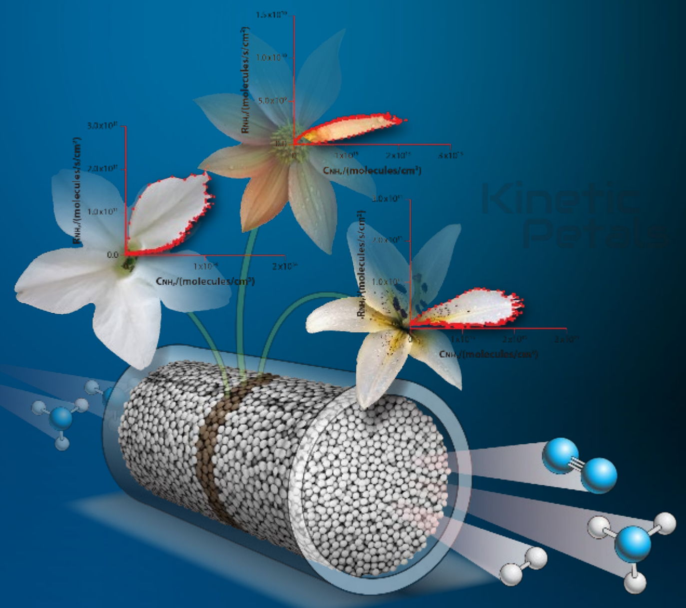
Structure/Kinetics of Complex, Industrial Catalysts

DOE/EERE/AMO Industry Roundtable
on Dynamic Catalyst Science

February 26, 2020, Houston, TX

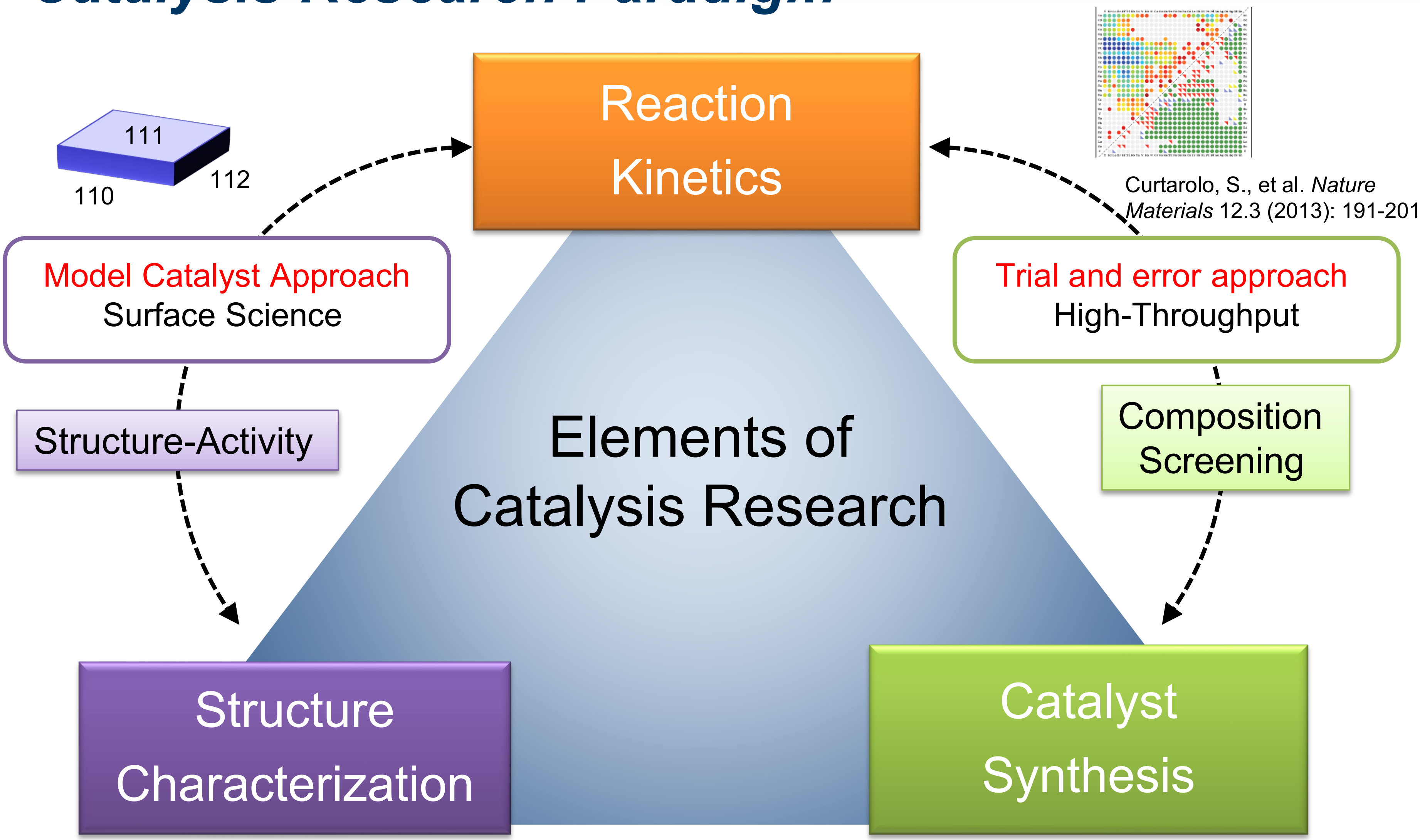
Rebecca R. Fushimi



www.inl.gov

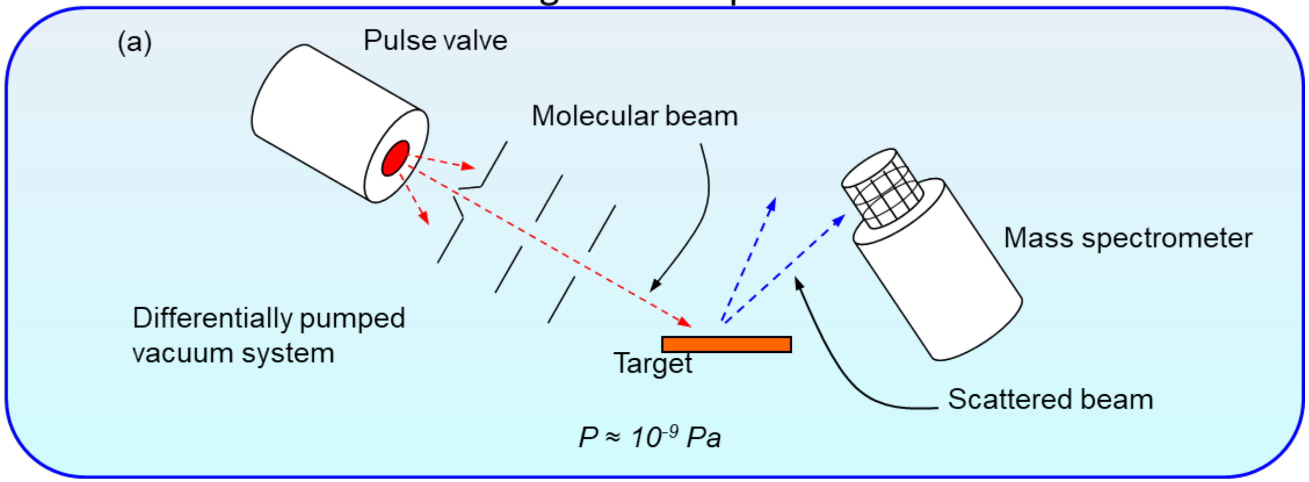
Idaho National Laboratory

Catalysis Research Paradigm



Molecular Beam Scattering vs. TAP

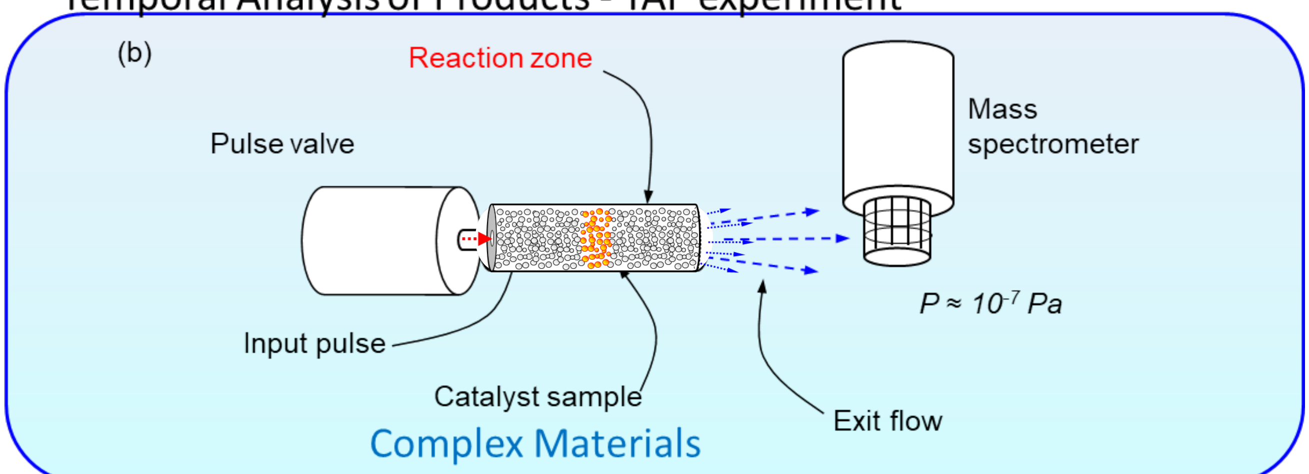
Molecular Beam Scattering – MBS experiment



Single crystals

Detailed, intrinsic kinetics

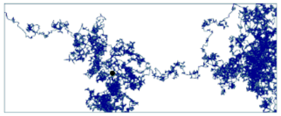
Temporal Analysis of Products - TAP experiment



Real catalysts

Detailed, intrinsic kinetics

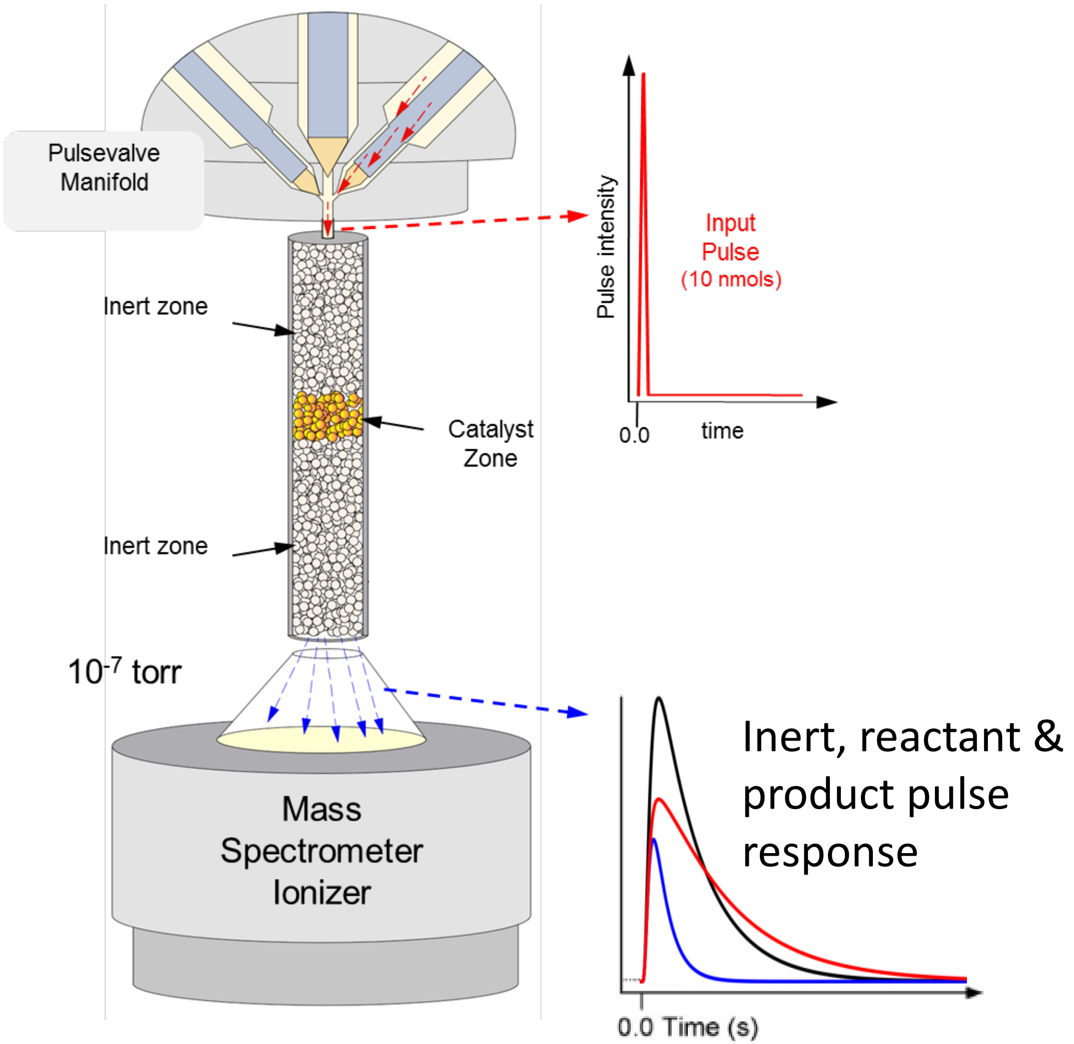
Knudsen Diffusion



1 active site receives 1000 collisions

Schuurman, Y., (2007) Catal. Tod. 121 p187

Temporal Analysis of Products (TAP)



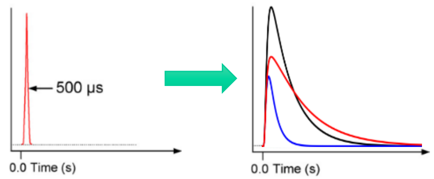
Distinguishing Features:

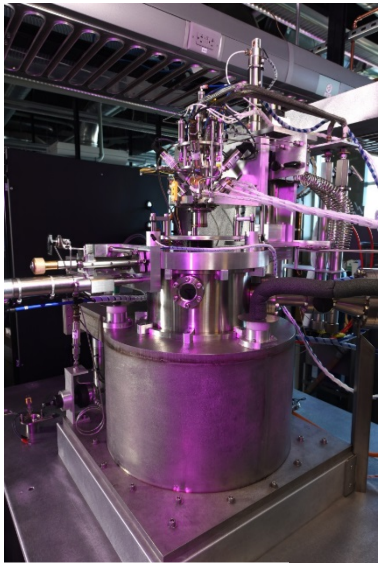
- Low pulse intensity 10 nmols
- Well-defined Knudsen transport
- Isothermal operation even for highly exothermic reactions
- Pulse-by-pulse, controlled titration of materials
- Separation of reactant inputs and product detection with high time resolution

Gleaves, J.T., *et al.* (1988) *Catal. Rev. Sci. and Eng. 30*(1), pp.49-116.
Morgan, K., *et al.* (2017) *Catal. Sci. & Tech. 7*(12), pp.2416-2439.

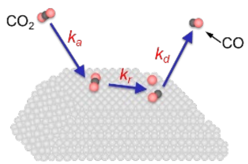
Temporal Analysis of Products (TAP)

- A low-pressure pulse response technique

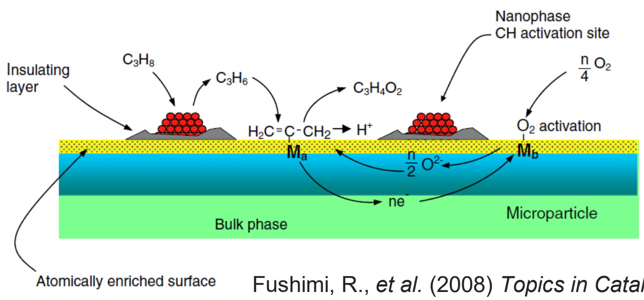




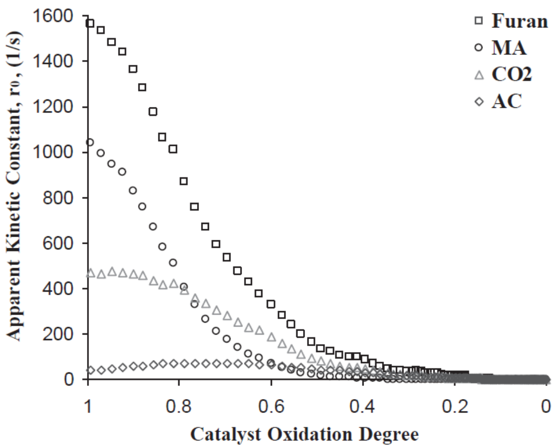
  – Understanding how catalysts work based on chemical response to pressure transients



  - Rate constants of elementary reaction steps
  - Incremental titration (chemical calculus) enables observation of material evolution
  - Development of detailed microkinetic models



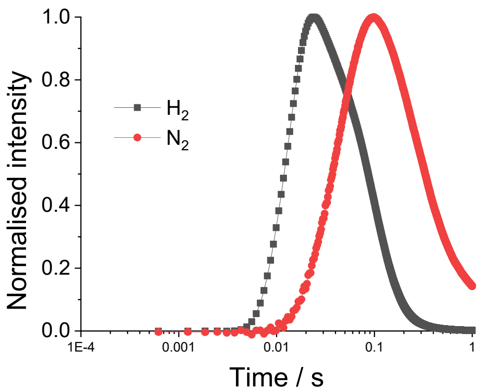
Fushimi, R., *et al.* (2008) *Topics in Catal.* *49*(3-4), 167-177.



Shekhtman, S. O., (2003) *Chem. Eng. Sci.*, *58*(21), 4843-4859.

Advances in Transient Data Analysis

Experimental Data
Exit flux (volts vs. time)

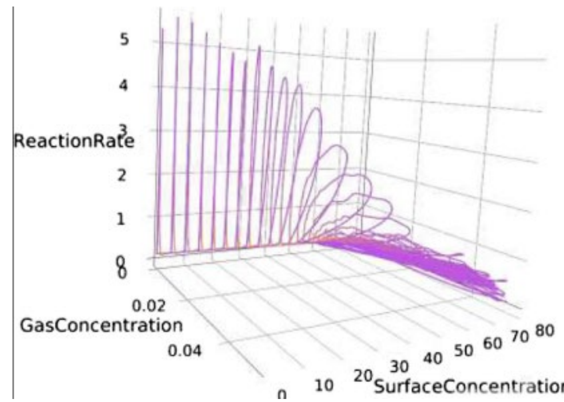


The exit flux contains transport and kinetic information

Preprocessing and Y-Procedure Analysis →

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

High-throughput kinetic analysis

Prior Art:
- Moment-based analysis
- Curve fitting

Y-Procedure

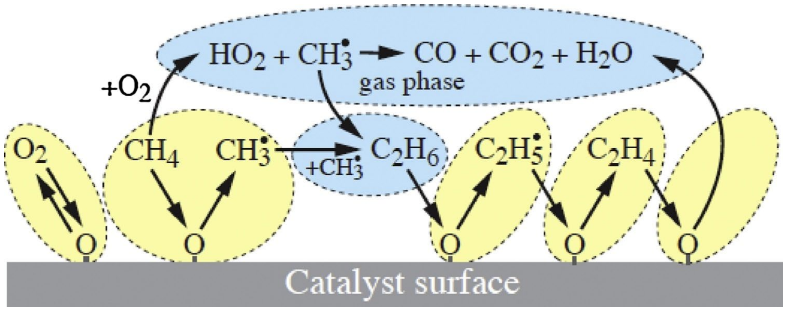
Yablonsky, G.S., *et al.*, (2007) Chem. Eng. Sci., *62*(23), 6754-6767.
Redekop, E.A., *et al.*, (2011) Chem. Eng. Sci., *66*(24), 6441-6452.
Kunz, M.R., *et al.*, (2018) Chem. Eng. Sci., *192*, 46-60.
Wang, Y., *et al.*, (2019) J. Phys. Chem. A, *123*, 8717.

Exit Flux →
Time-dependence Rate and Concentration

Advances in Measurement

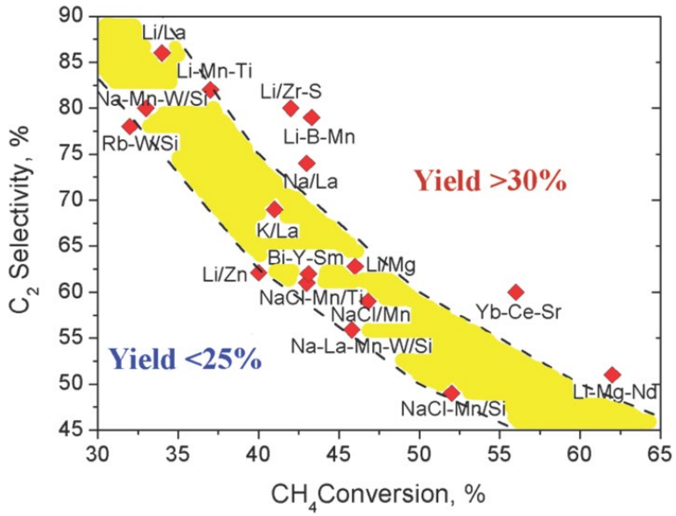
- Distinguishing active sites from a mixture
- Resolution of short-lived surface species
- Quantification of surface-to-bulk transport
- Distinguishing gas phase from gas/surface kinetics

Oxidative Coupling of Methane Reaction



Karakaya, C., *et al.*, 2018. *Catalysis Today*, *312*, pp.10-22.

U. Zavyalova, *et al.*, 2011. *ChemCatChem*, *3,* pp.1935-1947.

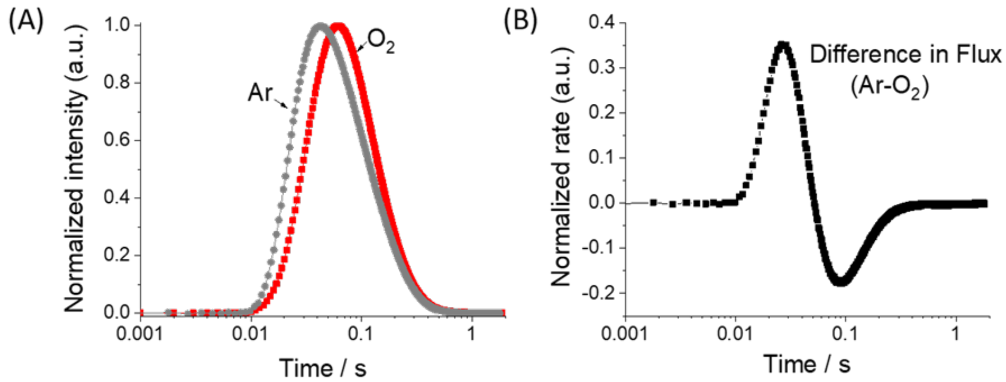


- Complex catalyst
  - $Mn_2O_3/Na_2WO_4/SiO_2$
- Aggressive environment, 850 °C
- Complex reaction mechanism
  - Both surface and gas phase reactions

- C_2 Yield is a key challenge

Reversible Adsorption of Oxygen

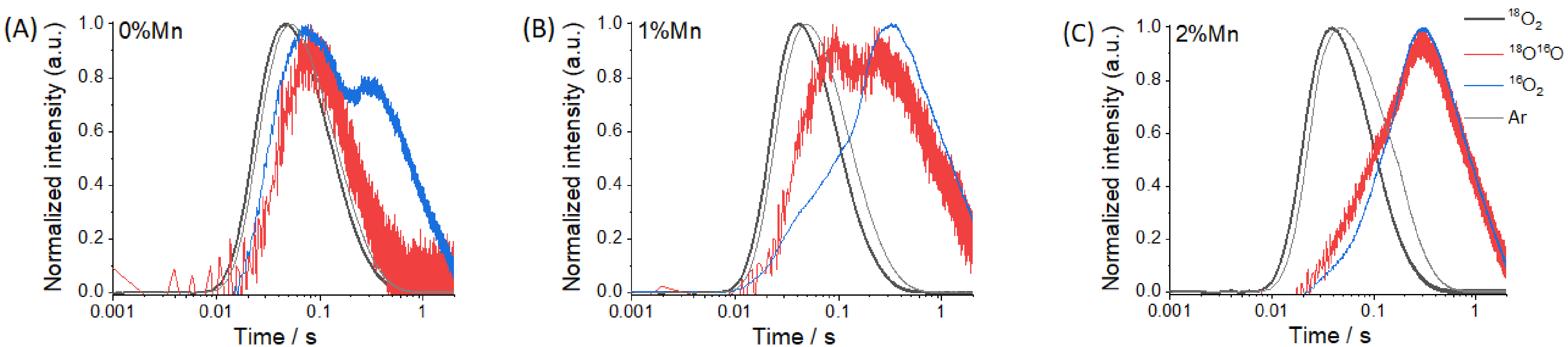
2%Mn/Na_2WO_4/SiO_2



Finite surface lifetime

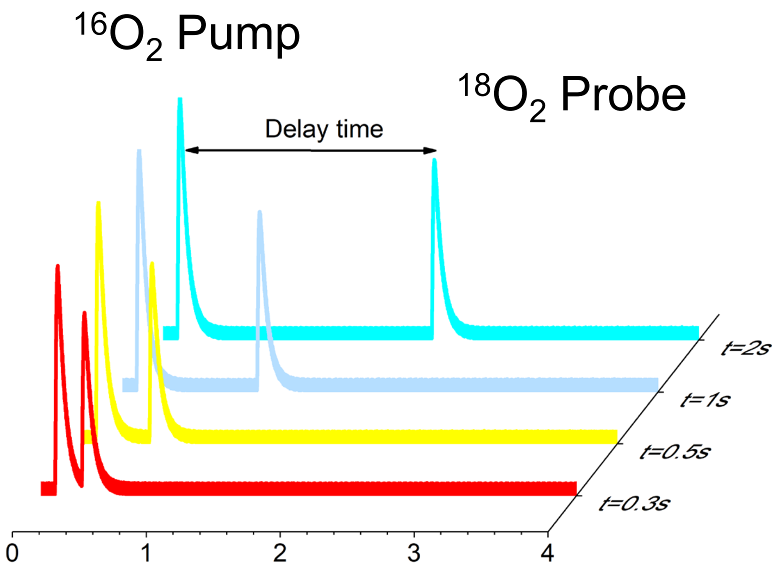
Time scale < 1s

Isotopic studies distinguish different forms of oxygen with distinct surface lifetimes

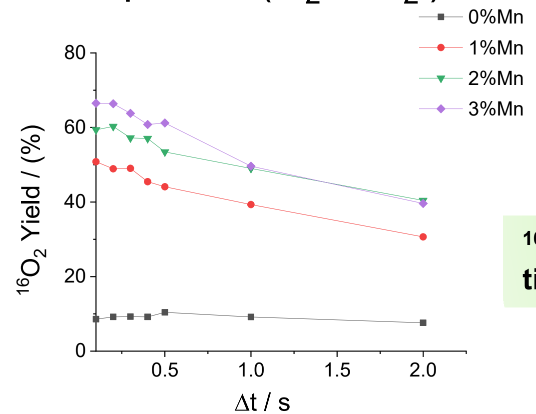


Reactive Oxygen Species – Surface Lifetime

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

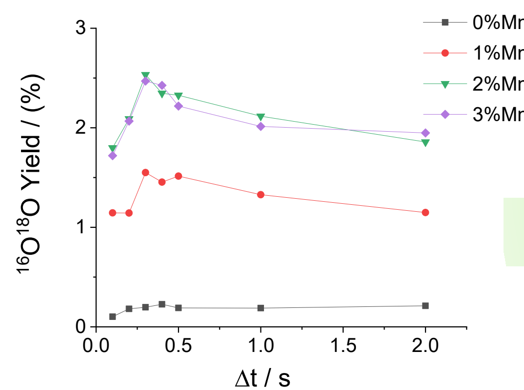


Dioxo species (O_2^{2-}, O_2^{-})



$^{16}O_2$ declines with time delay

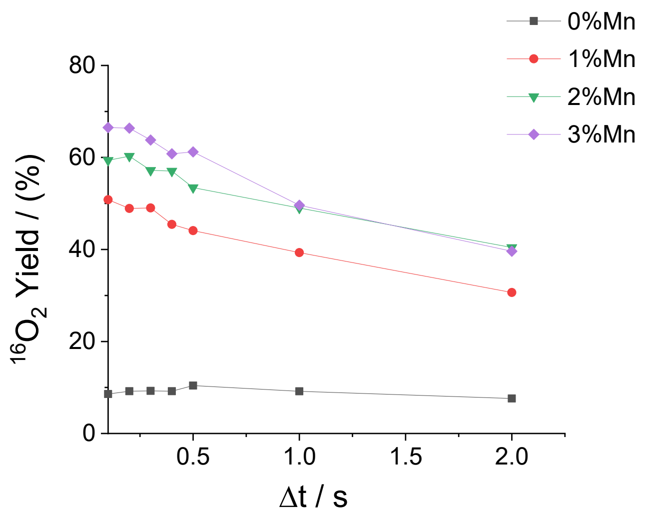
Monoxo species (O^-)

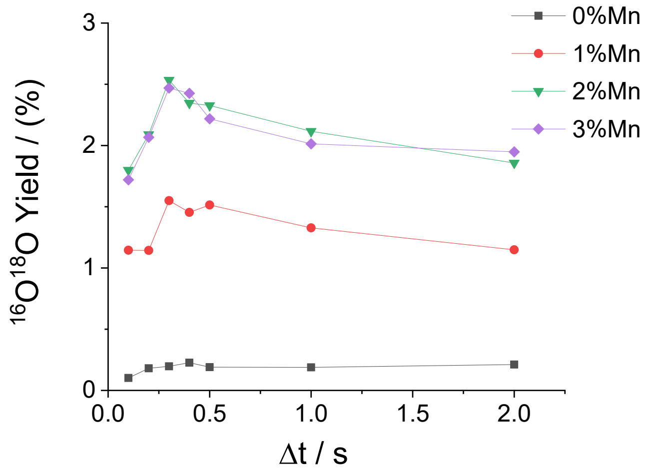


Maximum near 0.3 s

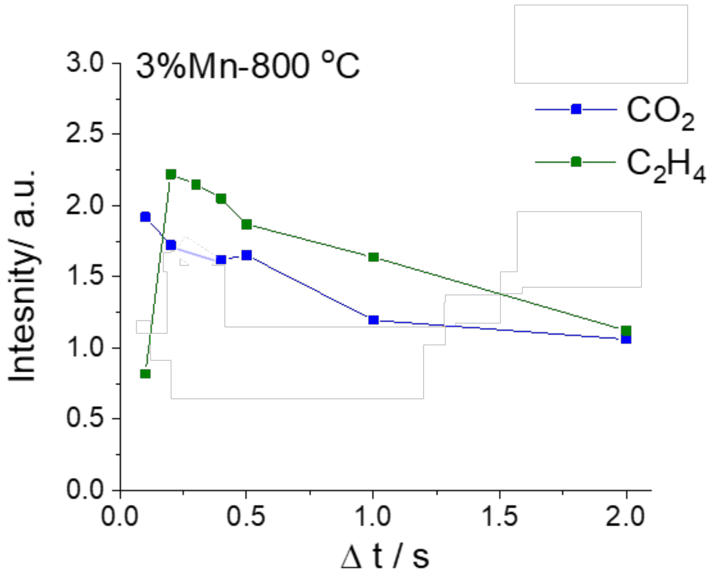
Amount and surface lifetime of different oxygen species changes with catalyst composition, %Mn

Reactive Oxygen Species – Kinetic Role





$^{16}O_2/^{13}CH_4$ Pump/Probe



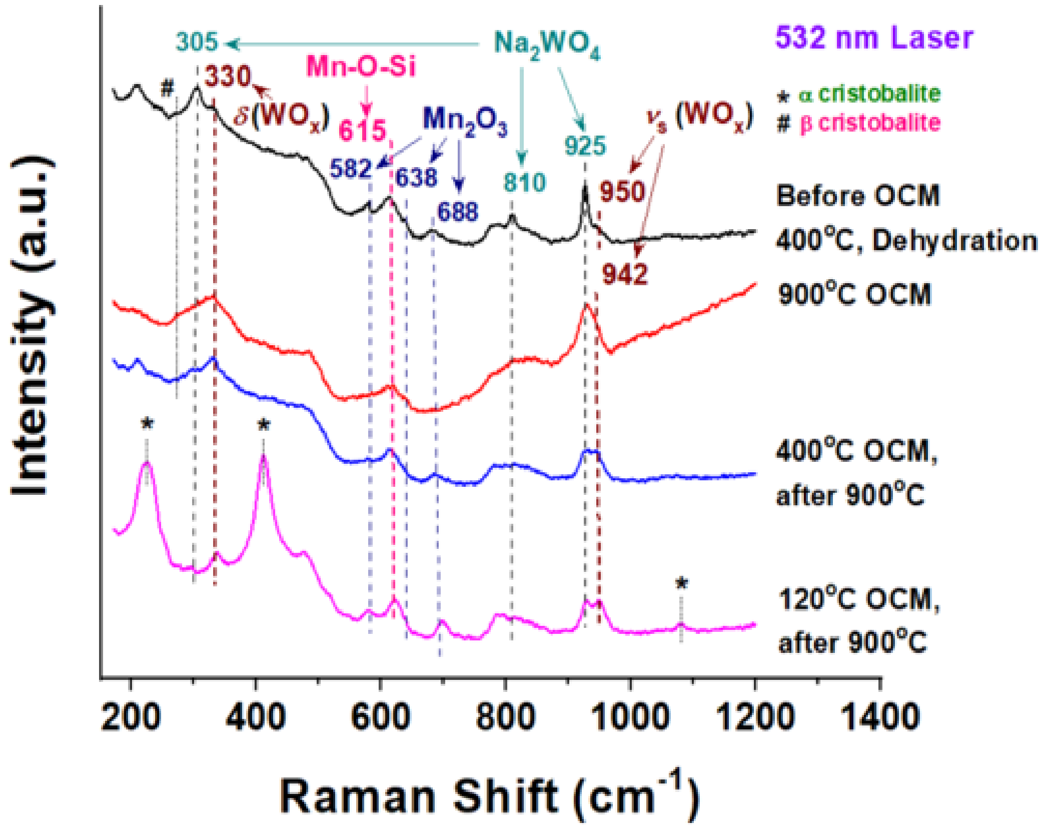
Dioxo species (O_2^{2-}, O_2^-) => CO_2 formation

Monoxo species (O^-) => C_2H_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_2O_3-Na_2WO_4/SiO_2 catalysts.* 17th International Congress on Catalysis, San Diego, CA, June 14 – 19, 2020

Operando *Spectroscopy State of the Art*

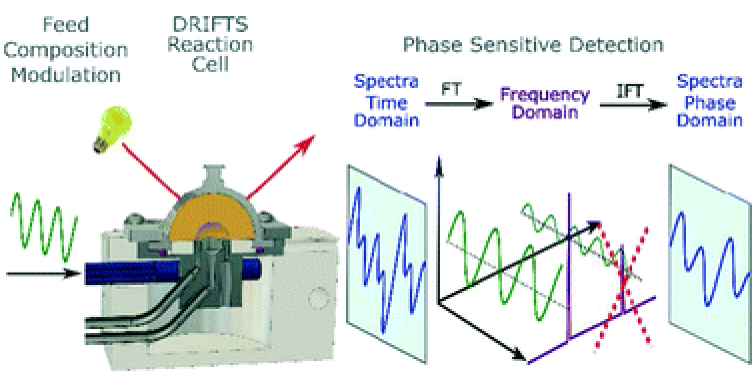
Operando Spectroscopy

Harrick Praying Mantis

Linkam CCR1000

- ✓ 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

Modulation Excitation



- ✓ 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?

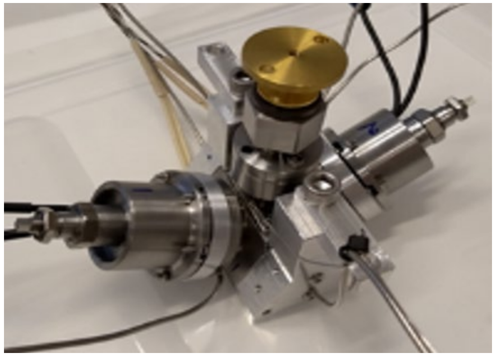
- ✓ Detailed, quantitative *intrinsic* kinetic information
- ✓ Well-developed theoretical tools for mechanism analysis
- ✓ High time resolution (milliseconds)
- ✓ Well-defined transport
  - Isothermal, far from equilibrium, well-mixed
- ✓ Fast (μs), precise dosing control (10 nmols) for superior modulation

Risks:

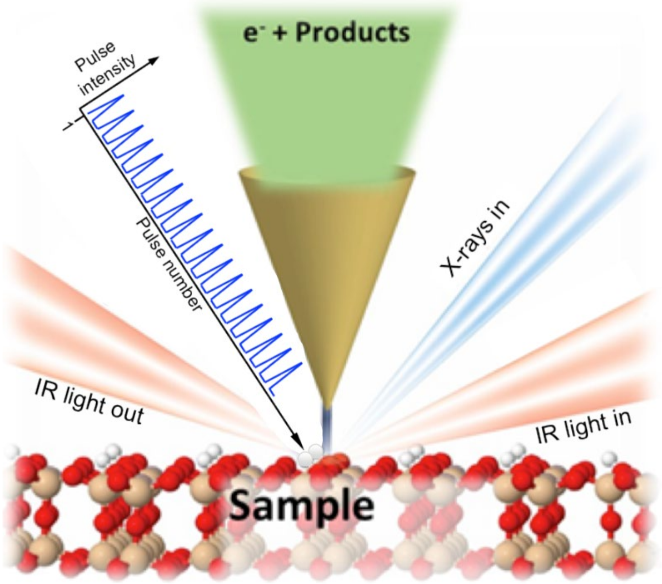
- ✗ Low spectral signal intensity (10 nmols)
  - ✓ Dispersive spectra collection mode
  - ✓ Higher pulse intensities

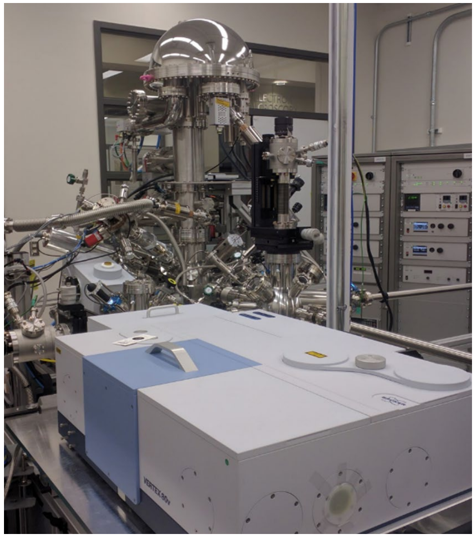
New Spectrokinetic Collaboration

- 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_2 versus C_2 selectivity
  - *Operando* tools
    - Need higher time-resolution
    - Coupled to detailed kinetic information, *Spectrokinetic*

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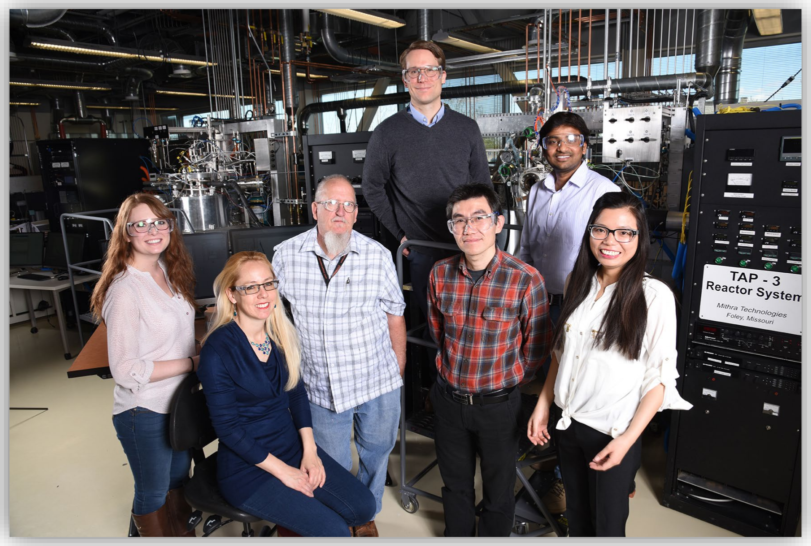

Collaborators

- John Gleaves (Washington University in Saint Louis)
- Gregory Yablonsky (Washington University in Saint Louis)
- Denis Constales (Ghent University, Belgium)
- Alessandro Fortunelli (University of Pisa)
- Jian Qian (Caltech)
- William A. Goddard (Caltech)

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