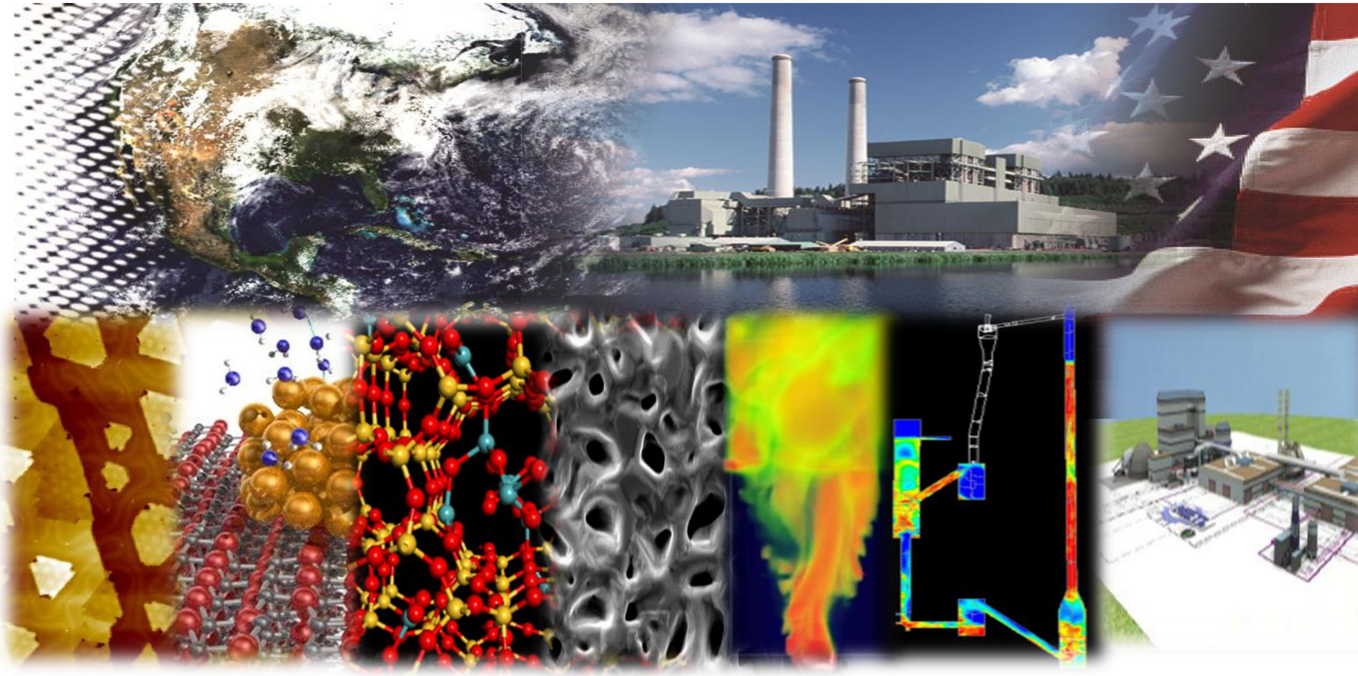
NATIONAL ENERGY TECHNOLOGY LABORATORY



Accelerating Technology Development

Catalyst/Sorbent Development & Commercialization

David A Berry

Director

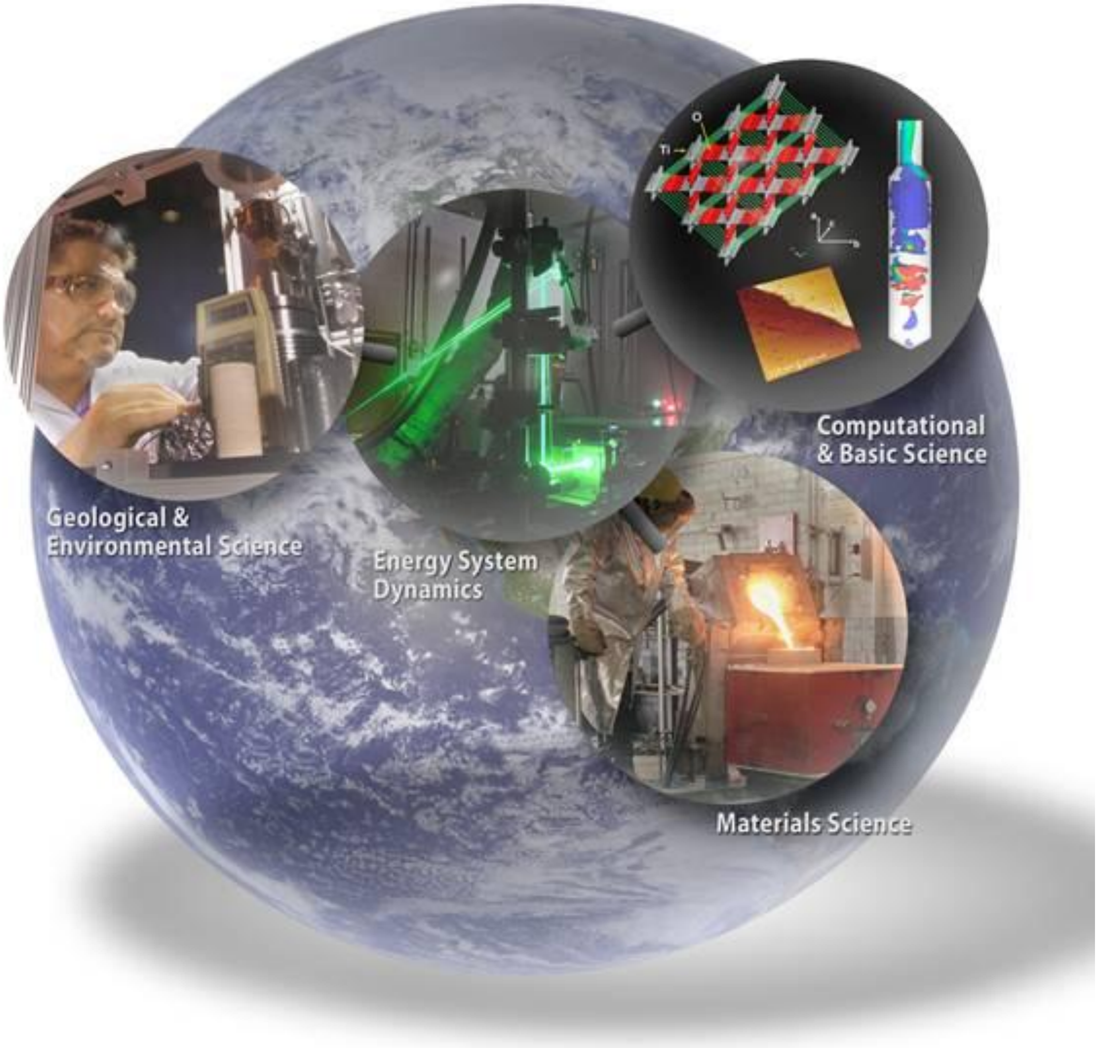
Separation & Fuel Processing Division

US DOE NETL

NETL-RUA Energy & Innovation Conference
November 28-29th, 2012

U.S. DEPARTMENT OF ENERGY

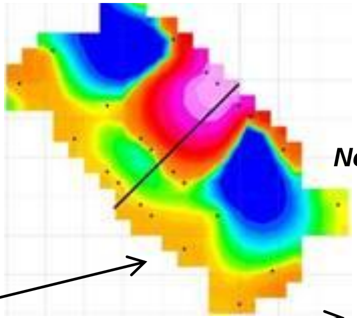
Catalysis
Fundamental backbone of chemical industry



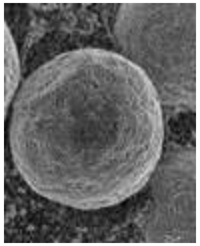
Recent ORD R&D 100 Awards

- **R&D 100 Awards**
  - 2007 – Armstrong Process CP Titanium and Titanium Alloy Powder and Products
  - 2007 – Multiphase Flow with Interphase eXchange (MFIX) software
  - 2007 – SEQURE™ Well Finding Technologies
  - 2008 – Palladium-based high temperature mercury sorbent
  - 2008 – Advanced Process Engineering Co-Simulator (APECS) software
  - 2009 - SEQURE™ Tracer Technology
  - 2009 - Clay-Liquid CO2 Removal Sorbent
  - 2009 - Thief Process for the Removal of Mercury from Flue Gas
  - 2009 - VE-PSI: Virtual Engineering Process Simulator Interface
  - 2010 - Cerium Oxide Coating for Oxidation Rate Reduction in Stainless Steels and Nickel Superalloys
  - 2010 – osgBullet
  - 2011 - APECS v2.0 with ANSYS® DesignXplorerTM and ROM Builder
  - 2011 - Mn-Co Coating for Solid Oxide Fuel Cell Interconnects
  - 2011 - Novel Platinum/Chromium Alloy for the Manufacture of Improved Coronary Stents
  - 2012 - Basic Immobilized Amine Sorbent (BIAS) Process for Carbon Dioxide (CO2) Capture (Environmental Technologies)
- Patents- 70 Applications in Process, 66 Total Issued Patents
- Active CRADAs-17, Patent Licenses-11

Field Test Results for Tracers



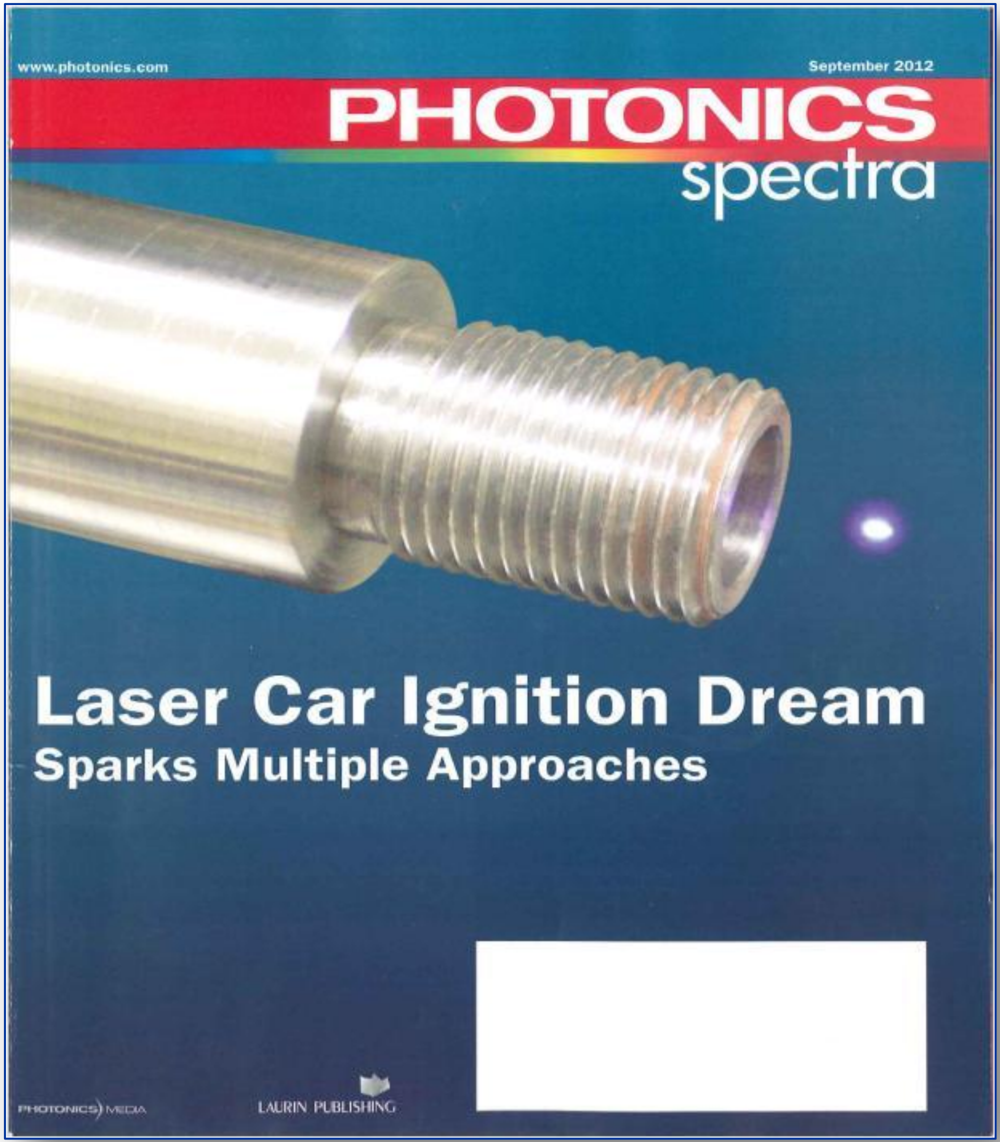
Novel CO2 sorbent



Thief Process Test on Commercial Burner

Virtual Process Engineering

NETL Technology in the News



- Prior NETL research on laser spark plug featured story in September 2012 Photonics Spectra trade magazine (circulation 95,000)
- Cover photo from NETL lab tests!
- Originally developed for emission reduction in natural gas engines.
- Attracting new interest this year.

Credit to Dustin McIntyre and Steve Woodruff

NETL Research is "Strikingly Original"

NETL-RUA researchers Mengning Ding, Alex Star, and Dan Sorescu have developed a methodology that utilizes carbon nanotube scaffolds to assemble gold nanowires, for potential H_2S sensor applications. Read more in their ***Journal of the American Chemical Society*** *article:*

J. Am. Chem. Soc., DOI: 10.1021/ja210278u

JACS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Article
pubs.acs.org/JACS

Welding of Gold Nanoparticles on Graphitic Templates for Chemical Sensing

Mengning Ding,[†,‡] Dan C. Sorescu,[†] Gregg P. Kotchey,[‡] and Alexander Star*[,†,‡]

[†]National Energy Technology Laboratory, U.S. Department of Energy, Pittsburgh, Pennsylvania 15236, United States
[‡]Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, United States

Supporting Information

ABSTRACT: Controlled self-assembly of zero-dimensional gold nanoparticles and construction of complex gold nanostructures from these building blocks could significantly extend their applications in many fields. Carbon nanotubes are one of the most promising inorganic templates for this strategy because of their unique physical, chemical, and mechanical properties, which translate into numerous potential applications. Here we report the bottom-up synthesis of gold nanowires in aqueous solution through self-assembly of gold nanoparticles on single-walled carbon nanotubes followed by thermal-heating-induced nanowelding. We investigate the mechanism of this process by exploring different graphitic templates. The experimental work is assisted by computational studies that provide additional insight into the self-assembly and nanowelding mechanism. We also demonstrate the chemical sensitivity of the nanomaterial to parts-per-billion concentrations of hydrogen sulfide with potential applications in industrial safety and personal healthcare.

INTRODUCTION

The bottom-up synthesis of complex architectures from nanoscale building blocks is a fascinating approach to achieve novel materials with unique structures and functions; yet this process remains extremely challenging because it requires careful and delicate control of the building blocks at a molecular level.[1−3] One representative example involves the fabrication of one-dimensional (1-D) gold nanowires (AuNWs) from zero-dimensional (0-D) gold nanoparticles (AuNPs), which have been extensively studied due to their potential applications in electronics,[4,5] photonics,[6] and sensors.[7] The difficulty with this system arises from the need to precisely place and interconnect individual NPs in a confined dimension.[8,9] Successful bottom-up fabrication of AuNWs has been accomplished through an "oriented attachment" method[10−12] where recognition of the anisotropic lattice and the reduction of surface energy played essential roles.[13,14] The welding of gold at the nanoscale was another approach for the bottom-up construction of gold nanostructures. Since this method does not require the templating of strong binding surfactants such as oleylamine, it is favorable for the fabrication of catalysts and chemical sensors. The welding of gold nanostructures has been successfully implemented by a number of methods such as laser heating,[15] Joule heating,[16] and cold welding.[17] Combining nanowelding with self-assembly of AuNPs provides another promising bottom-up strategy for the fabrication of AuNWs from AuNPs; one example of such a strategy has been successfully demonstrated by Belcher and co-workers utilizing biological templates.[18]

Progress made on controlled fabrication of Au nanostructures will significantly benefit the development of chemical sensors. Au has been used in chemical sensors for decades[19] because of its chemical inertness and high conductivity, which changes upon adsorption of different molecules. Hydrogen sulfide (H_2S), for example, has been detected using Au thin films,[20] AuNPs,[21] and most recently AuNPs-decorated carbon nanotubes (CNTs).[22,23] Despite the excellent sensitivity achieved by AuNPs for H_2S, there has been minimal advance in the development of H_2S sensors based on AuNWs. 1-D nanostructures have been considered to be an ideal sensor architecture because their Debye length is comparable to the cross-sectional radius;[24,25] therefore, it is of great interest to explore the H_2S sensitivity of 1-D AuNWs.

Here we report a bottom-up approach for the synthesis of AuNWs using AuNPs as building blocks in aqueous suspensions of single-walled carbon nanotubes (SWNTs). Citrate-stabilized AuNPs first underwent a 1-D self-assembly process enabled by 1-pyrenesulfonic acid (PSA)-decorated SWNT templates, and AuNWs were subsequently formed through a nanowelding process of aligned AuNPs induced by thermal heating. In addition to performing control experiments with different graphitic templates, we used density functional theory (DFT) calculations to understand the underlying mechanism of the entire self-assembly and nanowelding processes. We further demonstrated the use of AuNW-SWNTs hybrid material for sensitive and selective detection of H_2S gas. We established that, with its ultrasensitivity to H_2S at concentrations as low as parts-per-billion (ppb) and no obvious cross-sensitivity toward major components of natural

Received: November 9, 2011

Breaking the Paradigm
Materials Development Continuum

Leveraging multi-disciplinary, multi-scale research accelerates development, increases innovation, reduces risk

Materials Genome Initiative, for Global Competitiveness (2011)

Discovery or Application

What comes first?

Industry

Applications Oriented

Market Pull

NETL

Academia / National Laboratory

More fundamental in nature

Technology Push

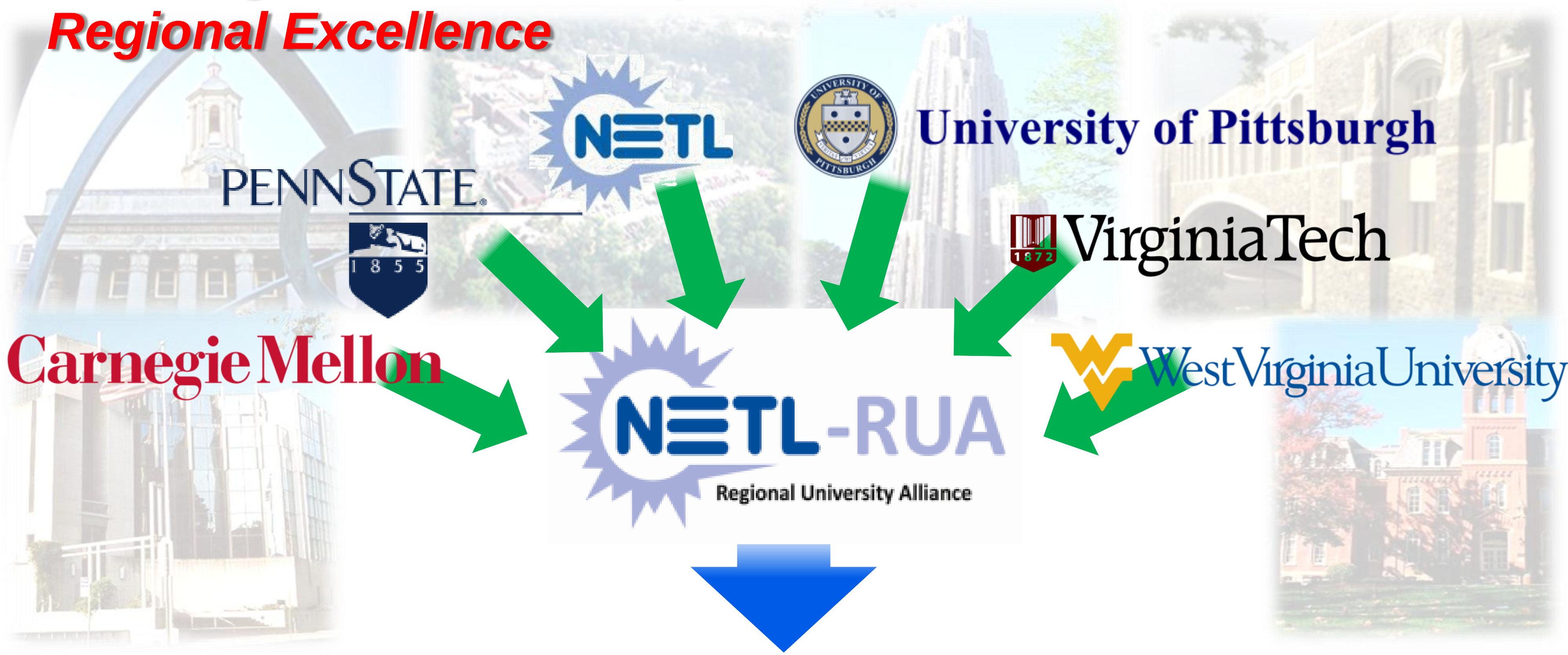
The Goal

Targeted, use-inspired integrated R&D

I want my technology NOW !

Strategic Partnerships

Regional Excellence



Shared Resources + Shared Intellect = Targeted Innovation

Create and enable dynamic teams to do targeted research that effectively provides solutions to the Nation's most challenging problems

Computational & Basic Sciences - Energy Systems Dynamics - Geological & Environmental Systems - Materials Science & Engineering

Back to Catalysis
Challenges

- **The problem:**

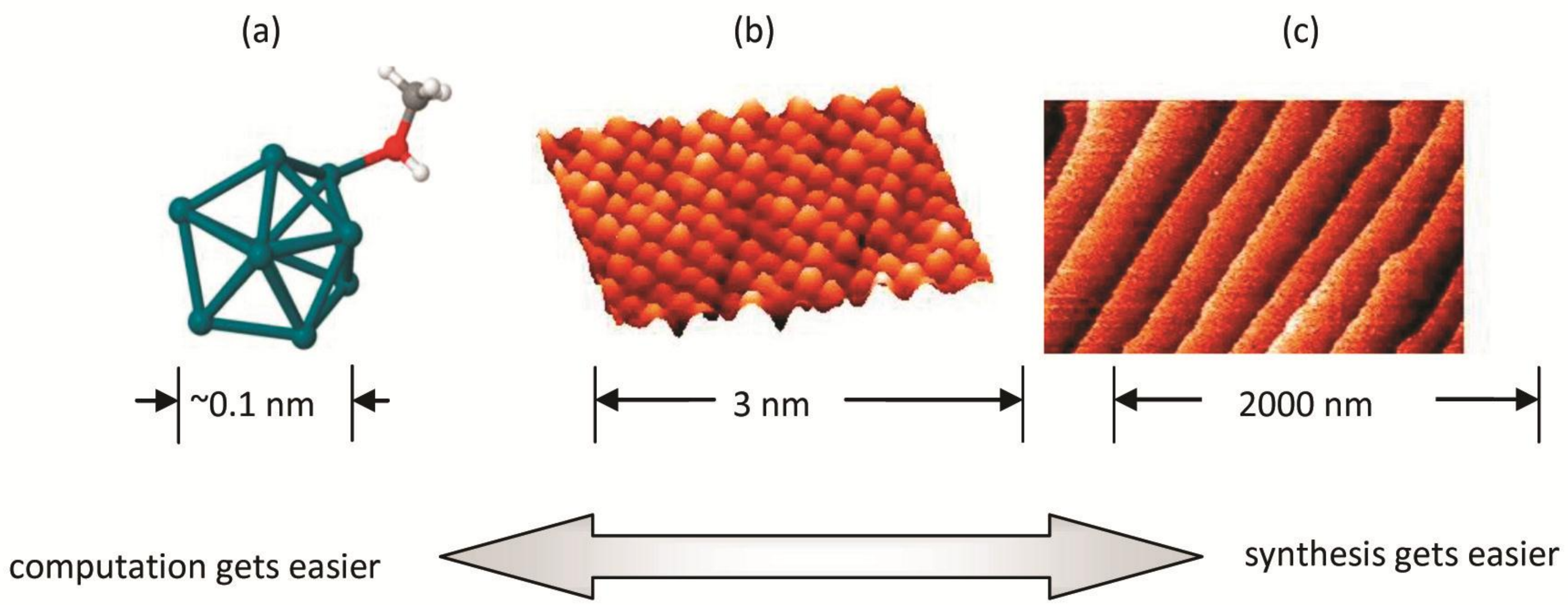
"Currently, there is a large divide between surface scientists …and most catalysis researchers …caused by the inability of existing experimental and theoretical techniques to deal with the real-world nanomorphologies. "[1]

"The ultimate goal is to have enough knowledge of the factors determining catalytic activity to be able to tailor catalysts atom-by-atom."[2]

[1] *Basic Research Needs for Clean and Efficient Combustion of 21st Century Fuels., DOE/BES, 2007, p. 32.*
[2] *J. K. Nørskov, T. Bligaard, J. Rossmeisl and C.H. Christensen, Nature Chemistry, 1 (2009) 37-46.*

Computational Approach

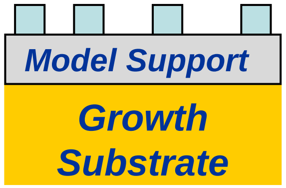
Prediction & Catalyst Design

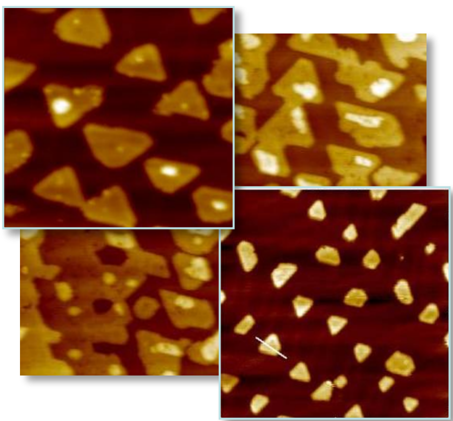


Understanding Catalyst Structure & Reactivity

Growth

Model catalysts

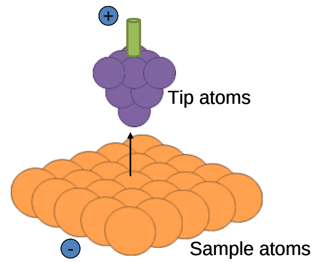


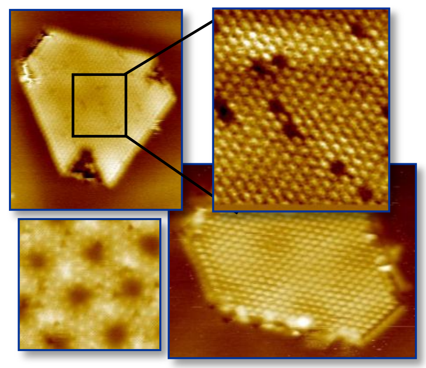


Model Fe Catalysts

Characterization

STM

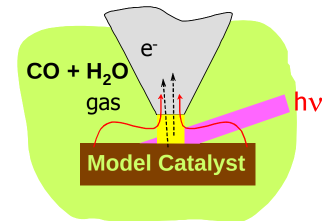


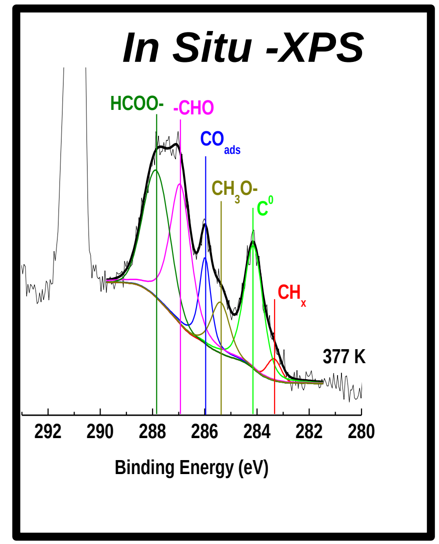


Atomically Resolved Fe-oxide

Reactivity Testing

In Situ-XPS (Synchrotron)





WGS Rxns on Fe-oxide catalysts

Collaborators:

BERKELEY LAB

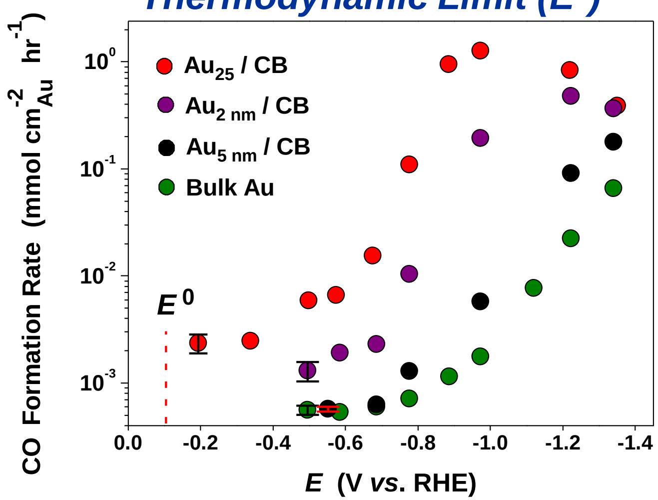
PITT

New Catalyst Discovery

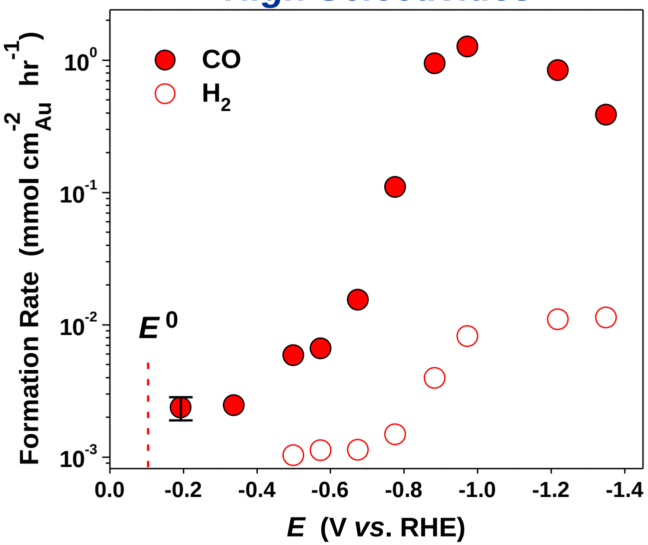
Experiments & Theory Explain Au_{25} Reactivity

Au_{25} is 10-100 times more efficient than any other reported technology

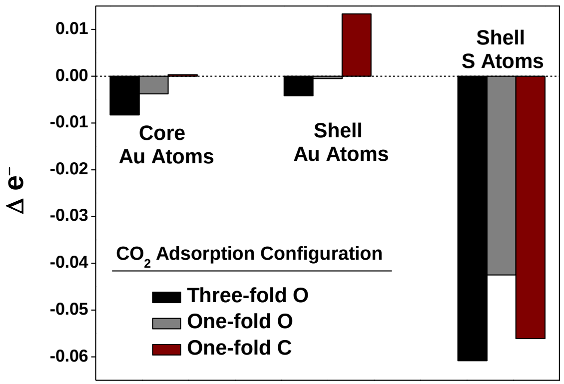
CO_2 Conversion to CO at the Thermodynamic Limit (E^0)

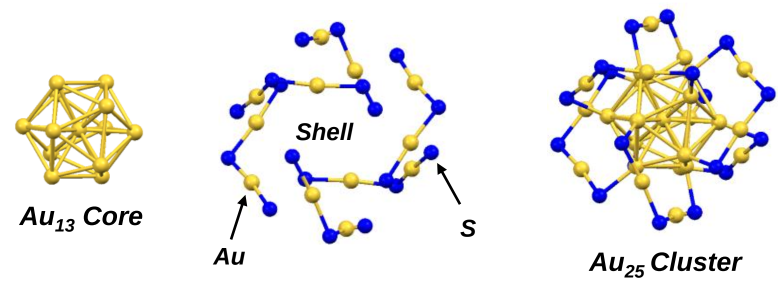


High Selectivities



CO_2 "Pushes" Charge During Adsorption



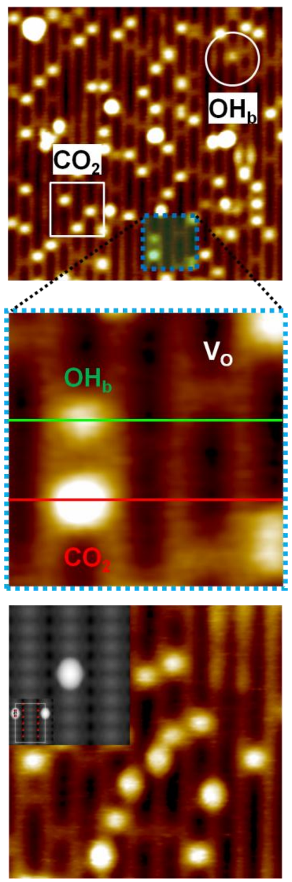


Kauffman et. al. Journal of the American Chemical Society, 10237 (2012)

Understanding Catalyst Structure & Reactivity

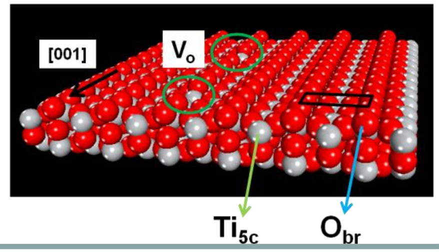
Experiments & Theory Watch Single Molecules React on Surfaces

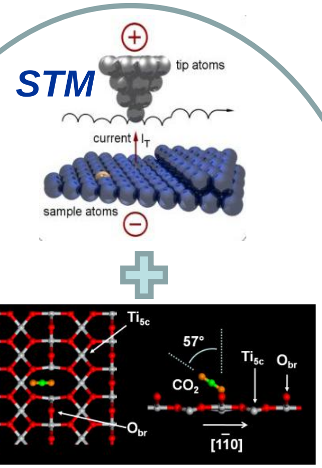
Adsorption sites



$CO_2/TiO_2(110)$

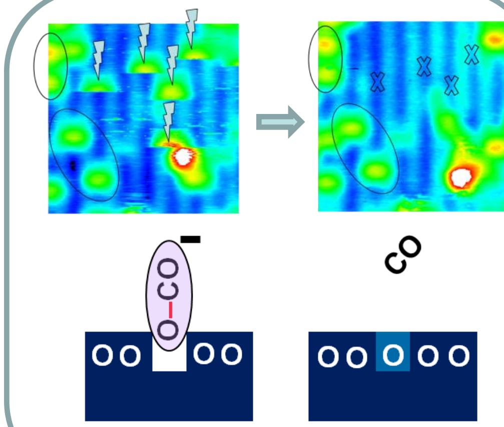
Model Photocatalyst – $TiO_2(110)$





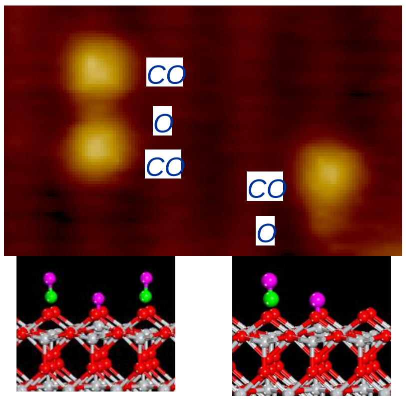
DFT Calculations

Electron-induced chemistry



$CO_2 + e^- \rightarrow CO + O$

Intermolecular interactions



$CO + O / TiO_2(110)$

Strategic Partnerships

Center for Atomic Level Catalyst Design

DoE Energy Frontier Research Center

The Center has the goal of advancing both:

• the ability of computational catalysis to accurately model reactions, and

• the tools of materials synthesis/characterization → allowing atomically precise catalysts identified by computation to be prepared and characterized unambiguously.

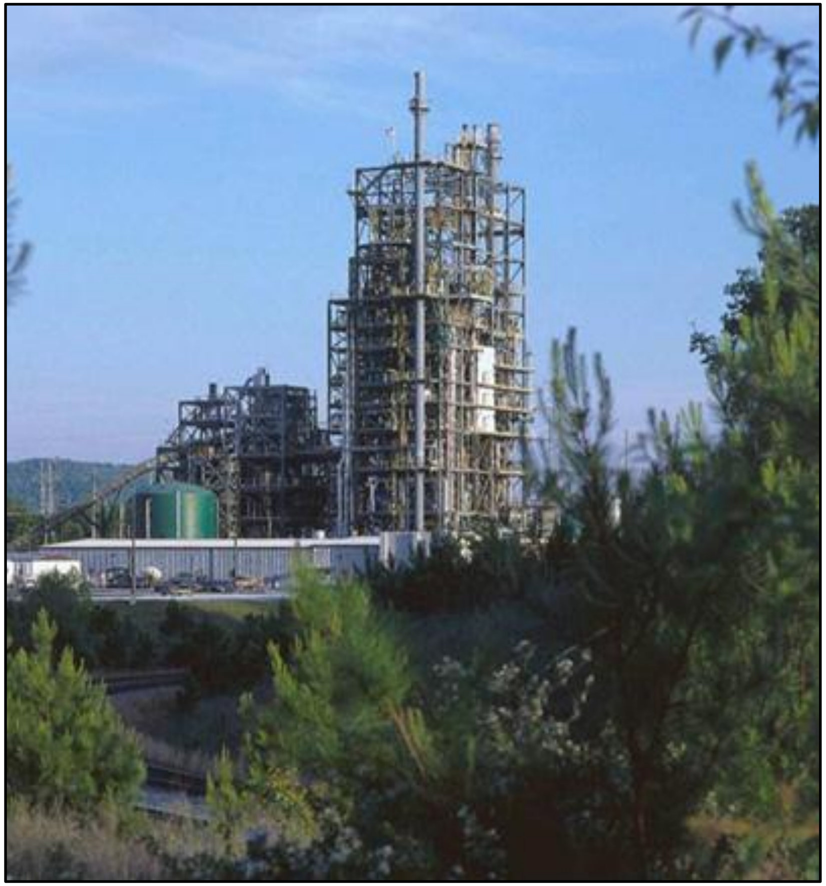
Performance Reactors

Variety of operating range/scale

Reactor	P (atm)	T (°C)	Mode of operation	Flow	Diameter	Reaction Length (in)	Gases allowed	Liquids allowed	Unattended operation	Comment
B3, 150										
HPR1	1,34	800, 600	Fixed	500 sccm	20 mm		H2S, inert			
HPR2	1,34	800,600	Fixed	500 sccm	8mm		H2S, inert			
MIR	40.8	800	Fluid/Fixed	300 scfh	2 inches		H2S, inert			
B25, 110										
Parr reactor	102	650	Fixed	2000 sccm	1 inch		H2S,inert			
B13										
Torrefaction	1	350	Fluid/Fixed	125 scfm	4 inch		inert			
B3/150										
Catalyst Screening Unit	35	1000	Fixed	2000 sccm	1 inch		CO, H2, inerts, CH4, H2S, C3H8, C3H6	Diesel, ethanol, jet fuels, or their surrogates	No	Equipped with radio frequency (RF)-assisted catalytic reaction
B4/West Bay										
Fuel Processing Unit	4	982	Fixed	300 slpm	1 inch		CO, H2, inerts, CH4, H2S, C3H8, C3H6	Diesel, ethanol, jet fuels, or their surrogates	Yes	Gliding-arc plasma reforming capability
B25/201										
Micro Performance Reactor 1	6 (30)	982 (650)	Fixed	1500 sccm	8 or 13 mm		CO, H2, inerts, CH4, H2S, C3H8, C3H6	Diesel, ethanol, jet fuels, or their surrogates	Yes	
Micro Performance Reactor 2	6 (30)	982 (650)	Fixed	1500 sccm	8 or 13 mm		CO, H2, inerts, CH4, H2S, C3H8, C3H6	Diesel, ethanol, jet fuels, or their surrogates	Yes	
B25/204										
Fischer-Tropsch Reactor	65	700	Fixed	1000 sccm			CO, H2, inerts, CH4, H2S, C3H8, C3H6	Diesel, ethanol, jet fuels, or their surrogates	Yes	Staged cooling for product separation
B22										
Circulating Fluid Bed	3	25	Transport/packed/fluid circulating bed	2,500 scfm	12 inch		air	55 ft		
Minimum fluidization rig	1	25	Bubbling Fluid bed	50 scfm	2.5 inch		air	5 ft		
10-cm BFB	1	25	Bubbling Fluid bed	100 scfm	4 inch		air	6 ft		
Rectangular Bed	1	25	Bubbling Fluid bed	400 scfm	3x9 inch		air	5 ft		
C2U	1	120	Transport/packed/fluid/circulating beds	2000 slpm	5.5 and 2 inch		air, N2, CO2, H2O	10 ft		
B6										
PPC	10	1700	continuous (gas phase reactions)	2 lb/s (1600 scfm)	7-inch		POC (air + nat. gas; H2 fuels)	Combustion R&D		
LECTR/SimVal	20	1700	continuous (gas phase reactions)	3 lb/s (2400 scfm)	7-inch		POC (air + nat. gas; H2 fuels)	Combustion R&D		
B4										
CLR	1	1000	circulating fluid bed	50 scfm	6-inch 8-inch		air, NG, inert	Chemical Looping & Circulating Reactor Studies		
B13										
SFBR	1	1000	fluid/fixed	14000 sccm (0.5 scfm)	2.5 - inch		air, NG, inert			

National Carbon Capture Center at the Power Systems Development Facility (PSDF)

Wilsonville, AL



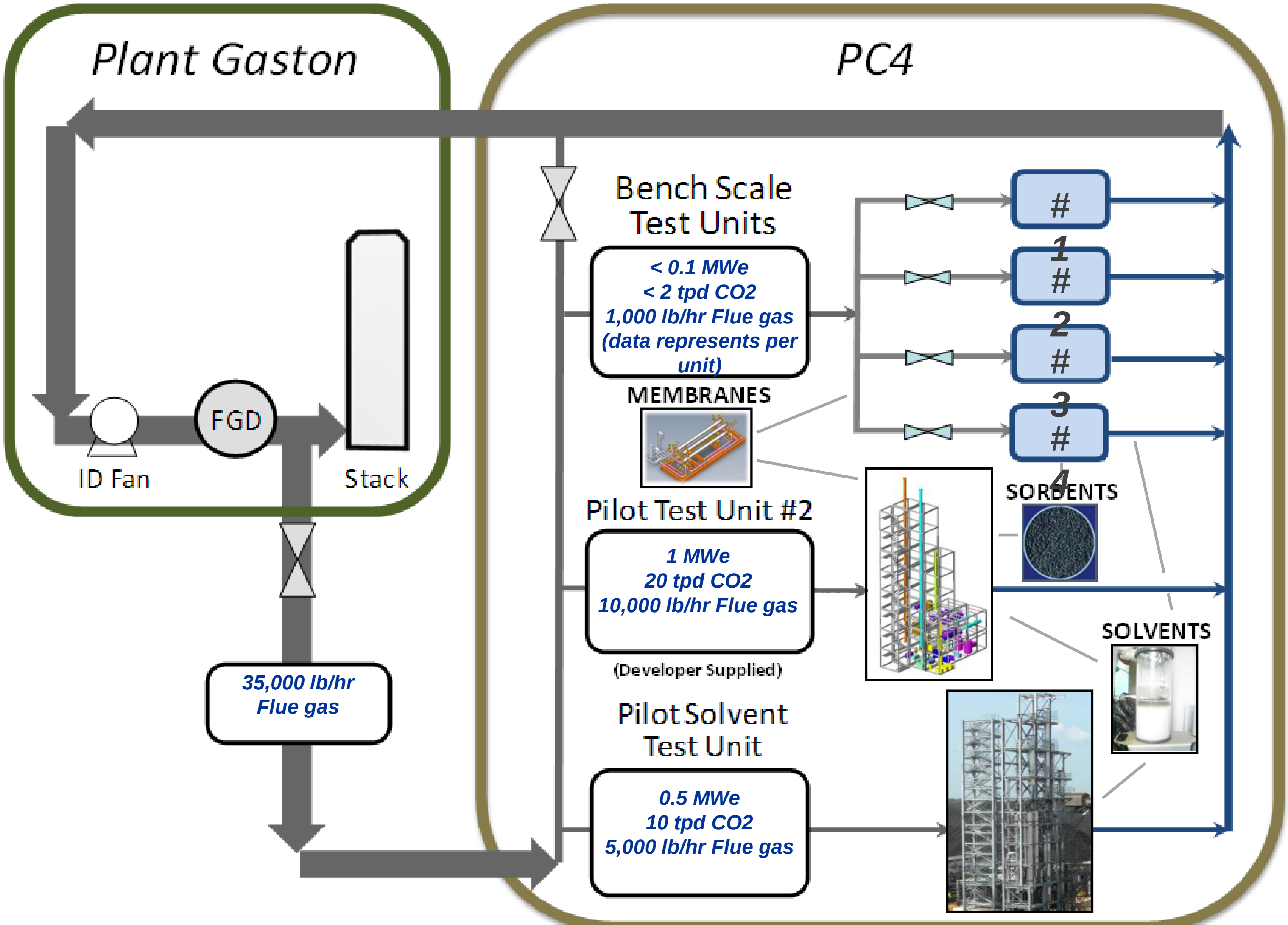
Southern Company Services

- 3 MW – 35,000 lbs/hr flue gas slip stream from post-combustion – from 880 MW Plant Gaston

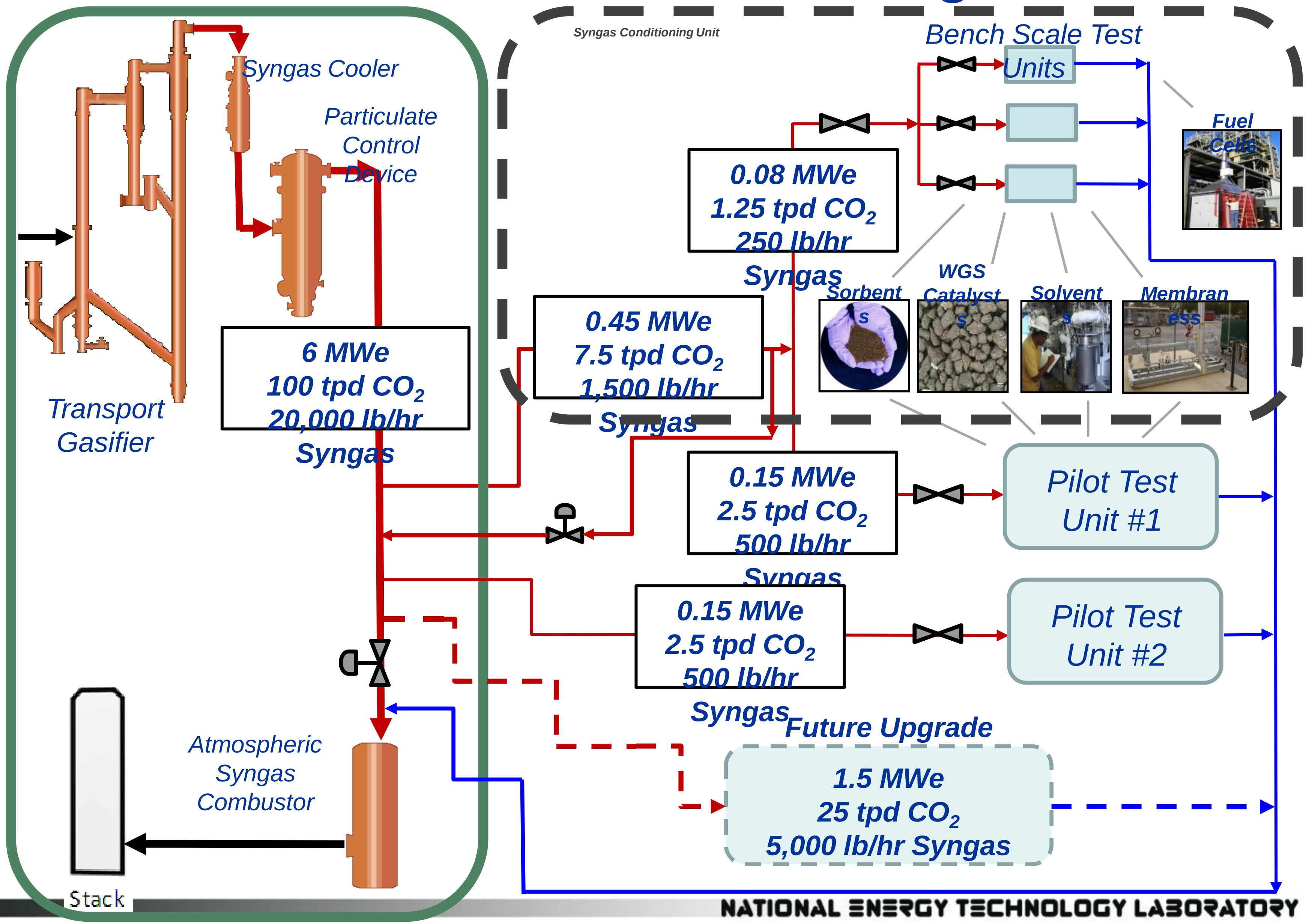
- 6 MWe -100tpd CO_2 – 20,000lb/hr. syngas from TRIG gasifier at PSDF

*Offer a unique **flexible R&D facility** where processes can be tested on coal-derived gas at various scales*

Post-Combustion Test Diagram



Pre-Combustion Test Diagram



A short story – Pyrochlore Catalyst…

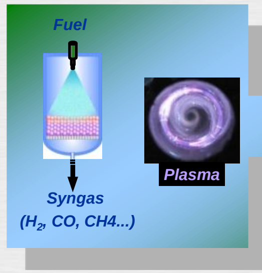
Fuel Cell Systems

NETL Fuels Processing R&D program is addressing the need of future fuel cell systems to operate on conventional hydrocarbon fuels by investigating:

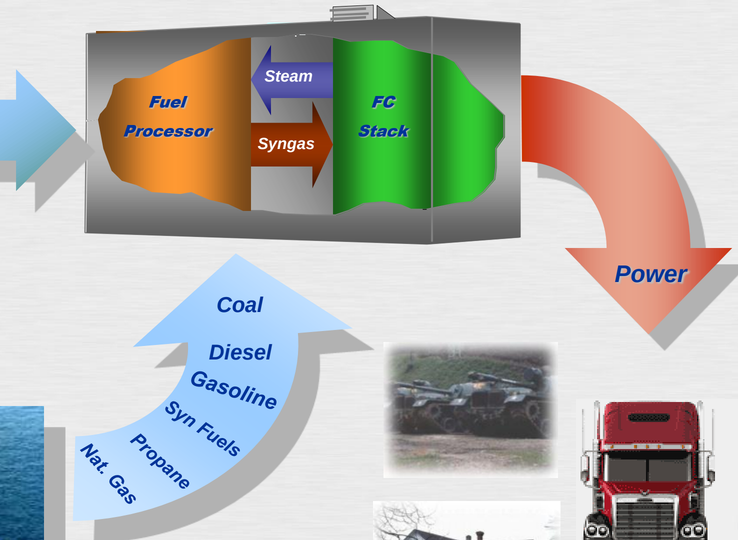
- Reforming options for high energy density fuels such as gasoline, coal-based, diesel, JP-8, military logistics fuels…for conversion into a fuel gas that is high in hydrogen and carbon monoxide
- Fundamental understanding of reforming mechanisms and overcoming deactivation associated with poisoning of both reforming catalysts & fuel cell anodes via sulfur and carbon deposition

High efficiency solid state fuel cell systems must be:

- Coupled and thermally integrated with fuel processors;
- Capable of achieving specifications required for various applications including stationary and mobile power systems



Reforming Technologies



Fuel Sources

Applications

- Stationary
- Military
- Transportation

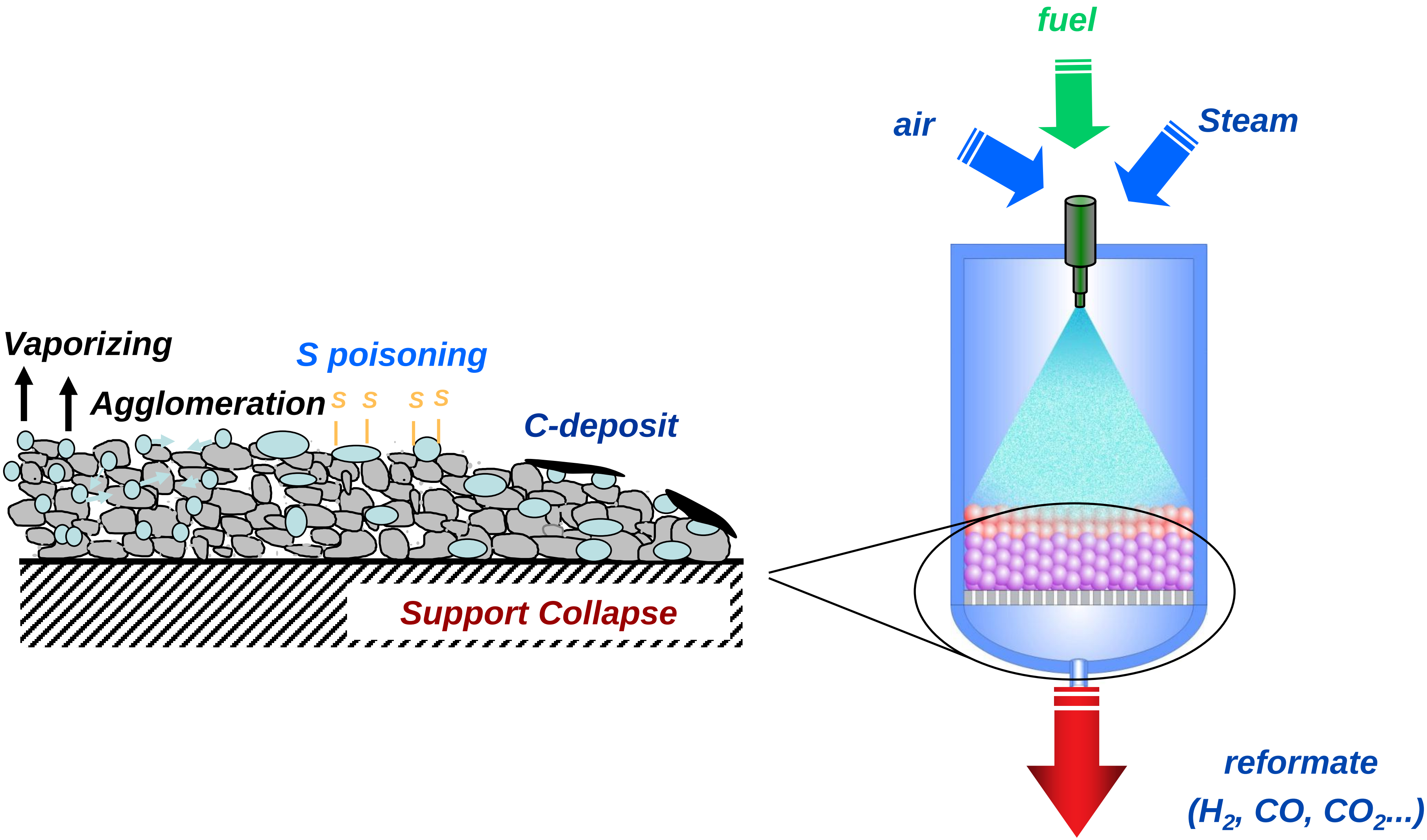
Research areas being investigated include:

- Advanced Oxide-Based Catalysis for Hydrocarbon Fuel Reforming
- Alternative Non-traditional Reforming Concepts
  - Plasma
  - RF

➢Research Capabilities:

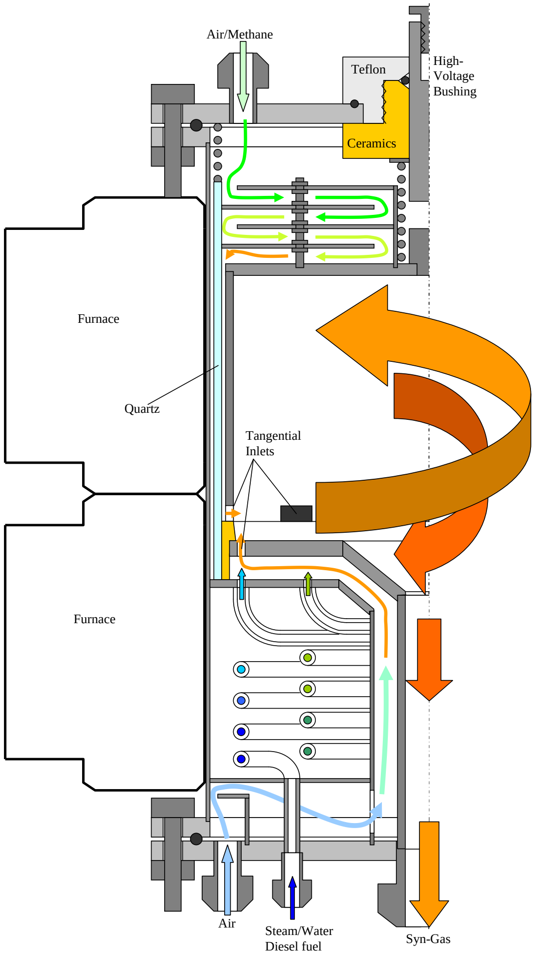
- Full R&D for fuel reforming, desulfurization, & fuel cell integration.
- Comprehensive analytical and test capability ranging from laboratory-scale to multi-KWe integrated systems.

Understanding the Problem
Conventional Reforming Technology



Technology Options

Thinking outside the box – Alternative Concepts

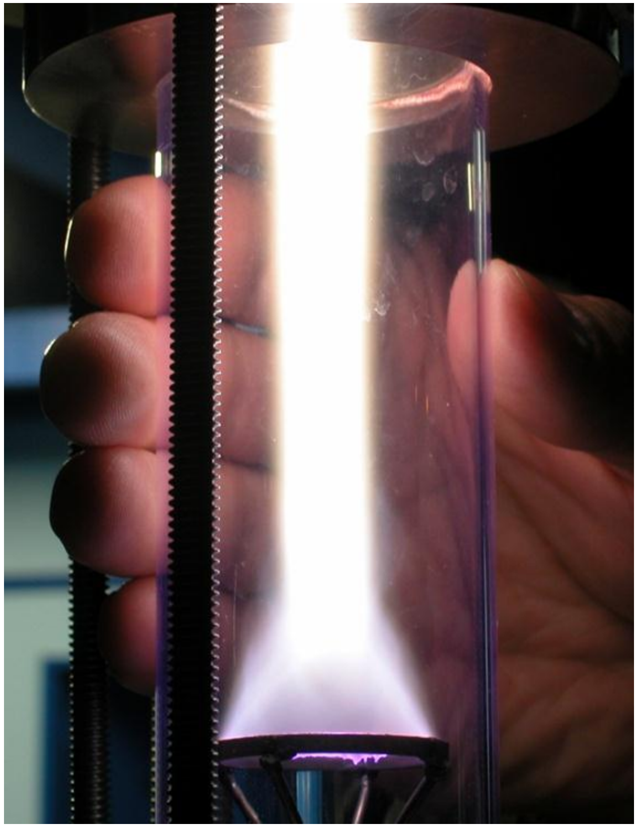


Thermal Plasma – conventional technology

- *All species are in thermal equilibrium – high temperature*
- *Very high plasma power and density*
- *Little chemical selectivity can be obtained*

Non-thermal plasma

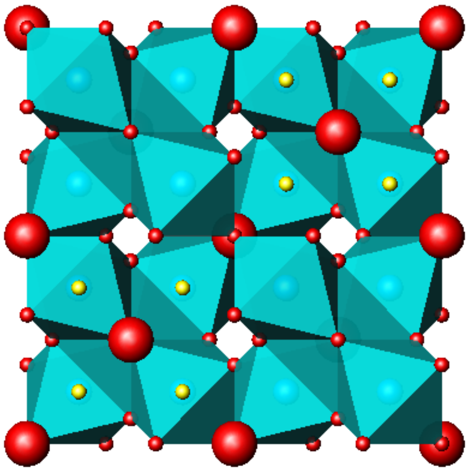
- *High electron temperature but low gas temperature*
- *Low power density*
- *High chemical selectivity possible*



[1]Fridman et al., Conversion of hydrocarbons into syn-gas simulated by non-thermal atmospheric pressure plasma (Drexel University)

Technology Solutions

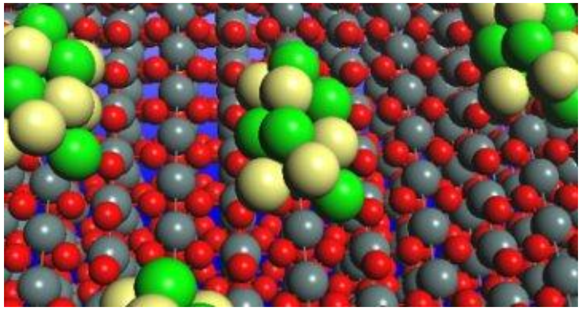
Ockhams Razor

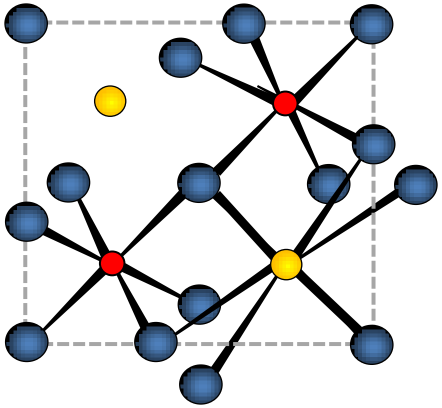


$A_2B_2O_7$

Individual surface atoms in the Pyrchlore catalyst impart unique properties and require less precious metals

A conventional catalyst is formed with metal clusters sitting on a support surface





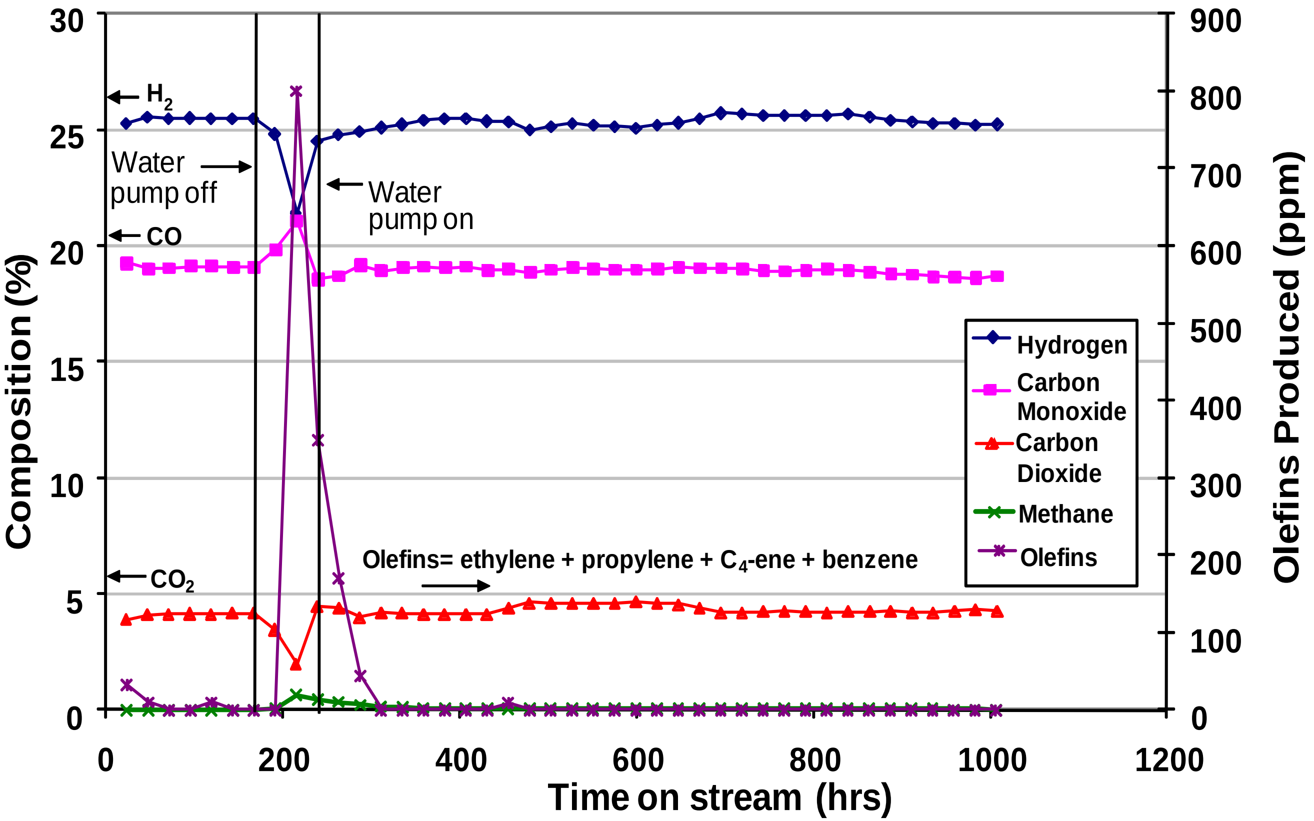
Highly-dispersed catalytic atoms yield excellent activity, thermal stability and resistance to poisons

- *Long term activity for diesel/JP8 reforming with excellent resistance to sulfur poisoning (fuel cell applications)*
- *Exceptional activity for gas reforming to hydrogen (refining applications)*

Validating the Technology

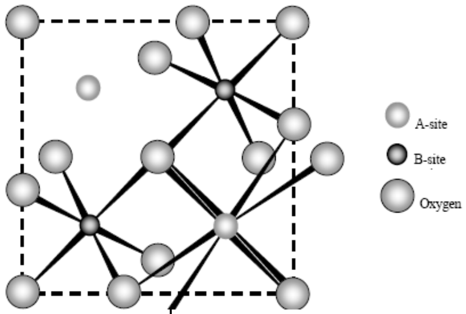
Long-term 1000-hr Test

- ✓Fully reformed local pump diesel
- ✓ Equilibrium syngas yields achieved
- ✓Survived multiple system upsets
- ✓ O/C=1, H_2O/C=0.5, *T=900°C, SV= 25,000 sccm/g-hr*



Economic Viability

Evaluating catalyst synthesis



Pyrochlore - $A_2B_2O_7$

Pechini

- *Good for small scale (lab)*
- *Results in well-mixed, uniform catalyst*
- *Most active material (1000 hr catalyst)*
- *Economic scale-up?*

Hydrothermal

- *Trade-off between compositional uniformity (mixing) and batch size.*
- *Was not able to get Rh into pyrochlore structure.*
- *Activity not as good as Pechini. to date*

Combustion Method

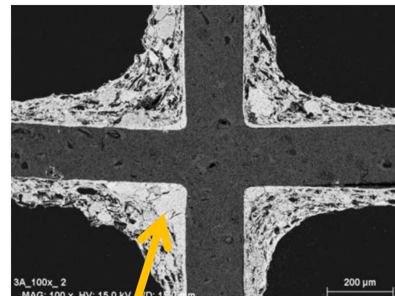
- *Under development*
- *Potential for high throughput*
- *Ideally material produced would be similar to Pechini.*

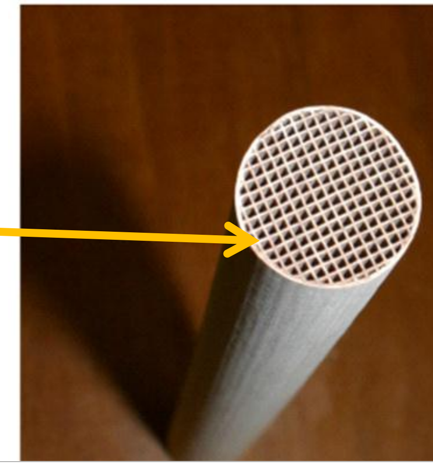
Solid State Mixing (Industrial Methods)

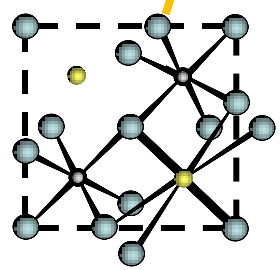
- *Economical for large batches.*
- *Requires high temperatures and long firing times to form pyrochlore.*
- *Catalyst uniformity a potential issue*

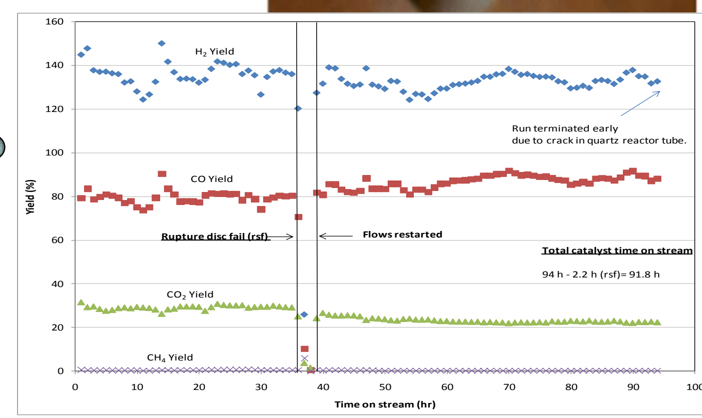
NETL Wins 2012 CCR Collaboration Award for Pyrochlore Catalyst

- Council for Chemical Research (CCR) recognizes NETL's collaboration efforts regarding the development of pyrochlore catalysts
- Technology used to reform hydrocarbon fuels to generate hydrogen-rich synthesis gas
- Exclusive license to Pyrochem Catalyst Company
- NETL collaborators recognized: EG&G (URS), LSU, WVU, Delphi, PCI



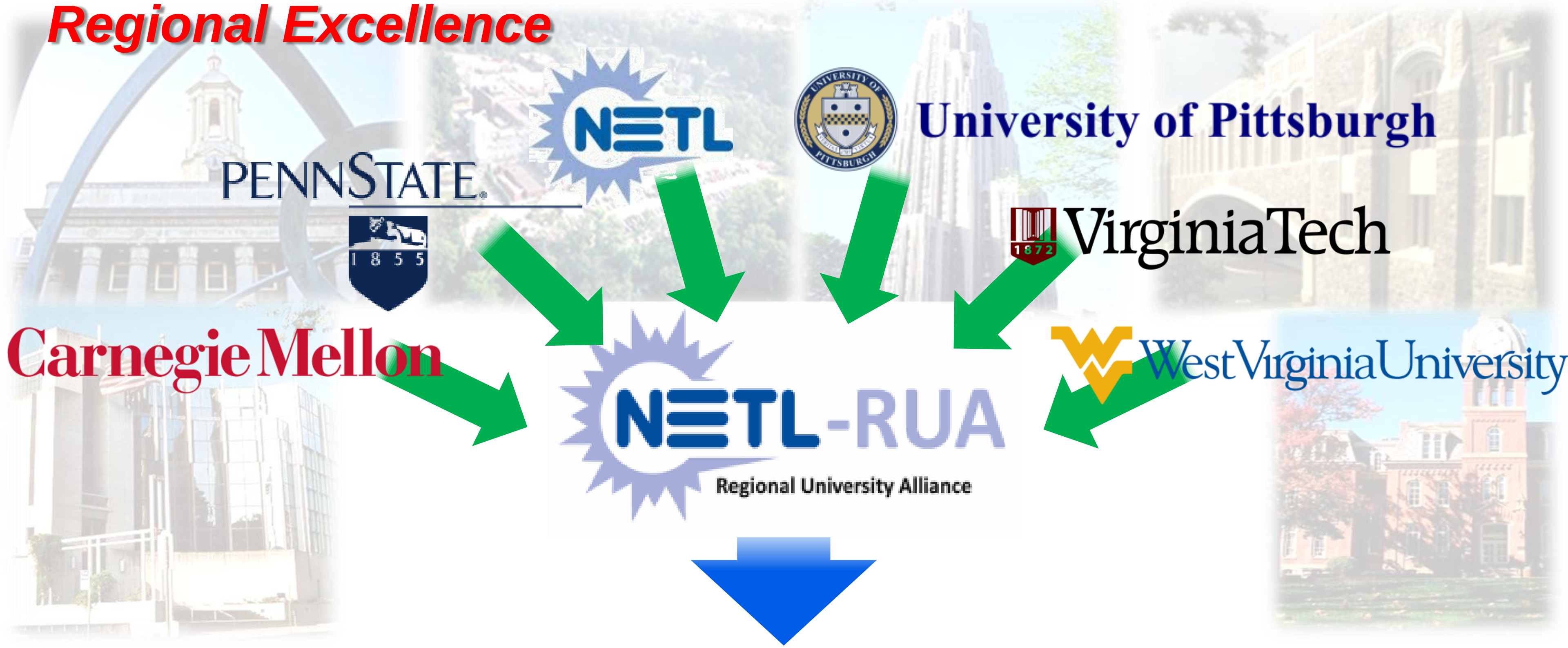






Strategic Partnerships

Regional Excellence



Shared Resources + Shared Intellect = Targeted Innovation

Create and enable <u>dynamic</u> teams to do <u>targeted</u> research that effectively provides solutions to the Nation's most challenging problems

Computational & Basic Sciences - Energy Systems Dynamics - Geological & Environmental Systems - Materials Science & Engineering