Entwicklung von Reaktionsmechanismen für heterogen-katalysierte Reaktionen

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Objective: Development of appropriate models for heterogeneous 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,
- recrystallisation phenomena,
- temporal history,
- surface structures,
- method of manufacture,
- type and structure of washcoat,
- solid bulk modification.

Global kinetics (macroscopic behavior)

Elementary kinetics

Mechanistic approach

Single microscopic steps

(mean field approximation)

Global kinetics

OD_01_103
Modeling heterogeneous-catalytic reactions: Mean field approximation

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

\[
\frac{L}{\theta} \exp \left( \frac{E}{RT} (\theta) \right) \prod_{s} \theta_s = (\frac{L}{\theta})^{\frac{N}{\theta}}
\]

Reaction rate:

\[
k_{rx} = \frac{A}{\Theta_{1} \Theta_{2} \ldots} \exp \left( -\frac{E}{RT} \right)
\]

Assumptions:

- Adsorbates are assumed to be randomly distributed on the surface
- Surface is viewed as being uniform; the local environment (edges, defects, terraces) is not directly taken into account
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Catalytic combustion of methane over platinum: Proposed scheme of surface reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
</tr>
</thead>
</table>
| H2 + 2Pt(S) => 2H(S) | 0.046 | 0.0 | 0 | STICK, FORD/PT(S) 1/
| 2H(S) => H2 + 2Pt(S) | 3.70E+21 | 0.067 | 400 | 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 | 0.021 | 320 | COV/O(S) 0 0 -6000 /
| 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) | 1.00E+13 | 0.04 | 300 |
| OH + Pt(S) => OH(S) | 1.00 | 0.0 | 0 | STICK |
| OH(S) => OH + Pt(S) | 1.00E+13 | 0.019 | 280 |
| H(S) + O(S) => OH(S) + Pt(S) | 3.70E+21 | 0.011 | 500 |
| H(S) + OH(S) => H2O(S) + Pt(S) | 3.70E+21 | 0.017 | 400 |
| OH(S) + OH(S) => H2O(S) + O(S) | 3.70E+21 | 0.048 | 200 |
| CO + Pt(S) => CO(S) | 0.84 | 0.0 | 0 | STICK, FORD/PT(S) 2/
| CO(S) => CO + Pt(S) | 1.00E+13 | 0.012 | 500 |
| CO2(S) => CO2 + Pt(S) | 1.00E+13 | 0.02 | 500 |
| CO(S) + O(S) => CO2(S) + Pt(S) | 3.70E+21 | 0.01 | 500 |
| CH4 + 2Pt(S) => CH3(S) + H(S) | 0.01 | 0.0 | STICK, FORD/PT(S) 2.3/
| CH3(S) + Pt(S) => CH2(S) + H(S) | 3.70E+21 | 0.02 | 300 |
| CH2(S) + Pt(S) => CH(S) + H(S) | 3.70E+21 | 0.02 | 300 |
| CH(S) + Pt(S) => C(S) + H(S) | 3.70E+21 | 0.02 | 300 |
| C(S) + O(S) => CO(S) + Pt(S) | 3.70E+21 | 0.062 | 800 |
| CO(S) + Pt(S) => C(S) + O(S) | 1.00E+18 | 0.018 | 400 |

H2, CO, CH4, O2, Pt on Pt in SURFACE CHEMKIN format

Proposed scheme of surface reactions for modeling catalytic ignition of H2, CO, CH4, O2, Pt on Pt in SURFACE CHEMKIN format

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

Reactivity scheme for modeling catalytic ignition of H2, CO, CH4, O2, Pt on Pt in SURFACE CHEMKIN format
Survey of the methodology of the development of a surface reaction mechanism

- Reactor models (including appropriate gas chemistry & transport models)
- Numerical simulation
- Experiments - integrated data (ign. & ext. temperatures, selectivity, conversion)
- Experiments - detailed data (spatial & temporal profiles, coverages)
- Revised surface reaction mechanism
- Sensitivity analysis => re-evaluation of crucial kinetic data
- Analogy to gas phase kinetics
- Analogy to organo-metallic compounds
- Transition-State theory
- Collision theory
- Heats of adsorption & -desorption calculations
- Surface science studies
- Ab-initio ab-initio calculations
- Tentative surface reaction mechanism
- Comparison of experiment and simulation
- BOC-MP UBI-QEP ab-initio calculations
- Metallic compounds
Kinetic data for surface reactions at practically relevant conditions and for technically used catalysts.
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.

\[ \alpha = \frac{\rho CH_4}{\rho CH_4 + \rho O_2} \]

\[ \alpha = \frac{\rho CH_4}{\rho CH_4 + \rho O_2} \]

\[ \alpha = \frac{\rho H_2}{\rho H_2 + \rho O_2} \]
Transient Modeling of Catalytic Ignition of Hydrogen and Methane Oxidation on Pt: Temperature and Coverage Conditions:

- H₂/O₂ mixture (6% diluted by 94% N₂, p = 1 bar), α = p_H₂/(p_H₂ + p_O₂) = 0.5, circles: experiment.

- CH₄/O₂ mixture (6% diluted by 94% N₂, p = 1 bar), α = C_CH₄/(p_CH₄ + p_O₂) = 0.5.


OD_99_314
gas-phase and surface reaction mechanisms.

The two-dimensional simulation of a single monolith channel is coupled with detailed transport and heterogeneous and homogeneous reaction mechanisms.

\[
\begin{align*}
\text{C}_2\text{H}_6 + \text{H}_2 \text{O} & \rightarrow \text{H}_2\text{O} + \text{C}_2\text{H}_4 + \text{CO} + \text{CO}_2 \\
\text{C}_2\text{H}_6 + \text{H}_2 & \rightarrow \text{C}_2\text{H}_5 + \text{H}_2
\end{align*}
\]

O. Deutschmann, XXXIV. Jahrestreffen Deutscher Katalyker / Fachtreffen Reaktionskinetik, Weimar, 21.-23.3.2001
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, O2: 30 sccm, Ar: 105 sccm at a total pressure of 20 mbar.
Lateral adsorbate interactions: Monte Carlo simulations of elementary surface processes on Pt(110), PEEM, 0.2 x 0.3 mm², T = 427 K, pO₂ = 3.2 · 10⁻³ mbar, pCO = 3 · 10⁻³ mbar, ∆t = 4.1/30 s.

Target pattern on Pt(100), ∆t = 10 s, 1000 x 1000 lattice, 0.25 x 0.25 mm², T = 490 K, pO₂ = 50 · 10⁻³ mbar, pCO = 1.5 · 10⁻³ mbar.

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


Multi-step mechanisms for simple heterogeneous-catalytic reactions such as
- oxidation of H₂, CO, CH₄, C₂H₆ on noble metals
- NO reduction on noble metals (3WCC)
- methanol and ammonia synthesis

Advanced experimental techniques such as SFG and SHG help to overcome the pressure and materials gap.

Challenges

- Still too little is known about the elementary steps, in particular at high pressures.
- Combination of the detailed reaction mechanisms with the macroscopic processes to the overall picture of the catalyst.
- Combination of the experimental observations of single elementary steps.
- Mass and heat transport in the surrounding reactive flows, the washcoat, and the solid bulk.

Summary and Outlook
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