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Oxidation and reforming of light hydrocarbons over platinum catalysts: Development of a unified surface reaction mechanism

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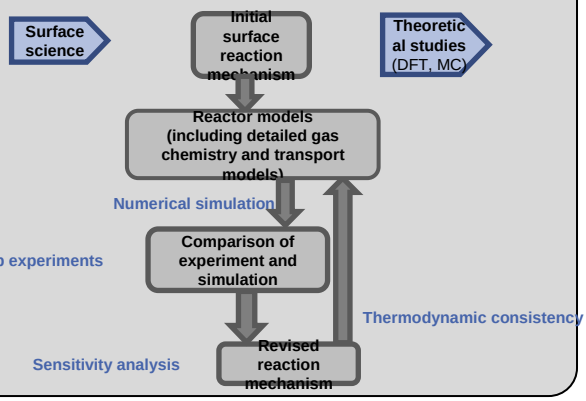
Introduction

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.

For a better understanding of the kinetics of the elementary-step reactions on platinum coated catalysts detailed modeling and simulation techniques are useful. A detailed surface mechanism is developed using numerous experimentally derived data.

To set up a reliable unified surface mechanism of light hydrocarbons over platinum, we first established several sub-mechanisms (H_2/O_2, CO/O_2, CH_4/O_2) applicable for a wide range of temperature and C/H/O ratios. Coupling of these mechanisms lead to an initial mechanism of C_nH_{2n} - hydrocarbons. We expanded this mechanism by important side reactions and by coverage dependencies of activation energies.

Modeling approach



Methods

Molar net production rate: $\dot{s}_i = \sum_k^{K_s} \nu_{ik} k_{f_k} \prod_j^{N_g+N_s} c_j^{\nu'_{jk}}$ (heterogeneous reactions)

Surface coverage: $\frac{\partial \Theta_i}{\partial t} = \frac{\dot{s}\sigma_i}{\Gamma}$

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

Computational simulations are performed using the software package DETCHEM [6]. It contains routines for calculation of reaction rates and transport coefficients. Different reactor models, such as plug flow and packed bed, are implemented that resort to these routines.

(Pt) + (Pt) + O2 ⇌ O(Pt) + O(Pt)
H2 + (Pt) + (Pt) ⇌ H(Pt) + H(Pt)
H + (Pt) → H(Pt)
CH4 + (Pt) + (Pt) ⇌ CH3(Pt) + H(Pt)
H2O + (Pt) ⇌ H2O(Pt)
OH + (Pt) ⇌ OH(Pt)
CO + (Pt) ⇌ CO(Pt)
CO2 + (Pt) ⇌ CO2(Pt)
CH3(Pt) + (Pt) ⇌ CH2(Pt) + H(Pt)
CH2(Pt) + (Pt) ⇌ CH(Pt) + H(Pt)
CH(Pt) + (Pt) ⇌ C(Pt) + H(Pt)
H(Pt) + O(Pt) ⇌ OH(Pt) + (Pt)
OH(Pt) + H(Pt) ⇌ H2O(Pt) + (Pt)
OH(Pt) + OH(Pt) ⇌ H2O(Pt) + O(Pt)
CO(Pt) +O(Pt) ⇌ CO2(Pt) +(Pt)
C(Pt) +O(Pt) ⇌ CO(Pt) +(Pt)
CO(Pt) + OH(Pt) ⇌ COOH(Pt) + (Pt)
CO(Pt) + OH(Pt) ⇌ HCOO(Pt) + (Pt)
(Pt) + HCOO(Pt) ⇌ H(Pt) + CO2(Pt)
CO2(Pt) + OH(Pt) ⇌ HCOO(Pt) + O(Pt)
CO(Pt) + H(Pt) ⇌ HCO(Pt) + (Pt)
CO(Pt) + OH(Pt) ⇌ CO2(Pt) + H(Pt)
OH(Pt) + C(Pt) ⇌ H(Pt) + CO(Pt)
...

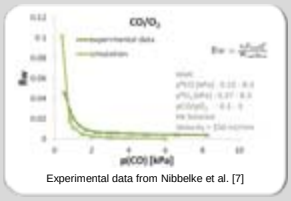
Experiments

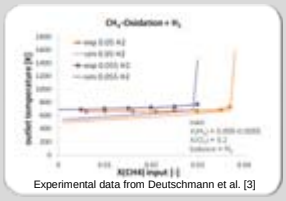
To support the development of the mechanism, laboratory experiments were performed in a flow reactor.

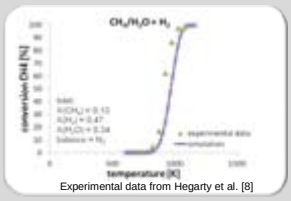
- Well-defined boundary conditions
- 20g/ft³ loaded Pt/Al_2O_3 monolith catalyst
- Homogenous pulse free reactant flow (2 – 4 slpm)
- Analyzed by FTIR and MS

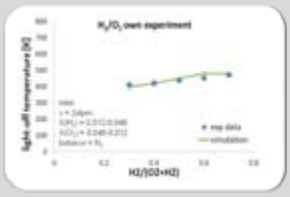
Simulation Results

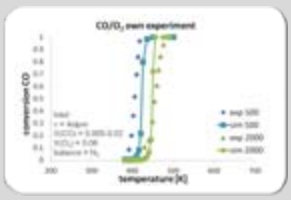
The unified C1-mechanism consists of 49 elementary-step reactions among 9 gas phase and 14 surface species. With these simulations we could figure out that the specific reactions of H_2O and CH_x of the reforming mechanism works via the HCOO-intermediate.

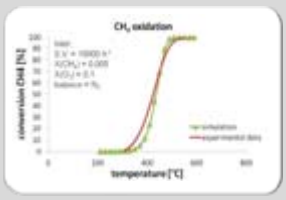

Experimental data from Nibbelke et al. [7]

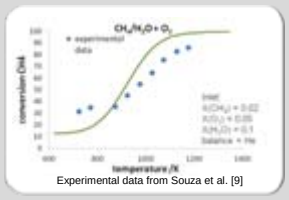

Experimental data from Deutschmann et al. [3]


Experimental data from Hegarty et al. [8]








Experimental data from Souza et al. [9]

The developed C1-mechanism for oxidation and reforming reactions of CH_4 are applicable to different reactors and experimental set-ups. The mechanism also describes the influence of adduct/product inflow in systems like $CH_4/O_2 + H_2O$, $CH_4/CO_2 + H_2O$, etc.

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