Structure/Kinetics of Complex, Industrial Catalysts

DOE/EERE/AMO Industry Roundtable on Dynamic Catalyst Science

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Elements of Catalysis Research

- Reaction Kinetics
- Catalyst Synthesis
- Structure Characterization
- Structure-Activity Model Catalyst Approach
- Surface Science
- Trial and error approach High-Throughput
- Composition Screening

Molecular Beam Scattering vs. TAP

Molecular Beam Scattering – MBS experiment

1 active site receives 1000 collisions

$P \approx 10^9 \text{ Pa}$

Single crystals
Detailed, intrinsic kinetics

Real catalysts
Detailed, intrinsic kinetics

Knudsen Diffusion

1 active site receives 1000 collisions

Temporal Analysis of Products (TAP)

Distinguishing Features:

- Low pulse intensity 10 nmols
- Well-defined Knudsen transport
- Isothermal operation even for highly exothermic reactions
- Pulse-by-pulse, controlled titration of materials
- Separation of reactant inputs and product detection with high time resolution

Temporal Analysis of Products (TAP)

- A low-pressure pulse response technique
  - Understanding how catalysts work based on chemical response to pressure transients
- Rate constants of elementary reaction steps
- Incremental titration (chemical calculus) enables observation of material evolution
- Development of detailed microkinetic models


Advances in Transient Data Analysis

Experimental Data
Exit flux (volts vs. time)

Preprocessing and Y-Procedure Analysis

The exit flux contains transport and kinetic information

3D Kinetic Mapping

$$Rate = f(C_{gas}, C_{surface}, k, T, N)$$

Reaction rates,
Rate constants,
Numbers of active sites,
Activation energies,
Surface residence time,
Mechanism

Prior Art:
- Moment-based analysis
- Curve fitting

Y-Procedure

Exit Flux →
Time-dependence Rate and Concentration

**Advances in Measurement**

- Distinguishing active sites from a mixture
- Resolution of short-lived surface species
- Quantification of surface-to-bulk transport
- Distinguishing gas phase from gas/surface kinetics

**Oxidative Coupling of Methane Reaction**

- Complex catalyst
  - $\text{Mn}_2\text{O}_3/\text{Na}_2\text{WO}_4/\text{SiO}_2$
- Aggressive environment, 850 °C
- Complex reaction mechanism
  - Both surface and gas phase reactions

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*C$_2$* Yield is a key challenge
Reversible Adsorption of Oxygen

Isotopic studies distinguish different forms of oxygen with distinct surface lifetimes

Time scale < 1s

Finite surface lifetime

2% Mn/Na₂WO₄/SiO₂

(A) 100% Mn
(B) 1% Mn
(C) 2% Mn

Normalized intensity (a.u.) vs. Time / s
Reactive Oxygen Species – Surface Lifetime

TAP Pump/Probe Experiment at reaction temperature, 750 °C

Dioxo species ($O_2^{2-}$, $O_2^-$)

Monoxo species ($O^-$)

Amount and surface lifetime of different oxygen species changes with catalyst composition, %Mn
Reactive Oxygen Species – Kinetic Role

Dioxo species ($O_2^{2-}$, $O_2^{-}$) => CO$_2$ formation

Monoxo species ($O^-$) => C$_2$H$_4$ formation

• Short-lived surface intermediates and their role in product formation can be studied
• Not observable under steady-state
• Need link to composition/structure
Reactive Oxygen Species – Structural Information

Catalyst is changes dramatically with temperature.

Sourav, S., Kiani, D., Baltrusaitis, J. Fushimi, R., Wachs, I., *Determination of catalytic active site for oxidative coupling of methane over supported Mn$_2$O$_3$-Na$_2$WO$_4$/SiO$_2$ catalysts.* 17th International Congress on Catalysis, San Diego, CA, June 14 – 19, 2020
Operando Spectroscopy State of the Art

Operando Spectroscopy

- Structural features, operating environment
- Changes due to reaction, e.g. effects of moisture
- Switch between oxidation/reduction
- Poor reactor design
  - Bypassing, readosorption, temperature gradients, holdup, complex hydrodynamics
- Low time-resolution (seconds)
- Coarse kinetic data

- Improved time-resolution of FT instruments
- Inadequate switching time (milliseconds)
- Large switching volumes (microliters)
- No theory for mechanistic analysis
- Coarse kinetic data
- Only qualitative structure/kinetics link hereto now
**Transient Spectrokinetic Reactor Concept**

TAP (Temporal Analysis of Products) Pulse Response + Spectroscopic Probe

Directly addressing the materials **structure/activity** knowledge gap:

*How do specific structural features control complex reaction mechanisms?*

- Detailed, quantitative *intrinsic* kinetic information
- Well-developed theoretical tools for mechanism analysis
- High time resolution (milliseconds)
- Well-defined transport
  - Isothermal, far from equilibrium, well-mixed
- Fast (µs), precise dosing control (10 nmols) for superior modulation

**Risks:**

- Low spectral signal intensity (10 nmols)
  - Dispersive spectra collection mode
  - Higher pulse intensities
New Spectrokinetic Collaboration

• Mithra Technologies, SBIR Phase I Award
  – Developing a fast gas delivery system for transient spectroscopic measurements
• BNL, NAP backfilling lab-scale XPS
• INL, Performance validation using TAP system

First-generation capillary gas delivery prototype developed by Mithra Technologies

SPECS NAP-XPS system including Bruker Vertex 80V for IRRAS measurement at BNL.
Conclusion

• Dynamic Catalyst Science
  – TAP pulse response experiments
    • Complex industrial catalysts
    • Decoupling of transport and kinetics
    • Detailed kinetic information
  – Oxidative Coupling of Methane
    • Measurement surface lifetime of short-lived oxygen species
    • Role in CO\textsubscript{2} versus C\textsubscript{2} selectivity
  – Operando tools
    • Need higher time-resolution
    • Coupled to detailed kinetic information, Spectrokinetic
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