When atomic-scale resolution is not enough: Heat and mass transfer effects in \textit{in-situ} model catalyst studies

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Catalysis research triangle

Testing/Validation (Kinetics)

Preparation  Characterization
Challenges across the scales

Self-consistent coupling to reactive flow field and appropriate heat balance

Accurate (first-principles) energetics of individual elementary processes

Quantitative transient and steady-state surface kinetics

Surface chemistry: adsorption, diffusion, reaction, desorption

Transport of momentum, energy, species

Gas-phase reactions

Heat transport in solid wall

Thermal radiation
The Surface Science disclaimer: Mind the gap(s)!

Supported "real" catalyst

Model catalysts

Going *in situ*: It’s not just like opening a valve…

**Reactor STM**

P.B. Rasmussen *et al*.,

**in situ XPS**

S. Yamamoto *et al*.,

A. Stierle and A.M. Molenbroek (Eds.), MRS Bull. 32 (2007)
A tour from electrons to the reactor

Part I  First-principles microkinetics

Part II  Integrating 1p-kMC into CFD
The “Quantum Engines”: Electronic structure methods

Potential energy for fixed nuclear positions \( \{ R_I \} \):

\[
E_0 (\{ R_I \}) = \min_\Psi <\Psi | H^e \{ R_I \} | \Psi >
\]

1. Wavefunction based methods (“Quantum Chemistry“)

Ansatz for \( \Psi \): Hartree-Fock, post-HF (MP2, CI, CC,…)

2. Density-functional theory

\[
\Psi = \Psi [n(r)] \quad \text{(Hohenberg-Kohn, 1964)}
\]

\[
\Rightarrow E_0 (\{ R_I \}) = \min_{n(r)} E_{\{ R_I \}} [n]
\]

\[
E_{\{ R_I \}} [n] = T_s [n] + \int d^3r \, \nu_{\{ R_I \}}^{\text{nuc}} (r) n(r) + \frac{1}{2} \int \int d^3r \, d^3r' \, \frac{n(r) n(r')}{|r - r'|} + E^{xc} [n]
\]

(Kohn-Sham, 1965)

\[
E_{\text{LDA}}^{xc} [n] = \int d^3r \, n(r) \, \varepsilon^{xc} (n_o) \bigg|_{n_o = n(r)}
\]

\[
E_{\text{GGA}}^{xc} [n] = \int d^3r \, n(r) \varepsilon^{xc} (n_o, \nabla n_o) \bigg|_{n_o = n(r)}
\]
Electronic regime: Energetics of elementary processes

- Active site model
- "Level of theory"

„The“ active site: The effective to atomistic gap

* vs.

- Generic active site independent of operation conditions dominant over other sites (one site model)
- Lately: move towards „multi-site“ models (multi = 2,...)

- Atomistic active site model every atom counts generally insufficient experimental characterization
- Manifold of possibly active site types on which one to focus? consider how many?
Mesoscopic regime: Tackling rare-event time scales

Transition State Theory

\[ k_{i\rightarrow j} = \left( \frac{k_B T}{\hbar} \right) \frac{Z_{TS(i\rightarrow j)}}{Z_i} = \Gamma \exp \left( -\frac{\Delta E_{i\rightarrow j}}{k_B T} \right) \]

First-principles kinetic Monte Carlo simulations for heterogeneous catalysis: Concepts, status and frontiers
Mean-field approximation: Rate equations

\[ \frac{dP_i(t)}{dt} = -\sum_j k_{i\rightarrow j} P_i(t) + \sum_j k_{j\rightarrow i} P_j(t) \]

\[ \frac{d\theta(O^{\text{cus}}, t)}{dt} = f_1 \left\{ k_{i\rightarrow j}, \theta(O^{\text{cus}}, t), \theta(O^{\text{br}}, t), \theta(CO^{\text{cus}}, t), \theta(CO^{\text{br}}, t) \right\} \]

\[ \frac{d\theta(O^{\text{br}}, t)}{dt} = f_2 \left\{ k_{i\rightarrow j}, \theta(O^{\text{cus}}, t), \theta(O^{\text{br}}, t), \theta(CO^{\text{cus}}, t), \theta(CO^{\text{br}}, t) \right\} \]

\[ P(O^{\text{br}}, CO^{\text{cus}}, t) \downarrow \]

\[ \theta(O^{\text{br}}, t) \cdot \theta(CO^{\text{cus}}, t) \]

...
CO oxidation at RuO$_2$(110): 1p-kMC model

26 elementary processes (site-specific):
- O$_2$ adsorption/desorption (dissociative/associative)
- CO adsorption/desorption (unimolecular)
- O and CO diffusion
- CO + O reaction

Surface structure and composition in the reactive environment

\[ T = 600 \text{ K}, p_{O_2} = 1 \text{ atm}, p_{CO} = 7 \text{ atm} \]

CO oxidation at RuO\(_2\)(110)

Steady-state and transient parameter-free turnover frequencies


Key ingredients to "predictive-quality" microkinetic modeling

Accurate rate constants:

Transition state theory and beyond
DFT functionals: „self-interaction“
van der Waals interactions

Reaction mechanism:

Process identification
Lattice mapping / spatial distributions
„Hot chemistry“ beyond Markov

\[ k_{i\rightarrow j} = \Gamma_0 \exp \left( \frac{-\Delta E_{i\rightarrow j}}{k_B T} \right) \]
„E pluribus unum“: Water-gas-shift at Rh(111)

Microscale

\[ \text{COOH}^* + \text{OH}^* \rightarrow \text{CO}^* + \text{OH}^* \]
\[ \text{CO}^* + \text{OH}^* \rightarrow \text{COOH}^* + \text{H}^* \]
\[ \text{COOH}^* + \text{H}^* \rightarrow \text{CO}_2^* + \text{H}_2\text{O}^* \]
\[ \text{CO}_2^* + \text{H}^* \rightarrow \text{HCOO}^* \]
\[ \text{HCOO}^* \rightarrow \text{CO}_2^* + \text{H}^* \]
\[ \text{CO}_2^* + \text{H}_2\text{O}^* \rightarrow \text{COOH}^* + \text{OH}^* \]
\[ \text{HCOOH}^* + \text{OH}^* \rightarrow \text{CO}_2^* + \text{H}_2\text{O}^* \]
\[ \text{CH}^* + \text{H}^* \rightarrow \text{CH}_2^* + \text{H}^* \]
\[ \text{CH}_2^* + \text{H}^* \rightarrow \text{CH}_3^* + \text{H}^* \]

\[ \text{CH}_3^* + \text{O}^* \rightarrow \text{CH}_2^* + \text{OH}^* \]
\[ \text{CH}_2^* + \text{OH}^* \rightarrow \text{CH}_3^* + \text{O}^* \]
\[ \text{CH}_3^* + \text{OH}^* \rightarrow \text{CH}_2^* + \text{O}^* \]
\[ \text{CH}_2^* + \text{O}^* \rightarrow \text{CH}^* + \text{OH}^* \]

~ \(10^2\) potential steps @ different coverages

Macroscale

\[ \text{CO}_2 + 2\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O} \]
\[ \text{H}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O} + \text{H}_2 \]

Error propagation through rate-determining steps

CO oxidation at RuO$_2$(110)

Sensitivity analysis:

\[ X_{rc,i} = \left( \frac{k_i}{TOF} \right) \left( \frac{\partial TOF}{\partial k_i} \right)_{k_j,K_i} \]

C.T. Campbell,
J. Catal. 204, 520 (2001);

H. Meskine et al.,
Ertl Special Issue
More than Markov?

Heat dissipation during dissociative adsorption: O₂/Pd(100)

\[ k = \tilde{S}_c(T) \frac{pA_{uc}}{\sqrt{2\pi nk_B T}} \]

J. Meyer and K. Reuter (in preparation)
Part I  First-principles microkinetics

Part II  Integrating 1p-kMC into CFD
Stagnation flow: Heat and mass transfer

\[ T, p_{CO}, p_{O2} \]
Self-consistent coupling to the flow field

\[ \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \]

\[ \frac{\partial}{\partial t} (\rho \mathbf{v}) + \nabla \cdot (\rho \mathbf{v} \mathbf{v}) = -\nabla p + \nabla \cdot \left[ \mu (\nabla \mathbf{v} + (\nabla \mathbf{v})^T) - \frac{2}{3} \mu (\nabla \mathbf{v}) \mathbf{I} \right] + \rho \mathbf{g} \]

\[ \frac{\partial}{\partial t} (\rho \omega_k) + \nabla \cdot (\rho \omega_k \mathbf{v}) = -\nabla \cdot (\rho \omega_k \mathbf{v}) + \dot{\Omega}_k^{\text{hom}} \quad k = 1, \ldots, \text{NG} \]

\[ \rho \hat{C}_P \frac{\partial T}{\partial t} + \rho \hat{C}_P \mathbf{v} \nabla T = \nabla \cdot (\lambda \nabla T) - \rho \sum_{k=1}^{\text{NG}} \hat{C}_P \omega_k \mathbf{v}_k - \sum_{k=1}^{\text{NG}} \dot{H}_k^{\text{hom}} \dot{\Omega}_k^{\text{hom}} \]

\[ k_{\text{ad}} = S(T) \frac{pA_{uc}}{\sqrt{2\pi m k_B T}} \]

Computational Fluid Dynamics
with
chemical source terms
from 1p-kMC ?!
On time scales relevant to changes in flow profile surface chemistry adapts quasi-instantaneously to new steady-state

e.g. O. Deutschmann, “Computational Fluid Dynamics Simulation of Catalytic Reactors”, In: Handbook of Heterogeneous Catalysis (2008)

Precompute steady-state 1p-kMC TOFs on dense grid in \((T, p_{O_2}, p_{CO})\)-space

Interpolate using modified Shepard (ideal for grid-less scattered data)

Run CFD using continuous representation as boundary condition

The CatalyticFOAM project

Pre-Processing
- OpenFOAM® BlockMesh
- GAMBIT, Ansys, CFX, etc.

OpenFOAM® Framework
- Convection + Diffusion
  - segregated approach
  - discretization on unstructured meshes

CatalyticFOAM Framework
- Reactions
  - coupled approach
  - stiff ODE solvers

Paraview ®
Post-processing

www.catalyticfoam.polimi.it

M. Maestri    A. Cuoci
**In situ** TOFs in the isothermal limit: Mass transfer limitations

\[ u^{\text{inl}}, T^{\text{inl}}, p_{O_2}^{\text{inl}}, p_{CO}^{\text{inl}} \]

\[ T = \text{const} \]

\[ T = 600 \, \text{K} \]
\[ p_{O_2} = 0.3 \, \text{atm} \]
\[ u^{\text{inl}} = 1 \, \text{cm/sec} \]

When atomic scale resolution is not enough

$T = 600 \text{ K}, u_{\text{inl(max)}} = 20 \text{ cm/sec}$

$p_{O_2} = 0.3 \text{ atm}, p_{CO} = 1.9 \text{ atm}$

Planar Laser Induced Fluorescence (PLIF)

Laser-sheet stimulation of known excitation (here: CO$_2$ vibration)

→ 2D concentration profile above catalyst

Making mass transfer limitations „visible“

_in situ_ PLIF measurements of ambient CO oxidation at Pd(100)

together with
E. Lundgren _et al._ (Lund University)

CO:O$_2$ = 1:1, $p_{\text{tot}} = 1$ atm


S. Matera _et al._, in preparation
Incomplete heat dissipation in a real stagflow reactor: Rayleigh-Bénard convection

CO oxidation at RuO$_2$(110)

$\text{CO}:\text{O}_2 = 4:1$, $p_{\text{tot}} = 1$ atm
$T_{\text{inlet}} = 500$K, adiabatic limit

S. Döpking, S. Matera
First-Principles Multiscale Modeling: Where do we stand?

State-of-the-art in catalysis modeling:
- Prevalence of highly coarse-grained models based on effective parameters without true microscopic meaning
  - rate equation theory based on empirical rate constants
  - 1D flow models
- Emergence of ad-hoc 1p-microkinetic models
  - kMC and mean-field for model catalysts & show case reactions

Steps towards a predictive character multiscale catalysis modeling:
- Replace effective parameters by clean first-principles data fitted vs. DFT-based rate constants
  - battle the curse of complexity (off-lattice, complex networks)
  - electronic non-adiabaticity, heat dissipation
- Refined modeling at each individual level
  - reliable and efficient 1p-rate constants (where needed)
  - necessity to resolve spatial arrangement at surface
  - integrate 1p-surface chemistry into detailed reactor models
- Robust links between theories that enable reverse-mapping
  - sensitivity analysis to control flow of error across scales
Thanks so much!!!

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