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 9/30/2018

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Project Overview

Timeline

- Project commenced October 2016
- Projected end date September 2018
- Project 90% complete

Barriers

- Molecular-level knowledge of catalyst control of ammonia synthesis and methane activation chemistries.

Budget

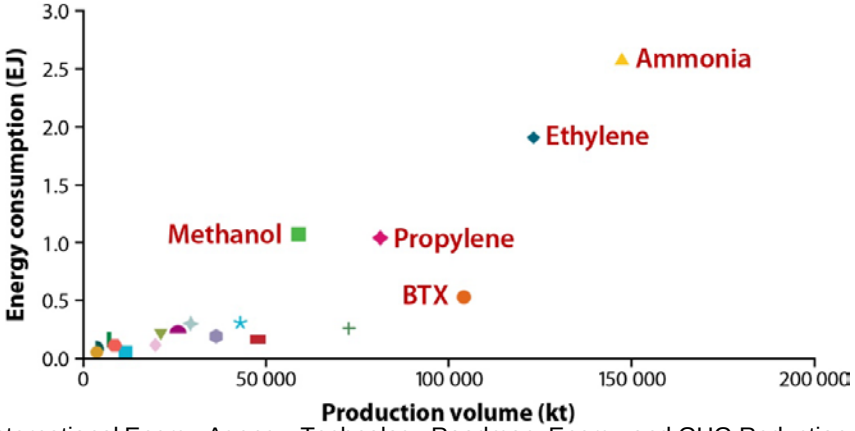
	FY 16 Costs	FY 17 Costs	FY 18 Costs	Total Planned Funding (FY 19-Project End Date)
DOE Funded	$850 k	$3.0 M	$2.7 M	$6.55 M
Project Cost Share	–	–	–	–

Partners

- Idaho National Laboratory
  - Transient kinetics
- Argonne National Laboratory
  - Atomic layer deposition of catalyst materials
- California Institute of Technology
  - Atomistic modeling
- University of Virginia
  - Homogeneous catalysis
- Georgia Institute of Technology
  - Data science and analytics

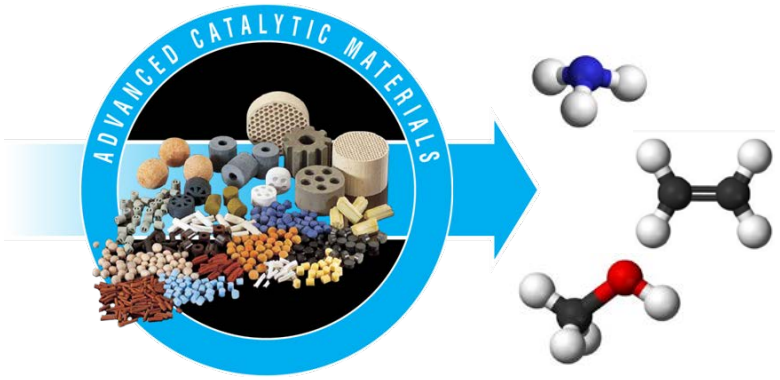
Project Objective

- <u>Challenge:</u> Reduce energy intensity chemical manufacturing
  - 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.

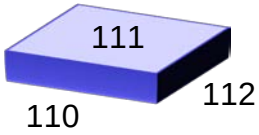
- <u>Barrier:</u> Catalyst development is primarily trial-and-error
  - Complex multistep reaction mechanism
  - Complex multicomponent, ill-defined materials
- <u>Goal:</u> Accelerate catalyst development through molecular-level knowledge provided by *transient kinetics*

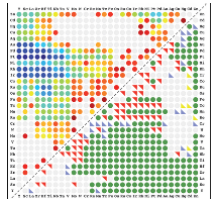


Technical Innovation

- 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.

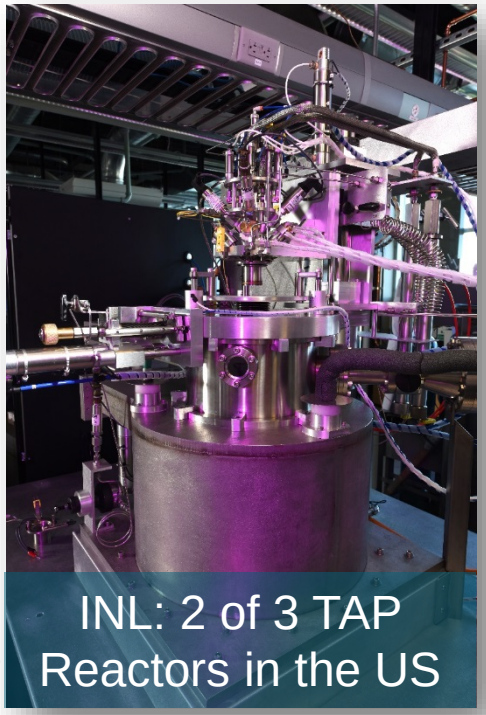
- New Approach: *Transient kinetics*

Temporal Analysis of Products (TAP) Reactor System

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

Exploiting data science tools around microkinetics

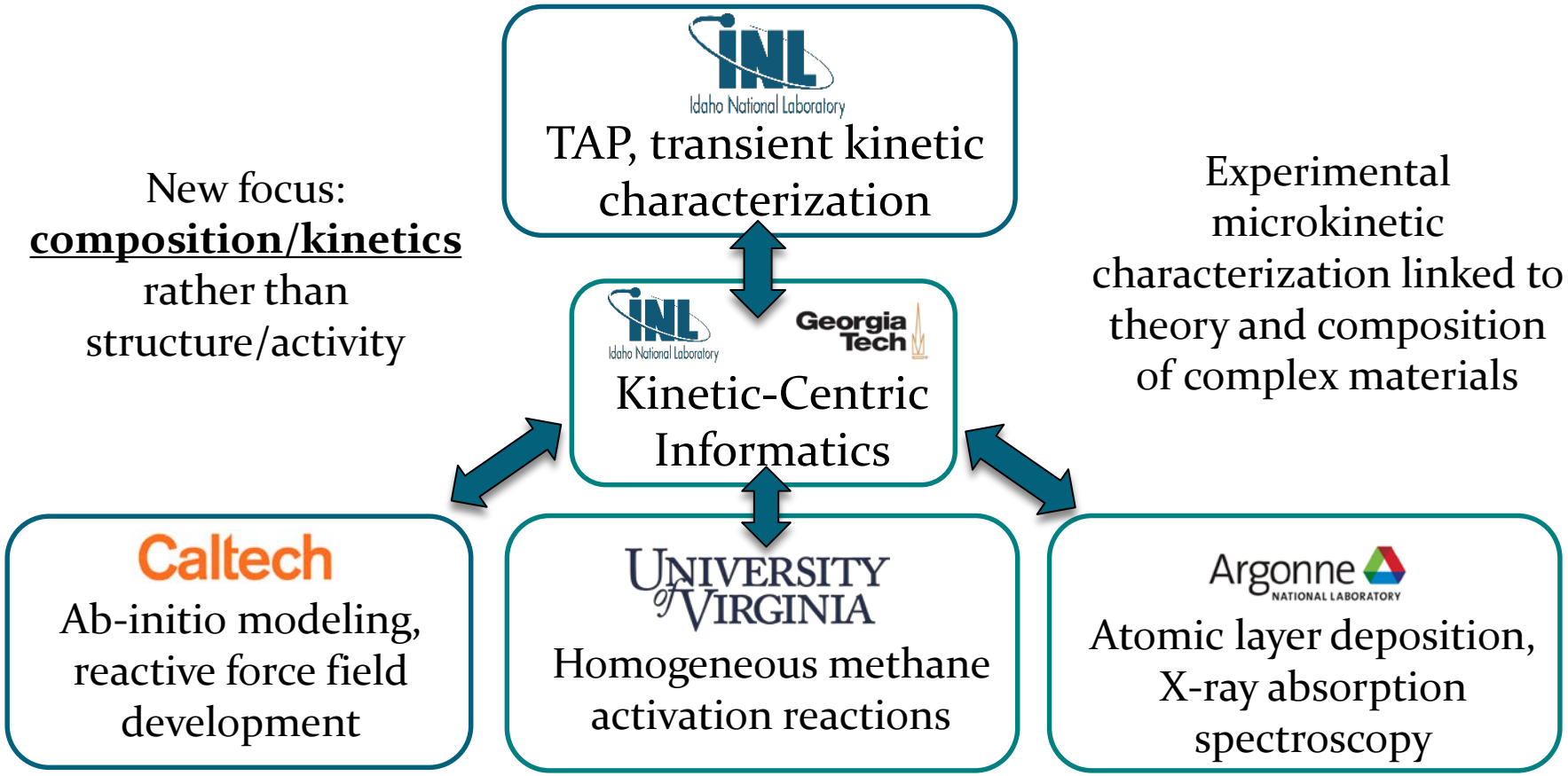
Understanding *how* and *why* materials function



- Technology Impact
  - Advanced catalysts (lower temperature & pressure)
  - Accelerating the catalyst development cycle

Technical Approach

- A new paradigm for catalyst development:
  Transient kinetic experiments
- Kinetic-Centric Informatics tool:
  More meaningful connections from complex data sources



Technical Approach

- Ammonia synthesis from 200 to 20 bar

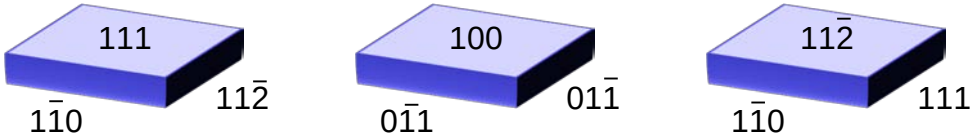
- Elementary reaction steps, N-N rupture, N-H formation
- Incremental surface coverage change, N, NH, H, etc.
- Material complexity

TAP Experimental

Theory

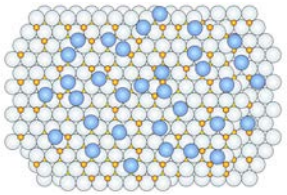
Fundamentals

Fe Single Crystals

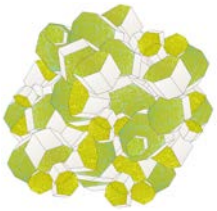


Polycrystalline Fe

Single site, Atomic cluster catalysts



Na, K, Ca Promoters



Commercial Catalysts

TAP + DFT

Experimental measurement theoretical predictions

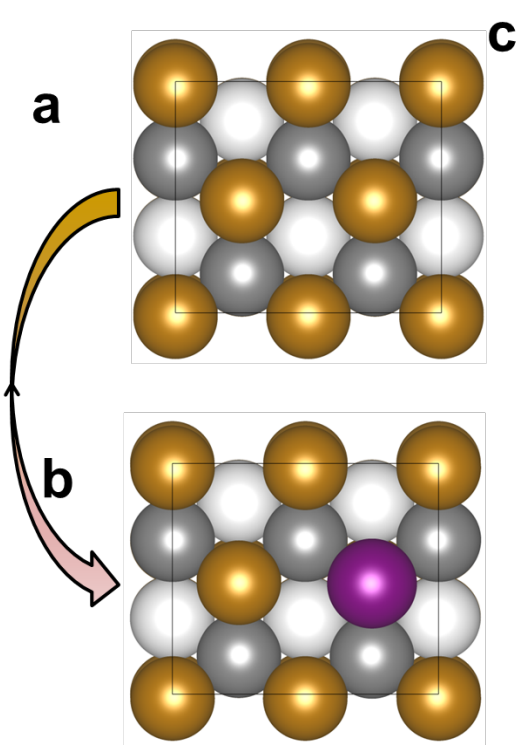
- Enthalpies, ΔH
- Rate constants, k_{ads}, k_r

Brings new direction for applying combinatorial tools to the right problem

Results and Accomplishments

- **Atomistic Modeling:**
  - Complete *ab initio* modeling of 17 key steps of ammonia synthesis on Fe(111)
    - Qian, J., An, Q., Fortunelli, A., Nielsen, R.J. and Goddard III, W.A., (2018) Journal of the American Chemical Society, 140(20), pp.6288-6297.
    - Modeling of Fe-alloys predict increase in NH_3 rate by 18,000x
    - Initial results of *in silico* screening of 34 alloy compositions

Colors indicate at which step dopants were eliminated in high throughput screening



N_2ads-dis-I | N_2ads-dis-II | hydrogenation | NH_3desorption | stability

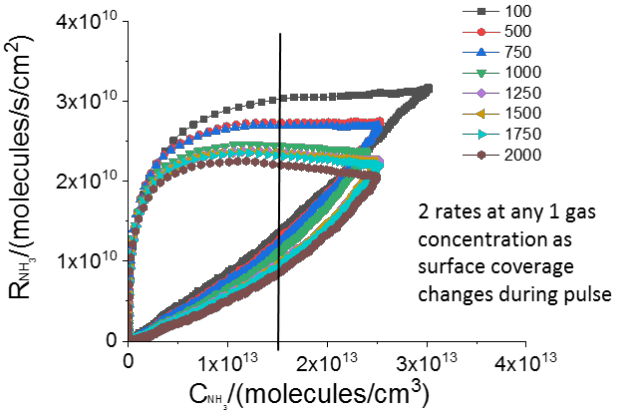
Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30
Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48
La 57	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80

Ce 58			Eu 63			Er 68	Tm 69		Lu 71

Results and Accomplishments

- **Accomplishments Transient Kinetics:**
  - TAP transient kinetic testing of NH_3 decomposition supporting atomistic predictions for NH_3 synthesis
  - Alloy testing: Materials prepared via incipient wetness, strong electrostatic adsorption, electroless deposition
  - Developed new data analysis techniques of transient data
    - Software for rate/concentration analysis of exit flux
    - Captures intrinsic rate constants as the pulse changes the concentrations
    - TAP becomes a high-throughput device for sampling kinetic states.

Medford, A.J., Kunz, M.R., Ewing, S.M., Borders, T. and Fushimi, R.R., 2018. *ACS Catalysis*. Accepted.



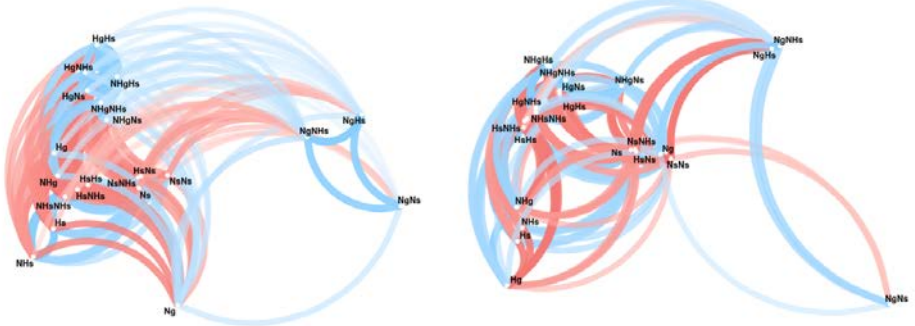
New Transient Analysis Theory and Software

R. Kunz, E.A. Redekop, T. Borders, L. Wang, G.S. Yablonsky, R. Fushimi, (2018) *Chem. Eng. Sci.* Submitted

Materials perform differently at a global level

Iron Catalyst

Iron Alloy Catalyst



New correlation structure analysis uses transient data to understand which reaction steps are important

Transition and Deployment

- Industry Engagement
  - 1 IDR, 7 publications submitted, 9 conference presentations
  - Industry Workshop, June 7, 2017
  - CRADA in development

Representatives from 12 companies attending

Developing a unique capability for industrial catalyst development

- Sustainment Model:

- Industrial Utilization: project results that speak to proprietary needs
- A specialized team surrounding transient kinetics
- Accelerate and derisk proprietary projects
- Advance the state-of-the-art: theoretical methods, advanced instrumentation, transient kinetics, high throughput *in silico* and experiment, data analytics

Questions?