Entwicklung von Reaktionsmechanismen für heterogen-katalysierte Reaktionen

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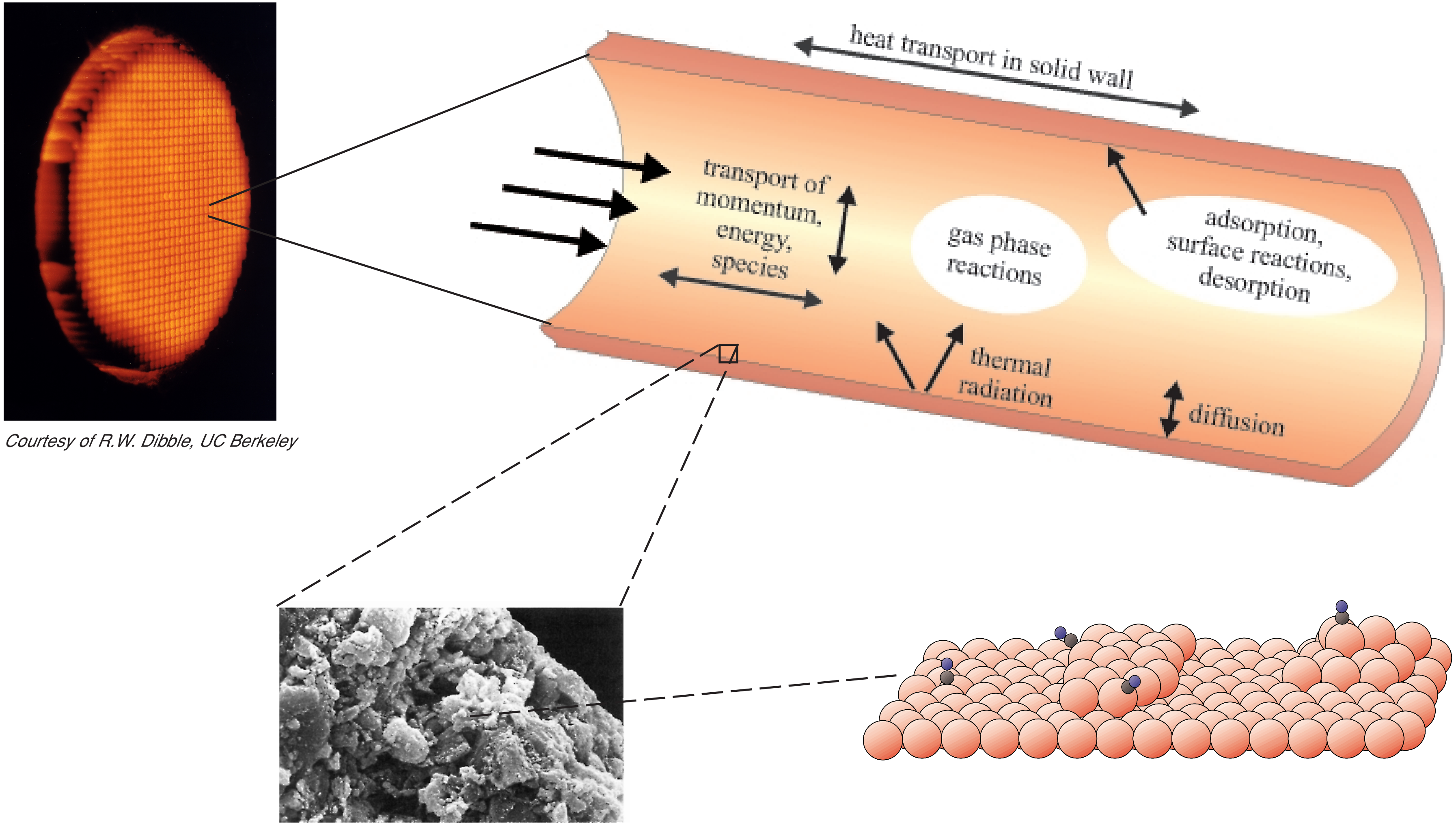
Objective: Development of appropriate models for hetereogenous-catalytic reactions



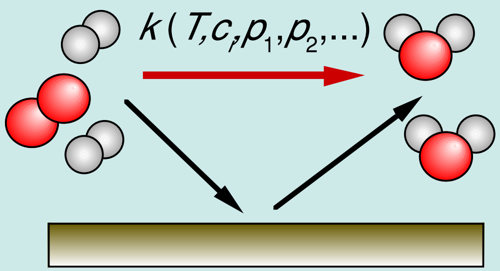
Courtesy of R.W. Dibble, UC Berkeley

Complexity of heterogeneous-catalytic reactions: Reaction rate is specific to the catalyst formulation

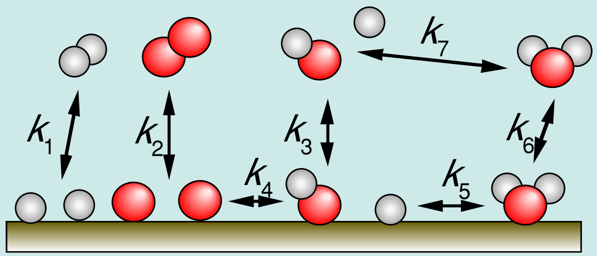
Reaction rate expression depends on:

- catalytic material type and catalyst support,
- type and structure of washcoat,
- method of manufacture,
- surface structures,
- temporal history,
- recrystallisation phenomena,
- solid bulk modification.

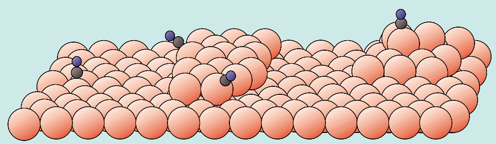
Global kinetics
(macroscopic behavior)



Mechanistic approach
(mean field approximation)



Elementary kinetics
(single microscopic steps)



Modeling heterogeneous-catalytic reactions: Mean field approximation

Assumptions:

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

Reaction rate:

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

Surface coverage:

$$\theta_i = \frac{c_i \sigma_i}{\Gamma}$$

Sticking coefficient:

$$k_{f_k}^{ads} = \frac{S_i^0}{1 - S_i^0 \theta_v / 2} \frac{1}{\Gamma_i^\tau} \sqrt{\frac{RT}{2\pi M_i}}$$

Rate coefficient:

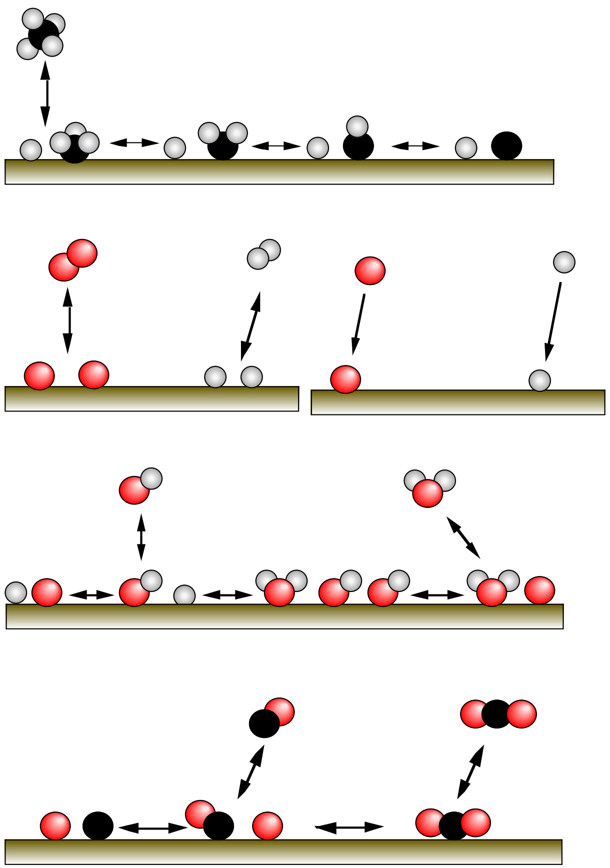
$$k_{f_k} = A_k T^{\beta_k} \exp\left[\frac{-E_{a_k}}{RT}\right] f(\theta_1, \theta_2 \ldots)$$

$$f(\theta_1, \theta_2 \ldots) = \prod_{i=1}^{N_s} \theta_i^{\mu_{i_k}} \exp\left[\frac{\epsilon_{i_k} \theta_i}{RT}\right]$$

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

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

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.

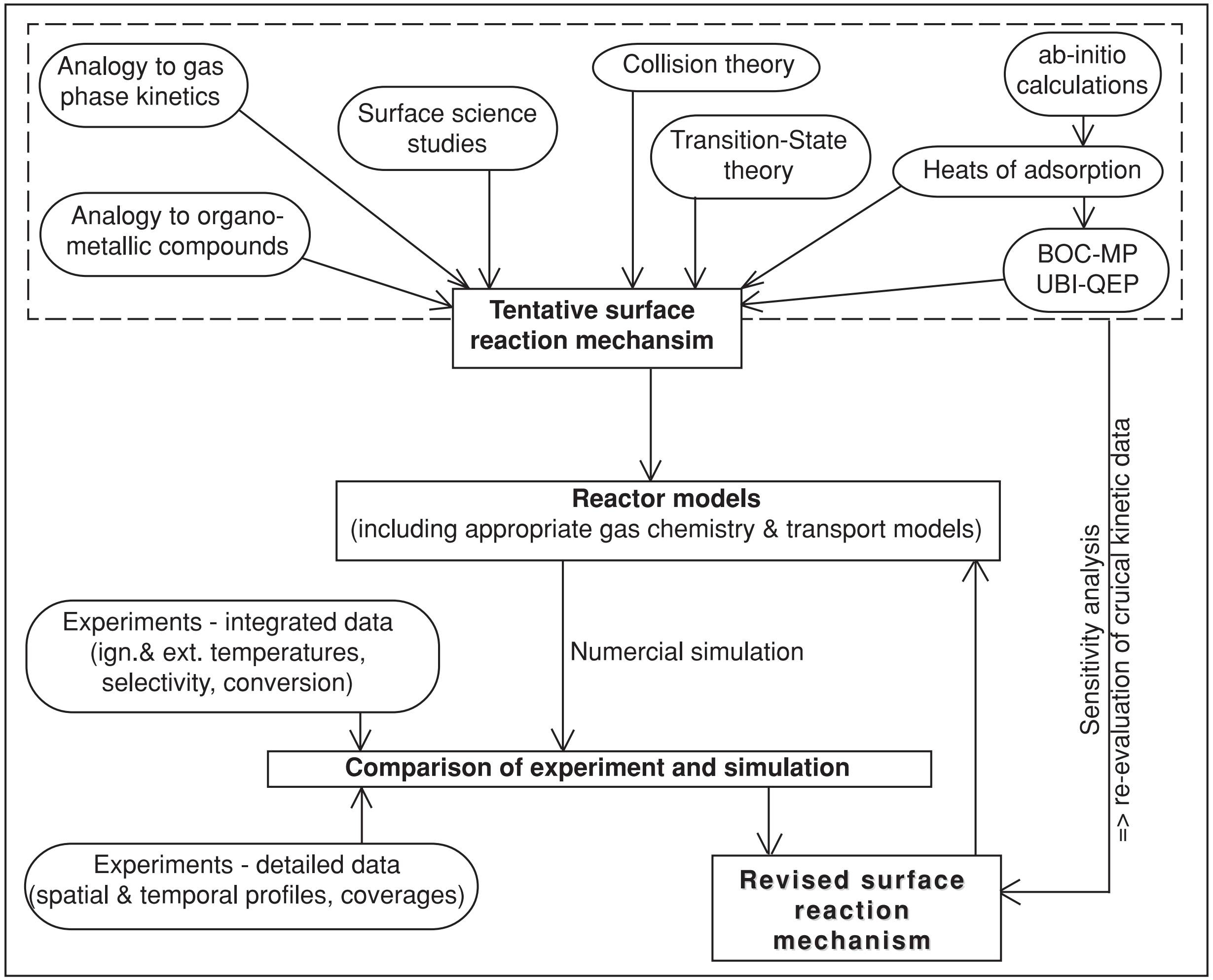
Reaction scheme for modeling catalytic ignition of H_2, CO, CH_4 on Pt in SURFACE CHEMKIN format

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	

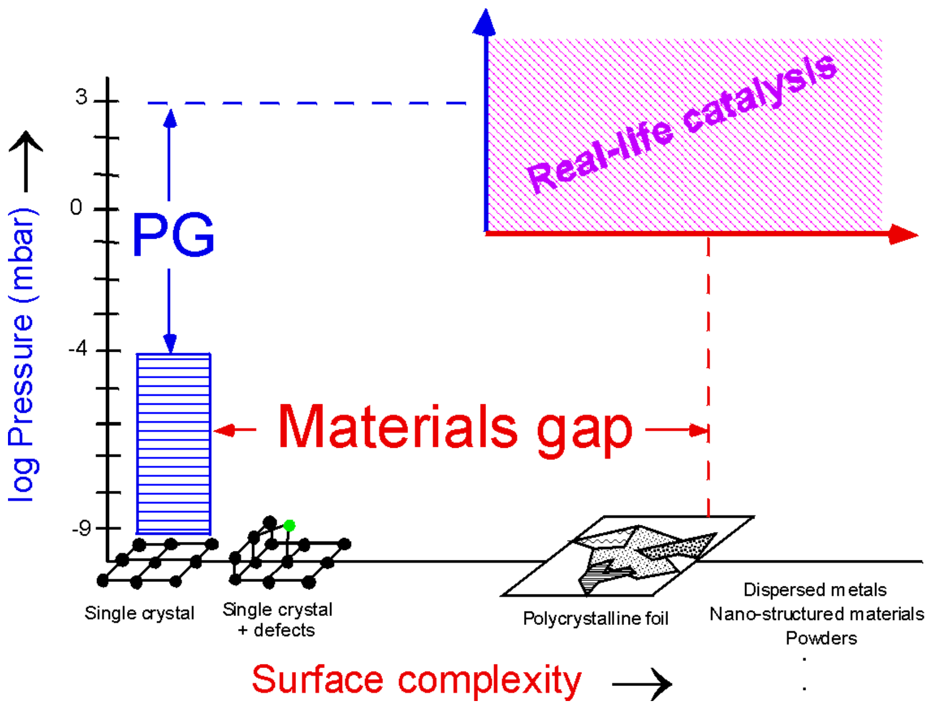
Courtesey of L.L. Raja, R.J. Kee, Colorad School of Mines
http://reaflow.iwr.uni-heidelberg.de/~dmann/sm_ch4_ox_1.2_SURFACECHEMKIN

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

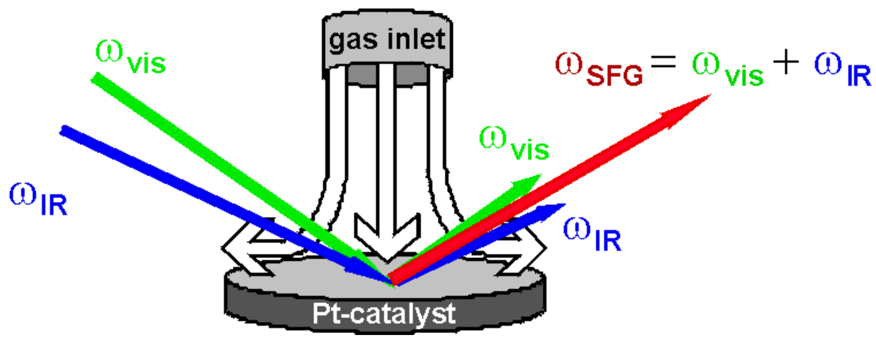
Survey of the methodology of the development of a surface reaction mechanism



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



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

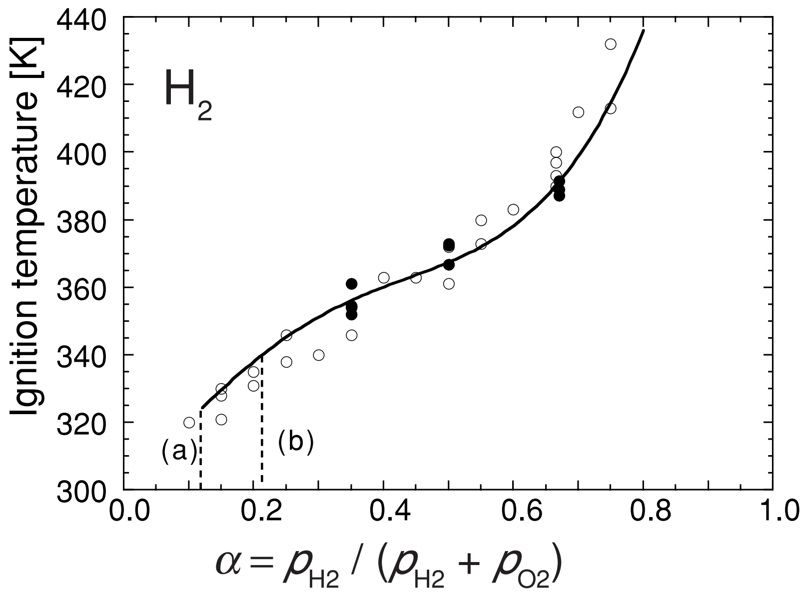


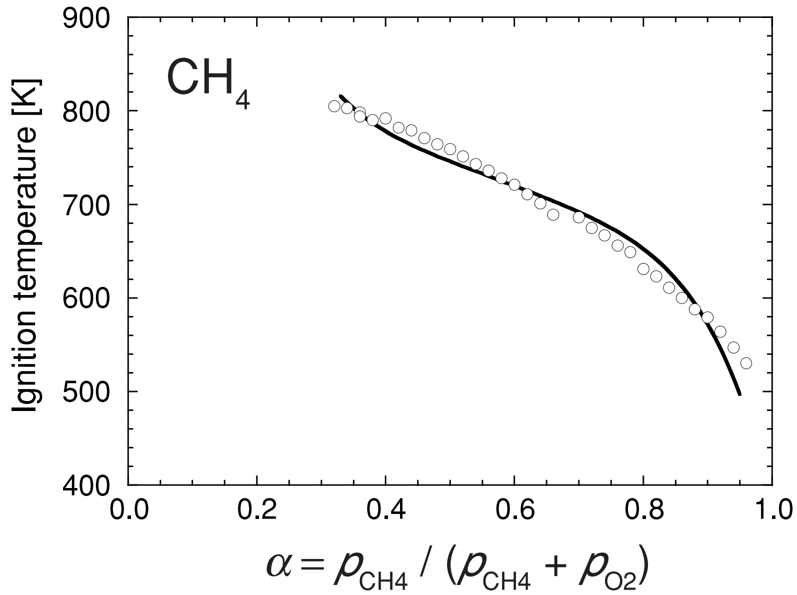
=> Quantitative determination of surface coverage with adsorbed species

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

Catalytic oxidation of hydrogen and methane on platinum: Ignition temperature

Comparison of measured and calculated ignition temperatures in a stagnation point flow on a platinum foil heated resistively.



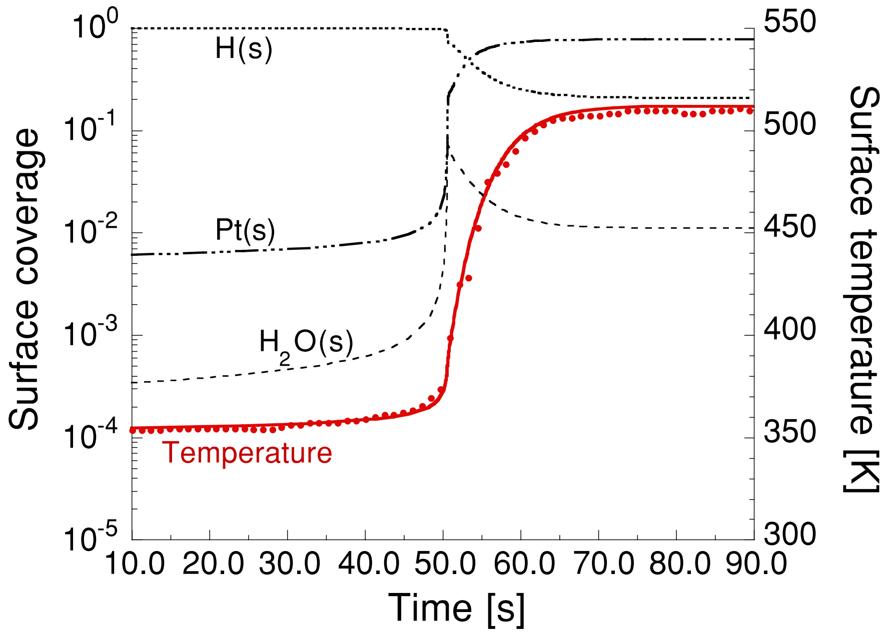


Conditions: T_0 = 298 K, p_{tot} = 1 bar (94% N_2), circles: experiment, line: simulation.

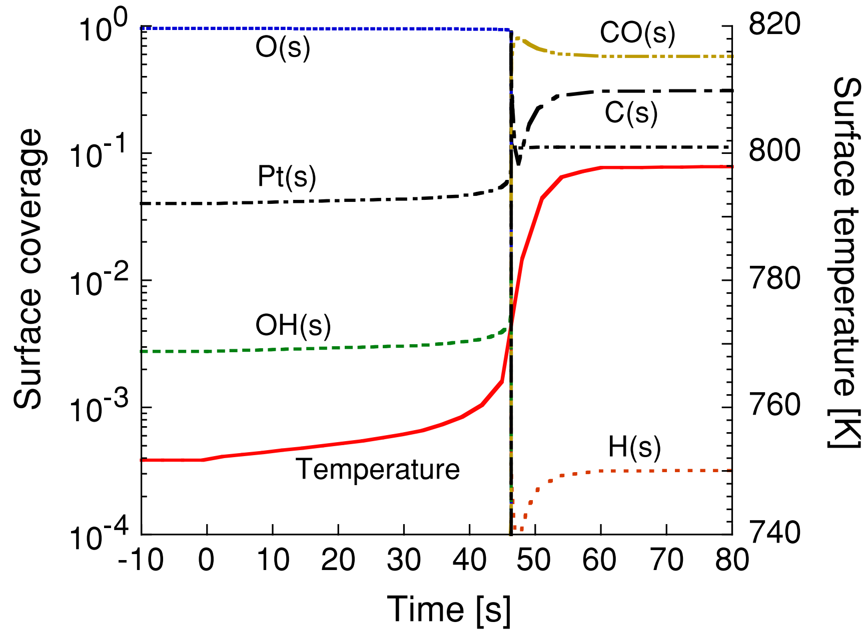
M. Rinnemo, O. Deutschmann, F. Behrendt, B. Kasemo. Combust. Flame 111 (1997) 312-326

O. Deutschmann, R. Schmidt , F. Behrendt, J. Warnatz. Proc. Combust. Inst. 26 (1996) 1747-1754

Transient Modeling of Catalytic Ignition of Hydrogen and Methane Oxidation on Pt: Temperature and Coverage



Conditions: H_2/O_2 mixture (6 % diluted by 94 % N_2, p = 1 bar), $\alpha = p_{H2}/(p_{H2}+p_{O2}) = 0.5$, circles: experiment.

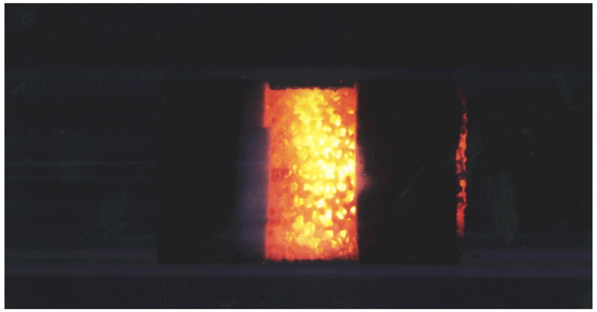


Conditions: CH_4/O_2 mixture (6 % diluted by 94 % N_2, p = 1 bar), $\alpha = C_{CH4}/(p_{CH4}+p_{O2}) = 0.5$.

O. Deutschmann, R. Schmidt, and F. Behrendt. in S. H. Chan (ed.), Transport Phenomena in Combustion, Vol. 1, p. 166-175, Taylor and Francis, 1996.

O. Deutschmann, R. Schmidt , F. Behrendt, J. Warnatz, 26th Symposium (International) on Combustion (1996) 1747-1754

Catalytic oxy-dehydrogenation of ethane: Interaction of transport and heterogeneous and homogeneous reactions

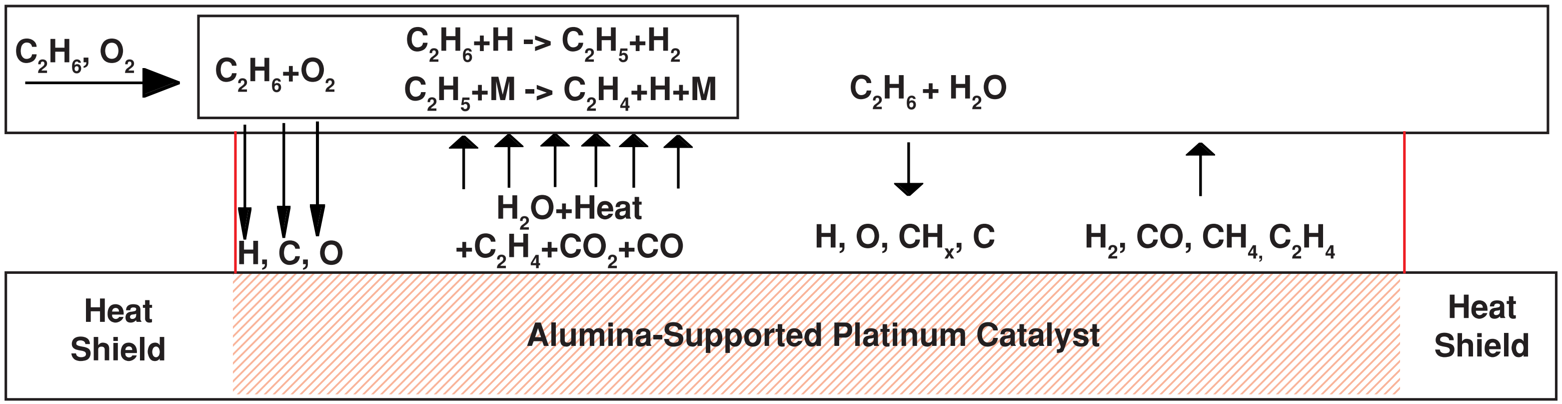


Platinum coated monolith, 1cm in length
Autothermal
Residence time: 5 ms
Ethylene selectivity: > 70%

M. Huff and L. D. Schmidt: AIChE J. 42 (1996), 3484
A. S. Bodke, D. A. Olschki, L. D. Schmidt, E. Ranzi: Science 285 (1999), 712

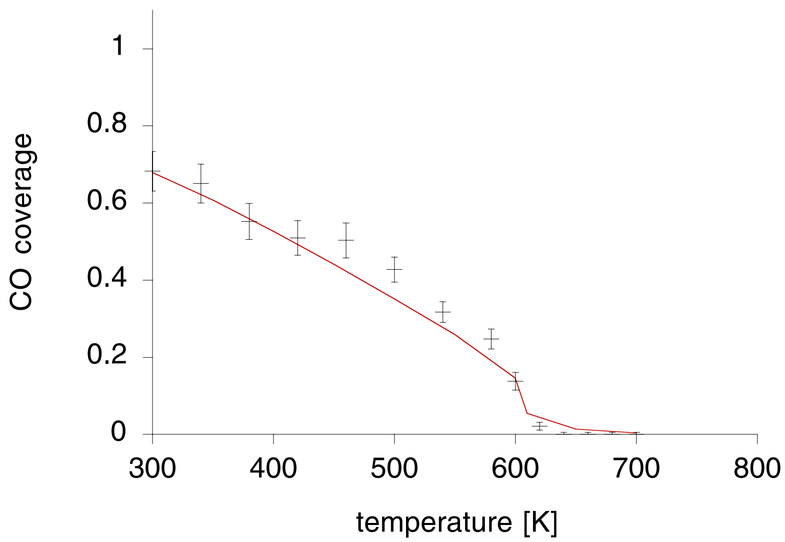
The two-dimensional simulation of a single monolith channel is coupled with detailed gas-phase and surface reaction mechanisms.

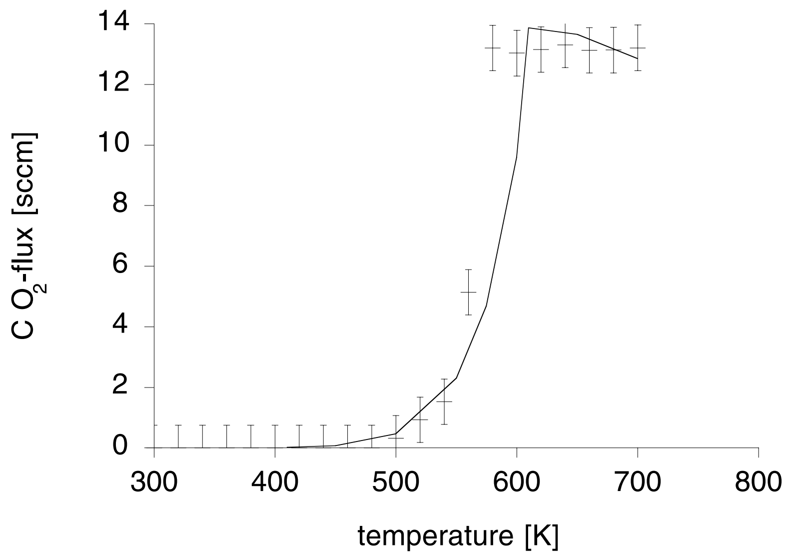
D.K. Zerkle, M.D. Allendorf, M. Wolf, O. Deutschmann. J. Catal.196 (2000) 18



Site heterogeneity of catalytic surfaces: Extension of the mean-field approximation leads to different sub-mechanisms

The CO oxidation on polycrystalline Pt is modelled by a *two-adsorption site* model. The predicted CO surface coverage is compared with data derived from optical sum-frequency generation (SFG) vibrational spectroscopy.



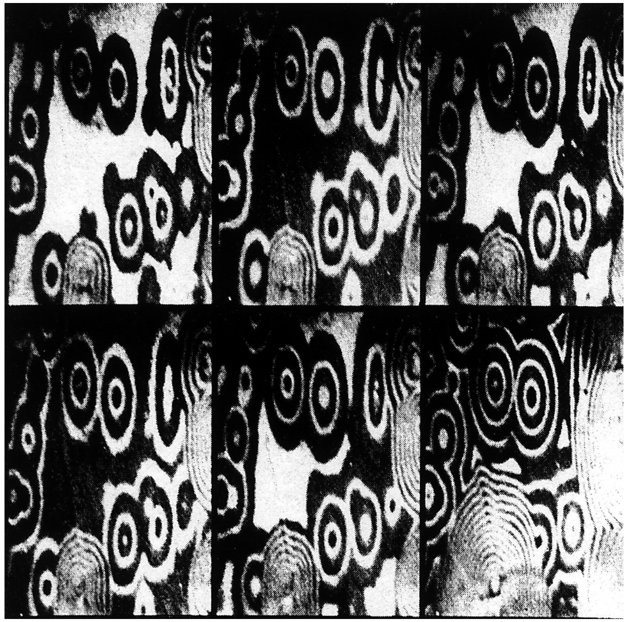


Conditions: CO: 15 sccm; O_2: 30 sccm, Ar: 105 sccm at a total pressure of 20 mbar

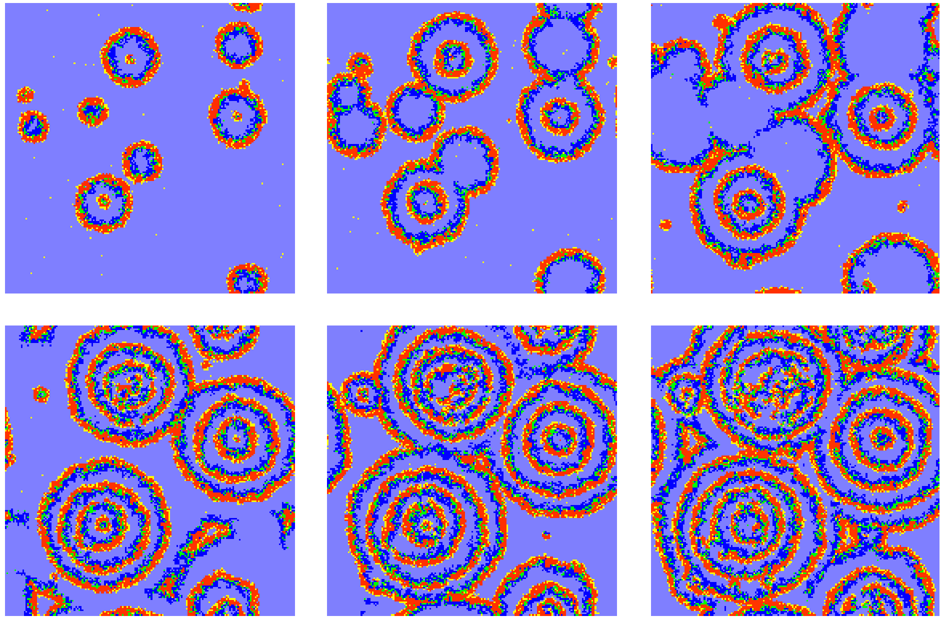
R. Kissel-Osterrieder, F. Behrendt, J. Warnatz, U. Metka, H.-R. Volpp, J. Wolfrum: Experimental and Theoretical Investigation of CO-Oxidation on Platinum: Bridging the Pressure and the Materials Gap, Proc. Combust. Inst. 28 (2000)

Lateral adsorbate interactions: Monte Carlo simulations of the elementary surface processes

Spatio-temporal patterns in catalytic oxidation of CO on platinum; 2D resolution of the non-homogeneous layers of adsorbed species



Pt(110), PEEM, 0.2 x 0.3 mm^2, T = 427 K, p_{O2}= 32·10^{-3} mbar, p_{CO} 3·10^{-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}= 50·10^{-3} mbar, p_{CO} 1.5·10^{-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)

Summary and Outlook

Multi-step mechanisms for simple heterogeneous-catalytic reactions such as

- oxidation of H_2, CO, CH_4, C_2H_6 on noble metals
- NO reduction on noble metals (3WCC)
- methanol and ammonia synthesis

Advanced experimental techniques help to overcome the pressure and materials gap

- high pressure STM
- nonlinear laser methods such as SFG and SHG

Challenges

- Still too little is known about the elementary steps, in particular at high pressure
- Combination of the experimental observations of single elementary steps to the overall picture of the catalyst
- Coupling of the detailed reaction mechanisms with the macroscopic processes (mass and heat transport in the surrounding reactive flow, the washcoat, and the solid bulk)

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