U.S. DEPARTMENT OF
ENERGY
Office of
ENERGY EFFICIENCY &
RENEWABLE ENERGY

AMMTO & IEDO JOINT PEER REVIEW
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Catalyst Evaluation for Deactivation and Remediation (CEDAR)| IEDO

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DE-FOA-0002252-1775| 9/1/21 – 9/30/24

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Project Overview

Addressing **catalyst deactivation** through Dynamic Catalyst Science (DCS) experimental, modeling and simulation tools

- Over 80% of chemical manufacturing processes rely on a heterogeneous catalyst
  - Wide ranging impact across the chemical manufacturing sector
- Progressive loss in catalyst performance reduces productivity and process efficiency
  - Results in waste and increased energy use in downstream separations
- Shutdown and replacement costs due to deactivation
  - Estimated in $B (billions of dollars)

Alignment with IEDO Mission:

- Accelerates innovation in cost-effective technology
  - Reducing catalyst replacement, regeneration, shut down costs
- Increases energy efficiency
  - Reduces nonselective side reactions, reduces energy required for separations
- Reduces greenhouse gas (GHG) emissions
  - Related to regeneration process, i.e., coke removal generating CO_2

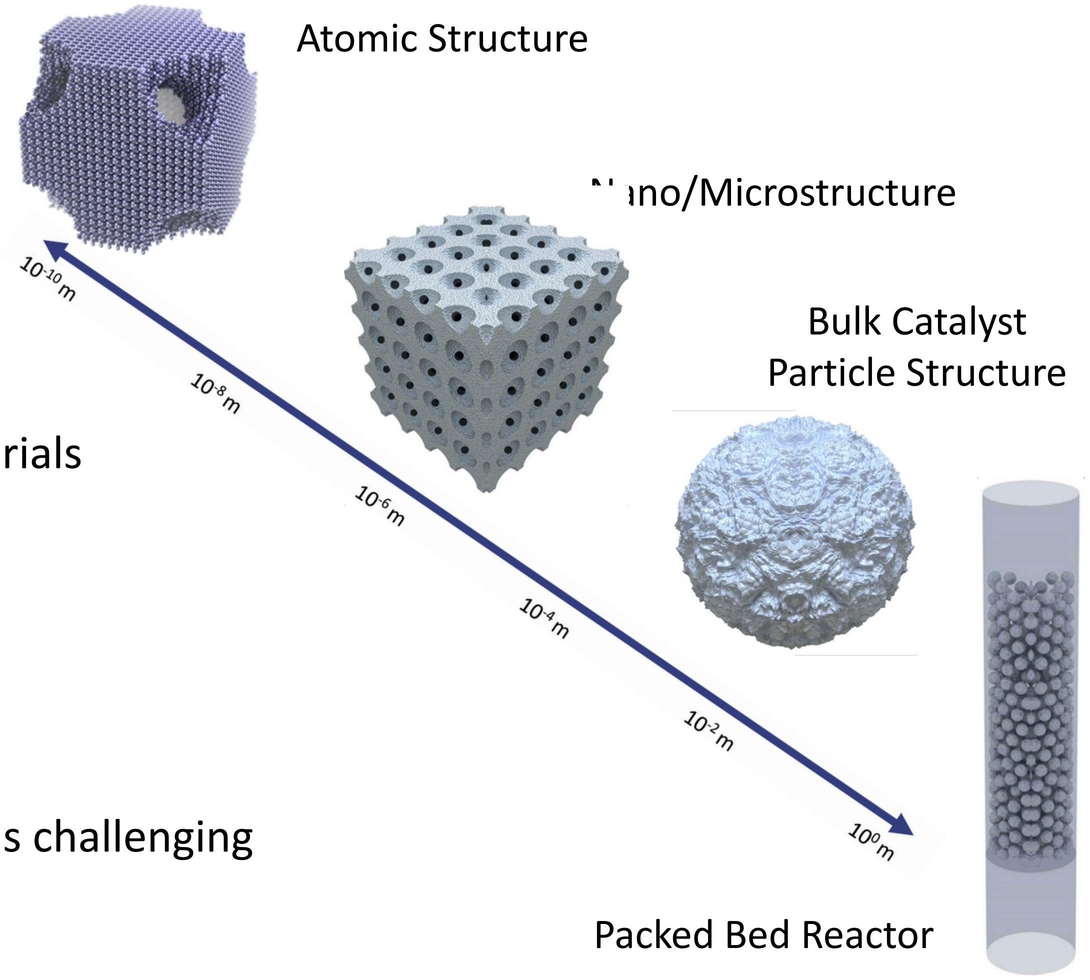
IMPACT Space

Energy, Emissions, & Environment: Reduced waste (catalyst replacement and nonselective side reactions), reduced energy usage for downstream product separations
Technical & Scientific: Faster development of advanced catalyst formulations, more productive reactor operation

Project Overview

Addressing **catalyst deactivation** through Dynamic Catalyst Science (DCS) experimental, modeling and simulation tools

- Main barriers:
  - Catalyst deactivation takes place on multiple time/length- scales with wide and varying phenomena
    - The lifetime of new catalysts is difficult to predict
  - Industrial catalysts are complex, multicomponent materials
    - Difficult to characterize under working conditions
  - Kinetic tools are based on gas phase measurement
    - Spectroscopic tools do not provide detailed kinetics
  - Dynamic experiments provide powerful information
    - Beyond the current reach of spectroscopy
  - Deterministic (physics based) analysis of dynamic data is challenging



Project Outline

Innovation: New research tools to address catalyst deactivation based on dynamics

Project Lead: Rebecca Fushimi, Idaho National Laboratory

Project Partners: Clariant Corporation, National Renewable Energy Laboratory, Georgia Institute of Technology, University of Houston

Timeline: 9/1/21 – 9/30/24, progress 50%

Budget: $5,000,000 Federal, $1,536,062 Cost Share

	FY22 Costs	FY23 Costs	FY24 Costs	Total Planned Funding
DOE Funded	$1,253,625	$1,498,550	$2,247,825	$5,000,000
Project Cost Share	$361,844	$469,687	$704,531	$1,536,062

End Project Goals:

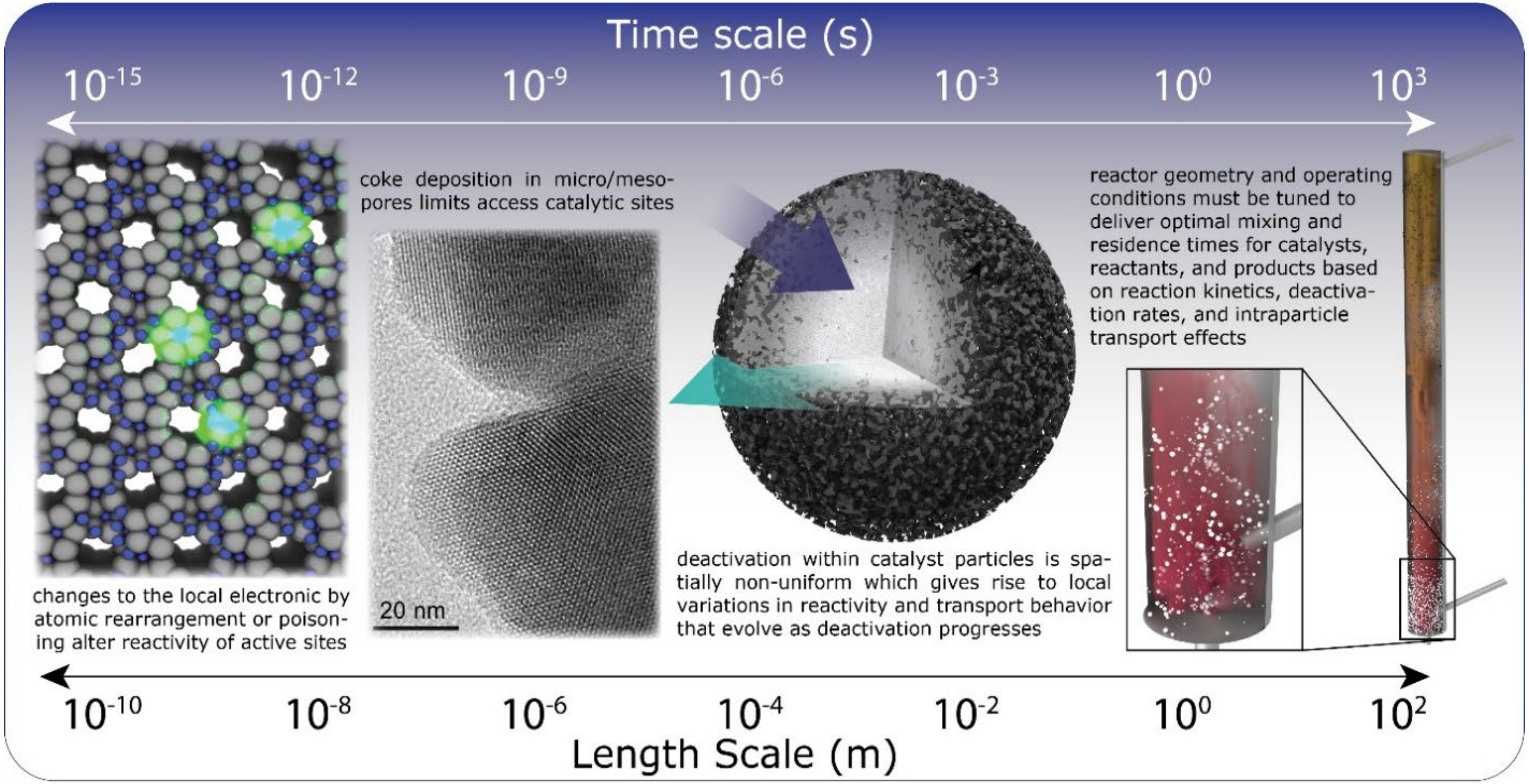
1) Demonstrate an experimental method for spectrokinetic analysis on the 10^{-3}s time scale,
2) Build an analytical tool for converting DCS data to machine-learned kinetic (MLK) models,
3) Demonstrate a multiscale process simulation tool that propagates MLK model to industrial time and length scales to reduce the time for predicting catalyst deactivation by 70%

Background & Strategic Approach

Catalyst Deactivation - *loss of activity over time*

- Comprises vast time and length scales
- Wide and varied phenomena
  - Chemical poisoning
  - Carbon accumulation
  - Solid state diffusion
  - Sintering/pore collapse
  - Mechanical/attrition
  - Leaching
  - Fouling
  - Etc.

No reliable methods to predict long-term deactivation



changes to the local electronic by atomic rearrangement or poisoning alter reactivity of active sites

coke deposition in micro/meso-pores limits access catalytic sites

deactivation within catalyst particles is spatially non-uniform which gives rise to local variations in reactivity and transport behavior that evolve as deactivation progresses

reactor geometry and operating conditions must be tuned to deliver optimal mixing and residence times for catalysts, reactants, and products based on reaction kinetics, deactivation rates, and intraparticle transport effects

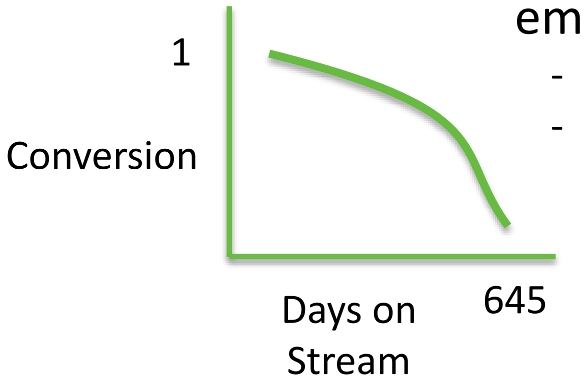
Background & Strategic Approach

Propane Dehydrogenation (PDH)

- ‘On purpose’ propylene = 2 Mt/yr U.S., 1.7 MMBtu/ton
- Significant energy savings compared to cracking
- Precursor for polypropylene (consumer products: packaging, bottles, textiles, etc.), acrylonitrile, acrylic acid, etc.

Chromia catalyst, Catofin® process
Short time scale reaction/regeneration
Multiple deactivation phenomena on different time-scales, reversible and irreversible:

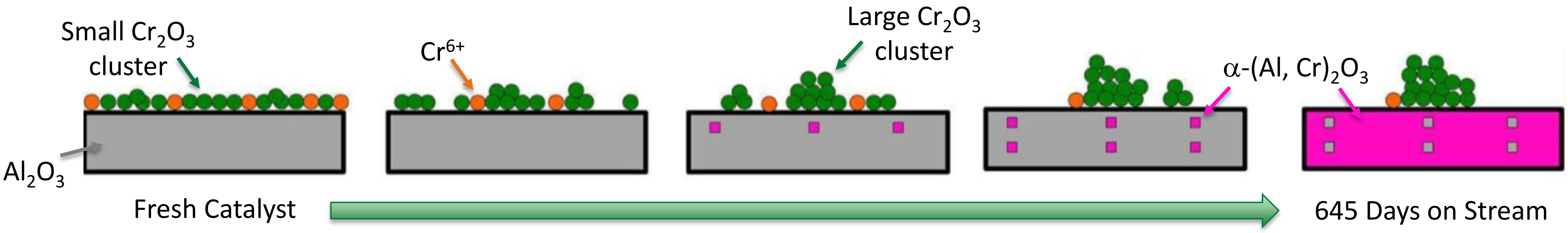
- Coke deposition/burn off
- Sintering of alumina (loss of surface area)
- Solid solution formation (migration of Cr^{3+} into alumina)



Currently used empirical models

- Based on historical data
- Unreliable for new regimes

Fridman and Xing (2017)
I&EC Research 56, 7937



Background & Strategic Approach

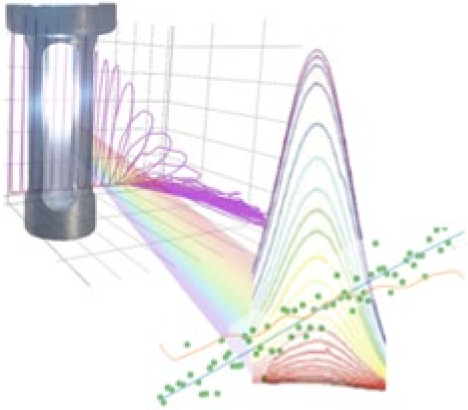
Our Approach: Dynamic Catalyst Science (DCS) – *The use of T, C or P transients to perturb the state of a chemical system, response or relaxation indicates how the system works.*

1. Develop dispersive-mode transient spectrokinetic method to improve the time-resolution of *operando* spectroscopy.
    - Current State-of-the-art 10^0 s $\Rightarrow$ need 10^{-3} s
2. High-volume transient spectrokinetic data is used to build Machine-Learned Kinetic (MLK) Models.

Hypothesis: Short time-scale chemical kinetic phenomena is predictive of long-term deactivation behavior.

3. Propagate MLK model through time- and length-scales using multiscale reactor simulation
4. Predict catalyst deactivation and developed advanced operational strategies.

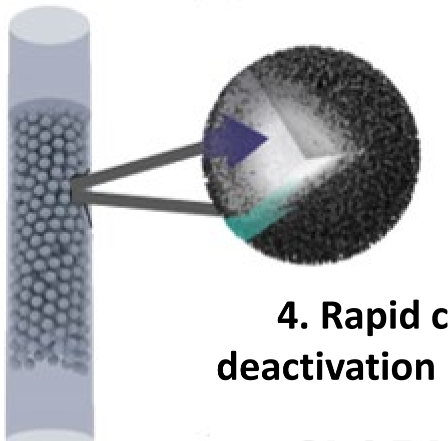
1. Transient spectrokinetic data



2. Machine-Learned Kinetic Models

$$R_i(t) = \sum_{k=1}^{N} \psi_{i,k}^{C} C_k(t) + \sum_{j=1}^{M} \psi_{i,j}^{U} U_j(t) + \sum_{k=1}^{N} \sum_{j=1}^{m} \psi_{i,k,j}^{CU} C_k(t) U_j(t) + \sum_{j=1}^{m} \sum_{j=1}^{m} \psi_{i,k,l}^{UU} U_j(t) U_l(t)$$

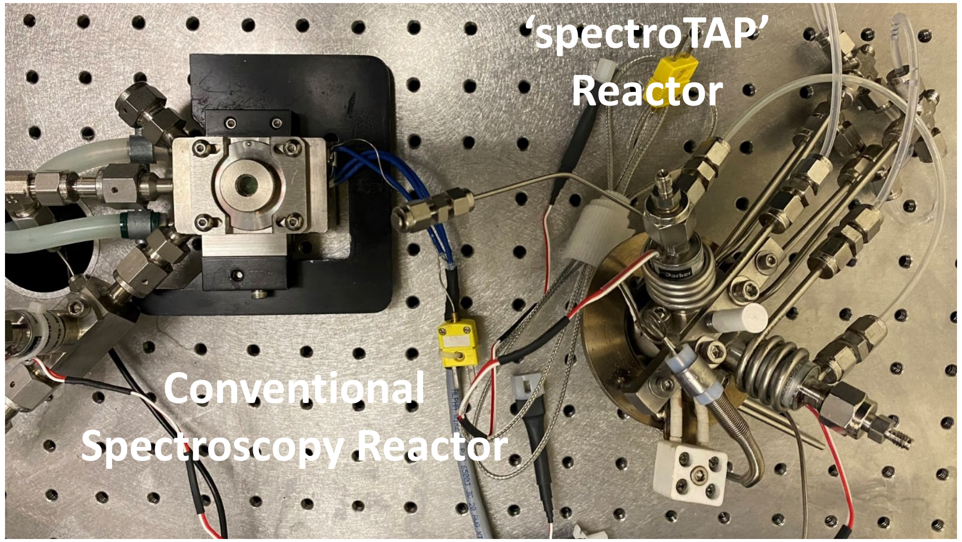
3. Multiscale reactor simulation



4. Rapid catalyst deactivation prediction

Results and Achievements

Advanced Transient Spectrokinetic Tool Demonstrated

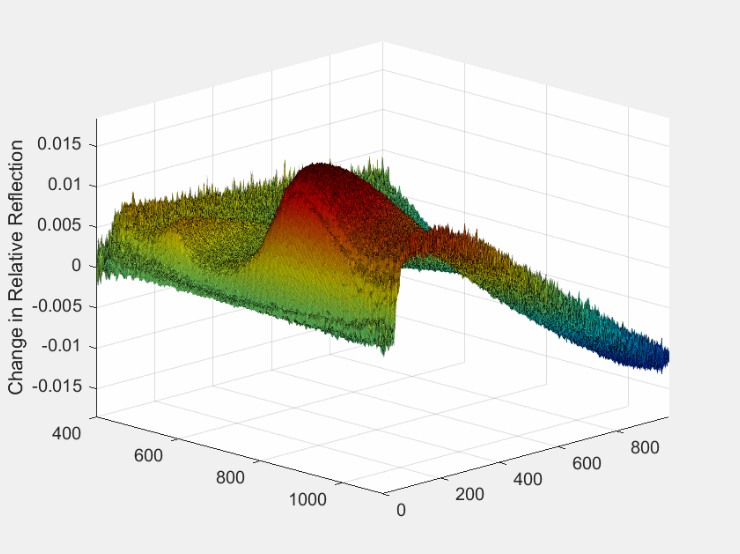


SpectroTAP Advantages:

- No dead volume
- Isothermal measurement (850 °C)
- Well-defined transport
- Separation of transport/kinetics
- Transient experiments
- 10^{-3} millisecond time-resolution

Custom built dispersion detector (not shown) with fast photodiodes enables high time resolution

spectroTAP: Pulsing Propane over an Oxidized CrO_x Catalyst



New Catalyst Information

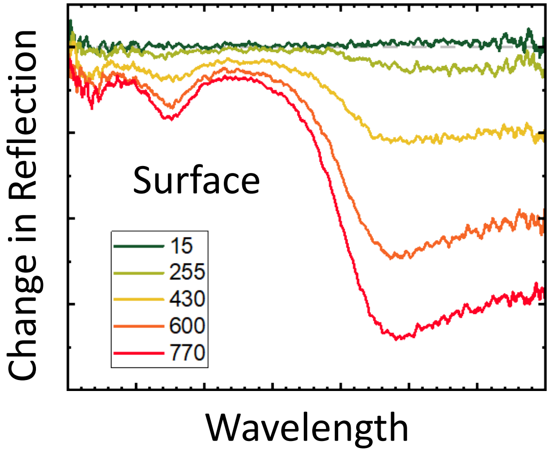
Propane pulsing:

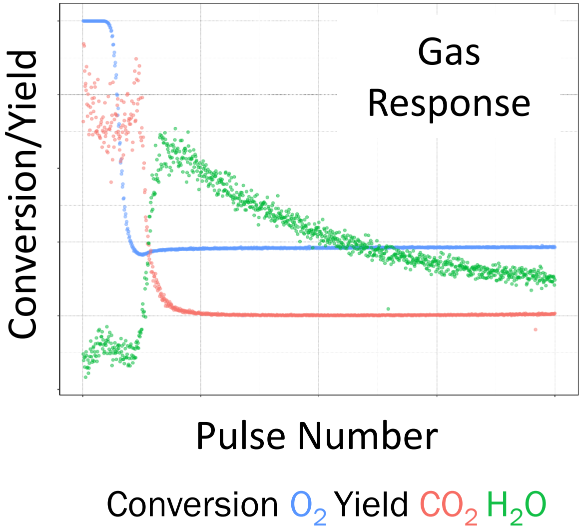
- Kinetics of coke accumulation separated from propylene formation

Oxygen pulsing:

- Kinetics of coke oxidation separated from catalyst reoxidation

Surface Change and Gas Response during Oxidation

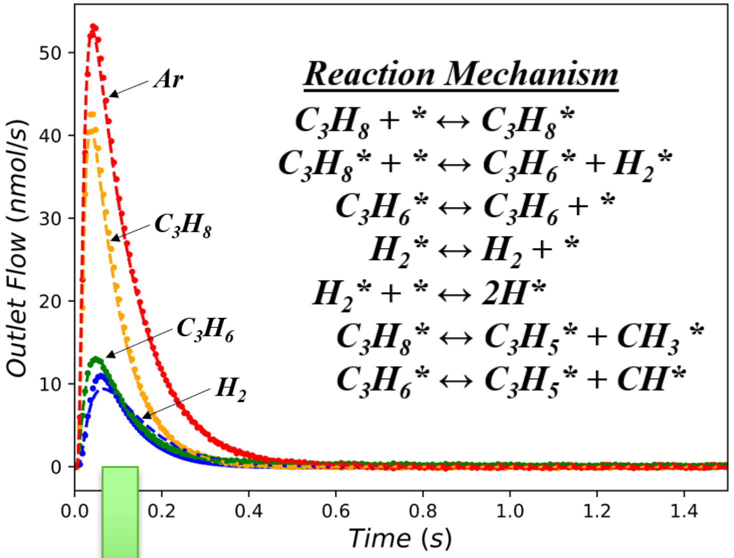




Results and Achievements

From TAP Pulses to Pellets to Packed Beds…

1 of 10,000 TAP pulse response cycles



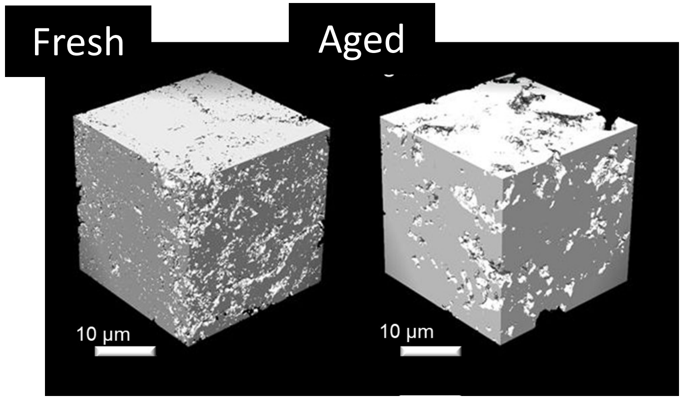
Reaction Mechanism

$$C_3H_8 + * \leftrightarrow C_3H_8*$$
$$C_3H_8* + * \leftrightarrow C_3H_6* + H_2*$$
$$C_3H_6* \leftrightarrow C_3H_6 + *$$
$$H_2* \leftrightarrow H_2 + *$$
$$H_2* + * \leftrightarrow 2H*$$
$$C_3H_8* \leftrightarrow C_3H_5* + CH_3*$$
$$C_3H_6* \leftrightarrow C_3H_5* + CH*$$

via Kinetic Informed Neural Net (KINN)

Rate Constant	Measured Value from TAP
k_{1f} [$m^3\ mol^{-1}\ s^{-1}$]	16.3
k_{1r} [$m^3\ mol^{-1}\ s^{-1}$]	1.97×10^{-6}
k_{2f} [s^{-1}]	9.54×10^{4}
k_{2r} [$m^3\ mol^{-1}\ s^{-1}$]	1.02×10^{3}
k_{3f} [s^{-1}]	143
k_{3r} [s^{-1}]	0

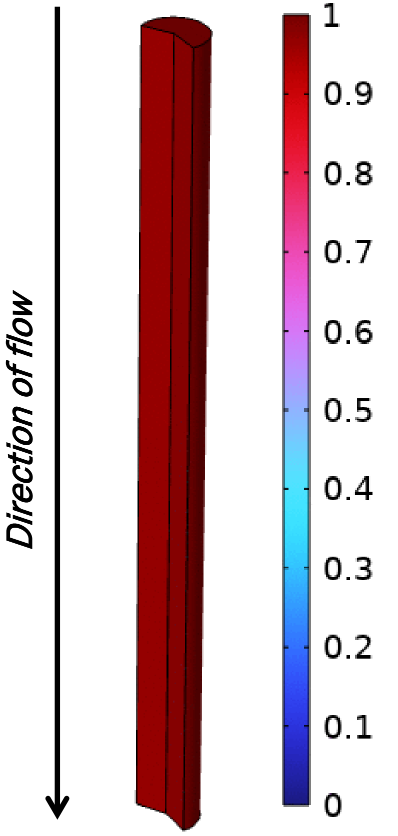
Nano-CT scan of industrial catalyst



Mesoflow simulation
250 µm catalyst particle

Concentration

Deactivation profile for spherical catalyst in packed bed



Active site consumption $[S]/[S]_0$

Future Work, Technology Transfer, & Impact

Future Work:

- Catalyst testing, compare kinetics and deactivation predictions for different compositions
- Advance neural net method for 10k pulse response analysis, Machine Learned Kinetic Models
- Connect TAP kinetics to industrial scale

Technology Transfer:

- Patent for analytical device and methodology, Copyright assertion on software tools
- Identify other catalyst deactivation challenges
  - E.g., Oleflex PDH, selective hydrogenation, methanol synthesis, selective oxidations, Fischer-Tropsch, alcohol dehydration, biomass/waste plastic fast pyrolysis, etc.
  - Adapt tools for customers (industrial catalyst developers, chemical manufacturers)
  - Enable access to tools/expertise

Impact:

- DCS tool investment broadly supports development of catalyst technology in other areas, e.g.,
  - ForgeNano, UOP, ‘Catalyst active site design by atomic layer deposition for advanced chemical manufacturing’
  - University of Houston, INEOS, ‘Resilient ammoxidation of small hydrocarbons using forced dynamic operation’

Reducing costs:	Faster assessment of improved catalyst stability, more productive reactor operation models
Increasing energy efficiency:	Reduces waste (catalyst replacement), maximizes selectivity, decreases energy load in downstream separations
Reducing GHG emissions:	Avoiding CO_2 emissions associated with catalyst regeneration

Questions?

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