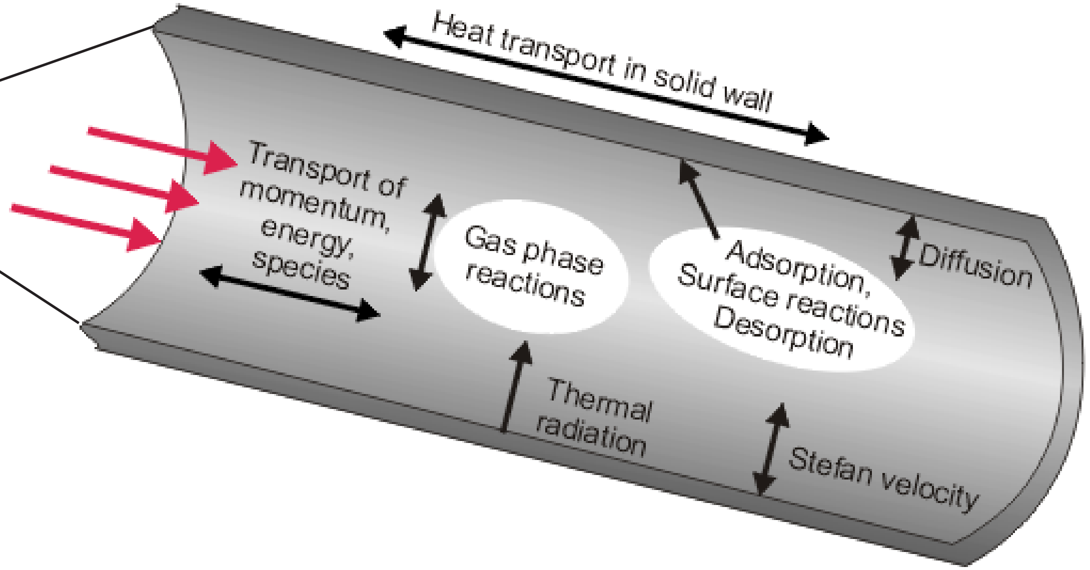
Catalytic converter

Courtesy of J. Eberspächer GmbH & Co.

Reactive flow in a single channel of a catalytic monolith: Varying levels of modeling the transport processes



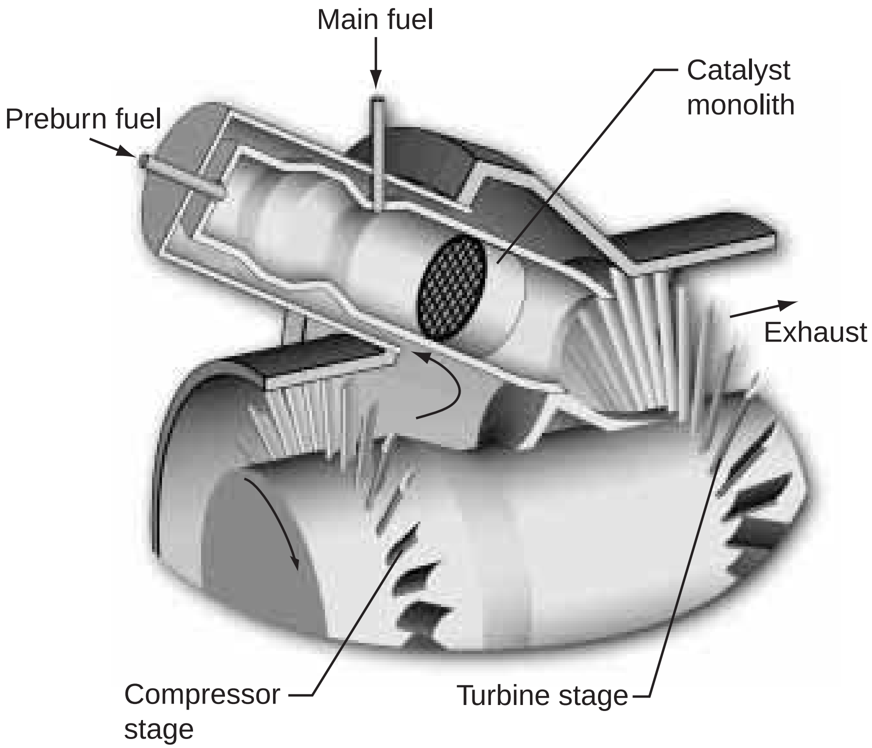
Courtesy of R.W. Dibble, UC Berkeley



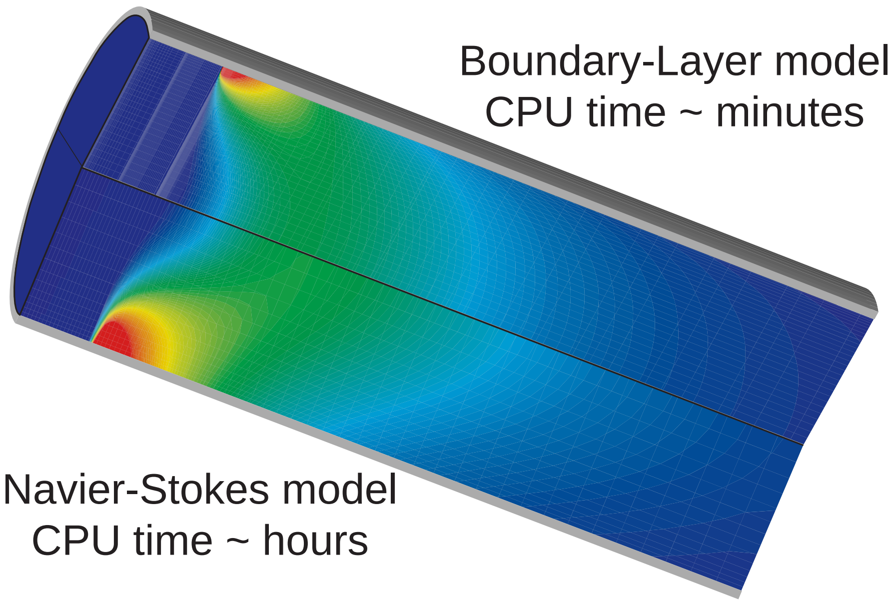
	Navier-Stokes	Boundary-Layer	Plug-Flow
Axial convection	yes	yes	yes
Axial diffusion	yes	no	no
Radial diffusion	yes	yes	no

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

Ultra-Low-Emission Gas-Turbine Technology: Modeling of the Catalytic Combustion Stage



Predicted CO mass fractions in a single channel

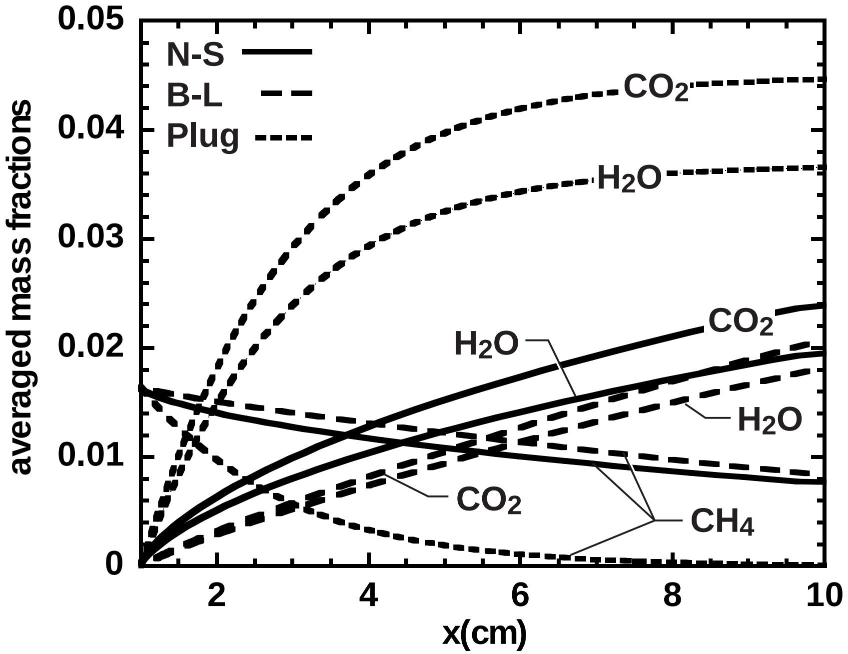


L.L. Raja, R.J. Kee, O. Deutschmann, J. Warnatz, L.D. Schmidt, Catal. Today 59 (2000) 47

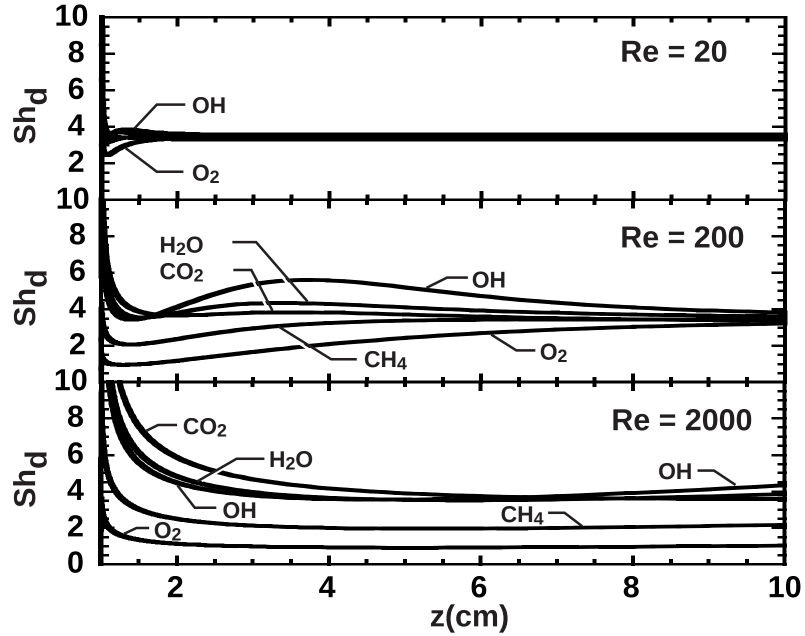
Picture: Courtesy of R.J. Kee, Colorado School of Mines

Mass transport limitation in a single channel of a catalytic monolith: Caution when using the Plug-Flow model

Averaged mass fraction species profiles from the Navier-Stokes, Boundary-Layer and Plug-Flow model



Mass-transfer coefficients for Plug-Flow model can be derived from full models

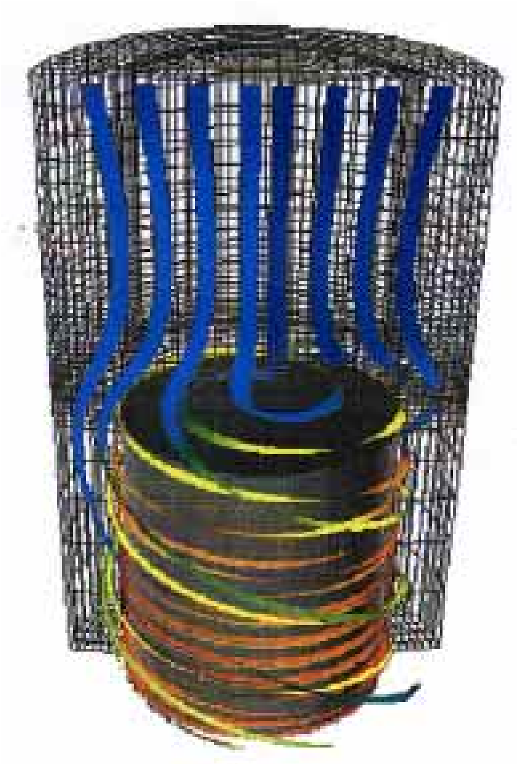


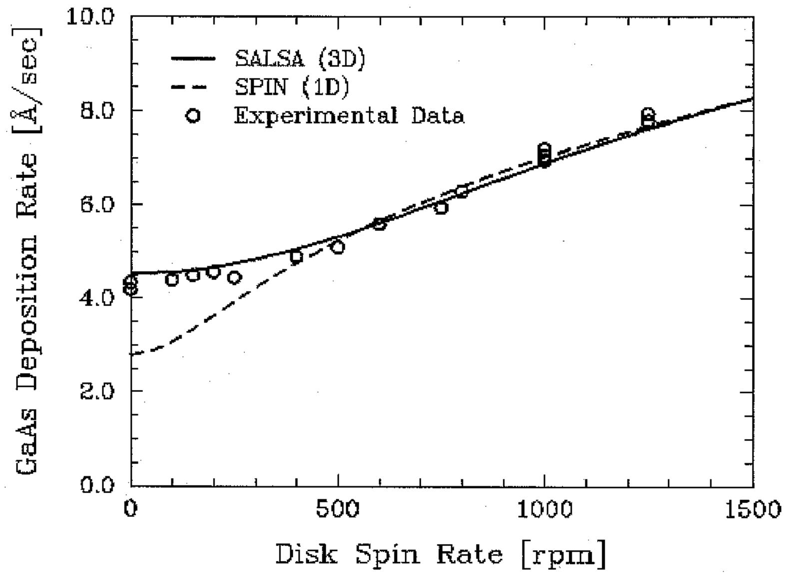
L.L. Raja, R.J. Kee, O. Deutschmann, J. Warnatz, L.D. Schmidt, Catal. Today 59 (2000) 47

Olaf Deutschmann, Second International Workshop on CHEMKIN in Combustion, Edinburgh/Scotland, July 30, 2000

Modeling CVD in a rotating disk reactor: Caution when using simplified models

Comparison of 3D (MPSalsa) and 1D (SPIN) simulation reveals weakness of the 1D model at low disk spin rates. Both codes use CHEMKIN software.

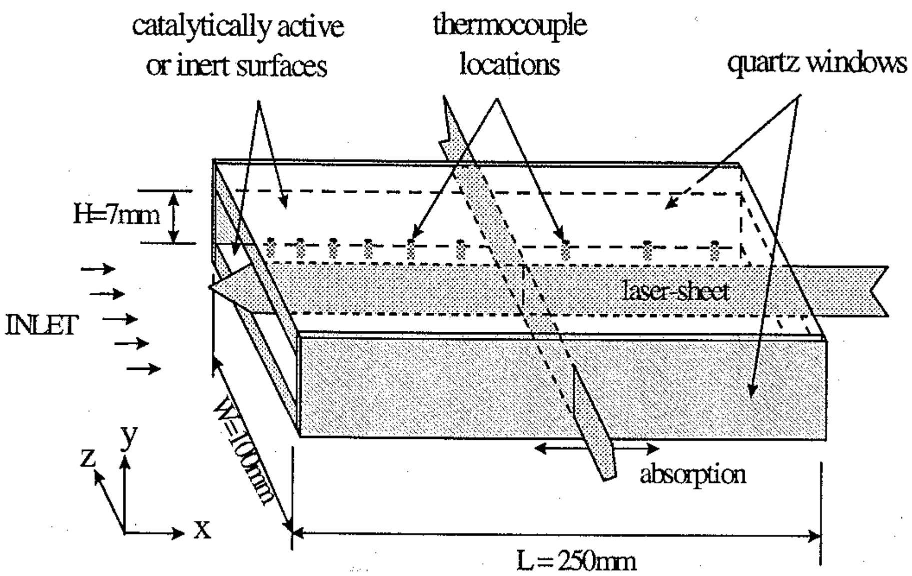


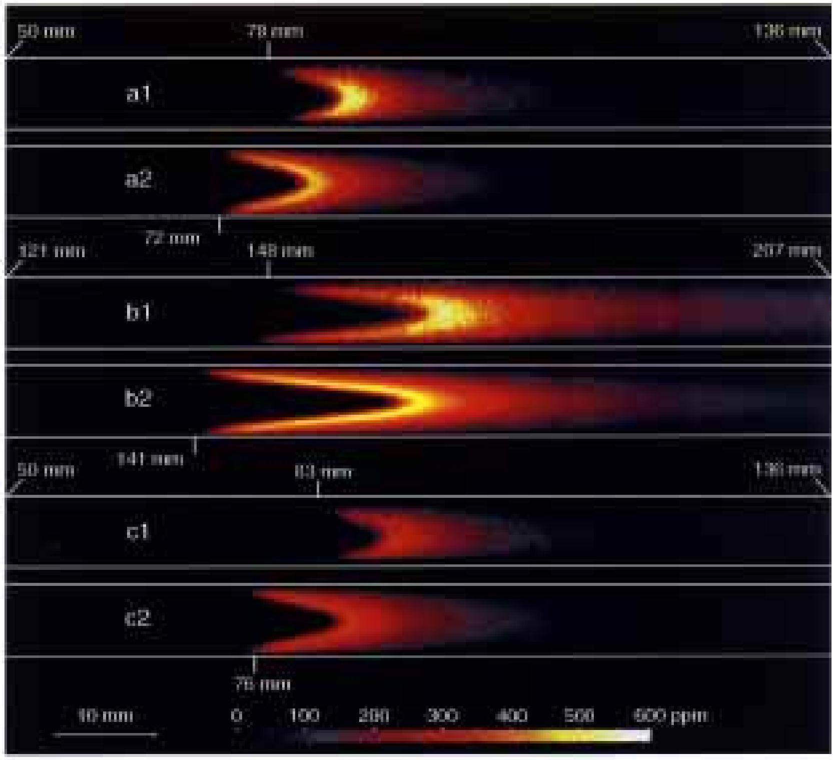


K.D. Devine, G.L. Hennigan, S.A. Hutchinson, A.G. Salinger, J.N. Shadid, R.S. Tuminaro: High Performance MP Unstructured Finite Element Simulation of Chemically Reacting Flows. Proc. of SC97, San Jose, CA, Nov. 15-21, 1997

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 using CHEMKIN) OH profiles in a laminar plane channel flow

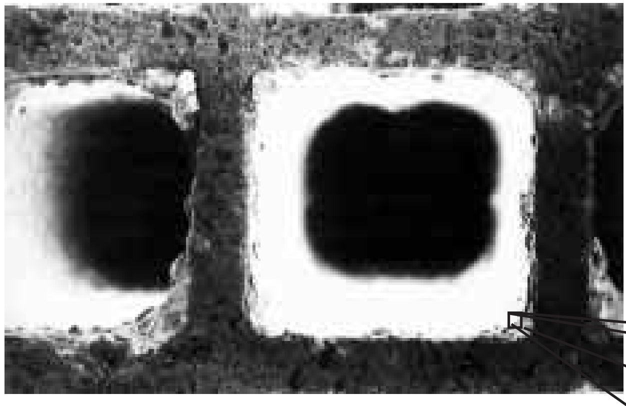




U. Dogwiler, J. Mantzaras, C. Appel, P. Benz, B. Kaeppeli, R. Bombach, A. Arnold. Proc. Combust. Inst. 27 (1998) 2275

Washcoat pore diffusion in catalytic monoliths: Potential source of transport limitation

Monolith channel: Diffusion and convection (gas phase)



Molecular diffusion

$$D_{eff} = \frac{\varepsilon_P}{\tau} D_{mol,i}$$

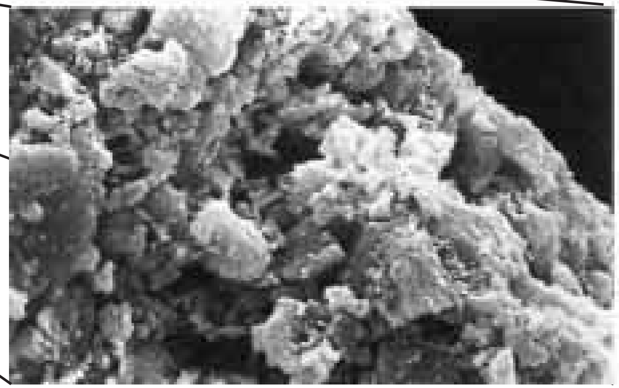
Knudsen-diffusion

$$D_{eff} = \frac{\varepsilon_P}{\tau} \frac{d_P}{3} \sqrt{\frac{8RT}{\pi M_i}}$$

Boundary condition at gas-surface interface

$$\eta F \dot{s}_i M_i = (j_{ir} + \rho Y_i v_{st})$$

$$\eta = \frac{tanh\,(\phi)}{\phi} \qquad \phi = L\sqrt{\frac{s_i \gamma}{D_{eff} c_{i,0}}}$$

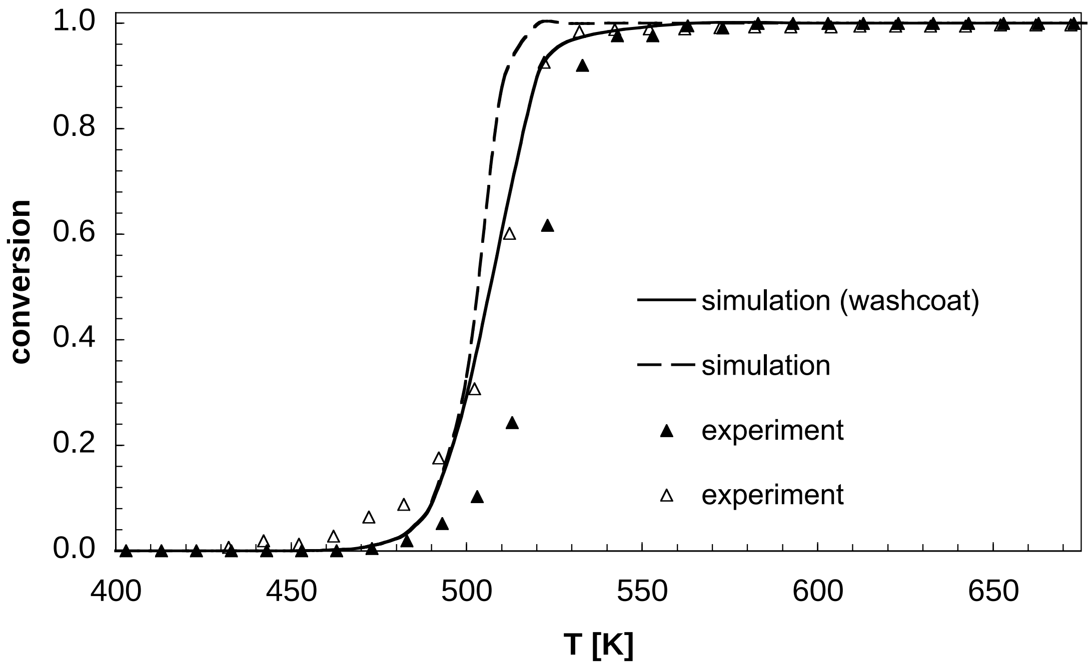


Washcoat: Diffusion in porous media

Washcoat in a single channel of an automotive catalytic converter: Impact of pore diffusion on conversion

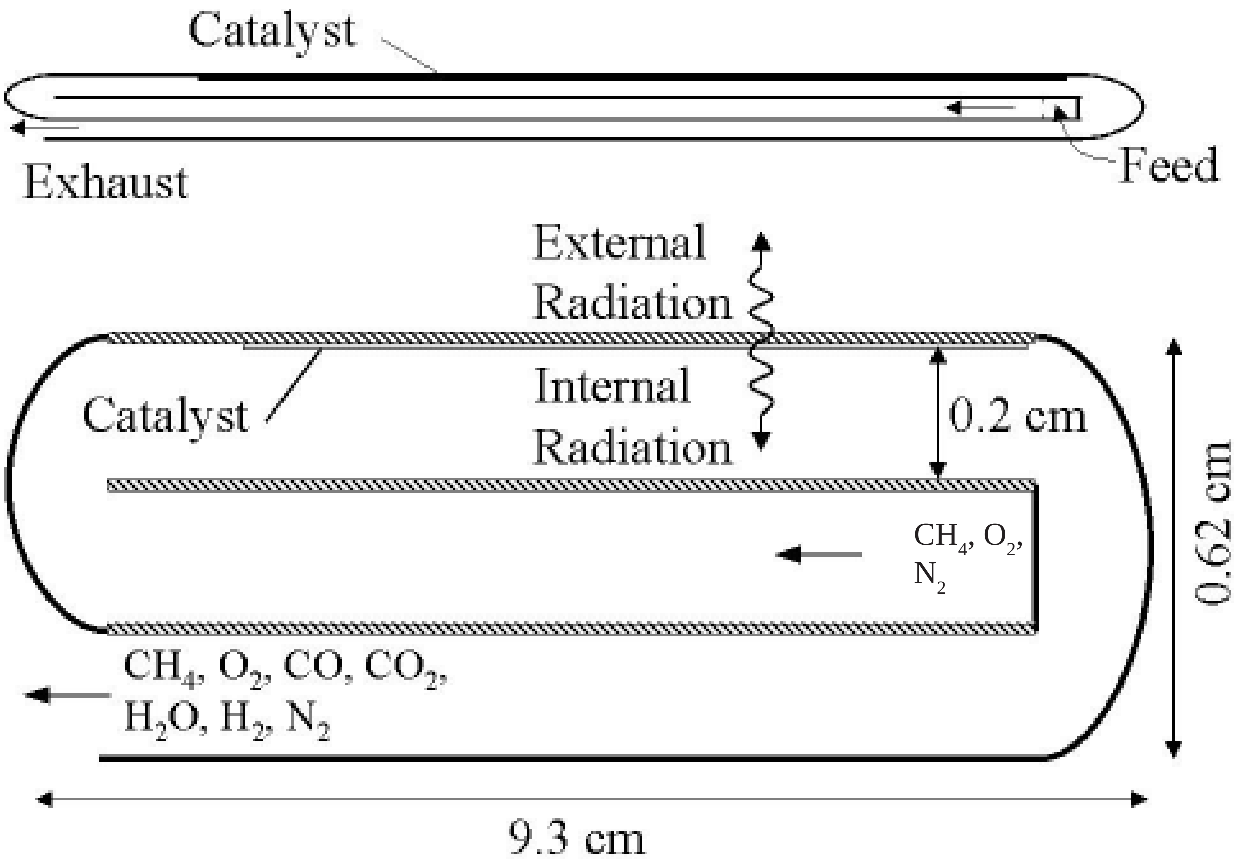
HC-SCR on Pt/Al_2O_3: Conversion of propane as a function of temperature, simulation vs. experiment

Picture: Courtesy of J. Eberspächer GmbH&Co.



(Chatterjee / Deutschmann / Warnatz, 2000)

Catalytic radiant burner with energy recuperation: Experimental setup

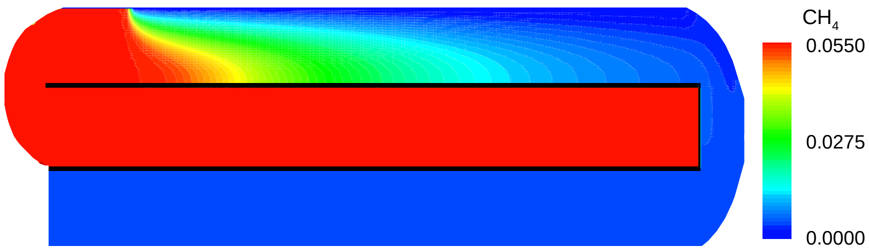


J. Redenius, L.D. Schmidt, O. Deutschmann, AIChE J. (submitted)

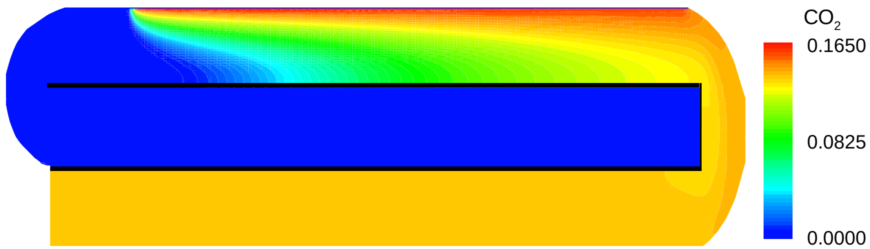
Catalytic radiant burner with energy recuperation: Simulation uses FLUENT and DETCHEM

IWR Universität Heidelberg

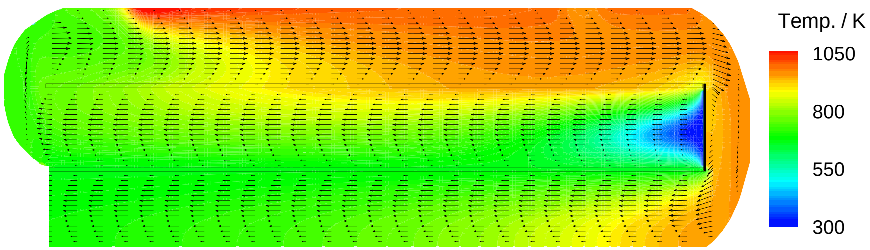
Methane



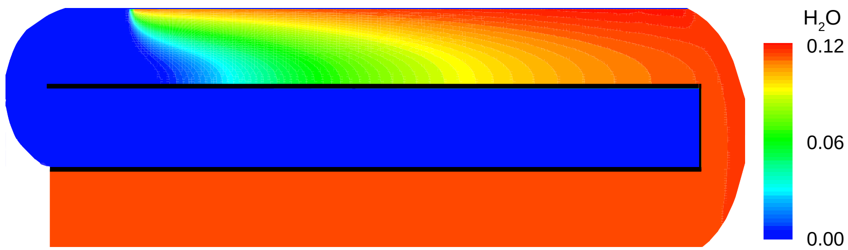
Carbon dioxide



Temperature



Water



J. Redenius, L.D. Schmidt, O. Deutschmann: AIChE J. (submitted)

FLUENT: http://www.fluent.com DETCHEM: http://www.reactive-flows.com

Modeling surface reactions in catalytic combustion: Kinetics depends on coverage and catalyst structure

Assumptions mostly made:

- Adsorbates are assumed to be randomly distributed on the surface (mean field approximation)
- Surface is viewed as being uniform, the local environment is not taken into account (edges, defects, terraces, different structures)

Reaction rate:

$$\dot{s}_i = \sum_{k=1}^{K_s} \nu_{ik} k_{f_k} \prod_{i=1}^{N_g+N_s+N_b} [X_i]^{\nu'_{ik}}$$

Sticking coefficient:

$$k_{f_i}^{\mathrm{ads}} = S_i^0 \frac{1}{\Gamma^\tau} \sqrt{\frac{RT}{2\pi M_i}}$$

Rate coefficient:

$$k_{f_k} = A_k T^{\beta_k} \exp\left[\frac{-E_{a\,k}}{RT}\right] f(\theta_1, \theta_2 \ldots)$$

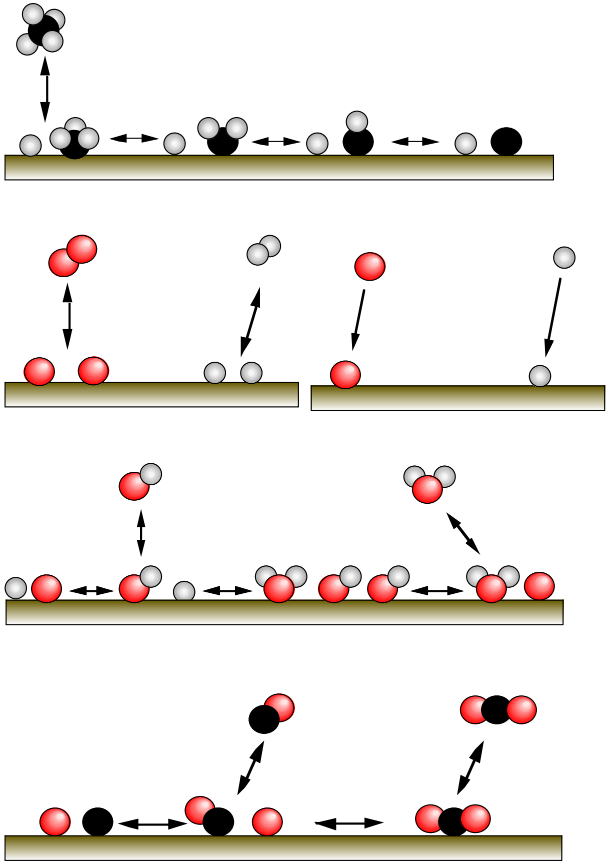
$$f(\theta_1, \theta_2 \ldots) = \prod_i 10^{\eta_i [\theta_i]} [\theta_i]^{\mu_i} \exp\left(\frac{\varepsilon_i \theta_i}{RT}\right)$$

$$k_{r_k}(T) = \frac{k_{f_k}(T)}{K_{c_k}(T)}$$

Binding states of adsorption on the surface vary with the surface coverage of all adsorbed species.

OD_00_092

Catalytic combustion of methane over platinum: Proposed scheme of surface reactions



D. A. Hickman, L. D. Schmidt, AIChE J. 39 (1993), 1164.
O. Deutschmann, F. Behrendt, and J. Warnatz: Catal. Today 21 (1994), 461.

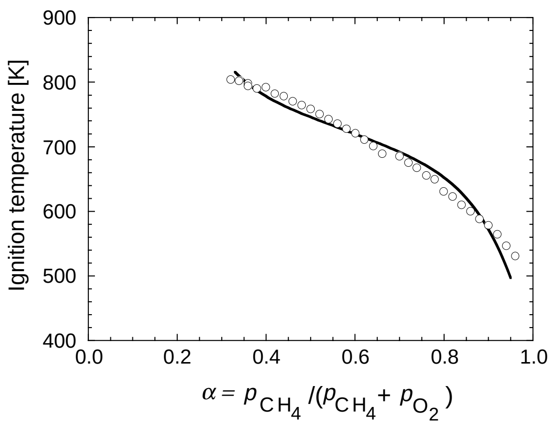
Reaction scheme for modeling catalytic ignition of H_2, CO, CH_4 on Pt in SURFACE CHEMKIN format

Reaction	A	b	E(J/mol)	Comment
H2 + 2PT(S) => 2H(S)	0.046	0.0	0	STICK, FORD /PT(S) 1/
2H(S) => H2 + 2PT(S)	3.70E+21	0.0	67400	COV /H(S) 0 0 -6000/
H + PT(S) => H(S)	1.00	0.0	0	STICK
O2+ 2PT(S) => 2O(S)	1.80E+21	-0.5	0	DUP
O2+ 2PT(S) => 2O(S)	0.023	0.0	0	STICK, DUP
2O(S) => O2 + 2PT(S)	3.70E+21	0.0	213200	COV /O(S) 0 0 -60000/
O + PT(S) => O(S)	1.00	0.0	0	STICK
H2O + PT(S) => H2O(S)	0.75	0.0	0	STICK
H2O(S) => H2O + PT(S)	1.0E13	0.0	40300	
OH + PT(S) => OH(S)	1.00	0.0	0.0	STICK
OH(S) => OH + PT(S)	1.00E13	0.0	192800	
H(S) + O(S) = OH(S) + PT(S)	3.70E+21	0.0	11500	
H(S) + OH(S) = H2O(S) + PT(S)	3.70E+21	0.0	17400	
OH(S)+ OH(S) = H2O(S) + O(S)	3.70E+21	0.0	48200	
CO + PT(S) => CO(S)	0.84	0.0	0	STICK, FORD /PT(S) 2/
CO(S) => CO + PT(S)	1.00E+13	0.0	125500	
CO2(S) => CO2 + PT(S)	1.00E+13	0.0	20500	
CO(S) + O(S) => CO2(S) + PT(S)	3.70E+21	0.0	105000	
CH4 + 2PT(S) => CH3(S) + H(S)	0.01	0.0		STICK, FORD/ PT(S) 2.3/
CH3(S)+ PT(S) => CH2(S)s + H(S)	3.70E+21	0.0	20000	
CH2(S)s + PT(S) => CH(S) + H(S)	3.70E+21	0.0	20000	
CH(S) + PT(S) => C(S) + H(S)	3.70E+21	0.0	20000	
C(S) + O(S) => CO(S) + PT(S)	3.70E+21	0.0	62800	
CO(S) + PT(S) => C(S) + O(S)	1.00E+18	0.0	184000	

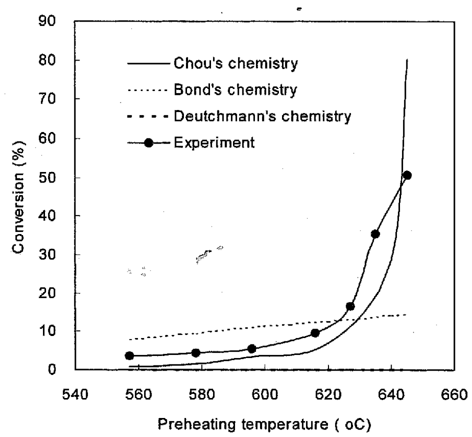
Courtesey of L.L. Raja, R.J. Kee, Colorad School of Mines
http://reaflow.iwr.uni-heidelberg.de/~dmann/sm_ch4_ox_1.2_SURFACECHEMKIN

O. Deutschmann, R. Schmidt, F. Behrendt, J. Warnatz: Proc. Comb. Inst. 26 (1996), 1747

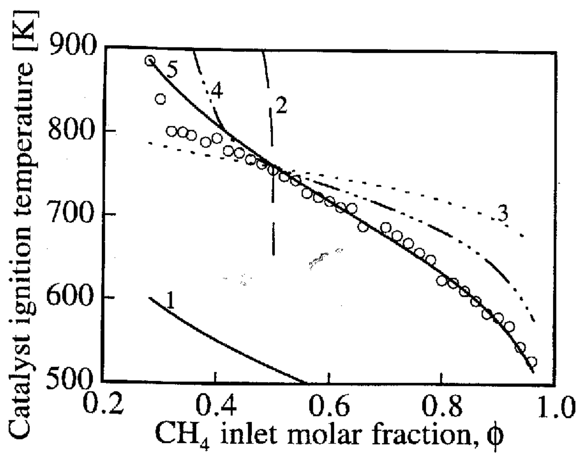
Different kinetics proposed for CH_4 combustion on Pt: Mechansisms are often based on few experimental data



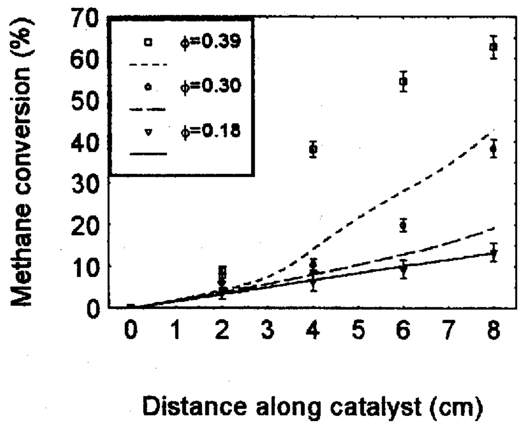
O. Deutschmann, R. Schmidt, F. Behrendt, J. Warnatz: Proc. Comb. Inst. 26 (1996), 1747



Y.S. Seo, S.J. Cho, S.K. Kang, H.D. Shin, Catal. Today 59 (2000) 75.

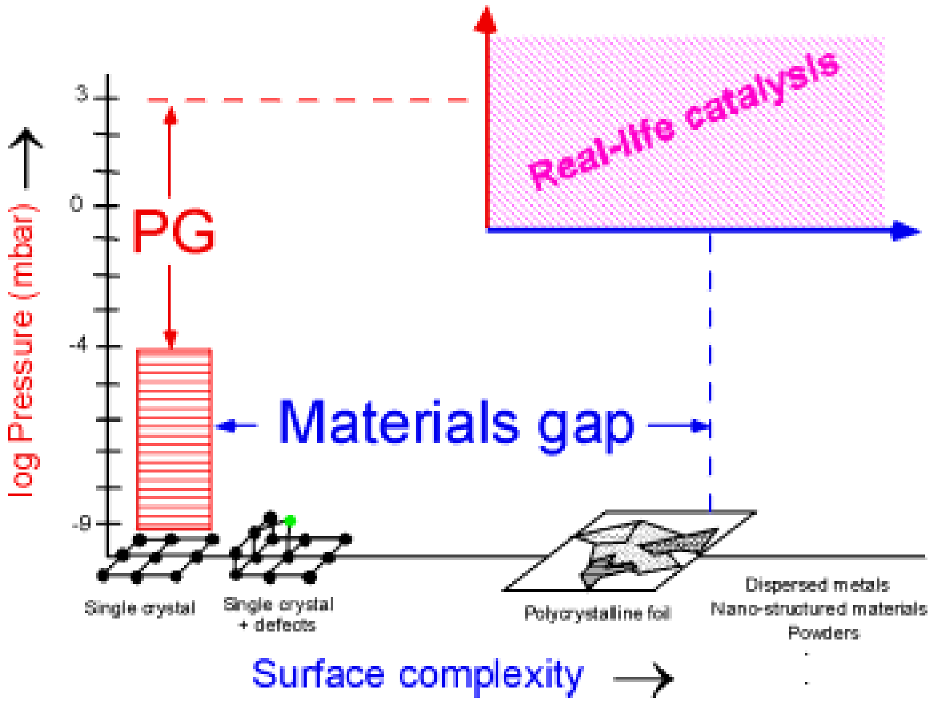


P.-A. Bui, D.G. Vlachos, P.R. Westmoreland, Surf. Sci. 385 (1997) L1029

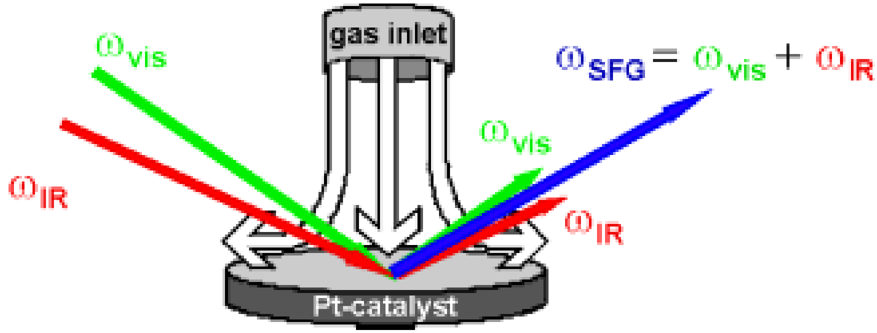


T.C. Bond, R.A. Noguchi, C.-P. Chou, R.K. Mongia, J.-Y. Chen, R.W. Dibble, Proc. Comb. Inst. 26 (1996) 1771

Kinetic data for surface reactions at practically relevant conditions and technically used catalysts



Laser-spectroscopic methods such as SFG (Sum Frequency Generation) can bridge the pressure and materials gap



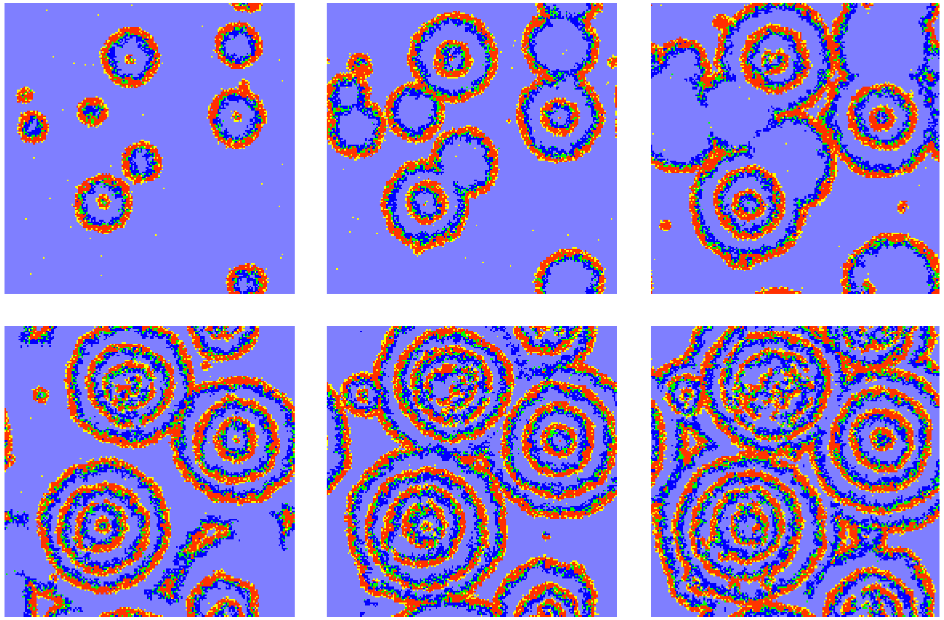
=> Quantitative determination of surface coverage with adsorbed species

R. Kissel-Osterrieder, F. Behrendt, J. Warnatz, U. Metka, H.-R. Volpp, J. Wolfrum. Proc. Combust. Inst. 28 (2000)

Coupling between surface structures and chemical reactions: Dynamic Monte-Carlo simulations

Catalytic oxidation of CO on platinum; 2D resolution of the non-homogeneous layers of adsorbed species; experiment vs. simulation

Pt(110), PEEM, 0.2 x 0.3 mm^2, T = 427 K, p_{O2}= $32 \cdot 10^{-3}$ mbar, p_{CO} $3 \cdot 10^{-3}$ mbar, Δt = 4.1/ 30 s



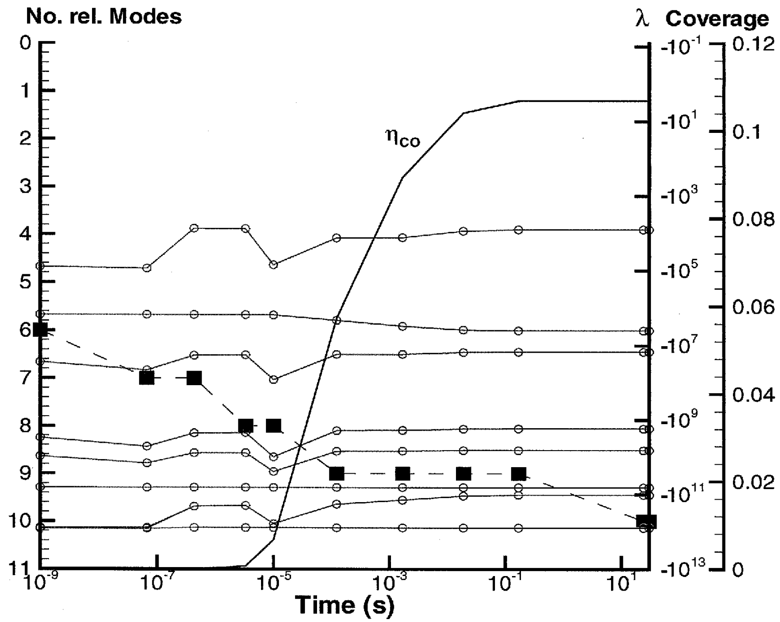
Target pattern on Pt(100), Δt = 10 s, 1000 x 1000 lattice, 0.25 x 0.25 mm^2, T = 490 K, p_{O2}= $50 \cdot 10^{-3}$ mbar, p_{CO} $1.5 \cdot 10^{-3}$ mbar

S. Jakubit, H.H. Rotermund, W. Engel, A.von Oertzen, G. Ertl. Phys. Rev. Lett. 65 (1990) 3013

R. Kissel-Osterrieder, F. Behrendt, J. Warnatz. Proc. Combust. Inst. 28 (2000)

Intrinsic Low-Dimensional Manifolds of Heterogeneous Combustion Processes

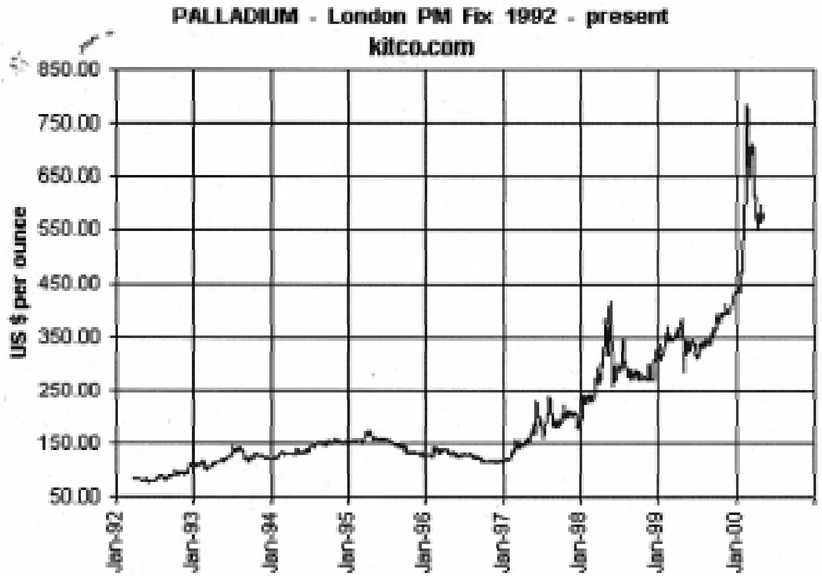
Application of the ILDM approach for the reduction of a detailed reaction mechanism describing the oxidation of methane on platinum in a stagnation point flow configuration

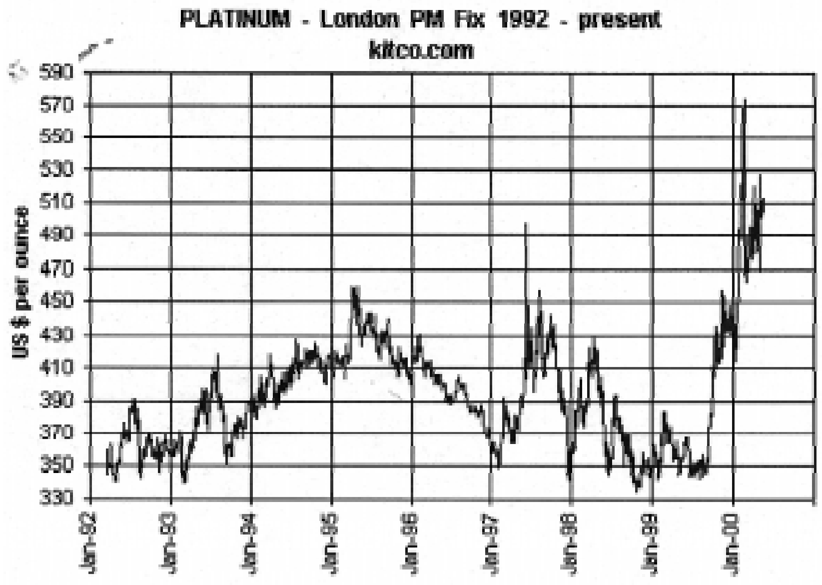


The number of relaxed modes (■) increases with time until all ten chemical time scales have relaxed (chemical equilibrium on the surface).

X. Yan, U. Maas. Proc. Comb. Inst. 28 (2000)

Catalyst materials for catalytic combustion: Variation of market prices of noble metals





Source: http://www.kitco.com, 20.07.2000

Palladium and metal-substituted hexaluminates: Catalyst materials for catalytic combustion

Palladium and metal-substituted hexaluminates are catalysts of great interest for gas turbine applications

Comparison of methane oxidation rate at 400°C, 2% CH_4 in air at 1 atm		
Material	Areal rate (10^{-7} mol m^{-2} s^{-2})	Surface area (m^2 g^{-1})
Pd/Al_2O_3	140	2
Pt/Al_2O_3	50	1
$Sr_{0.8}La_{0.2}MnAl_{11}O_{19}$	0.045	70

R.A. Dalla Betta. Catalysis Today 35 (1997) 129

Wide variety of studies on the complexity of Pd catalysts exists (phase transformation and activity of Pd/PdO, hydroxide formation, interaction with support, support sintering, vaporization, lightoff, aging)

but *no detailed reaction scheme has been established yet*

Catalytic combustion: Modeling needs

- Use of adequate flow field models for the simulation of catalytic combustion devices

- CFD tools including detailed chemistry models are meanwhile available
  but they are very time-consuming and still have problems solving very stiff systems

- Consideration of pore diffusion in washcoats

- More accurate development of heterogeneous reaction schemes needed
  (distribution of rxn mechanisms in electronic form, well-defined experiments,
  accurate description of flow field and potential homogeneous reactions)

- Studies of heterogeneous reaction kinetics at relevant conditions
  (pressure and materials gap)