Catalysis Development and Testing Program

A Transient Kinetic Approach to Catalytic Materials For Energy-Efficient Routes to Ammonia, Ethylene and Related Chemicals

Contract #32132

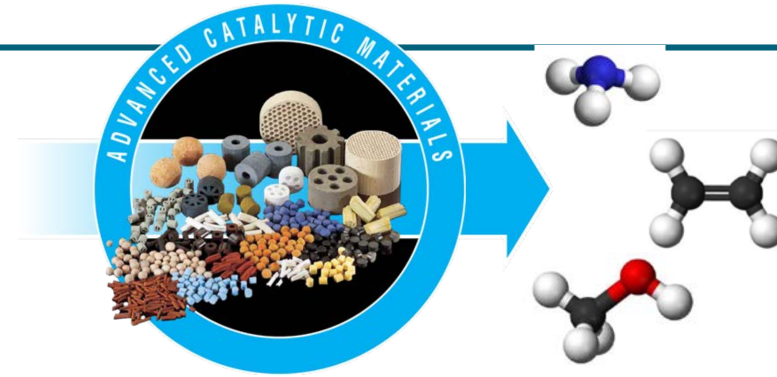
Chemical Catalysts Research and Testing/Idaho National Laboratory, Argonne National Laboratory

Project Period 10/1/2016 to 9/30/2021

Dr. Rebecca Fushimi, Idaho National Laboratory

U.S. DOE Advanced Manufacturing Office Program Review Meeting
Washington, D.C.
June 13-14, 2017

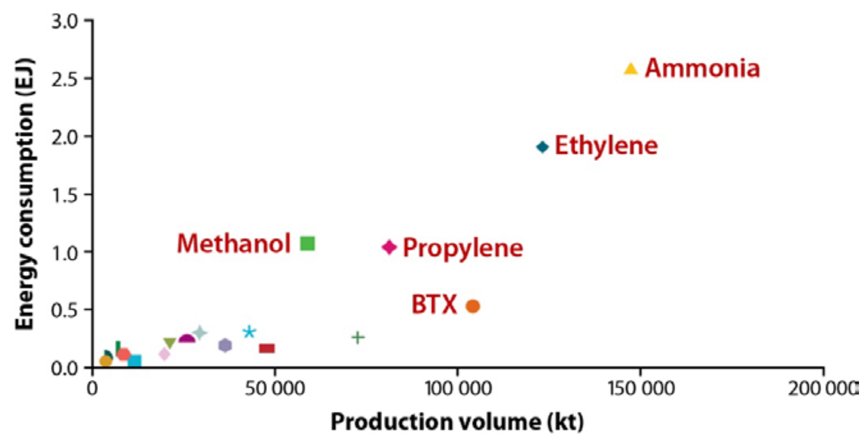
Project Objective



- A new paradigm for catalyst development based on transient kinetics

- Catalyst development is primarily trial-and-error to address:
  - Complex multistep reaction mechanism
  - Complex multicomponent, ill-defined materials

- New catalytic routes to ammonia, ethylene, etc.
  - Ammonia: 2% of the world's energy use
  - Ethylene: 30% energy saving with catalysis over current steam cracking practice

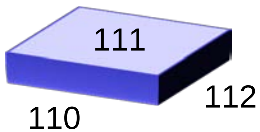


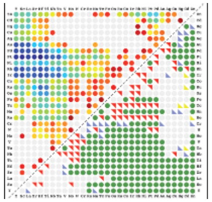
International Energy Agency, Technology Roadmap, Energy and GHG Reduction in the Chemical Industry via Catalytic Processes, 2013.

Technical Innovation

- Current practice of catalyst development

Surface Science	High-Throughput
– Detailed kinetics – Model materials	– Basic kinetics – Industrial materials





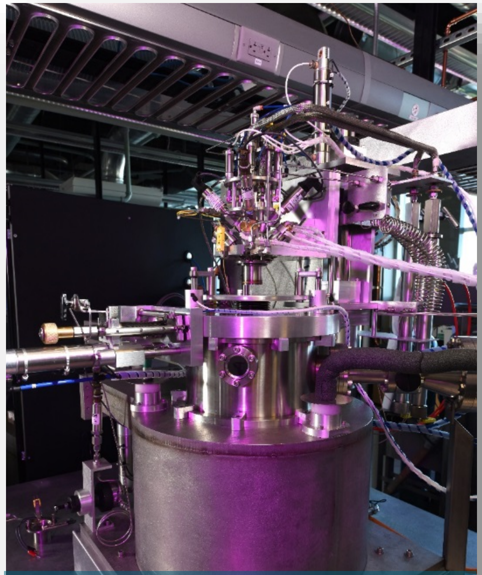
Curtarolo, Stefano, et al. *Nature materials* 12.3 (2013): 191-201.

- Transient kinetics

Temporal Analysis of Products (TAP) Reactor System

- Detailed kinetics : Complex mechanism
- Industrial materials : Complex materials

Understanding *how* and *why* materials function



INL: 2 of 3 TAP Reactors in the US

- Kinetic-Centric Informatics

Exploiting data science tools around microkinetics

- Experimental & Theoretical

- Accelerating the catalyst development

Technical Approach

- A new paradigm for catalyst development:

  Transient kinetic experiments

- Kinetic-Centric Informatics tool:

  More meaningful connections from complex data sources

Idaho National Laboratory

TAP, transient kinetic characterization

New focus:
composition/kinetics
rather than
structure/activity

Experimental microkinetic characterization linked to theory and composition of complex materials

Idaho National Laboratory · Georgia Tech

Kinetic-Centric Informatics

Caltech

Ab-initio modeling, reactive force field development

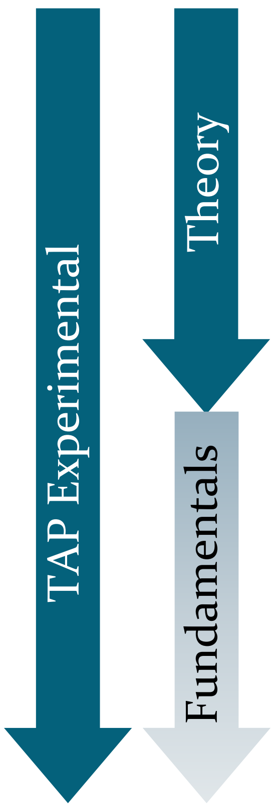
Argonne NATIONAL LABORATORY

Atomic layer deposition, X-ray absorption spectroscopy

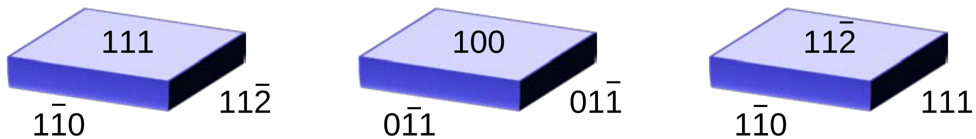
Technical Approach

- Ammonia synthesis from 200 to 20 bar

  - Elementary reaction steps, N-N rupture, N-H formation
  - Incremental surface coverage change, N, NH, H, etc.
  - Material complexity

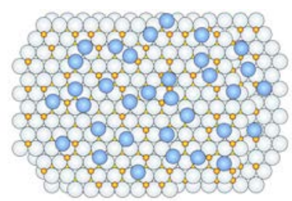


Fe Single Crystals

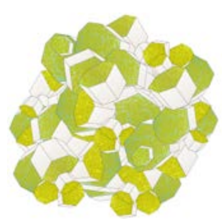


Polycrystalline Fe

Single site, Atomic cluster catalysts



Na, K, Ca Promoters



Commercial Catalysts

TAP + DFT

Experimental measurement theoretical predictions

- Enthalpies, ΔH
- Rate constants, k_{ads}, k_r

Brings new direction for applying combinatorial tools to the right problem

Transition (beyond DOE assistance)

- Transient Kinetics User Portal

Developing a unique capability for industrial catalyst development

- A specialized team surrounding TAP
- Accelerated research execution and analysis
- Partners provide broader expertise and resources
- *Kinetic-Centric Informatics* connects resources and enables better decisions
- Accelerate and derisk proprietary projects

- Sustainment Model:
  - Industrial Utilization: project results that speak to proprietary needs
  - Advance the state-of-the-art: theoretical methods, advanced instrumentation
    - Spectroscopy, catalyst modification methods, multiscale systems
  - Beyond catalysis
    - Chemical sensors, advanced sorbents, photo and electrochemical systems, energetic reactions, materials characterization, etc.

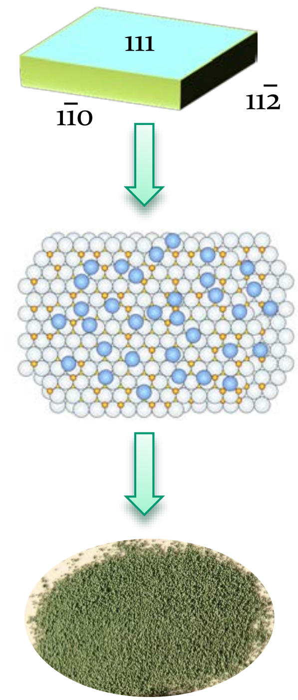
Measure of Success

- Moving catalyst development beyond trial-and-error
- Enduring benefit
  - A unique capability to support industrial research
  - Changing the way materials are studied and designed
- Measurement
  - Industry participation (CRADA and SPP Agreements)
  - Advancement of catalytic technologies through TRL
- Oxidative dehydrogenation of ethane
  - 30% energy savings over steam pyrolysis
  - 900 – 325 °C, 98% selectivity, eliminate cryogenic separations

- Wide-adoption of TAP and understanding of transient kinetics
- Move beyond catalysis to other gas/solid reaction applications
- Adoption of more-efficient transient chemical processes

Project Management & Budget

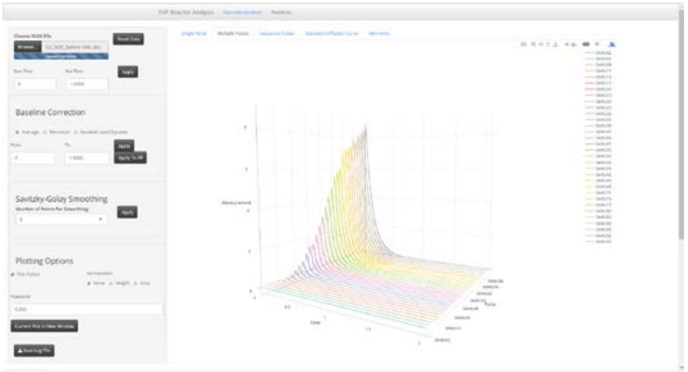
- 5 year project
- First year key project tasks
  - Establish industrial advisory board
  - Atomistic predictions guiding catalyst synthesis
  - Atomic layer deposition sample preparation
  - Link TAP measurements to DFT predictions
  - Advanced TAP methodologies
    - Analysis & viz. software, complex transport/reaction modeling
  - Kinetic-centric informatics model building



Total Project Budget	
DOE Investment	FY17 \$3.6M, FY18 \$3M, FY19 \$3M
Cost Share	FY18 – FY19 10-20% addition through industrial contracts
Project Total	\$9.6M

Results and Accomplishments

- Industrial Advisory Board Meeting – June 7
  - DOW, AramcoServices, Shell, Sabic, BASF, UOP
- Analysis and viz. tool
- Informatics data sources identified
- QM reaction barriers for 20 steps on Fe (111)
  - Overall rate predictions compare with experiment
  - Working on more complex systems with K, Li, Na, Rb, Cs



- TAP experiments
  - N_2 desorption induced by H_2 pulsing
  - Distinguishing H_2O pathways from H_2 and NH_3
- Working on identifying synthesis targets
  - Atomic layer deposition precursors