Dynamics at the Interface for Advancing Efficient Manufacturing (DIAdEM): Developing new methods to understand catalysts for ethylene production

Contract # 34921

Idaho National Laboratory, Georgia Institute of Technology, Wayne State University

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Overview

Project Title: Dynamics at the Interface for Advancing Efficient Manufacturing (DIAdEM): Developing new methods to understand catalysts for ethylene production

Timeline:

Project Start Date: 10/01/2018

Budget Period End Date: 09/30/2019

Project End Date: 09/30/2021

Barriers and Challenges:

- 60% ethane/ethylene yield is needed to enable an economically viable industrial oxidative coupling of methane (OCM) process
- Current SOTA catalysts offer 30% C_2 yield
- Conventional catalyst development methods have stymied
- Transient kinetic tools can close key knowledge gaps to understand how/why materials perform differently

AMO MYPP Connection:

- Process Intensification
- Microkinetic data on catalyst performance supports improved catalyst design, potentially leading to the 60% ethane/ethylene yield target.
- High catalyst activity/selectivity enables:
  - Decentralized manufacture of ethylene matched to the size/location of the end user
  - Significantly reduce the energy intensity in comparison to steam cracking
    - Higher selectivity to eliminate separation steps
    - Lower operating temperature

Project Budget and Costs:

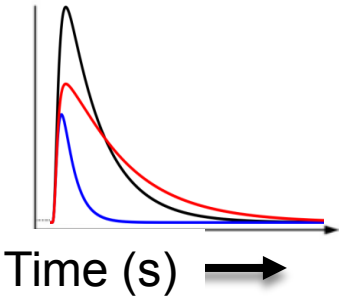
Budget	DOE Share	Cost Share	Total	Cost Share %
Overall Budget	$5,000,000	$0	$5,000,000	0%
Approved Budget (BP-1&2)	$1,967,815	$0	$1,967,815	0%
Costs as of 3/31/19	$770,074	$0	$770,074	0%

Project Team and Roles:

- Idaho National Laboratory – Transient kinetic characterization, method development, catalyst evaluation, project management
- Georgia Institute of Technology – Modeling and analytical tools for transient kinetics data
- Wayne State University – Synthesis and structural characterization of novel layered oxide structures and new catalysts

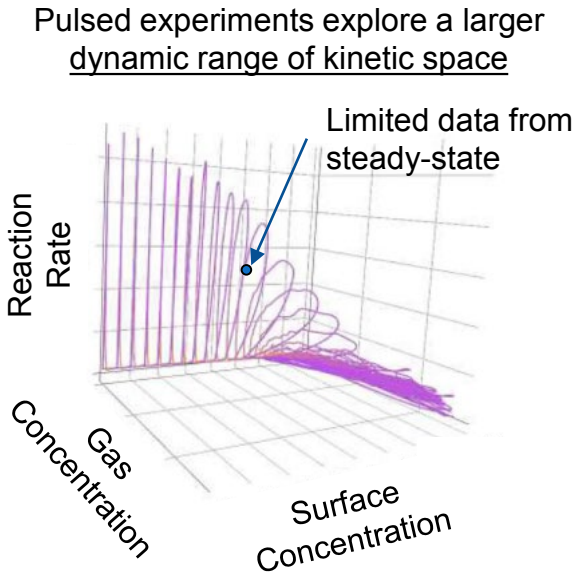
Project Objectives

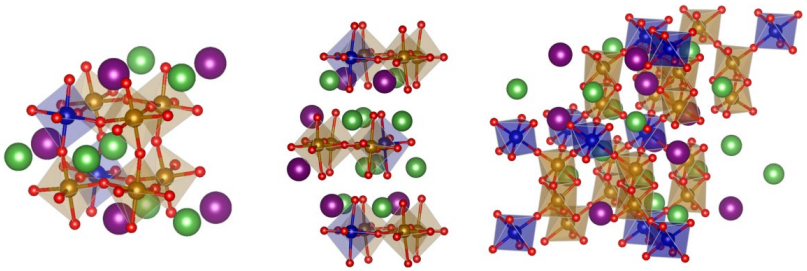
- Ethylene production via steam cracking is centralized and energy intensive
- Catalytic OCM is a promising alternative route to ethylene
  - Higher selectivity, lower temperature: 30% energy reduction
  - $100/t cost advantage and a 90% reduction in scale to match with delocalized end-users
  - Process economics require > 60% C_2 yield, SOTA: 30% yield
- OCM catalyst development has stymied, conventional kinetic tools are limited to a global picture of a complex mechanism
- <u>Objectives:</u>
  - Develop transient kinetic tools to address key knowledge gaps in catalyst function (OCM and beyond)
  - Create advanced oxides for testing/performance
  - Advance modeling and analytical tools for transient data



Technical Innovation

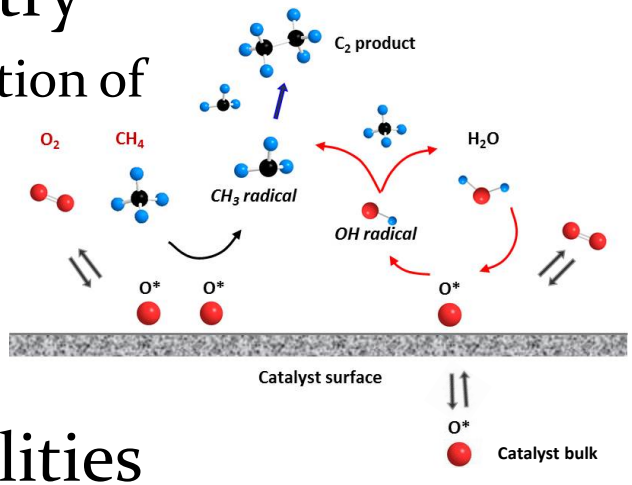
- Today: Conventional kinetic analysis at steady-state
  - Parallelized reactors can screen large libraries of composition
  - Only coarse kinetic information about conversion, selectivity
- Innovation: Transient kinetic methods
  - Greater details of *microkinetic* properties; info. about how/why A is better than B
  - TAP pulse response method can directly study complex industrial materials
  - Transient experiments = high throughput *kinetic* sampling
  - New tools for transient analysis, modeling and simulation
- Advanced nonstoichiometric layered oxides

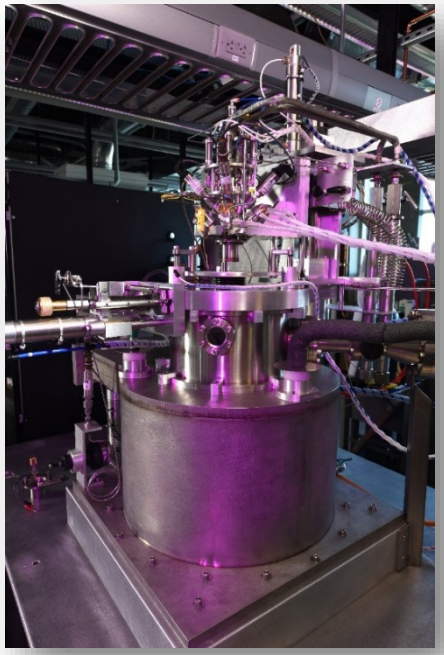




Technical Approach

- Key knowledge gaps for OCM chemistry
  - Influence of catalyst composition on distribution of selective/nonselective oxygen species
  - Regulation of oxygen between surface/bulk
  - Role of gas phase vs. surface chemistry

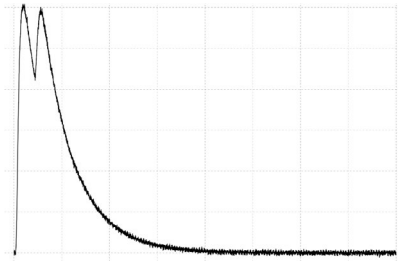




TAP Reactor System at INL
(2 of 3 systems in US)
Transient Kinetic Leadership Position

- INL Roles/Responsibilities

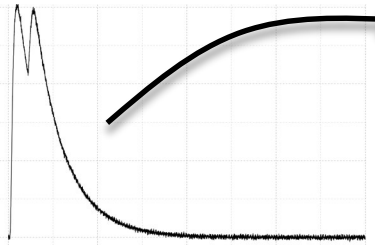
Transient Kinetic Experiments



- Oxygen screening
  - Pump/probe surface dynamics
  - >90% confidence interval for discriminating 2 or more surface oxygen species
- Surface/bulk transport
  - Modulated pulse intensity, variable anneal time
  - Nanomole precision
- Gas/gas vs. gas/solid chemistry
  - NonKnudsen pulsing regime

Technical Approach

- Georgia Tech
  - Kinetic modeling of transient data
  - Software for mechanism generation
  - Connection to density functional theory
  - Multiscale transport/kinetic modeling



$$R = Ae^{-(E_a/RT)} C_a^{\alpha} C_b^{\beta}$$

Primary initiation

$CH_4 + O_2 \rightleftharpoons CH_3^{\bullet} + HO_2^{\bullet}$ (6)

$CH_3^{\bullet}$ generation

$CH_4 + H^{\bullet} \rightleftharpoons CH_3^{\bullet} + H_2$ (7)

$CH_4 + O^{\bullet} \rightleftharpoons CH_3^{\bullet} + OH^{\bullet}$ (8)

$CH_4 + OH^{\bullet} \rightleftharpoons CH_3^{\bullet} + H_2O$ (9)

$CH_4 + HO_2^{\bullet} \rightleftharpoons CH_3^{\bullet} + H_2O_2$ (10)

$CH_3^{\bullet}$ oxidation

$CH_3^{\bullet} + O_2 \rightleftharpoons CH_3O^{\bullet} + O^{\bullet}$ (11)

$CH_3^{\bullet} + HO_2^{\bullet} \rightleftharpoons CH_3O^{\bullet} + OH^{\bullet}$ (12)

$CH_3^{\bullet} + O_2 \rightleftharpoons CH_2O + OH^{\bullet}$ (13)

$CH_3^{\bullet}$ coupling

$CH_3^{\bullet} + CH_3^{\bullet} + M \rightleftharpoons C_2H_6 + M$ (14)

Oxidation of $CH_3O^{\bullet}$ and CH_2O

$CH_3O^{\bullet} + M \rightleftharpoons CH_2O + H^{\bullet} + M$ (15)

$CH_2O + OH^{\bullet} \rightleftharpoons CHO^{\bullet} + H_2O$ (16)

$CH_2O + HO_2^{\bullet} \rightleftharpoons CHO^{\bullet} + H_2O_2$ (17)

$CH_2O + CH_3^{\bullet} \rightleftharpoons CHO^{\bullet} + CH_4$ (18)

$CHO^{\bullet} + M \rightleftharpoons CO + H^{\bullet} + M$ (19)

$CHO^{\bullet} + O_2 \rightleftharpoons CO + HO_2^{\bullet}$ (20)

$CO + HO_2^{\bullet} \rightleftharpoons CO_2 + OH^{\bullet}$ (21)

Dehydrogenation of C_2

$C_2H_6 + H^{\bullet} \rightleftharpoons C_2H_5^{\bullet} + H_2$ (22)

$C_2H_6 + OH^{\bullet} \rightleftharpoons C_2H_5^{\bullet} + H_2O$ (23)

$C_2H_6 + CH_3^{\bullet} \rightleftharpoons C_2H_5^{\bullet} + CH_4$ (24)

$C_2H_6 + O^{\bullet} \rightleftharpoons C_2H_5^{\bullet} + OH^{\bullet}$ (25)

$C_2H_5^{\bullet} + M \rightleftharpoons C_2H_4 + H^{\bullet} + M$ (26)

$C_2H_5^{\bullet} + O_2 \rightleftharpoons C_2H_4 + HO_2^{\bullet}$ (27)

$C_2H_4 + O_2 \rightleftharpoons C_2H_3^{\bullet} + HO_2^{\bullet}$ (28)

$C_2H_4 + H^{\bullet} \rightleftharpoons C_2H_3^{\bullet} + H_2$ (29)

$C_2H_4 + O^{\bullet} \rightleftharpoons C_2H_3^{\bullet} + OH^{\bullet}$ (30)

$C_2H_4 + OH^{\bullet} \rightleftharpoons C_2H_3^{\bullet} + H_2O$ (31)

$C_2H_4 + CH_3^{\bullet} \rightleftharpoons C_2H_3^{\bullet} + CH_4$ (32)

$C_2H_3^{\bullet} + M \rightleftharpoons C_2H_2 + H^{\bullet} + M$ (33)

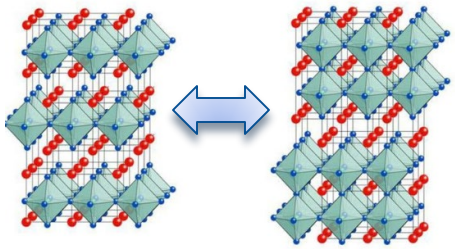
$C_2H_3^{\bullet} + O_2 \rightleftharpoons C_2H_2 + HO_2^{\bullet}$ (34)

Decomposition of C_2H_4

$C_2H_4 + O^{\bullet} \rightleftharpoons CH_3^{\bullet} + CHO^{\bullet}$ (35)

$C_2H_4 + OH^{\bullet} \rightleftharpoons CH_3^{\bullet} + CH_2O$ (36)

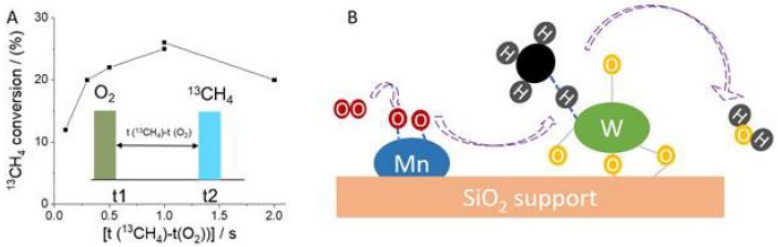
- Wayne State University
  - Advanced oxide synthesis and structural characterization
  - Steady-state catalyst testing
  - Ruddlesden-Popper (RP) layered oxides
    - Substoichiometric characterization/manipulation
    - Thermodynamic properties
    - Structure-stability relationships

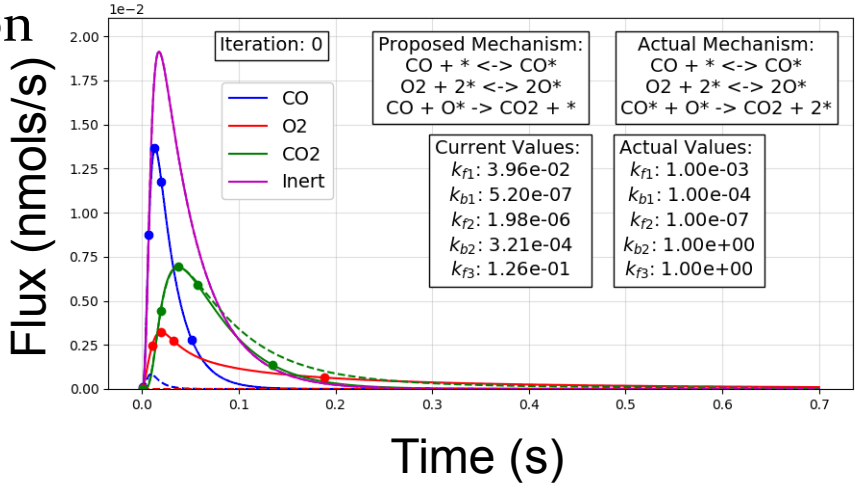


Results and Accomplishments

- Y1Q1: Prepare OCM catalyst library for testing
- Y1Q2: Transient kinetic data, supporting characterizations
  - First generation performance on par with industry preparations, SOTA
  - Early results in TAP pump/probe experiments
    - CO formed in gas phase, CO_2 on surface
    - Mn significantly enhances oxygen exchange and surface/bulk diffusion, full exchange for CO_2, more reactive than W
    - Metal promoters identified, linked to change in W binding energy
  - Early success in modeling/simulation for CO oxidation
- Y1Q4 Go/No-Go
  - >90% confidence interval in statistical discrimination of 2 or more surface oxygen distributions
- Y2Q1: 2nd generation materials

$Mn/Na_2WO_4/SiO_2$

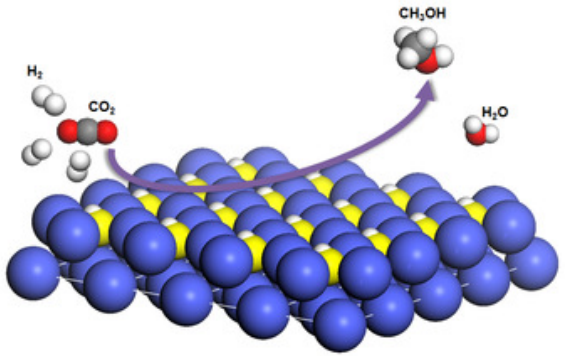




Transition (beyond DOE assistance)

- Industrial collaborations
  - Transient kinetic tools will be used to develop promising pre-commercial OCM catalysts for industry
  - Current partnership with Precision Combustion Inc.

- Transient kinetic methods applied beyond OCM
  - Selective oxidation catalysts
  - Oxidative dehydrogenation catalysts
  - Chemical looping materials
  - Solid oxide electrolytes
  - Sorbents and separations



- Intellectual property license of new RP-oxide based catalyst for OCM