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Development of an unified surface reaction mechanism of oxidation and reforming reactions of light hydrocarbons over platinum

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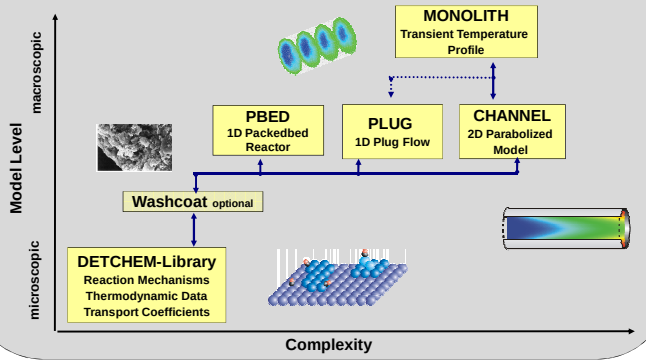
Introduction

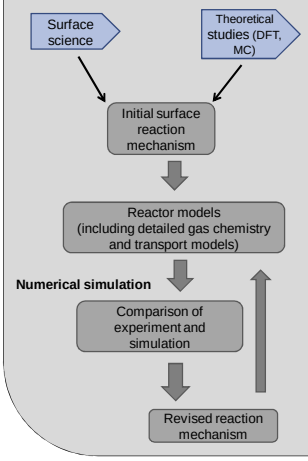
Reforming and partial oxidation of hydrocarbons [1,2], combustion of natural gas [3,4], and the reduction of pollutant emissions from automobiles [5] are important examples for catalytic reactions over platinum.

The application of reliable and predictive modeling of technical reactors used by CFD simulations calls for a better understanding of the kinetics and elementary-step reactions. A detailed surface mechanism is developed against numerous experimentally derived data.
The software DETCHEM [6] was applied for numerical simulation. Steady state and transient models of packed bed, channel and monolithic reactors have been evaluated concerning their ability to describe laboratory experiments specific.

Numerical Model, DETCHEM Package



Modeling approach

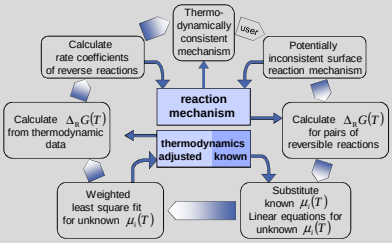


Thermodynamic Consistency

Equilibrium reaction

$$\nu'_1 A_1 + \nu'_2 A_2 + \ldots \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \nu''_1 A_1 + \nu''_2 A_2 + \ldots$$

$$\frac{k_f(T)}{k_r(T)} = \exp\left(-\frac{\Delta_R G^{\ominus}(T)}{RT}\right) \frac{\prod_i \left(c_i^{\ominus}\right)^{\nu'_i}}{\prod_i \left(c_i^{\ominus}\right)^{\nu''_i}}$$



Mean field approximation

- 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

Adsorption

$$\dot{s}_i = S_i^{\text{eff}} \sqrt{\frac{RT}{2\pi M_i}} c_i$$

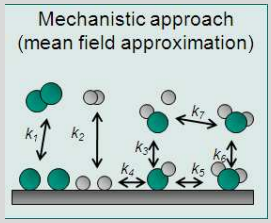
Surface coverage

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

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

Rate expression

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

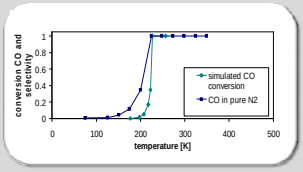


- Should include all possible paths for formation of the chemical species
- Should be applicable over a wide range of conditions
- Needs to be evaluated against numerous experimentally derived data
- Crucial steps in the mechanism ought to be define

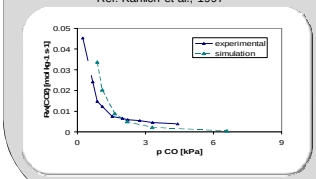
Simulation Results

Experimental CO oxidation results (dots) of different reactor systems were simulated (solid line) by corresponding DETCHEM software tools.

Packedbed

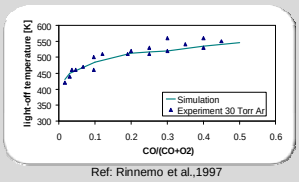


Ref: Kahlich et al., 1997

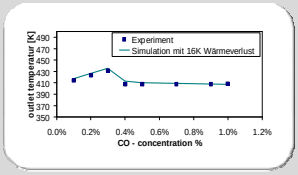


Ref: Nibbelke et al., 1997

Channel

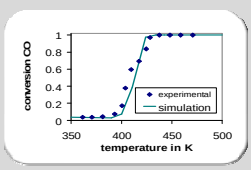


Ref: Rinnemo et al.,1997

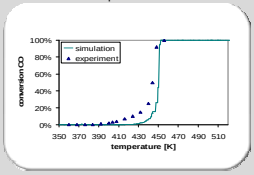


Ref: Sun et al., 2003

Monolith



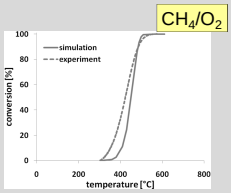
own experiment 2010



Ref: Salomons et al., 2006

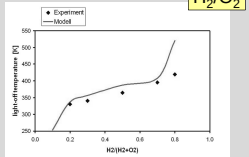
Further sub-mechanisms are verified against experimental measurements for hydrogen oxidation, methane partial oxidation and steam reforming of methane to develop a unified surface mechanism.

CH_4/O_2



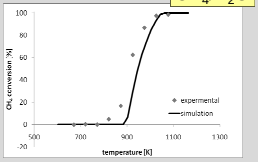
own experiment 2010

H_2/O_2



Ref: Rinnemo et al.,1993

CH_4/H_2O



Ref: Hegarty et al.,1998

The developed sub-mechanisms are applicable to different reactors and experimental set-ups. The simulations conform to the experimental data very well.

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