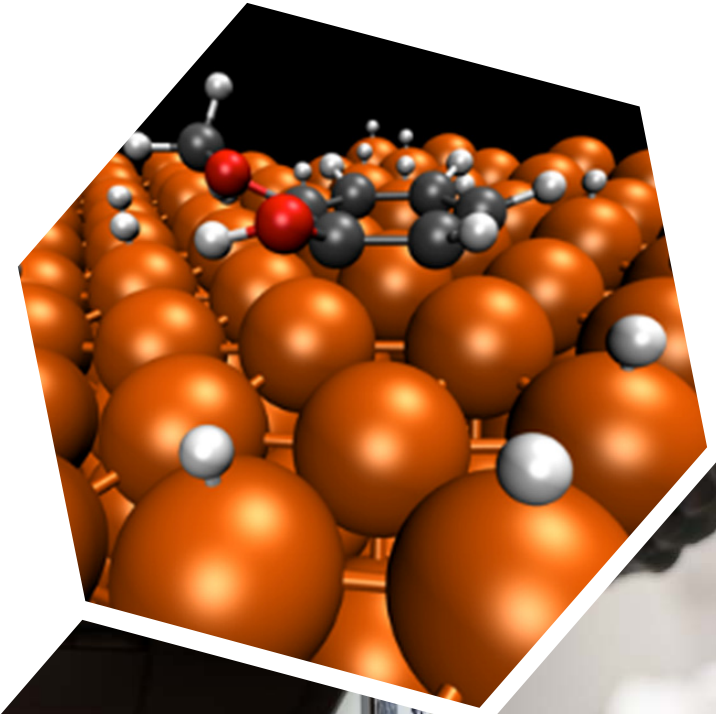
ChemCatBio
Chemical Catalysis for Bioenergy

Consortium for Computational Physics and Chemistry (CCPC)

PIs and Task Leads: Jim Parks (ORNL), Rajeev Assary (ANL), Larry Curtiss (ANL), Bill Rogers (NETL), Syam Madhava (NETL), David Robichaud (NREL), Peter Ciesielski (NREL), Roger Rousseau (PNNL), Asanga Padmaperuma (PNNL)
[full list of CCPC team on last slide]

Oak Ridge National Laboratory · Argonne National Laboratory · National Energy Technology Laboratory · NREL National Renewable Energy Laboratory · Pacific Northwest National Laboratory



ChemCatBio Webinar
November 14, 2018

U.S. DEPARTMENT OF ENERGY | Office of ENERGY EFFICIENCY & RENEWABLE ENERGY
BIOENERGY TECHNOLOGIES OFFICE

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A Multi-Scale Problem …
A Multi-Lab Solution

CCPC

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Oak Ridge National Laboratory
Pacific Northwest National Laboratory
National Energy Technology Laboratory
NREL National Renewable Energy Laboratory
Argonne National Laboratory

Energy Materials Network
U.S. Department of Energy

ChemCatBio
Chemical Catalysis for Bioenergy

BioPower

Biochemical Process Modeling and Simulation

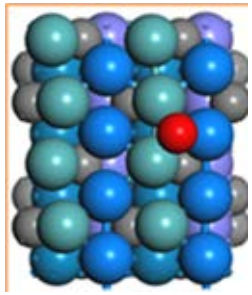
fcic
Feedstock-Conversion Interface Consortium

Bioprocessing Separations Consortium

- Accelerating catalyst/enzyme discovery for bioenergy conversion
- Optimizing process design for complexity associated with biomass feedstocks and products
- Enabling process integration and intensification via optimal coupling of catalysis and separation functions

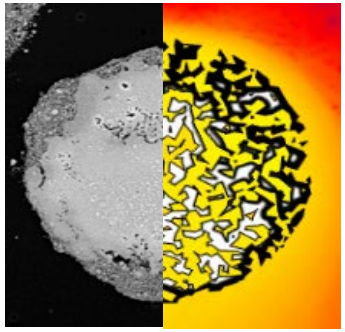
Consortium for Computational Physics and Chemistry (CCPC)

Atomic Scale Catalysis Modeling



Investigating novel catalyst material combinations and understanding surface chemistry phenomena to guide experimentalists

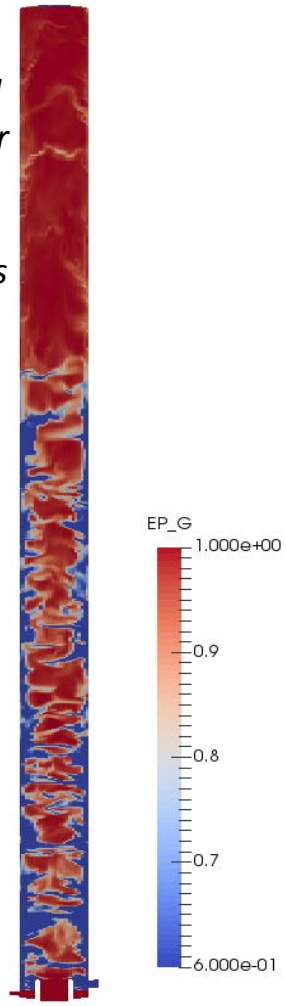
Meso Scale Particle Modeling



Understanding mass transport of reactants/products, reaction kinetics, and coking and deactivation processes

Process Scale Reactor Modeling

Determining optimal process conditions for maximum yield and enable scale-up of ChemCatBio catalysts



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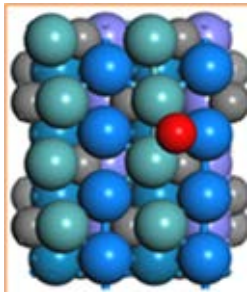
Atomic Scale Catalysis Modeling



Investigating novel catalyst material combinations and understanding surface chemistry phenomena to guide experimentalists

Dr. Seonah Kim (NREL)

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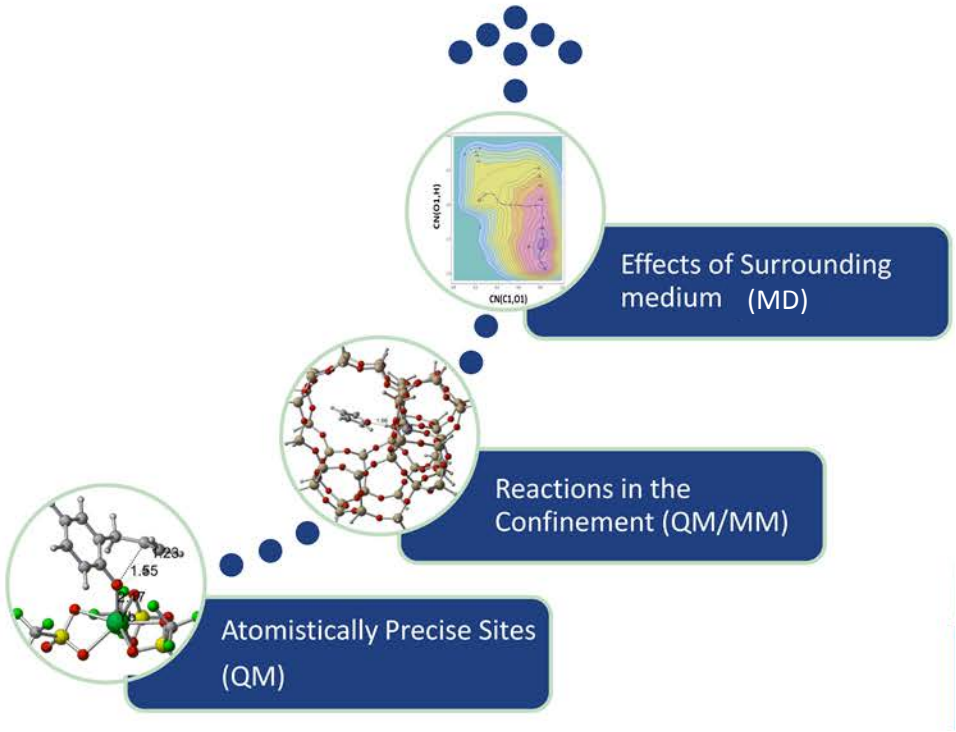
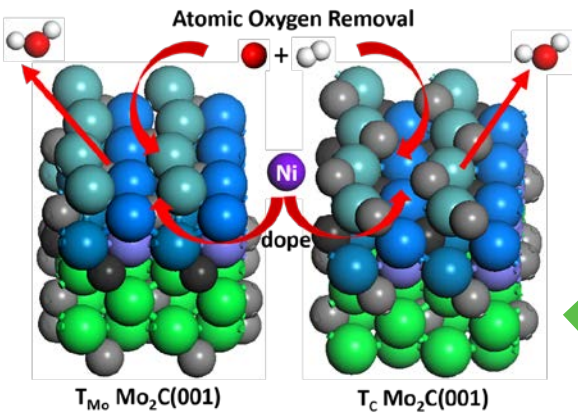
Guiding compositional catalysis design utilizes multiple atomistic toolsets



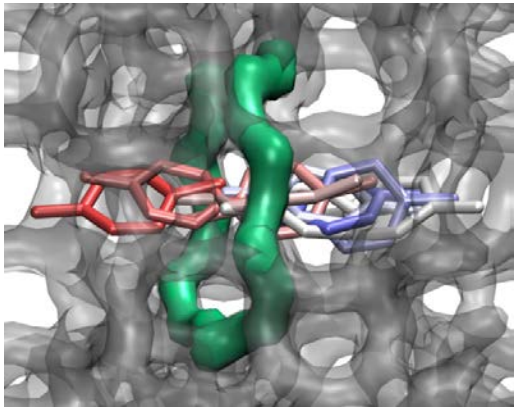
Atomistic simulations using static to dynamic models to support ChemCatBio:

- ***Understand*** catalyst activity and yield selectivity as a function of composition
- ***Guide*** new catalyst compositional synthesis (ACSC)
- ***Optimize*** operating conditions

Atomistic modeling is useful in a variety of ways

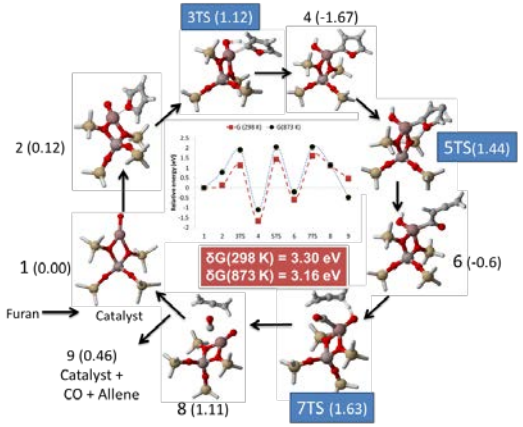


Modeling dopants to tailor product selectivity and balance multi-functional catalytic activity

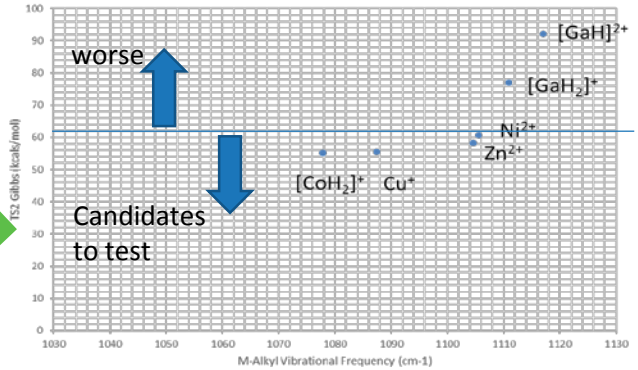


Exploring molecular-scale transport

Design Performance-Advantaged Catalysts



Exploring catalytic cycles and nature of active sites to identify structure/function relations

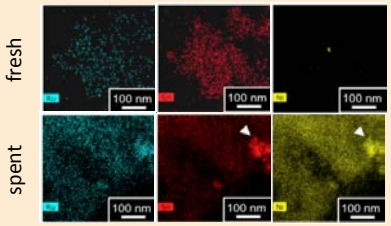


Screening catalysts to guide new syntheses

Developing a holistic view of inverse bimetallic catalysts for selective carboxylic acid reduction

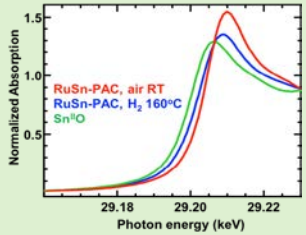
ORNL

SEM-EDS Spectroscopy



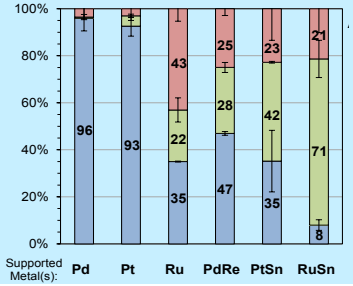
ANL

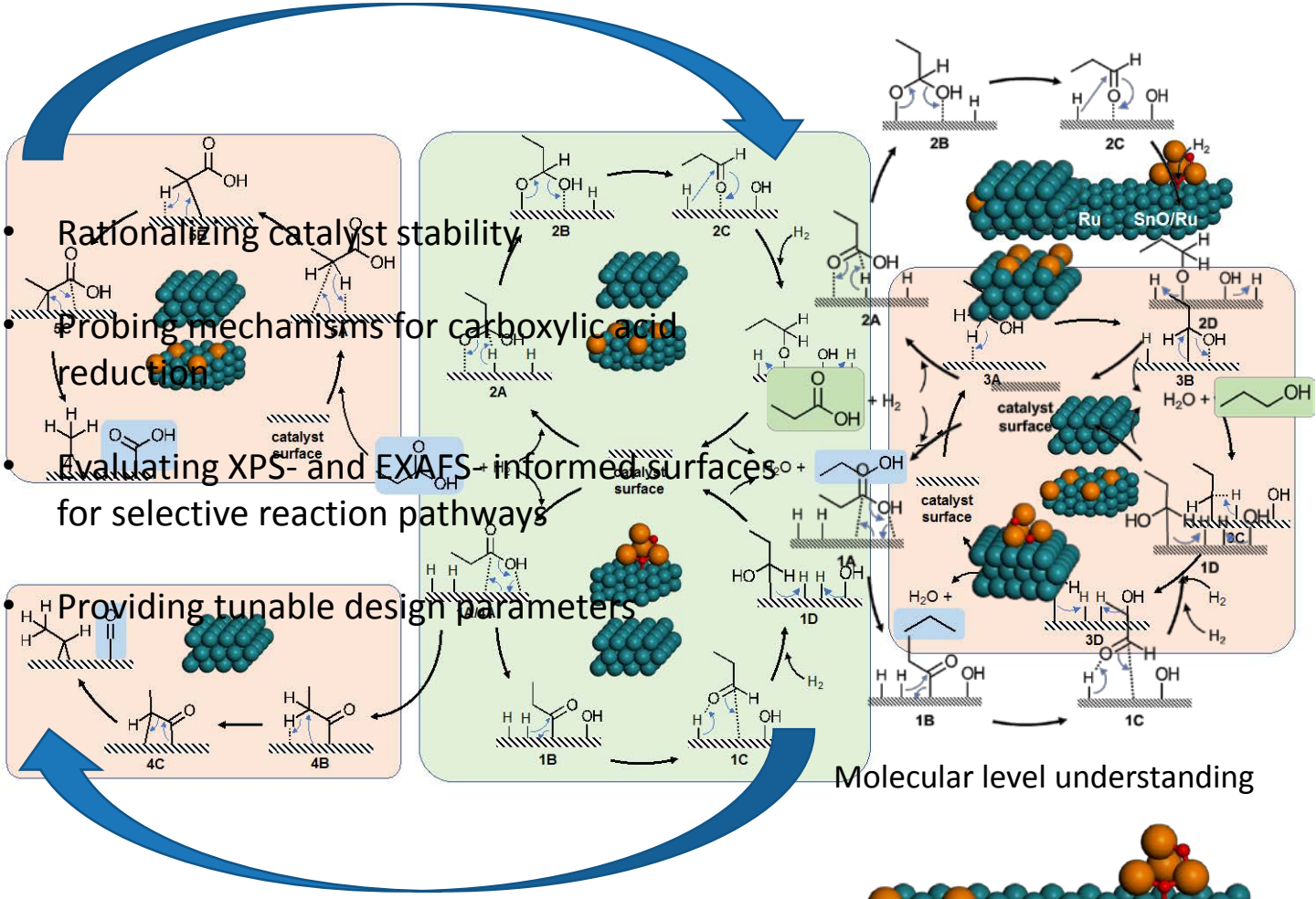
XAS/EXAFS/XANES



NREL

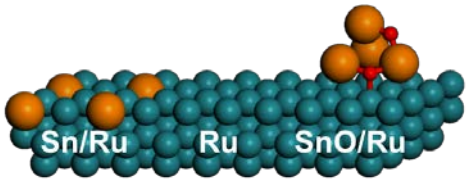
Catalytic testing





- Rationalizing catalyst stability
- Probing mechanisms for carboxylic acid reduction
- Evaluating XPS- and EXAFS-informed surfaces for selective reaction pathways
- Providing tunable design parameters

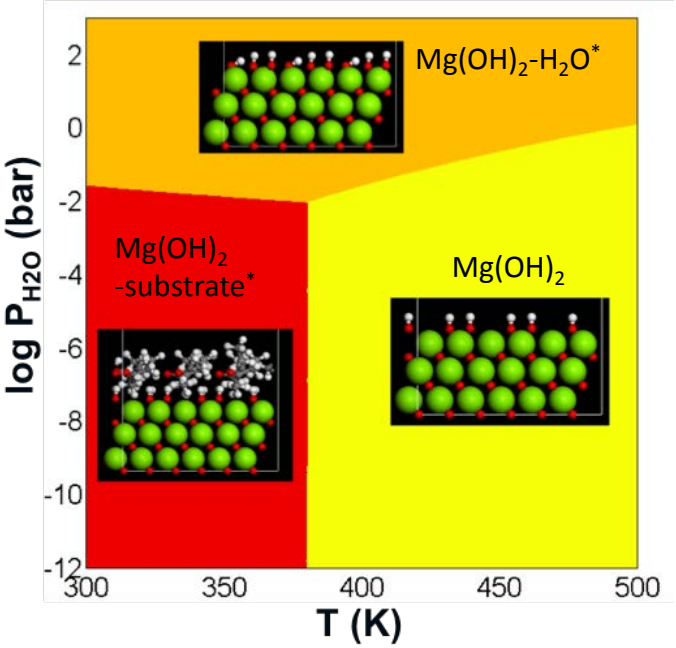
Molecular level understanding

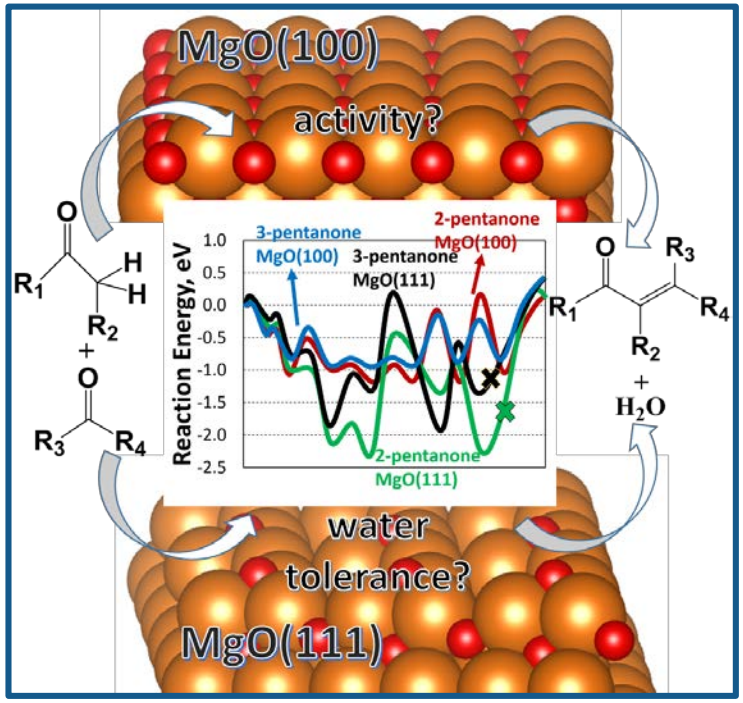


Vardon et al., *ACS Catal.*, **2017**, *7* (9), 6207-6219
Vorotnikov V, Eaton T, et al., ***in prep***.

Understanding water deactivation of metal oxide catalysts

- Predicting surface composition using equilibrium thermodynamics
- Discerning activation energy differences in aldol condensation of 2- and 3-pentanone over MgO surfaces
- Providing mechanistic insight into the role of water, hydroxyls to understand water tolerance



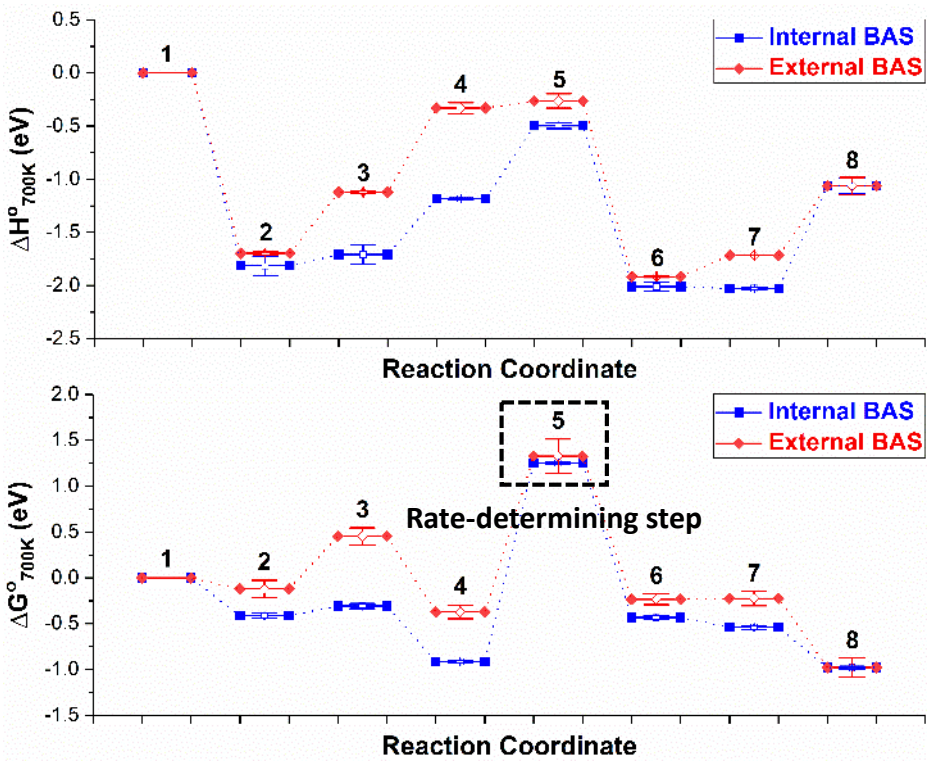


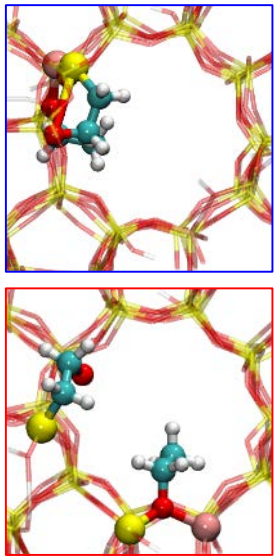
Mingxia Zhou, Rajeev S. Assary, Larry A. Curtiss (ANL)/ Vassili Vorotnikov, Derek Vardon

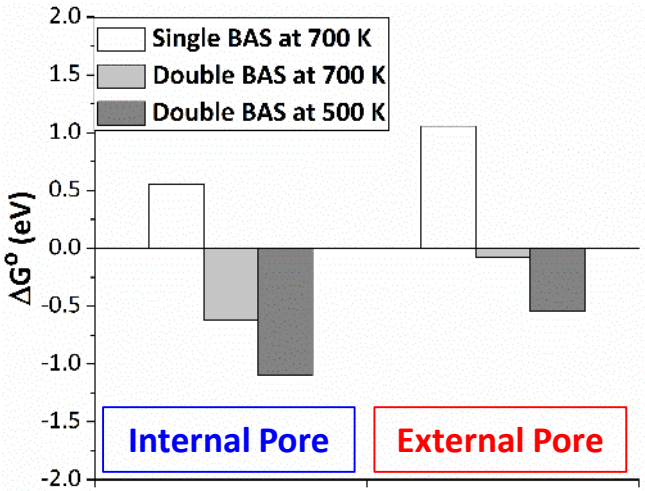
Considering the enthalpy and entropy contribution towards Gibbs free energy is critical for studying the ethanol upgrading over zeolite

$$\text{Ethoxy}^* + \text{Ethene}_{(g)} \leftrightarrow \text{Ethoxy_Ethene}^*_{\text{complex}}$$

Thermodynamic Profile of Ethanol Upgrading



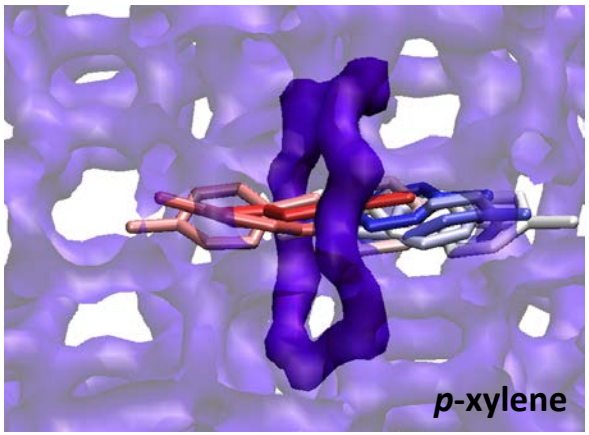


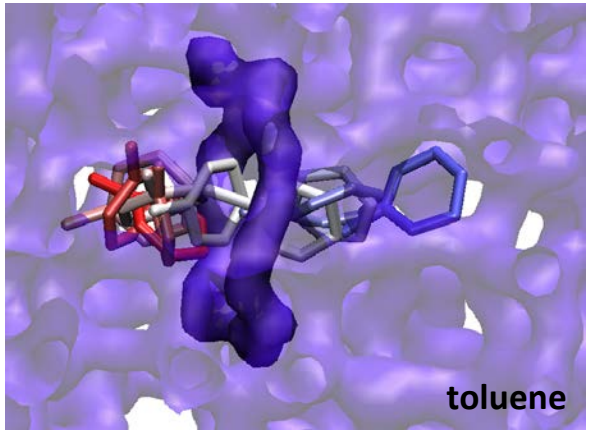


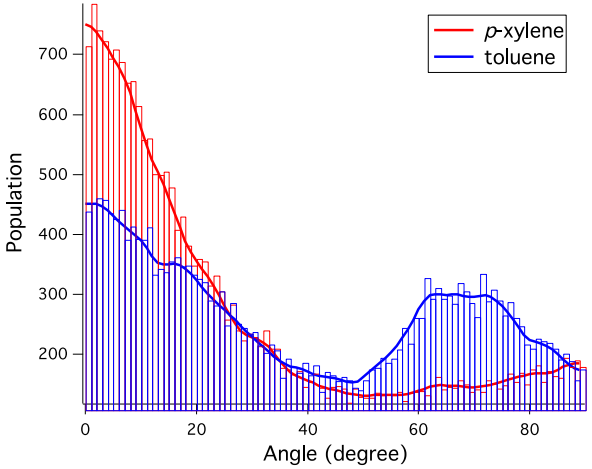
- Incorporation of entropy not only leads to different thermodynamic landscape, but also identifies the rate-determining step.
- Thermodynamic profiles of rate-determining step can further be tuned by increasing the **number of BAS** and lowering the **operating temperature**.

Simuck Yuk, Roger Rousseau (PNN

Diffusion in microporous and mesoporous catalysts

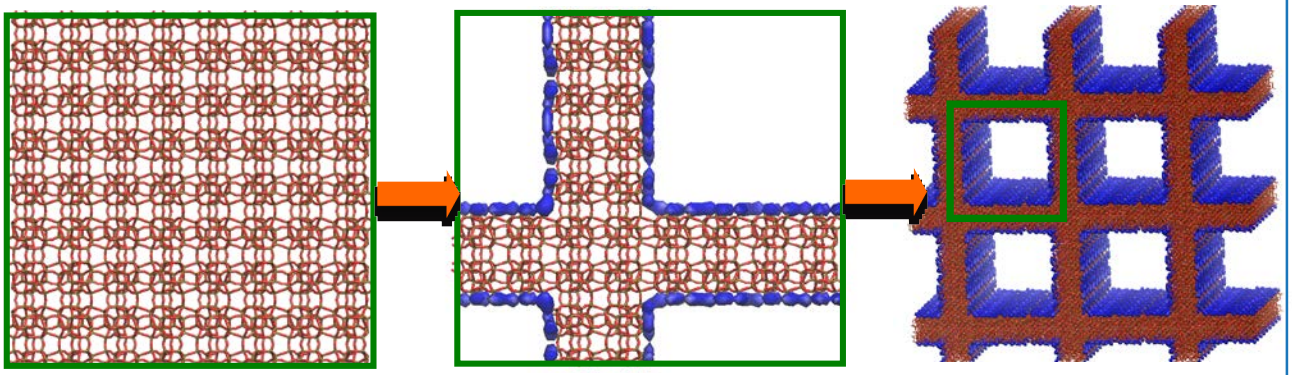




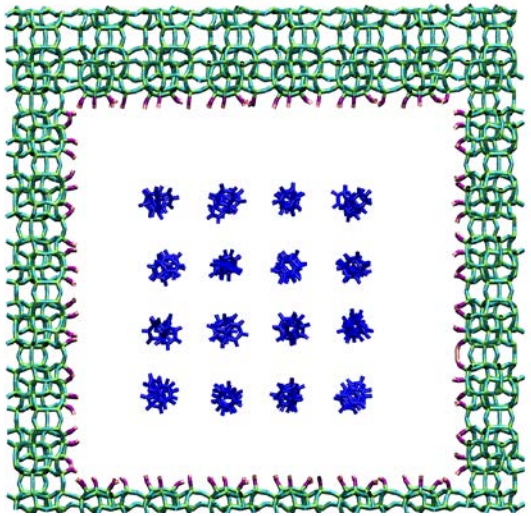


p-xylene and toluene diffusion in microporous H-ZSM-5 (Bu, *JPCC*, 2017)

Characterize the diffusivities of coke precursors in microporous and mesoporous H-ZSM-5



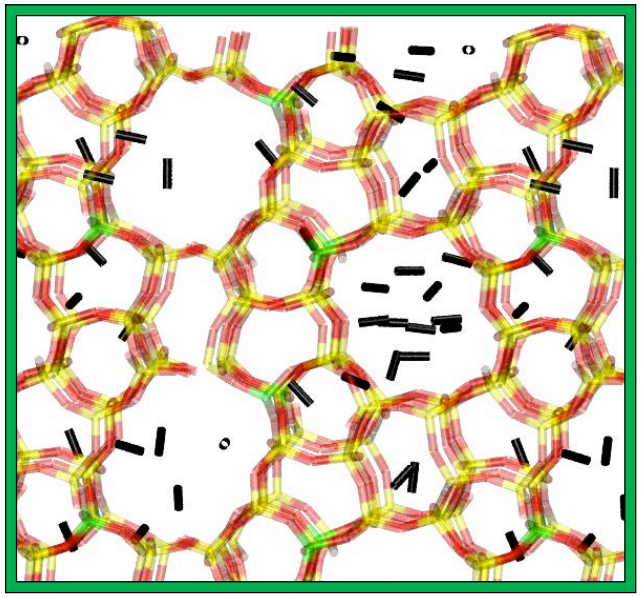
D_S ($10^{-10}m^2/s$,700K)	Micropore	Mesopore (20Å)	Mesopore (60Å)
benzene	0.74 ± 0.20	107 ± 15	260 ± 21
naphthalene	0.04 ± 0.01	40 ± 12	92 ± 14
anthracene	0.02 ± 0.01	17 ± 6	30 ± 7

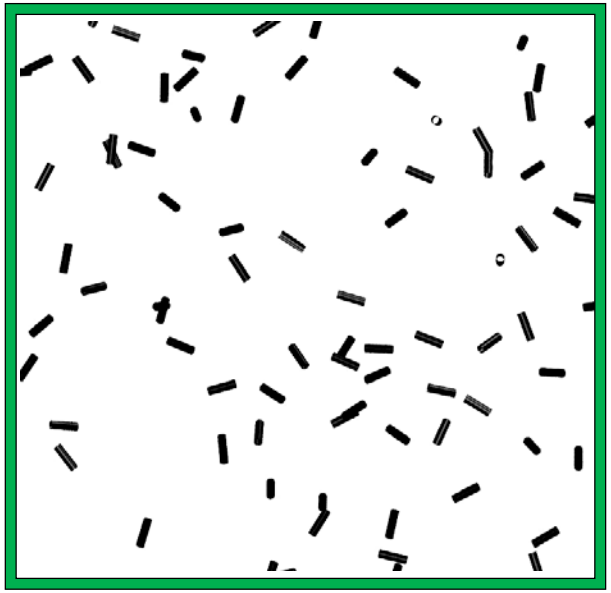


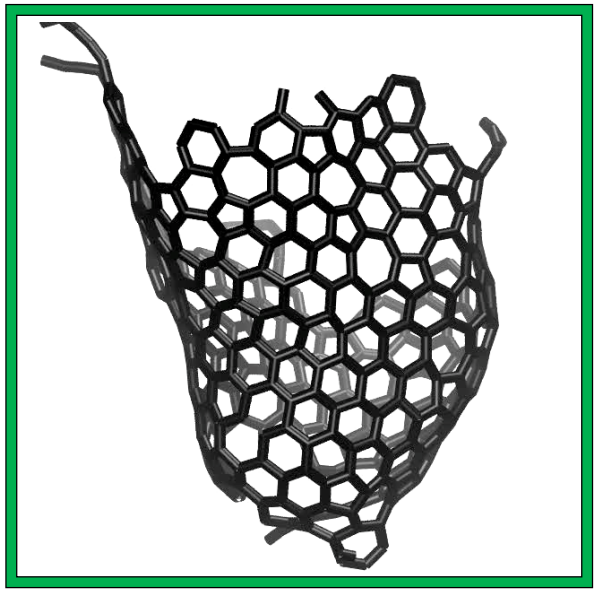
benzene diffusion in mesoporous H-ZSM-5 (Bu, *Catalysis today*, 2018)

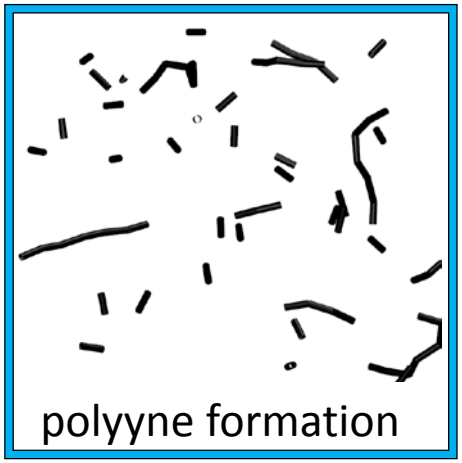
Diffusion in zeolites can impact coke formation, longevity of the catalyst, product selectivity, yields and separations.

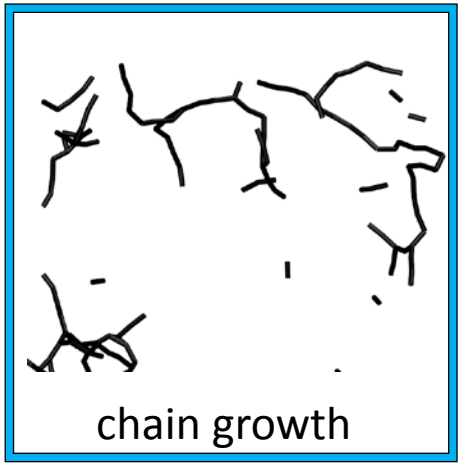
Coke formation via ReaxFF MD Simulation

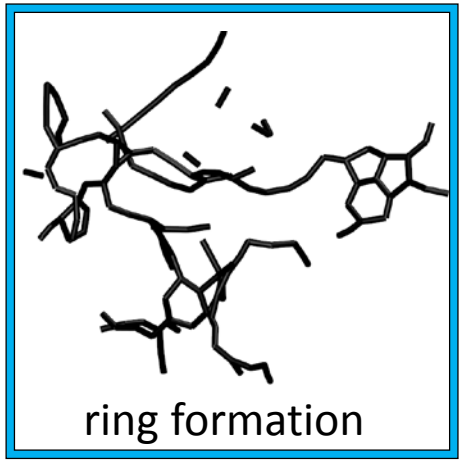


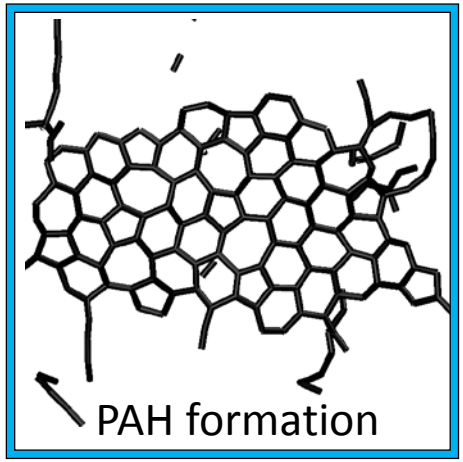










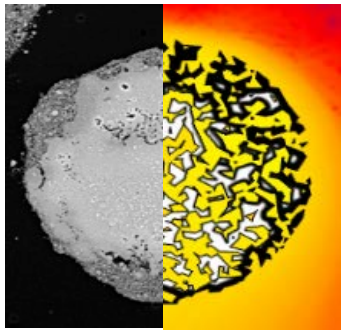


- Composition of coke formed inside zeolite and on the external surface might be different.
- Microporous topology confine the rearrangement of branched chains to form aromatic rings.

Lintao Bu (NREL

Consortium for Computational Physics and Chemistry (CCPC)

Meso Scale Particle Modeling



Understanding mass transport of reactants/products, reaction kinetics, and coking and deactivation processes

Dr. Peter Ciesielski (NREL)

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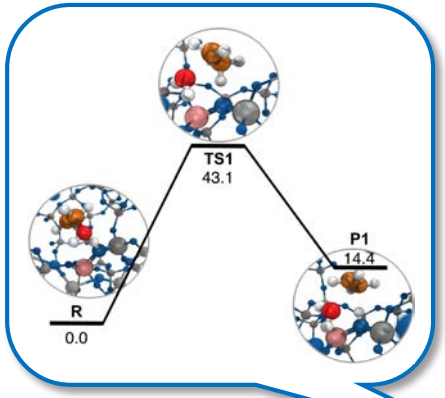
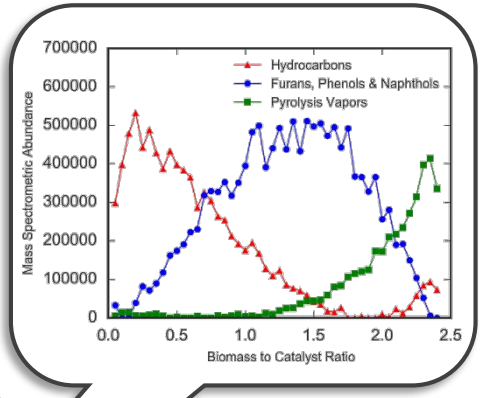
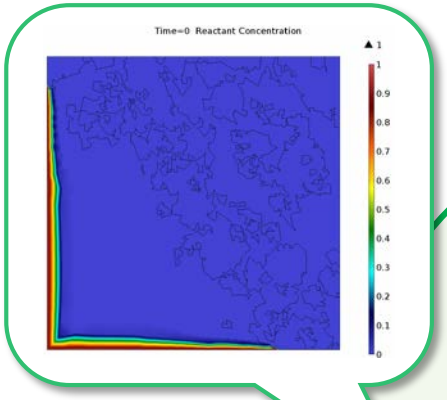
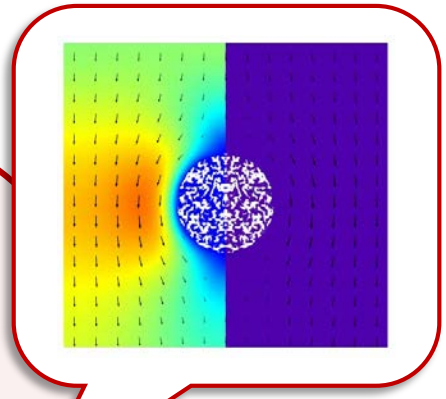
Experimentally observed “effective” catalytic reaction rates are dependent on system-specific parameters (particle size, porosity, flow, etc.)









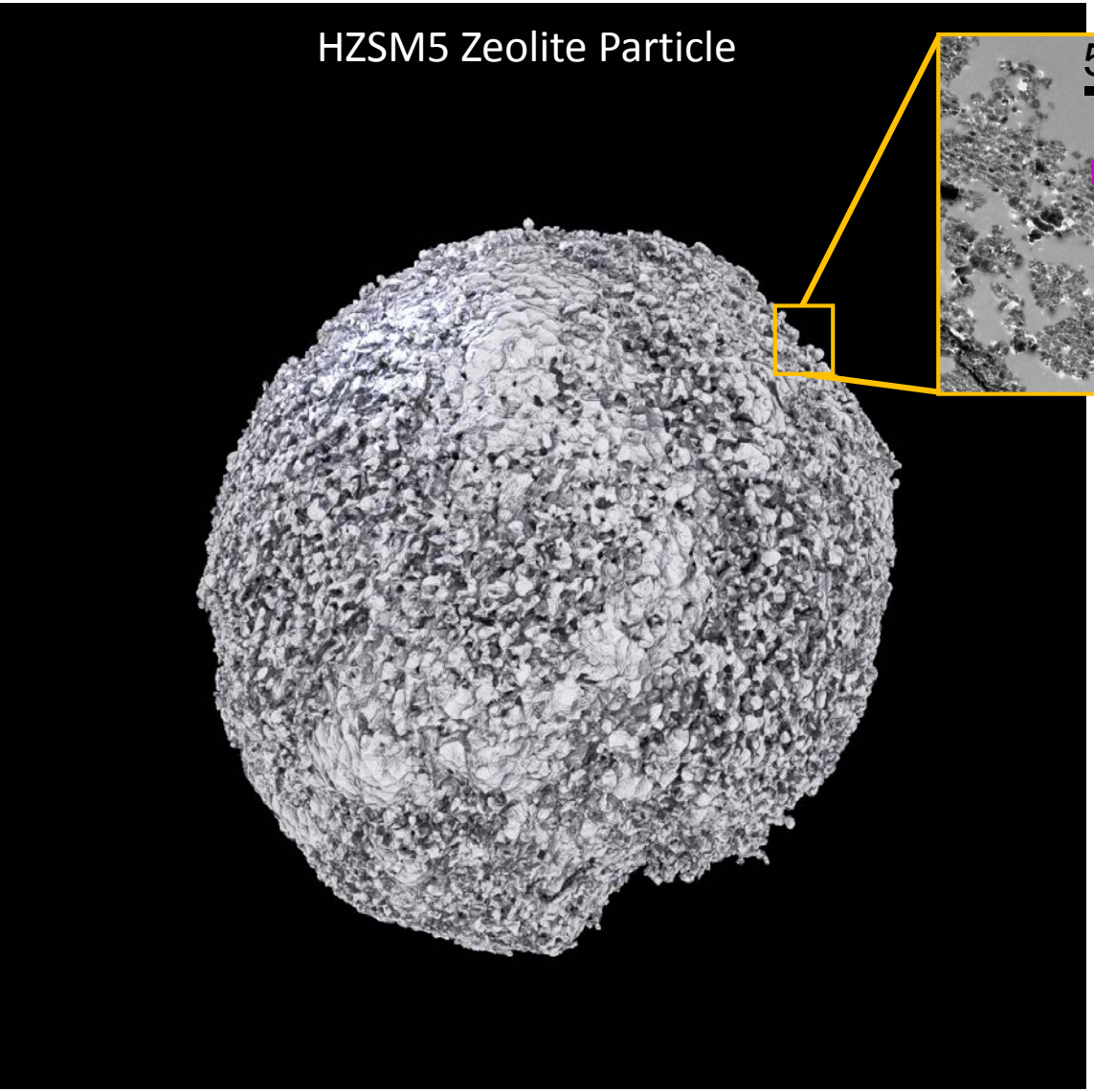
Intrinsic reaction kinetics

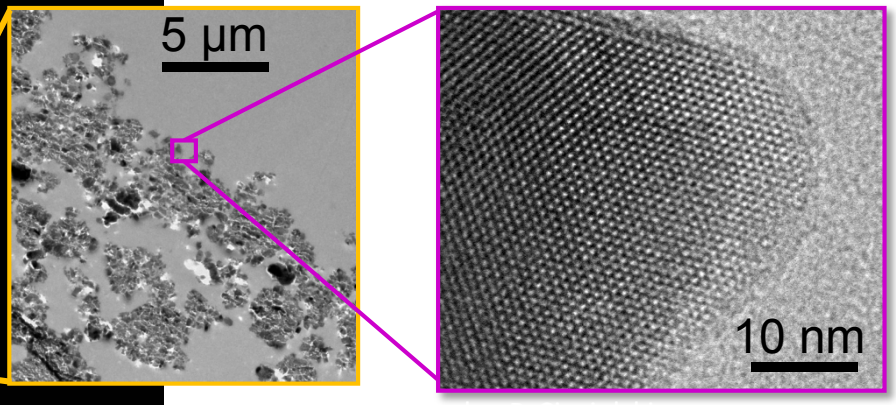
Observed reaction rate

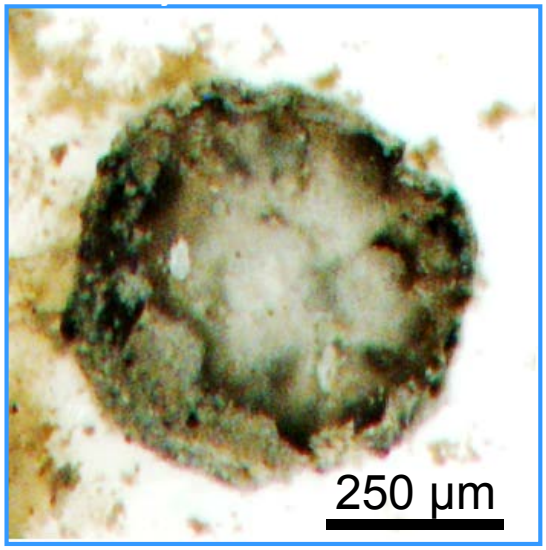
Intra-particle diffusion

Extra-particle diffusion and convection

Constructing accurate mesoscale models requires detailed structural characterization to parameterize the particle geometry and transport models



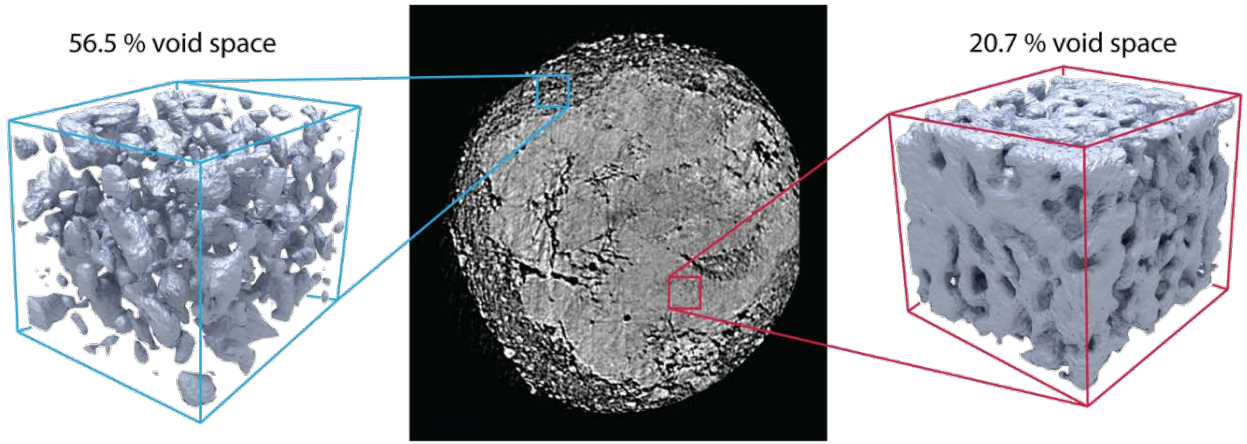




 XCT Data: B. Kappes, Colorado School of Mines; TEM Data: P. Ciesielski, NREL

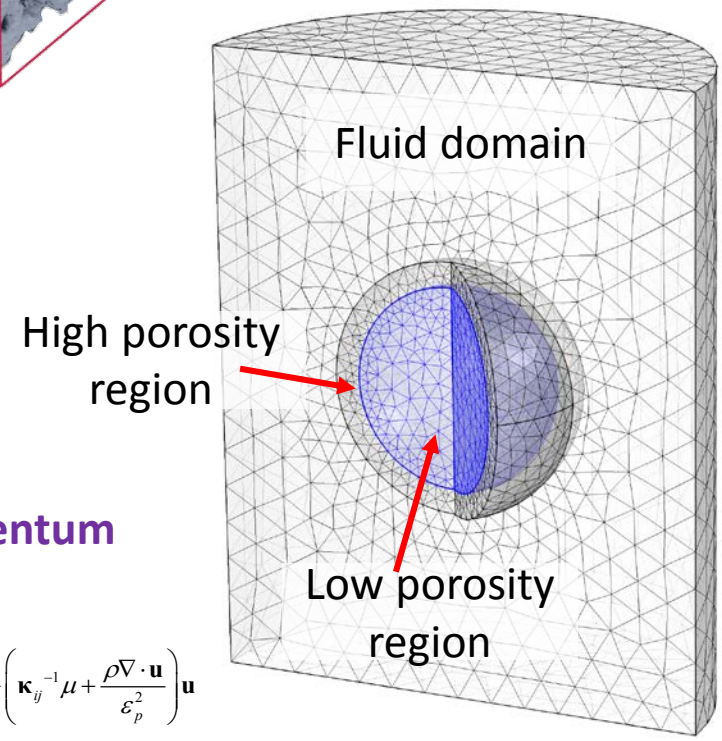
Particle porosity captured by XCT characterization forms basis for particle model

Experimental Characterization via XCT



- Porosity is present in 2 distinct, localized regimes
- These results were used to parameterize approximations for transport in porous media (Darcy's Law) in each regime

Particle Model with Two Distinct Porosity Zones



Conservation of Mass

$$\varepsilon_p \frac{\partial c_i}{\partial t} + \nabla \cdot \left(-D_i \nabla c_i\right) + \mathbf{u} \cdot \nabla c_i = \sum_n R_i$$

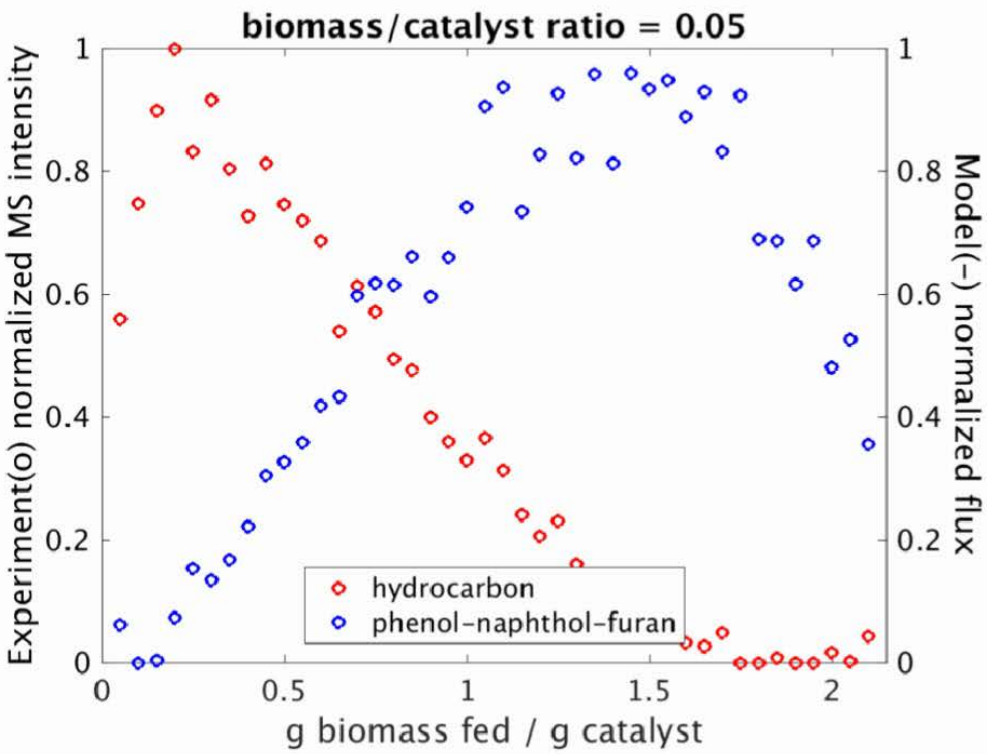
Conservation of Momentum

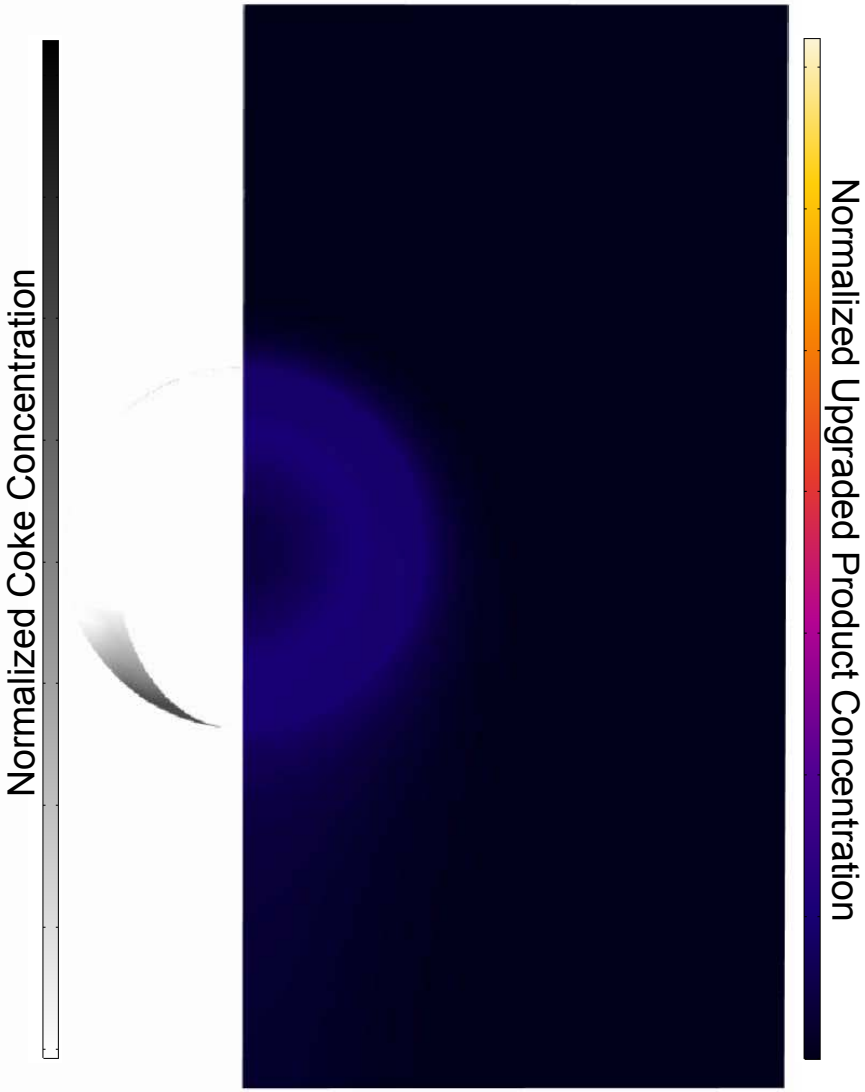
$$\frac{\rho}{\varepsilon_p}\left(\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u}\cdot\nabla)\frac{\mathbf{u}}{\varepsilon_p}\right) =$$

$$-\nabla p + \nabla \cdot \left\{\frac{1}{\varepsilon_p}\left(\mu\left(\nabla\mathbf{u} + (\nabla\mathbf{u})^T\right) - \frac{2}{3}\mu(\nabla\cdot\mathbf{u})\mathbf{I}\right)\right\} - \left(\kappa_{ij}^{-1}\mu + \frac{\rho\nabla\cdot\mathbf{u}}{\varepsilon_p^2}\right)\mathbf{u}$$

XCT Data: B. Kappes, Colorado School of Mines

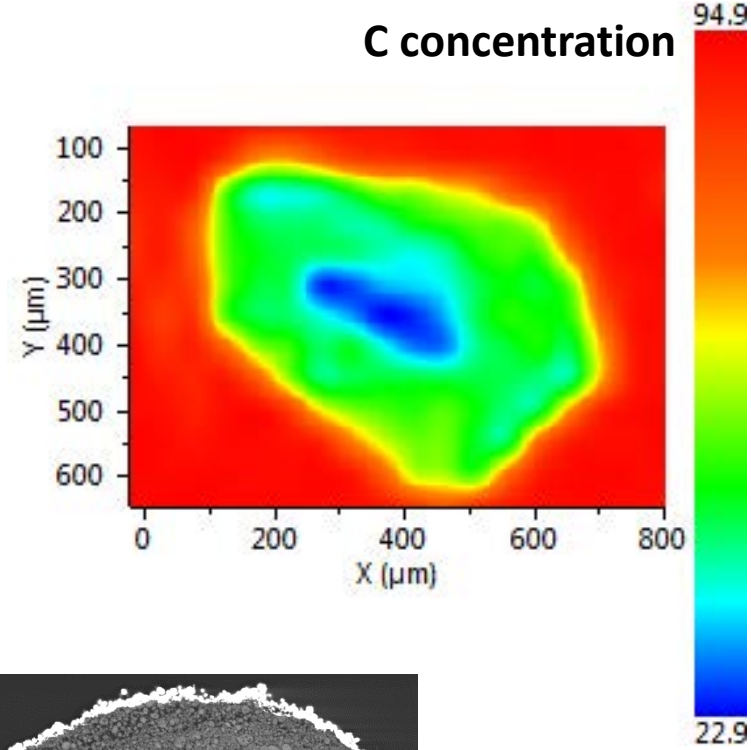
Simulation results with optimized kinetic parameters

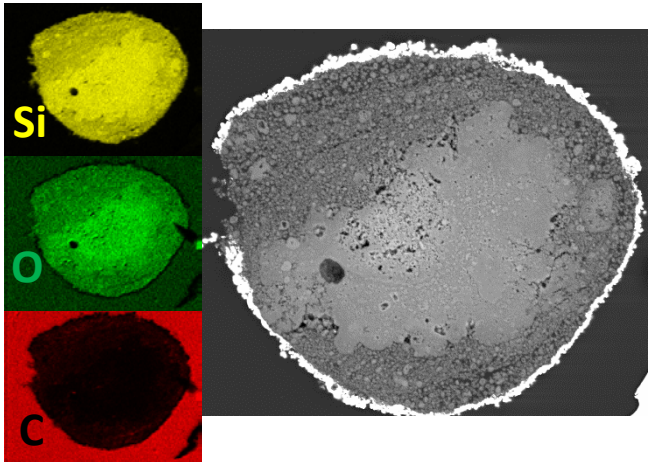




Validation of model coking results with microscopy and elemental analysis

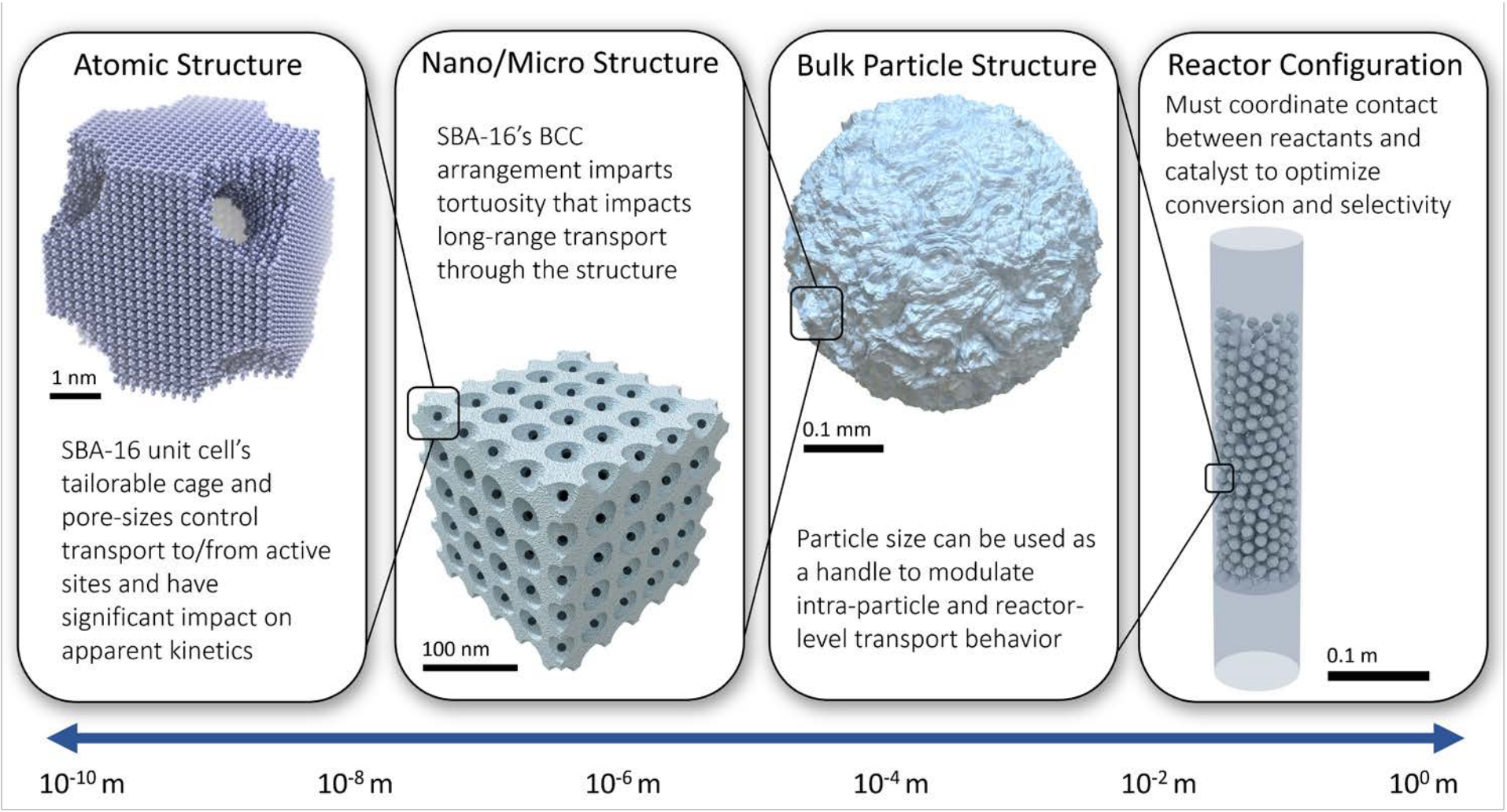
- Electron microscopy coupled with quantitative elemental analysis is being used to validate the particle coking model
- Catalyst particles that have been coked to different degrees have been imaged
- Coking differences as a function of particle radial distance are observed
- Ongoing effort which is complicated by variety of particle shapes and characteristics continues





Characterization by the Advanced Catalyst Synthesis & Characterization Project; Kinga Unocic (ORNL)

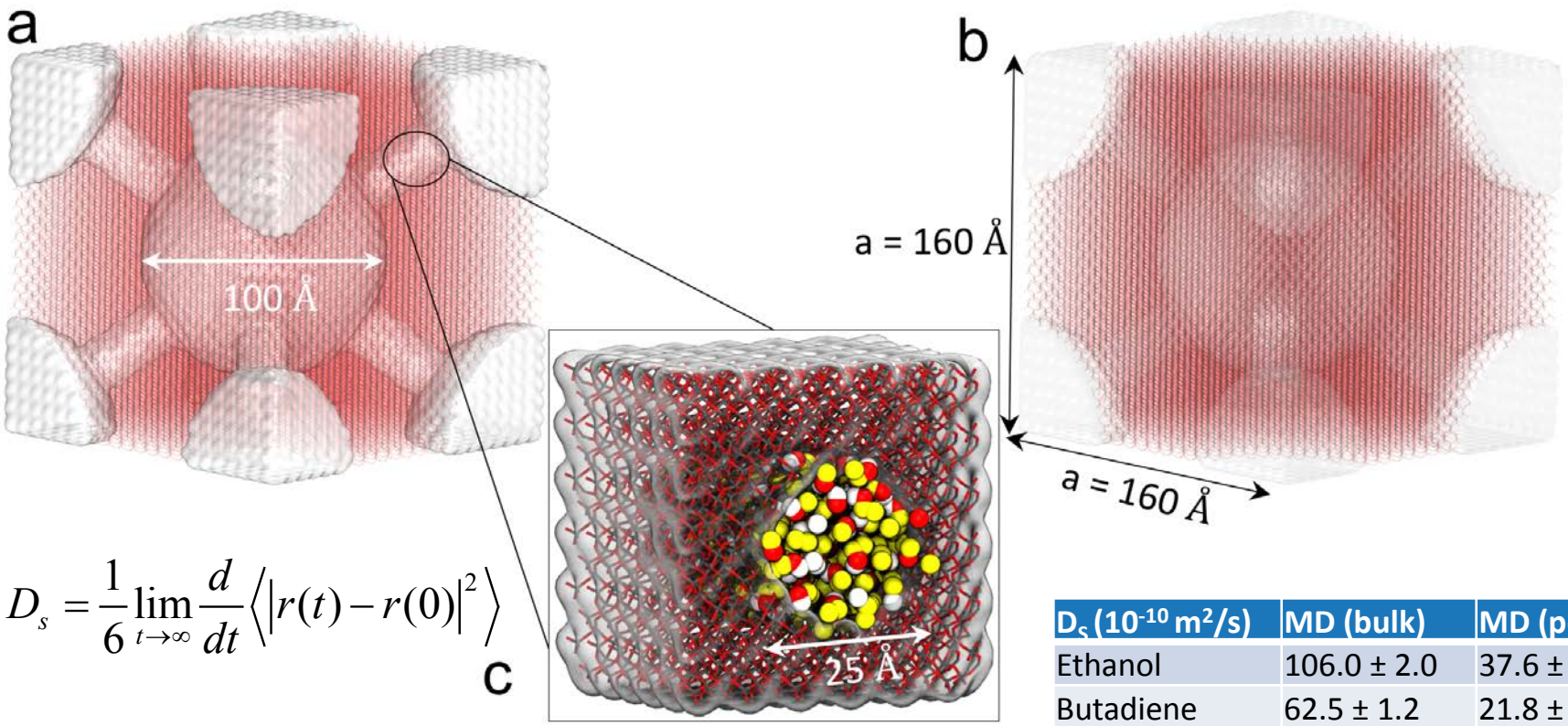
Modeling Structural Hierarchy in Catalytic Systems: SBA-16 Mesoporous Silica Catalyst Supports



Bharadwaj, Pecha, Bu, Lebarbier-Dagle, Dagle, and Ciesielski. *Under review*

Modeling Structural Hierarchy in Catalytic Systems: SBA-16 Mesoporous Silica Catalyst Supports

Atomic/Molecular Scale: Molecular Dynamics studies of reactants and products were performed in atomic models of SBA16 nanostructure to compute diffusion coefficients in each domain of the support



$$D_s = \frac{1}{6}\lim_{t\to\infty}\frac{d}{dt}\left\langle \left|r(t)-r(0)\right|^2 \right\rangle$$

D_s (10^{-10} m^2/s)	MD (bulk)	MD (pore)
Ethanol	106.0 ± 2.0	37.6 ± 2.7
Butadiene	62.5 ± 1.2	21.8 ± 2.0

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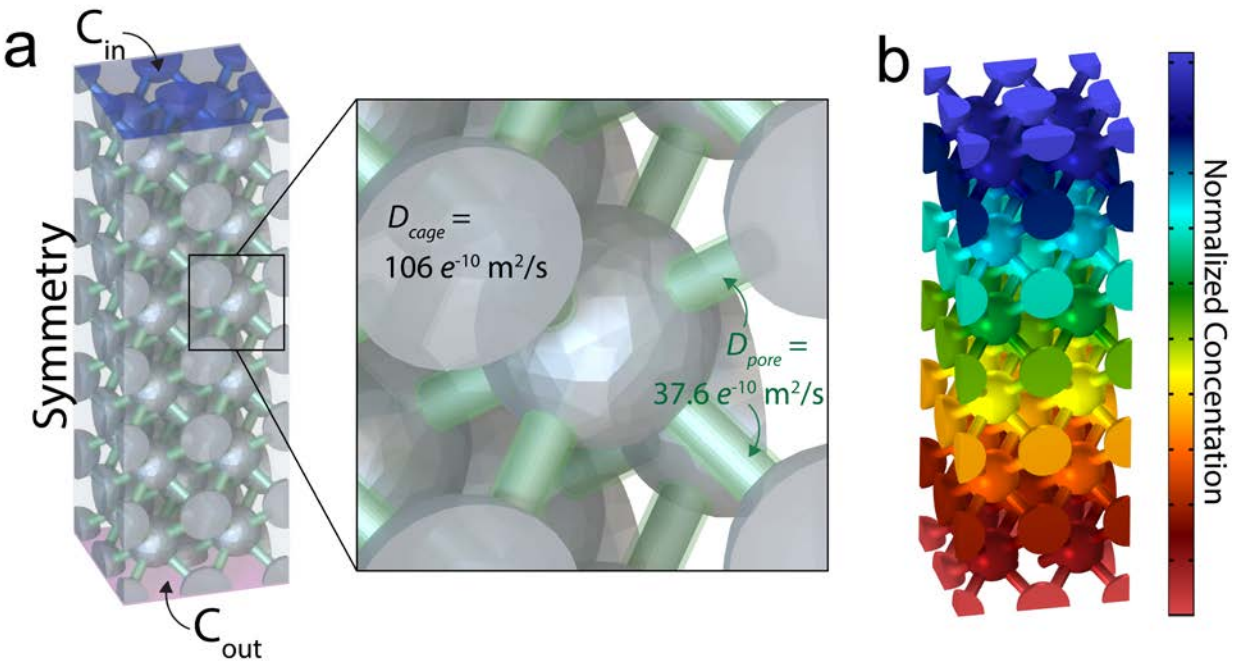
Modeling Structural Hierarchy in Catalytic Systems: SBA-16 Mesoporous Silica Catalyst Supports

Mesoscale: Diffusion coefficients from MD were used in explicit models for the pore structure of SBA16 to compute effective bulk diffusion coefficients. This enables implicit consideration of transport effects inherent to the SBA-16 microstructure in reactor-scale simulations.



$$J_i = D_{domain} \nabla \cdot C_i$$

$$D_{eff} = \frac{J_i * \Delta x}{\Delta C_i}$$

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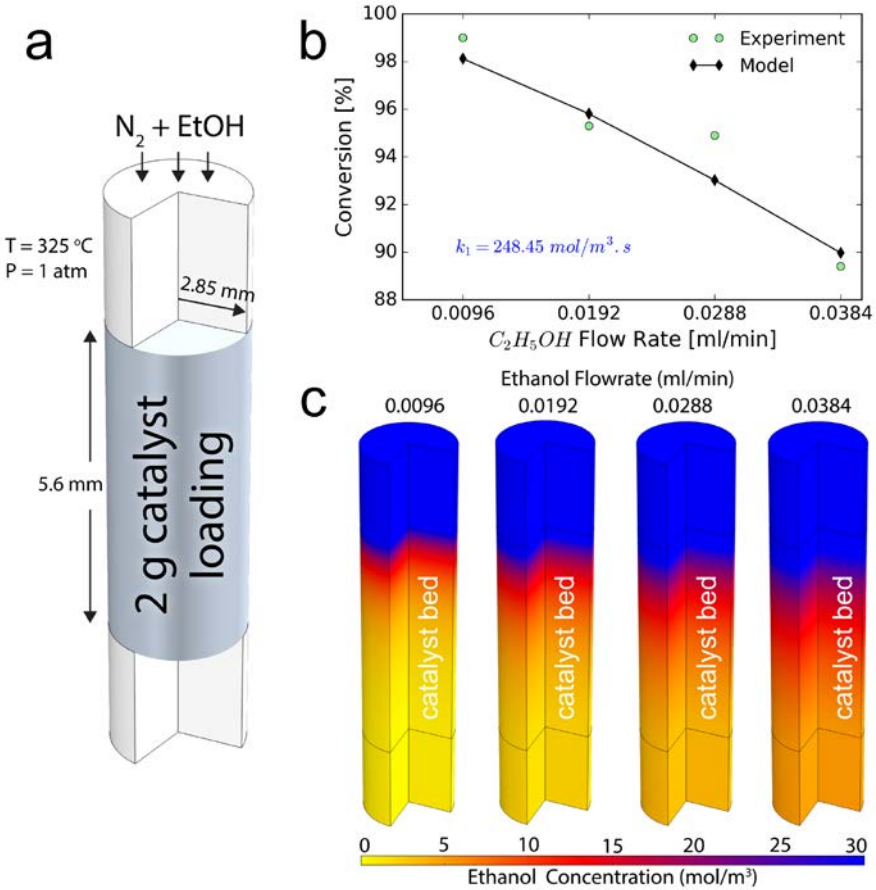
Modeling Structural Hierarchy in Catalytic Systems: SBA-16 Mesoporous Silica Catalyst Supports

Macroscale: The effective diffusion coefficients obtained from mesoscale models were used to model packed bed experiments performed by experimental partners at PNNL. The simulation was used to extract reaction kinetics from the experiments.



Conservation Equations

$$\frac{\rho}{\varepsilon_p}\left(\frac{\partial \mathbf{u}}{\partial t}+\frac{\mathbf{u}\cdot\nabla\mathbf{u}}{\varepsilon_p}\right)=-\nabla p+\nabla\cdot\left\{\frac{\mu}{\varepsilon_p}\left(\nabla\mathbf{u}+(\nabla\mathbf{u})^T-\frac{2}{3}(\nabla\cdot\mathbf{u})\mathbf{I}\right)\right\}-\left(\kappa_{ij}^{-1}\mu+\frac{\rho\nabla\cdot\mathbf{u}}{\varepsilon_p^2}\right)\mathbf{u}$$

$$\varepsilon_p\frac{\partial c_i}{\partial t}+\nabla\cdot(-D_i\nabla c_i)+\mathbf{u}\cdot\nabla c_i=\sum R_i$$

$$\frac{\partial \varepsilon_p\rho}{\partial t}+\nabla\cdot(\rho\mathrm{u})=\sum R_i$$

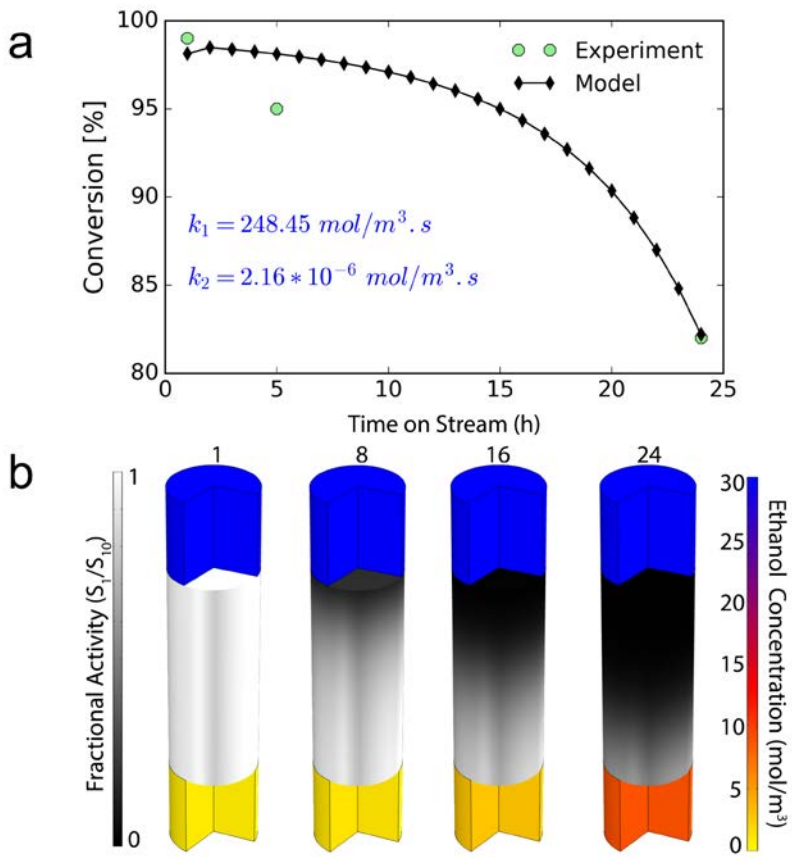
Transport-Delayed Rate Law

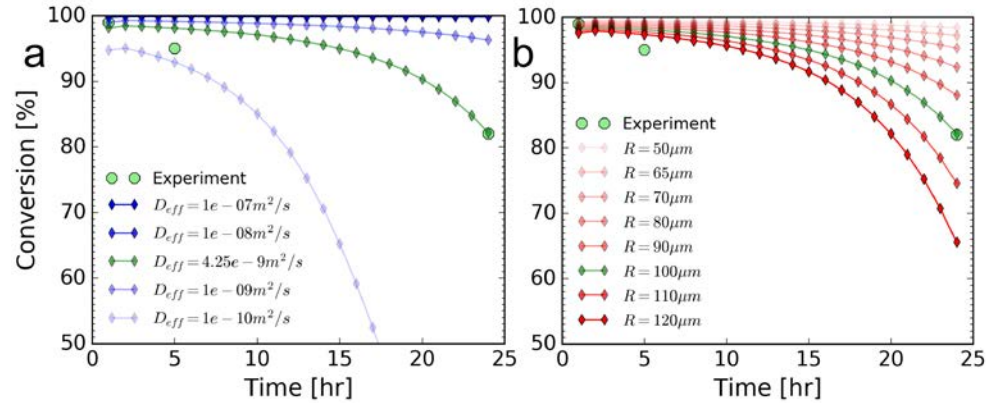
$$\frac{dC_{et}}{dt}=k_1C_{et}^2\frac{\theta}{\phi_1}\left[\frac{1}{\tanh(3\phi_1)}-\frac{1}{3\phi_1}\right]$$

Bharadwaj, Pecha, Bu, Lebarbier-Dagle, Dagle, and Ciesielski. *Under review*

Modeling Structural Hierarchy in Catalytic Systems: SBA-16 Mesoporous Silica Catalyst Supports

Macroscale: The calibrated model was used to perform sensitivity analysis of experimentally adjustable parameters. Actionable recommendations were provided to experimental partners to improve performance.





The results suggest that reducing the particle size and increasing the pore size of SBA-16s should result in improved catalyst activity lifetimes.

Bharadwaj, Pecha, Bu, Lebarbier-Dagle, Dagle, and Ciesielski. *Under review*

Consortium for Computational Physics and Chemistry (CCPC)

Dr. Jim Parks (ORNL)

ChemCatBio
Chemical Catalysis for Bioenergy

CCPC

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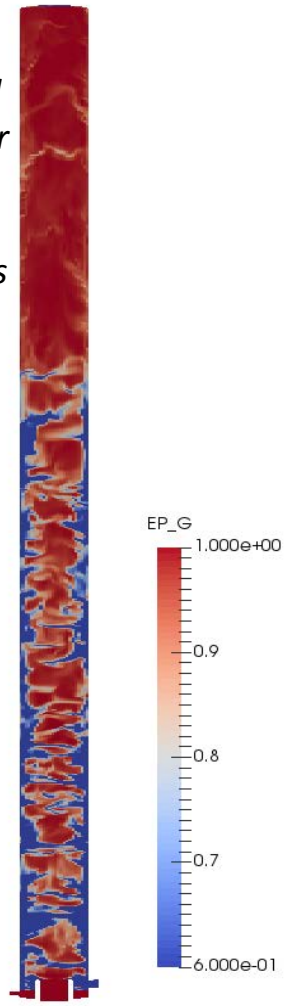
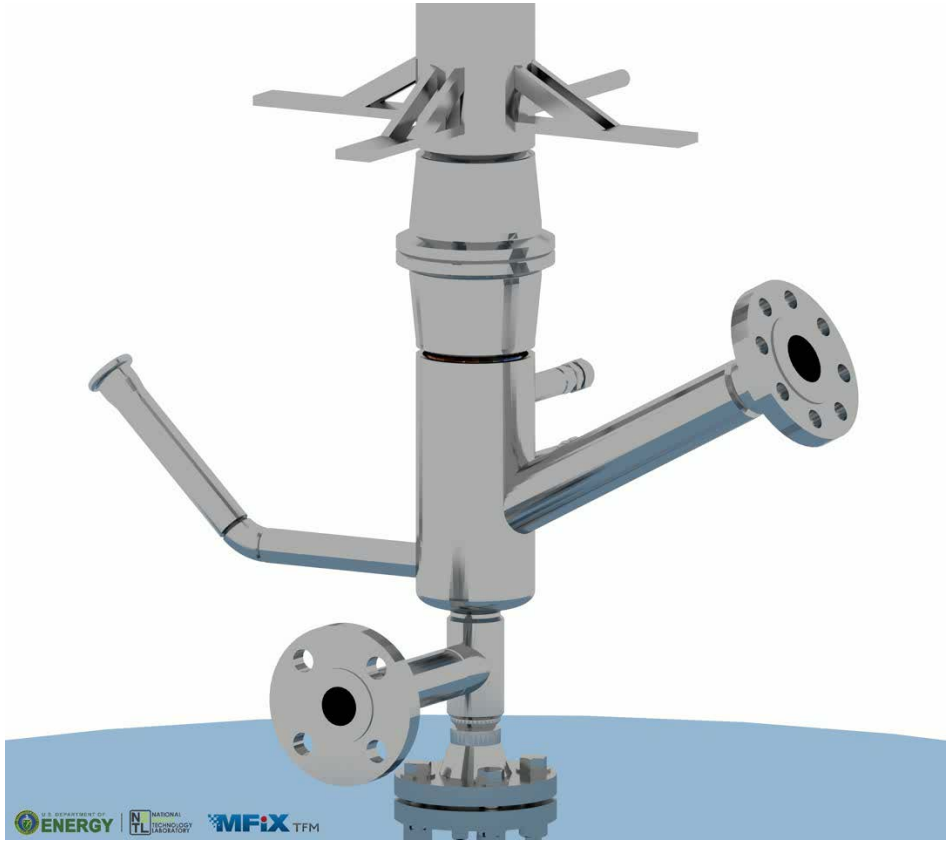
Process Scale Reactor Modeling

Determining optimal process conditions for maximum yield and enable scale-up of ChemCatBio catalysts



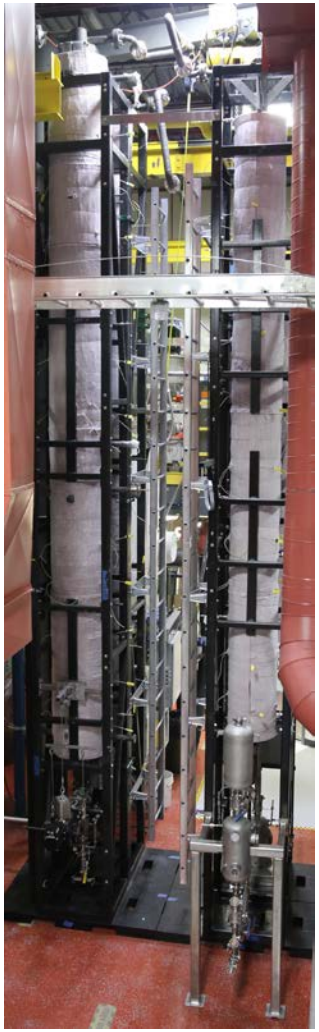
Process Scale Modeling Utilizes MFiX

MFiX CFD reactor models capture residence time and mixing effects



MFiX model of R-Cubed Catalytic Upgrading Reactor

CFD and reduced order models inform BETO reactor teams; experiments validate model results

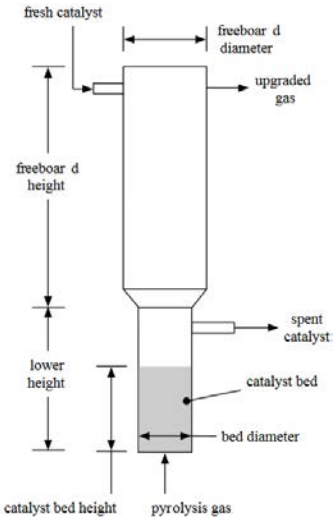


R-Cubed Catalytic Upgrading Reactor at NREL

MFiX (Multiphase Flow with Interphase eXchange) is a computational fluid dynamics (CFD) code developed by NETL

Experiments and modeling conducted across range of reactor scales to aid in ChemCatBio catalyst scale up

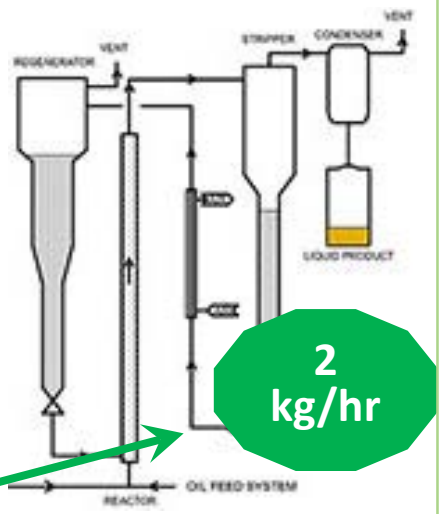
2" Fluidized Bed Reactor Upgrader*



0.5 kg/hr

Relevant to new BETO catalysts

Davison Circulating Riser (DCR) Reactor*

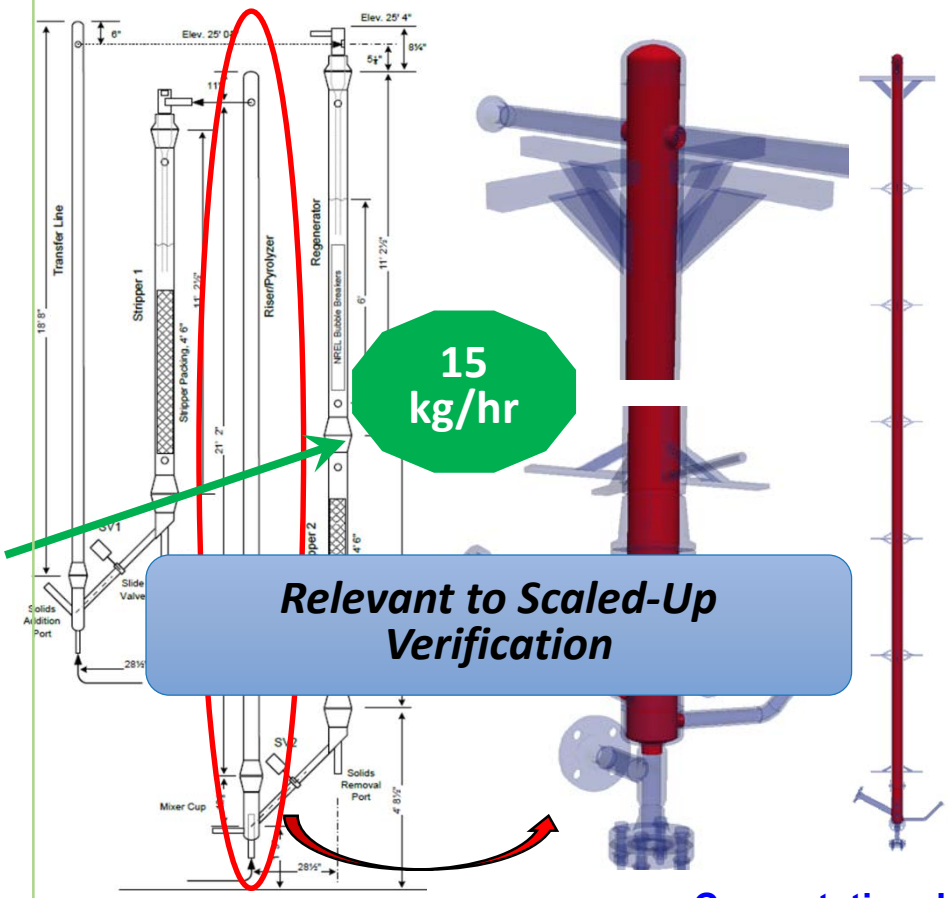


2 kg/hr

WR Grace

Relevant to Industry

TCPDU R-Cubed Upgrader*



15 kg/hr

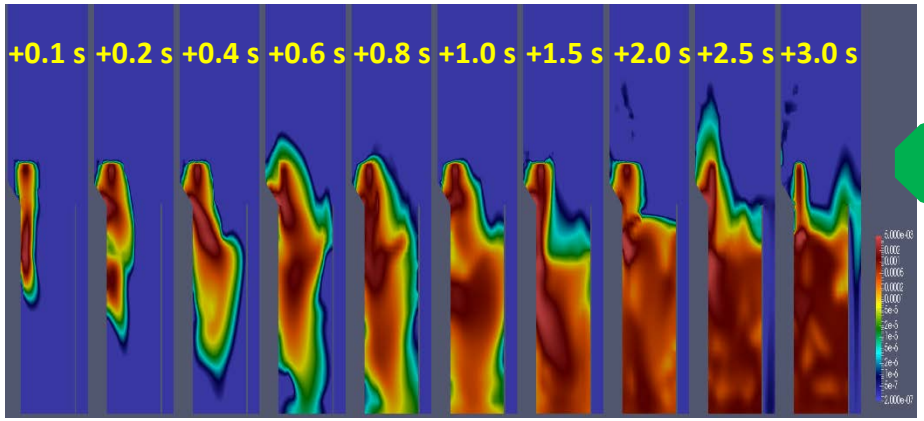
Relevant to Scaled-Up Verification

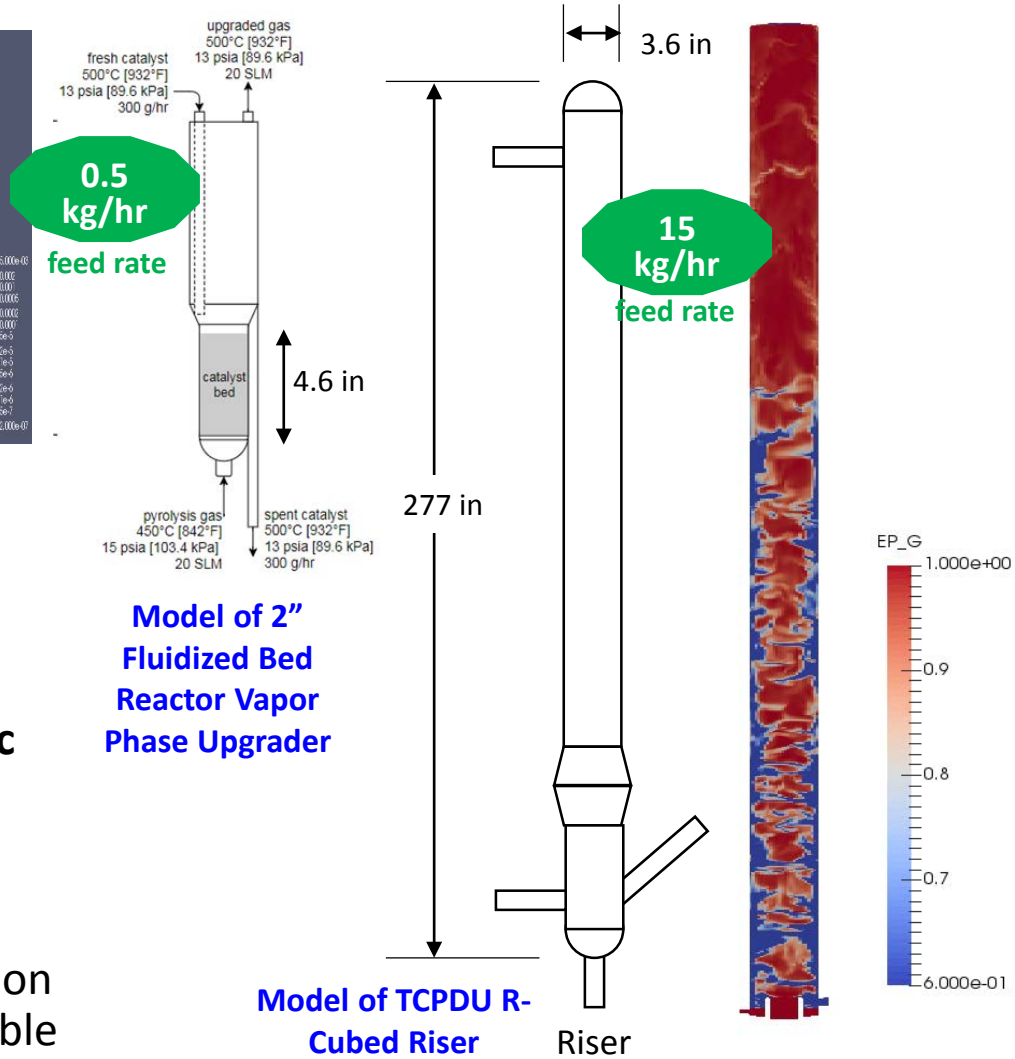
PSRI (redesign)

Computational Domain in Red

***All (3) Reactors at NREL**

Residence Time Distributions Vary with Reactor Design





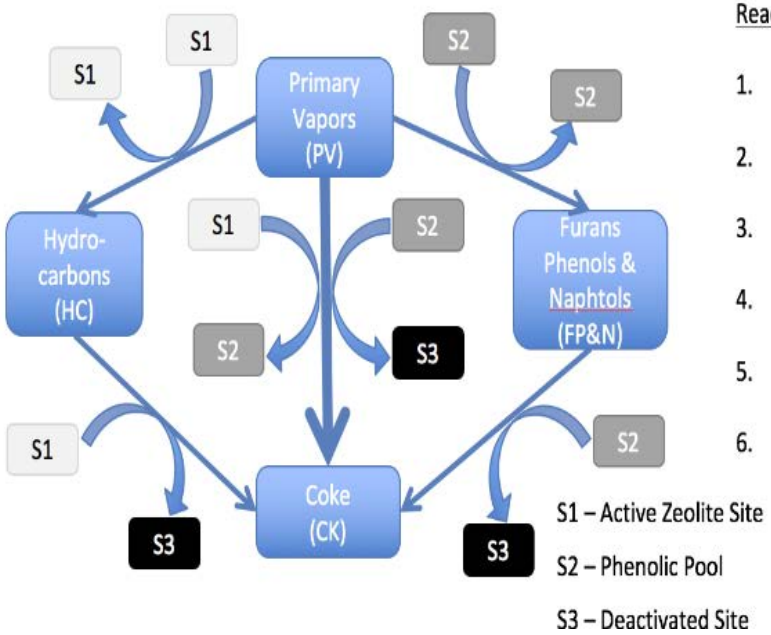
- MFiX simulations used to capture critical residence time distributions for catalytic upgrading reactors
- **Mean Residence Times:**
  - 2"FBR Vapor Phase Upgrader: **883 sec** (650 micron catalyst)
  - R-Cubed Riser: **139 sec** (85 micron catalyst)
- Models can be used to compare conversion processes across a range of scales to enable scale up of ChemCatBio developed catalysts

ORNL (CCPC): C. Finney, E. Ramirez, G. Wiggins, J. Parks
NETL (CCPC): B. Rogers, M. Syamlal, T. Li, X. Gao
NREL (experimentalists): K. Iisa, R. French, K. Smith, K. Gaston, D. Carpenter

Kinetics: Critical to Predicting Conversion at Process Scale

- Kinetic rates for catalytic upgrading of bio-specific oils are critical for models to predict conversion and yield
- Micro-Kinetics approach being pursued by universities (Northwestern Univ. - L. Boradbelt, Univ. of Delaware – M. Klein) is chemically comprehensive but computationally complex for bio oils
- Our approach: determine kinetic rates for grouped chemical products with specifically designed experiments and analysis

Kinetic Reaction Scheme and Rate Constants for Pine Pyrolysis Oil Upgrading with a ZSM-5 Catalyst



Reactions

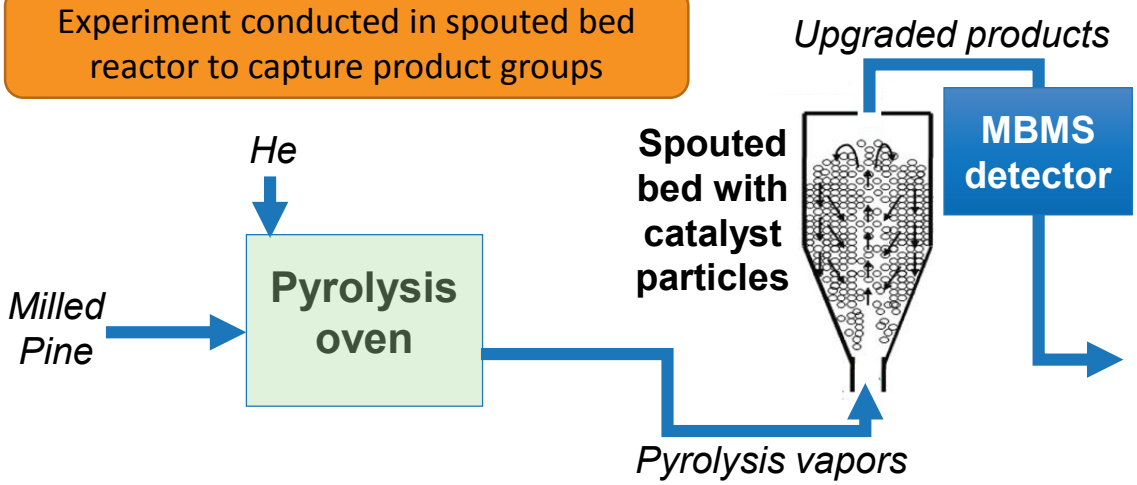
1. PV + S1 --> HC + S1
2. PV + S1 --> CK + S2
3. PV + S2 --> FP&N + S2
4. PV + S2 --> CK + S3
5. HC + S1 --> CK + S3
6. PN + S2 --> CK + S3

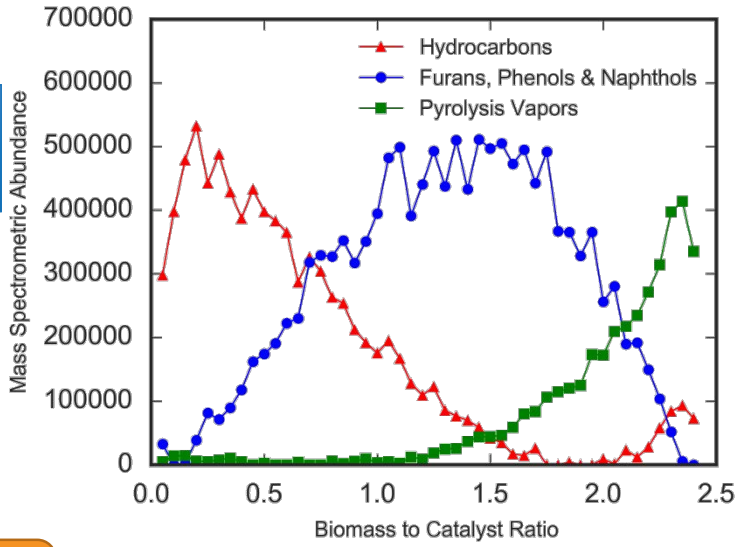
Preliminary Results

	Reaction	Rate Constant @500 °C [m³/(mol.s)]
1	PV + S1 → HC + S1	139.262
2	PV + S1 → CK + S2	40.876
3	PV + S2 → FP&N + S2	1.158
4	PV + S2 → CK + S3	69.79
5	HC + S2 → CK + S3	2.751
6	PN + S2 -> CK + S3	0.024

Close collaboration between experimentalists and modelers enables kinetic rate parameters to be determined

Experiment conducted in spouted bed reactor to capture product groups





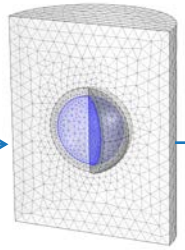
Kinetic rates extracted by using particle scale model to analyze data and extract rates

- Species
- Experimental Yields

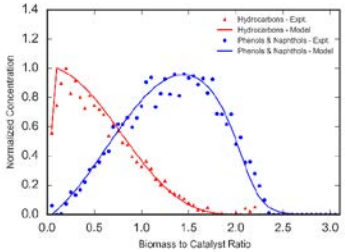
- Porosities
- Diffusivities
- Architecture
- Reaction Scheme

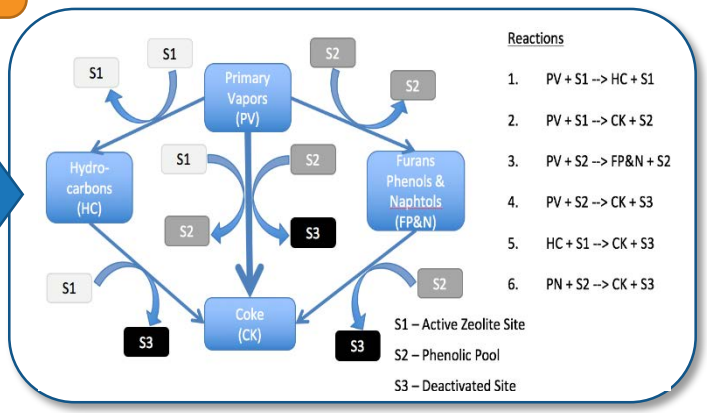
Initial Guess

- Kinetic Rate Parameters



FEM simulation

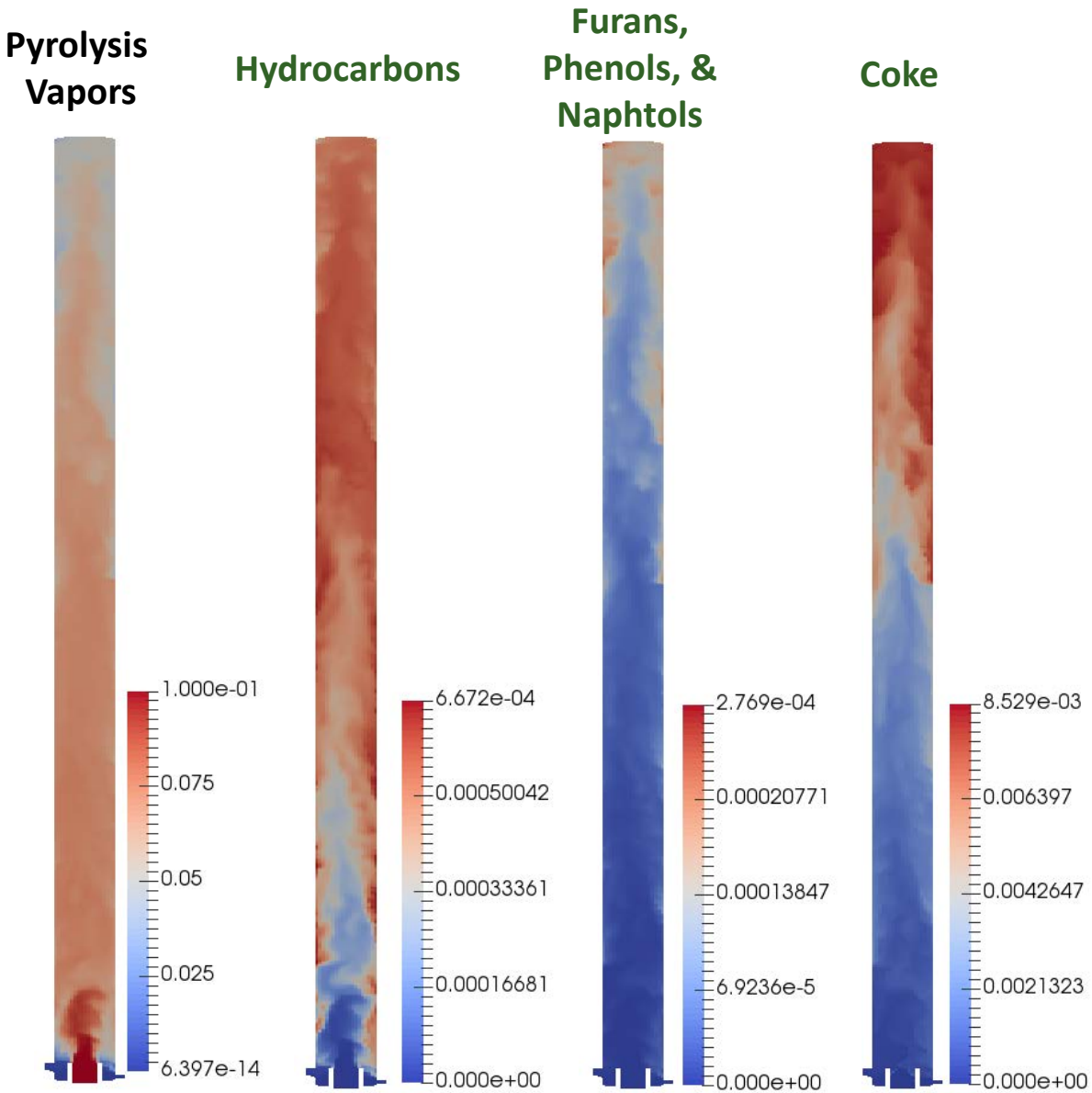




Reaction Pathway with Kinetic Rates

External optimization routine

Kinetics incorporated into R-Cubed reactor model

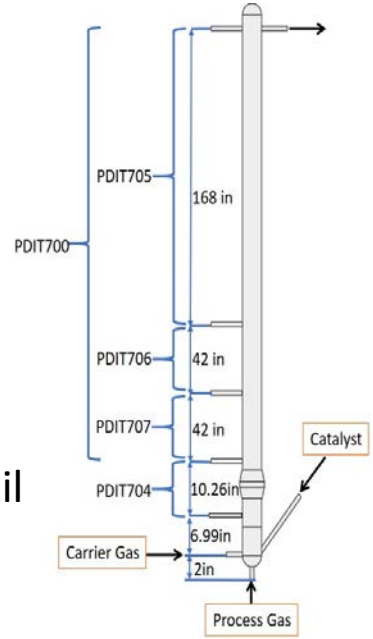


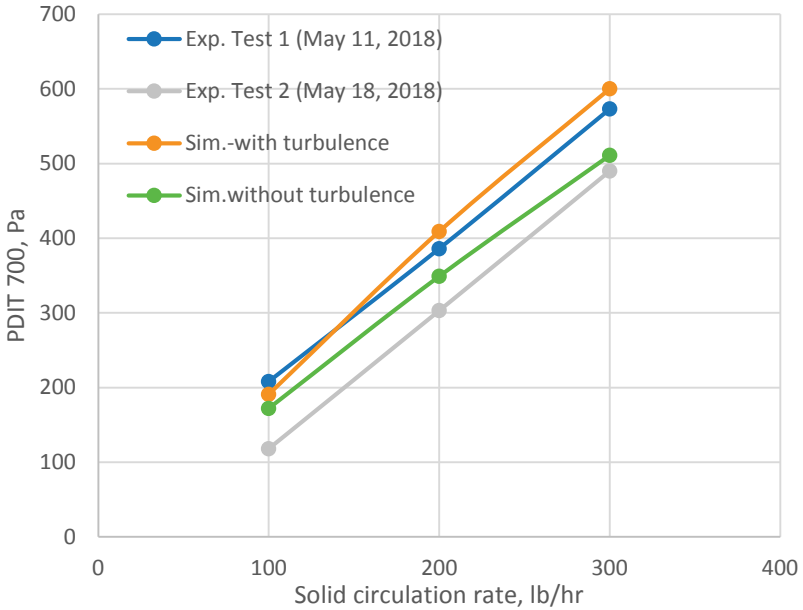
- Preliminary results obtained with MFiX model of R-Cubed riser with kinetic rates for pyrolysis vapor conversion to grouped products
- Current research focus is experimental validation of both hydrodynamics and catalytic conversion

Validation of R-Cubed Model: Ongoing Experiments

- Experimental matrix performed by reactor team on R-Cubed system with inert process gas
- Matrix included varying catalyst flow, temperature, etc.
- Pressure data utilized for validation of model
- Initial heterogeneous Sarkar drag model did not provide accurate model prediction
- Determined that Wen-Yu homogeneous model was more accurate
- Experiments are ongoing including upcoming experiments with pyrolysis oil upgrading

Experimental matrix						
No.	Process N2, SLM	Carrier N2, SLM	Heater temps, °C	Process gas temp, °C	Catalyst flow, kg/h (lb/h)	Front end pressure (kPa)
0	400	130	500	500	91 (200)	50
1	400	130	500	500	45 (100)	50
2	400	130	500	500	136 (300)	50
3	300	130	500	500	91 (200)	50
4	500	130	500	500	91 (200)	50
5	400	130	500	400	91 (200)	50
6	400	130	500	600	91 (200)	50
7	400	230	500	500	91 (200)	50
8	400	330	500	500	91 (200)	50
9	400	130	500	500	91 (200)	25
10	400	130	500	500	91 (200)	75





Summary

- Modeling support of ChemCatBio research is occurring across wide range of scales
  - Atomic scale modeling of surface chemistry
  - Meso scale modeling of particle scale effects
  - Process scale modeling of conversion in reactors
- Close collaboration with experimentalists is critical to all modeling activities
- Preliminary kinetics developed specific to bio oil conversion and incorporated into process models
  - This critical activity can enable translation of ChemCatBio catalysis success to larger scales relevant to industry
  - Validation ongoing with experimental reactor teams

Acknowledgements*

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Bill Rogers
Madhava Syamlal
Tingwen Li
Dirk VanEssendelft
Balaji Gopalan
Xi Gao

Argonne National Laboratory

Larry Curtiss
Rajeev Assary
Mingxia Zhou
Lei Cheng
Cong Liu
Dale Pahls

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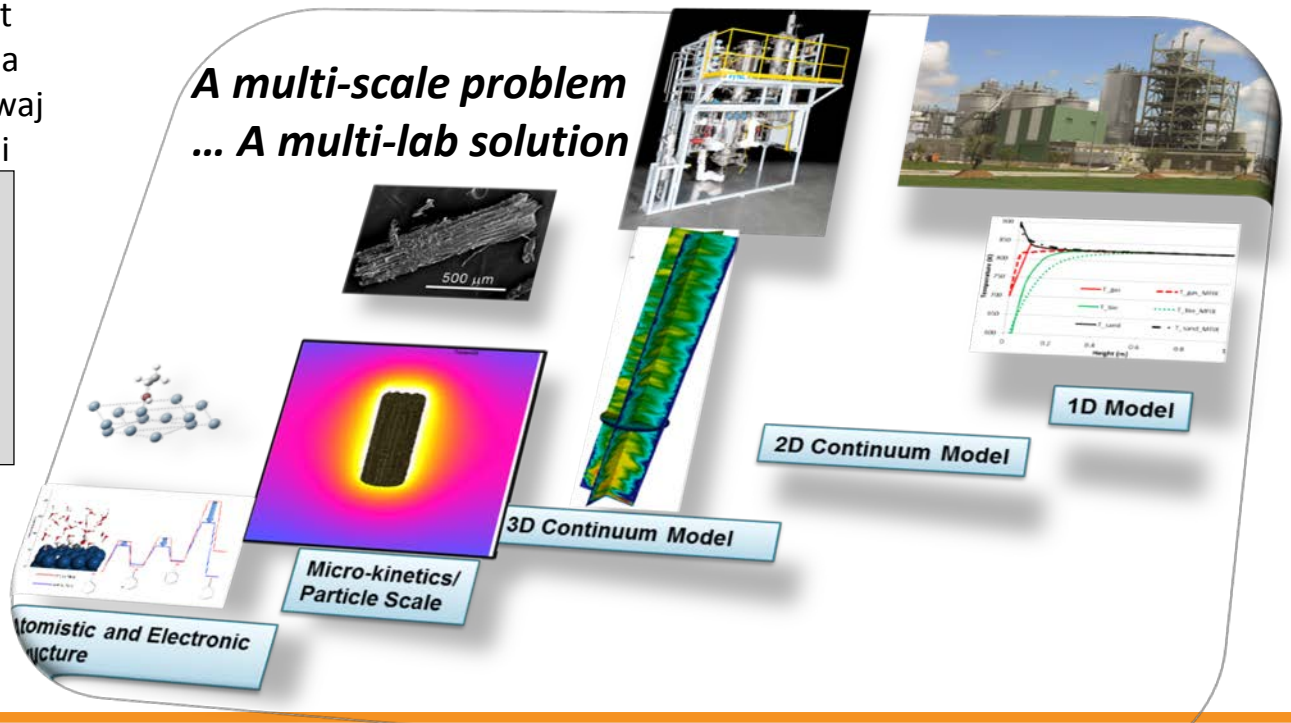
David Dayton (RTI), George Huff (MIT, retired BP),
Jack Halow (Separation Design Group), Mike Watson (Johnson Matthey), Steve Schmidt (WR Grace), Tom Flynn (Babcock & Wilcox)



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*includes current and former CCPC contributors

Thank you.

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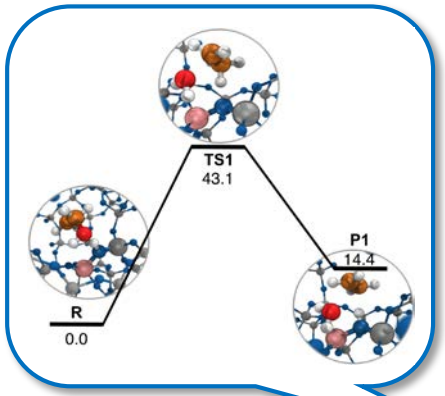
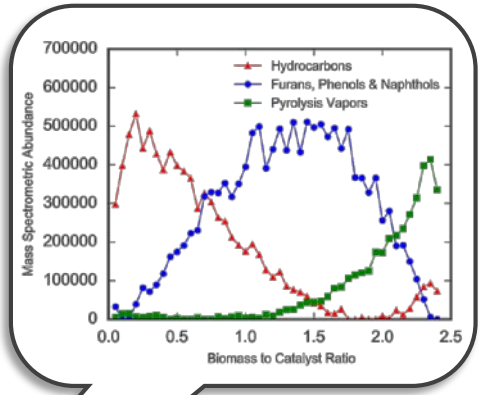
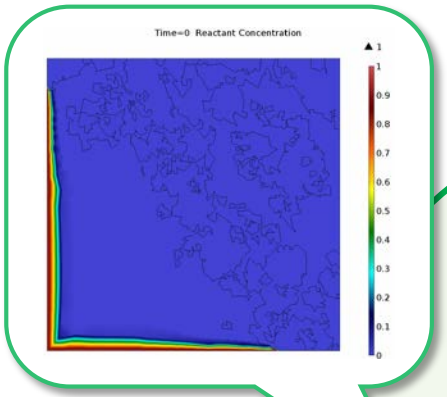
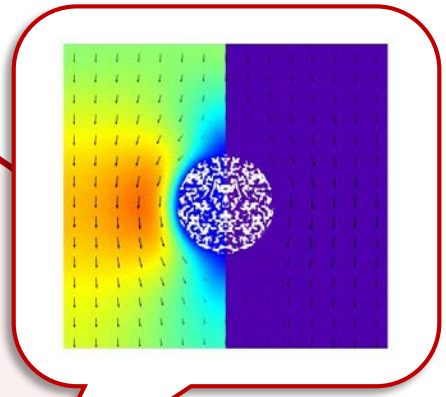
Experimentally observed, "effective" catalytic reaction rates are highly dependent on system-specific parameters

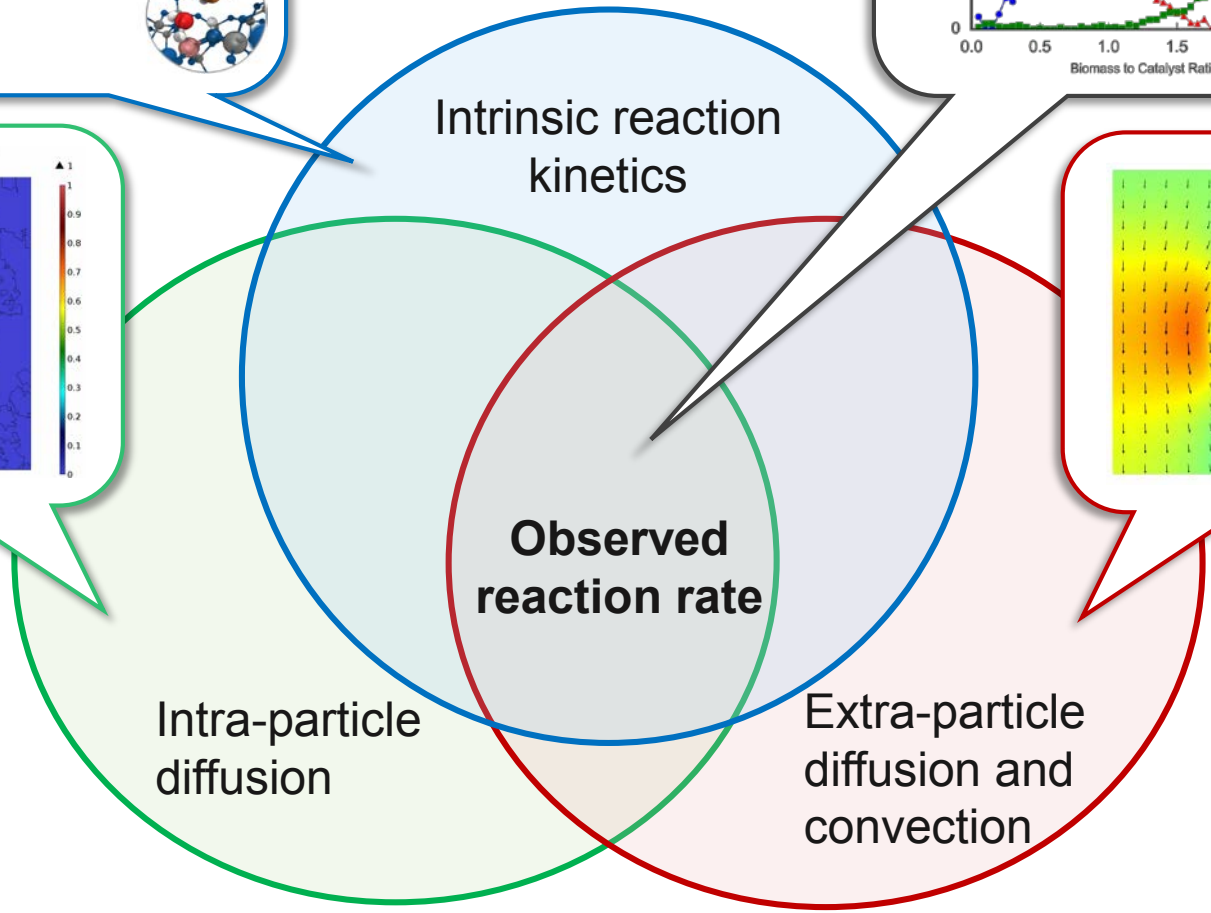


If transport phenomena are not accounted for, extracted kinetics are not extensible to other systems

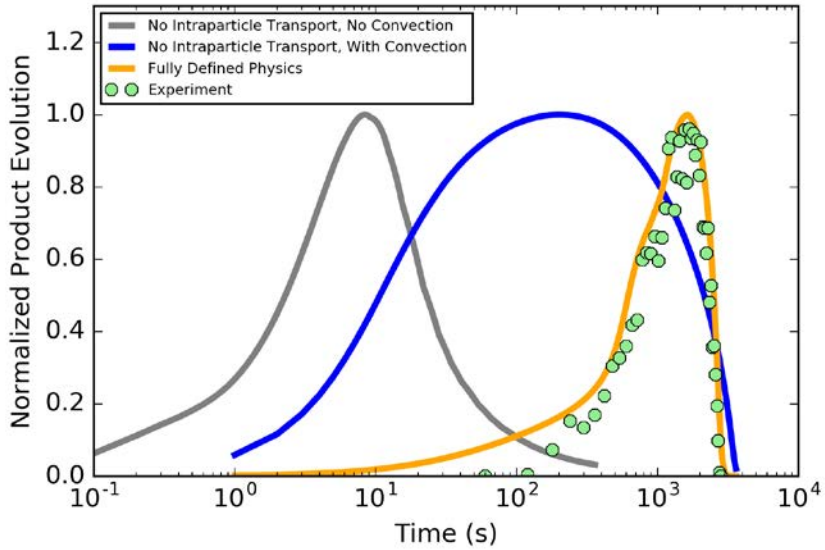




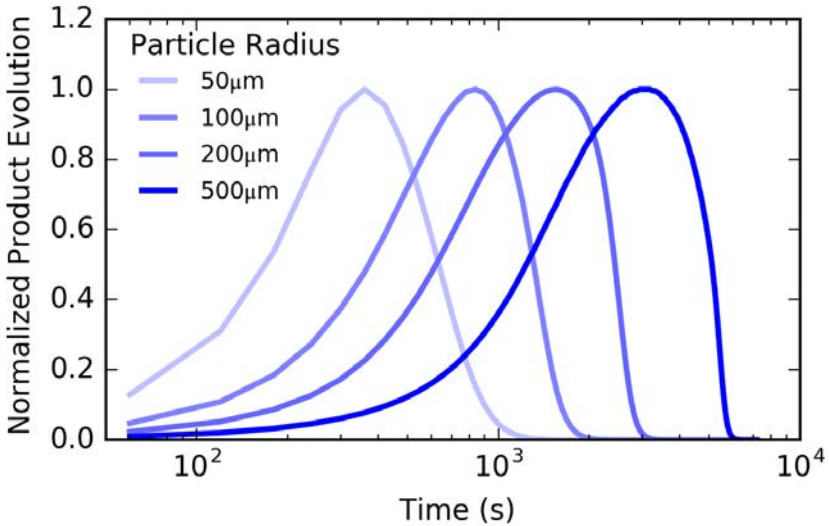




Mesoscale simulations can be used to extract reaction kinetics that are independent of system-specific parameters



- By "turning off" transport physics in the simulation, we can evaluate their affect on product evolution rates
- Transport phenomena can delay effective catalytic conversion rates by orders of magnitude



- Once transport-independent kinetics are obtained, the impact of catalyst parameters such as particle size and porosity can be investigated