Department of Energy
Washington, DC 20585

ARPA-E Rare Earth and Critical Materials Workshop
Breakout Session: Catalysts

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Rare Earths In Solid Oxide Fuel Cells

Scott A Barnett
Northwestern University

Rare Earths Are Ubiquitous in SOFCs

- Electrolytes:
  - Yttria-stabilized Zirconia (YSZ)
  - Gd-doped Ceria
  - $(La_{0.9}Sr_{0.1})(Ga_{0.8}Mg_{0.2})O_3$
- Cathodes:
  - $(La_{0.8}Sr_{0.2})MnO_3$
  - $(La_{0.6}Sr_{0.4})(Fe_{0.8}Co_{0.2})O_3$
- Anodes:
  - Ni-YSZ, Ni-Ceria
  - $(La_{0.5}Sr_{0.5})(Cr_{0.5}Fe_{0.5})O_3$ and related perovskites
- Contacting materials: rare-earth containing perovskites
- Interconnectors: steels or $LaCrO_3$

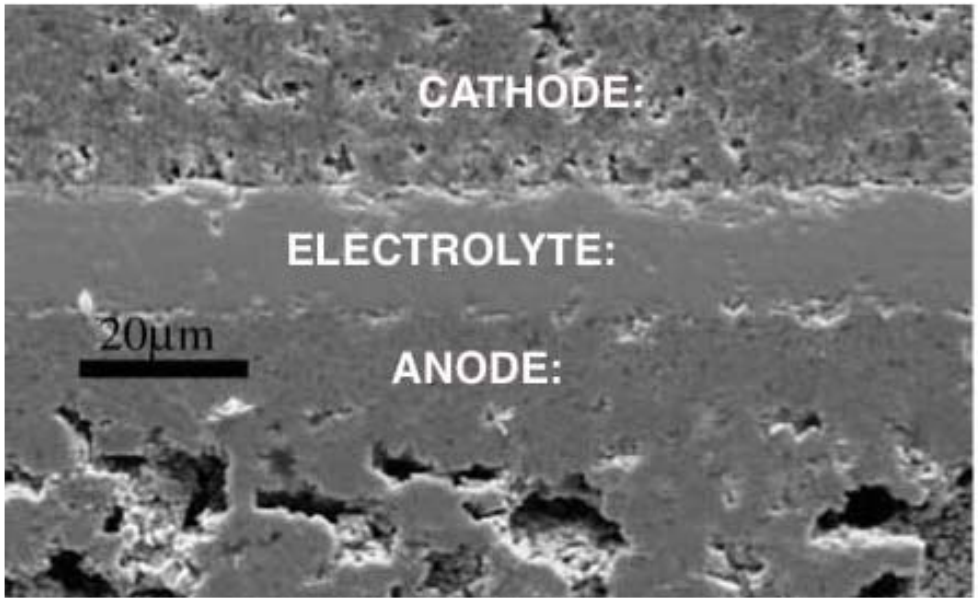
Reducing Rare Earth Amounts

- Cell design
  - Design to minimize use of rare-earth-rich compounds
- Materials design
  - Compositions with reduced rare-earth content
  - Rare-earth-free compositions?
- Use of un-refined rare-earth mixtures
  - Demonstrated for La-based cathodes

SOFC Geometry

- Basic choice - which part is thick structural element?
- Electrolyte support
  - Dense supporting material with good strength (YSZ)
  - Large thickness leads to large ohmic resistance
- Anode support
  - Thin electrolyte minimizes ohmic loss
  - Easy co-firing of YSZ and NiO-YSZ
- Cathode support
  - Not widely used due to interactions between cathode materials and YSZ at high co-firing temperatures

Anode-Supported SOFC Structure



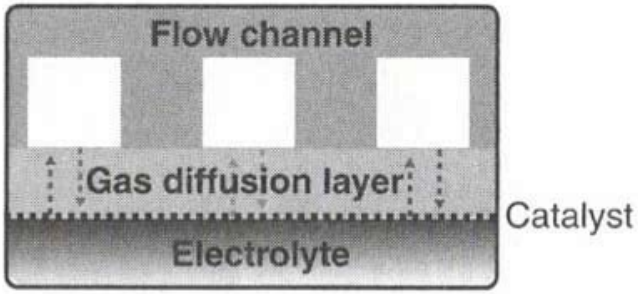
(La,Sr)(Mn)O_3 (LSM)

LSM-YSZ

Y-doped ZrO_2 (YSZ)

Ni-YSZ (active layer)

Ni-YSZ (porous support)



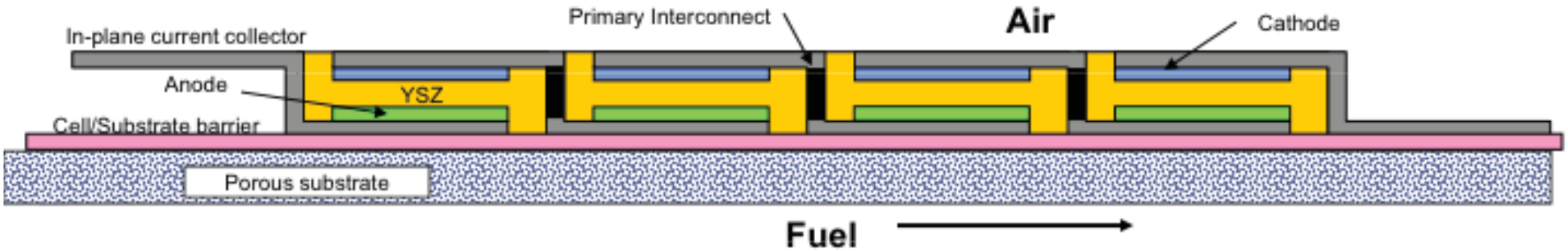
Design:

- Ni-YSZ anode is thick supporting layer
  - ~400 µm thick
  - 8 mol% Y in YSZ
- Electrolyte ~ 10 µm thick
- Cathode typically ~ 100 µm thick
  - High La content

Current collector thickness

- Must be sufficient for low resistance path to current collector
- Design to reduce current paths

Segmented-In-Series Structures

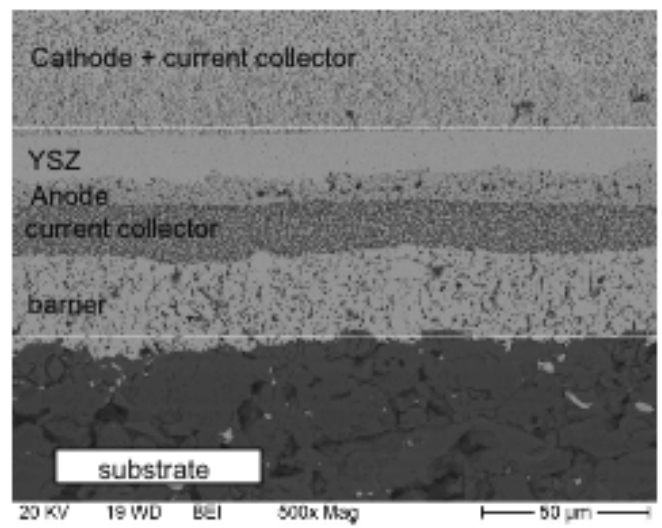


Integrated planar series arrangement

Series connected cell design for high voltage low current

Thin layers of active materials minimize cost

Ceramic support material uses low cost $MgO+Al_2O_3$ powder + low cost extrusion



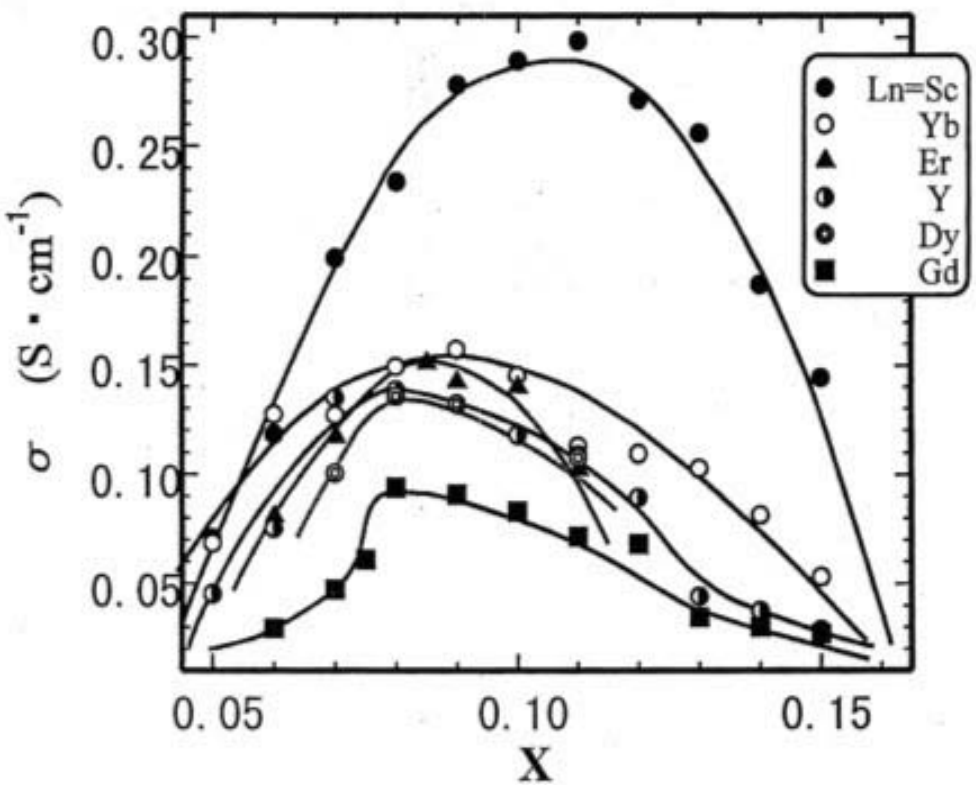
High voltage low current benefits

Easier hence cheaper for power electronics to convert low current DC to AC

High voltage facilitate direct conversion to 480 V AC grid requirement

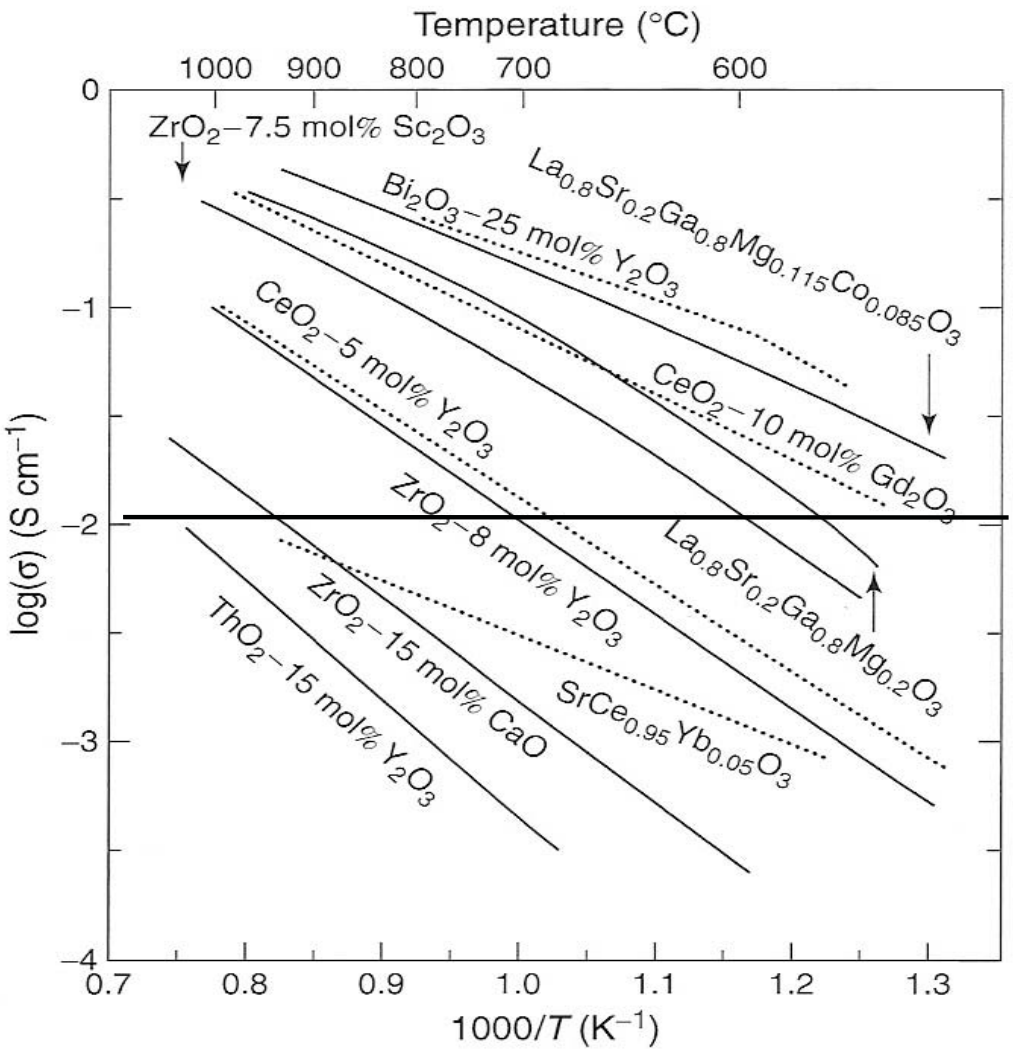
Low currents give low Ohmic I^2R losses offering greater materials options

ZrO_2 Conductivity Versus Dopant



- Conductivity versus dopant content at 1000°C
- Dopants stabilize cubic structure and introduce oxygen vacancies
- Y doping most common
  - Maximum σ: 8 mol% Y_2O_3
- Rare earths (Y, Yb, La, Sc, *etc.*)
  - Others: Ca, Mg
- Lower dopant content possible in anode support, where ionic conductivity is not essential

SOFC Electrolyte Conductivity

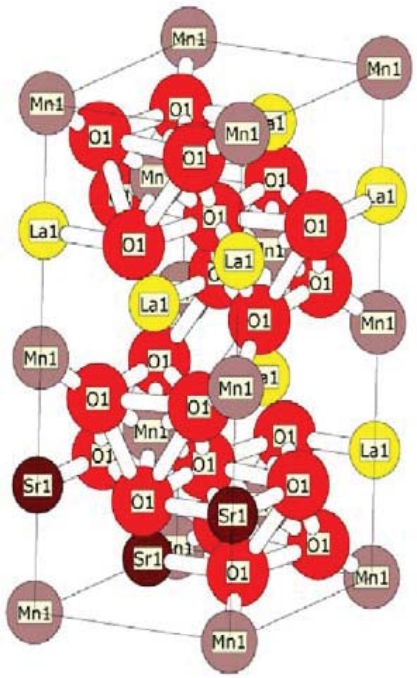


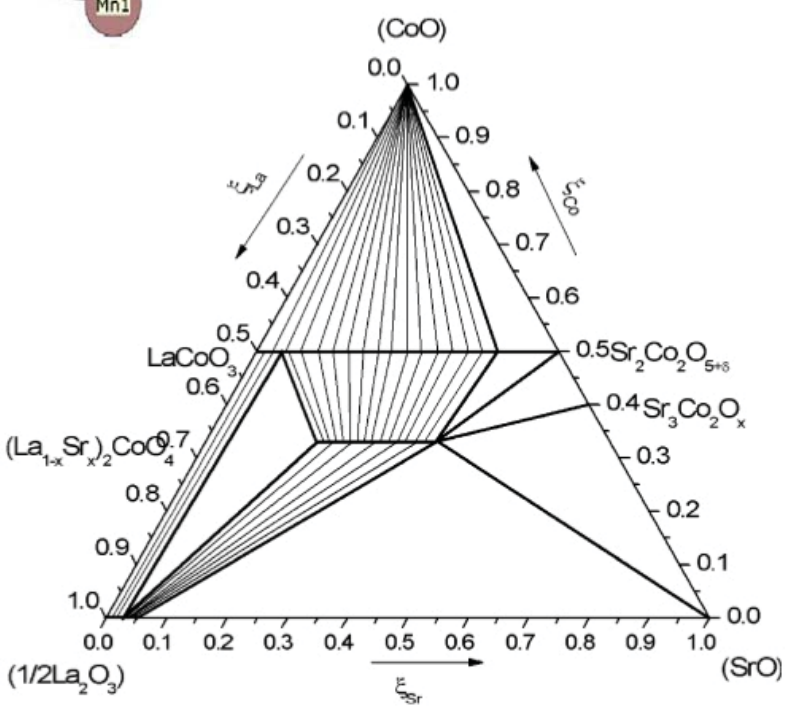
T. Ishihara, Handbook of Fuel Cells, p. 1109

- Conductivity decreases with decreasing temperature
- Common electrolytes
  - Y_2O_3-stabilized ZrO_2 (YSZ)
  - Sc_2O_3-stabilized ZrO_2 (SSZ)
  - Gd-doped CeO_2 (GDC)
  - $(La,Sr)(Ga,Mg)O_3$ (LSGM)
- Target area-specific resistance:

  $R_{electrolyte} = 0.1 \wedge cm^2$
  - Consistent with 1 W/cm^2
  - Line calculated for a 10 ⌠m thick electrolyte
- YSZ okay down to ~700°C
- Ca-stabilized zirconia not viable
- Alternate materials needed below 700°C
  - GDC, LSGM good to ~550°C

Cathodes: Perovskite Oxides



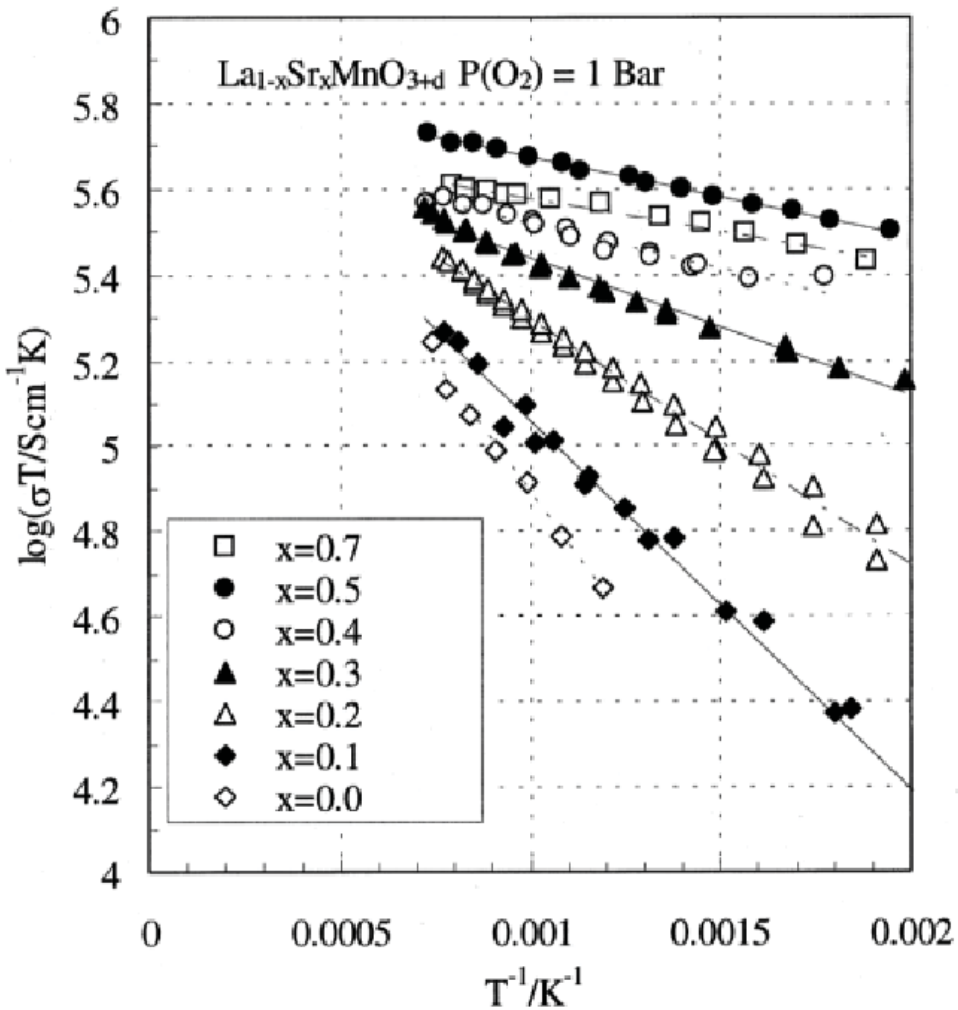


- Examples: doped $LaMnO_{3+TM}$, $LaFeO_{3+TM}$, $LaCoO_{3+TM}$,
- Most common cathode:
  - $(La_{1-x}Sr_x)MnO_{3+\delta}$
- Effect of doping:
- Substitution of Sr^{2+} ions for La^{3+} ions results in electron holes:

$$LaMnO_3 \xrightarrow{xSrO} La^{3+}_{1-x}Sr^{2+}_{x}Mn^{3+}_{1-x}Mn^{4+}_{x}O_3$$

  - Here some of the Mn ions switch to a Mn^{4+} valence to maintain charge neutrality
  - Effectively a hole (missing e^-) attached to a Mn

Conductivity: (La,Sr)MnO_{3+}™ (LSM)



- Mn^{4+} can "move" by holes hopping from Mn to Mn
  - Termed small polaron hopping
- Conductivity given by:

$$\sigma T = A\left(\frac{h\nu^{o}}{k_B}\right)c(1-c)\exp\left(\frac{E_a}{kT}\right)$$

  - ν^{o} = frequency factor (~10^{13} /s)
  - h = Planck's constant
  - c = occupancy probability
  - E_a = activation energy
- Maximum conductivity at 50:50 La/Sr ratio
- Other factors (stability with YSZ, mechanical strength) favor use lower Sr content

Use of Unrefined Lanthanides

- In 1997, Westinghouse reported that mixed Lanthanides could be used in place of pure La in $(La,Sr)MnO_3$
  - La plus Nd, Pr, Ce, and Sm
  - Only a slight reduction in cell performance
  - Suggested a 70% reduction in materials cost
- S. Singhal, in SOFC-V, Electrochem. Soc. Proc. 97-18, p. 37
- Probably would have little impact if used in cathode current collector

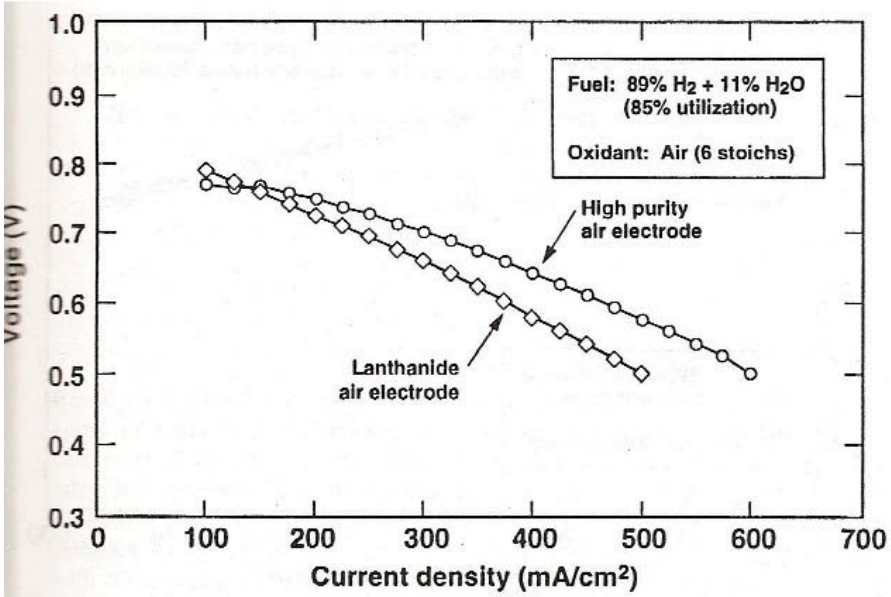
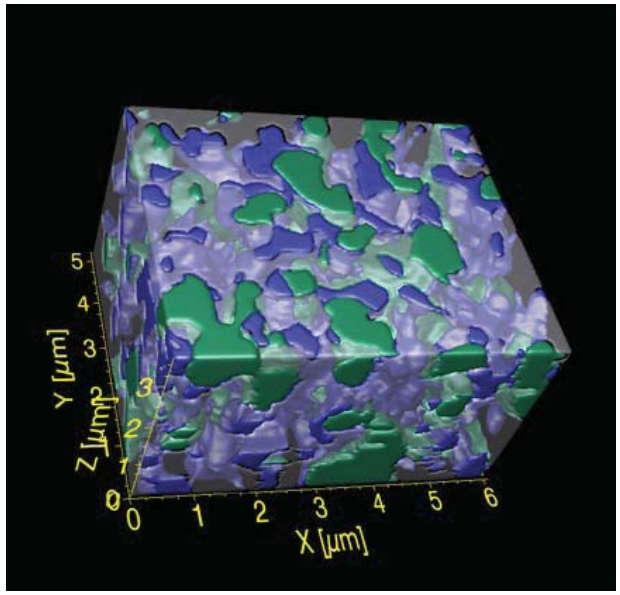


Fig. 9. Effect of air electrode material purity on the voltage-current characteristics of AES cells at 1000°C.

SOFC Anodes

- Ni-YSZ composite:
  - Could use non-RE dopant in thick support
- Alternative anode materials - mixed conducting oxides
  - $(La,Sr)CrO_3$ doped with Mn, Fe
  - $SrTiO_3$ doped with Y, La, etc.
  - $Sr(Mn,Mg,Mo)O_3$



SOFC Interconnectors

- Oxides that are stable and electronically conducting in both fuel and air environments
  - Doped $LaCrO_3$
  - Difficult to process, form, and fragile
- Metallic materials - readily formed and mechanically robust
  - Ni-Cr alloys
    - Expensive but retain strength at high T and form conducting oxide scales
  - Ferritic stainless steels - low cost but reduced creep strength at high T and can form very thick scale
  - Sometimes used with RE-containing coatings to minimize scale problems

Oxygen Membranes

- Mixed electronically and ionically conducting oxides
  - Examples: $(La,Sr)FeO_3$, $(La,Sr)CoO_3$, $(Ba,Sr)(Co,Fe)O_3$, La_2NiO_4 and related compounds
  - $(La,Sr)FeO_3$ membranes under development by Praxair for pure oxygen production
    - E.g., for oxygen-fired coal plants
  - Most have significant rare-earth content

Rare Earths in Catalysis

Presenter: Suresh Baskaran

Contributors: Dave King and Chuck Peden

(david.king@pnl.gov; chuck.peden@pnl.gov)

Pacific Northwest National Laboratory

ARPA-E Workshop, Dec 06, 2010

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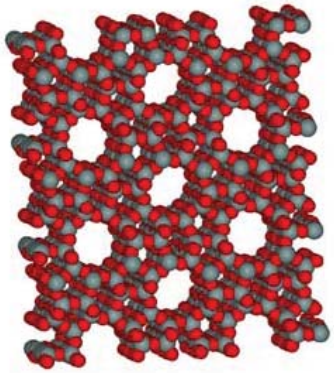
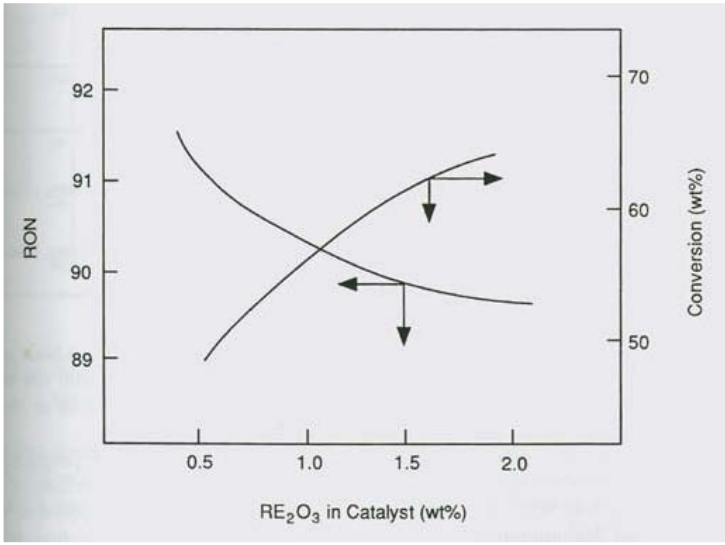
Rare Earths in Catalysis - Fluid Catalytic Cracking (FCC)

- Fluid catalytic cracking produces gasoline and diesel-range fractions from crude hydrocarbon feedstocks
  - Primary source of cracking activity derives from acid sites within an aluminosilicate zeolite that cleave carbon-carbon bonds and produce smaller molecules from large ones
  - Acidity correlates with the aluminum content within the zeolite, with an acidic proton accompanying each Al to balance framework charge
  - Under harsh cracking reaction conditions and in the presence of generated steam, Al may be extracted from the zeolite, leading to loss of acidity and ultimately zeolite collapse
  - Lanthanum or rare earth mixtures (rich in La, Ce) are incorporated into the zeolite structure by ion exchange techniques
  - They provide stability against loss of Al (i.e., maintain high conversion, with some loss of octane), through formation of a strong stable complex involving rare earth cations, water oxygens, and lattice oxygens



Zeolite cracking catalyst



Effect of rare earth content of FCC catalysts on activity and gasoline research octane

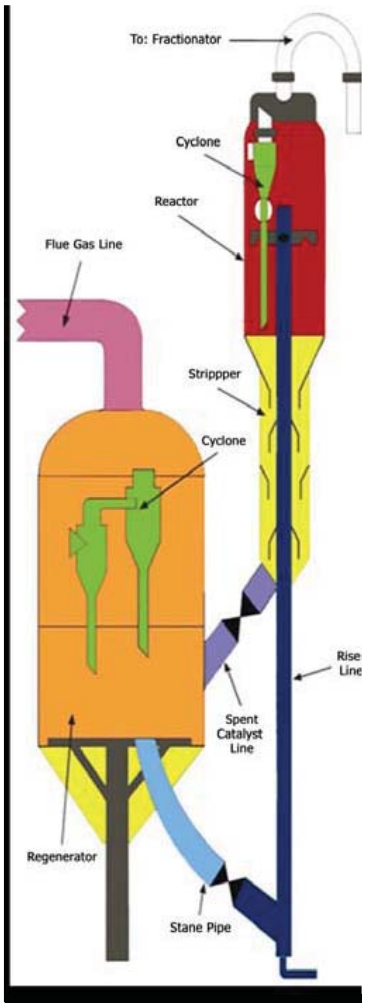
Rare Earth Replacements in Fluid Catalytic Cracking - Potential Research Approach

Characterization and Understanding of Baseline Materials

- Characterize the structure of rare earth containing zeolites before and after reaction
  - Location within the structure— understand specific siting locations of rare earths within the zeolite
  - Quantify stability of complexes involving rare earths exchanged into cracking zeolites
  - Quantify strength and nature of the interaction between rare earth and Al using techniques such as solid state NMR, EXAFS, infrared spectroscopy

Evaluation of Alternative Cations

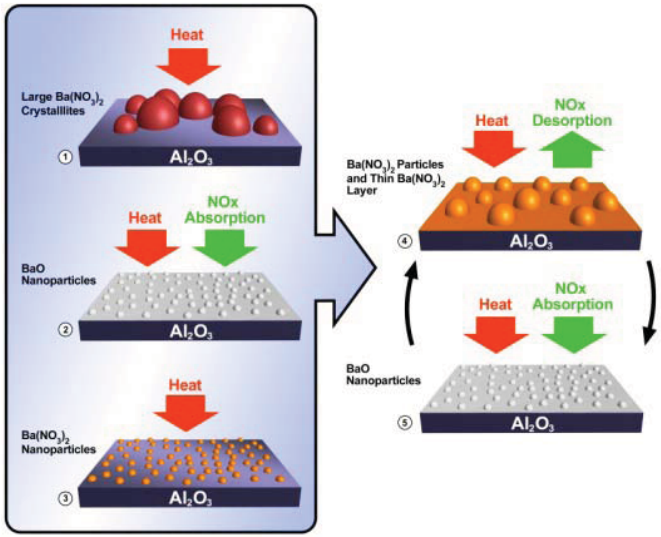
- Characterize the interaction of alternative cations with Al within the zeolite framework and compare with La or Ce interactions
  - Use molecular modeling techniques to gain additional quantitative insights
- Quantify the acidity generated by addition of alternative irreducible cations and down-select acceptable candidates
- Carry out extensive steam stability studies to compare effect of alternate exchanged cations with rare earths
- Examine effect of alternate stabilizing cations on product distribution from cracking reactions with selected model compounds

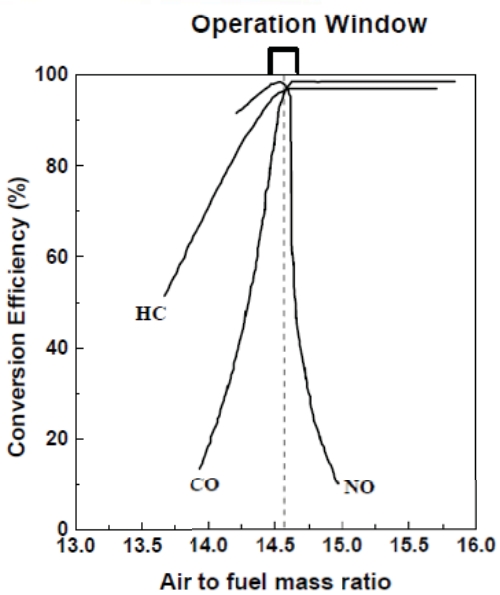


Fluid catalytic cracking unit

Rare Earths in Automotive Catalysts

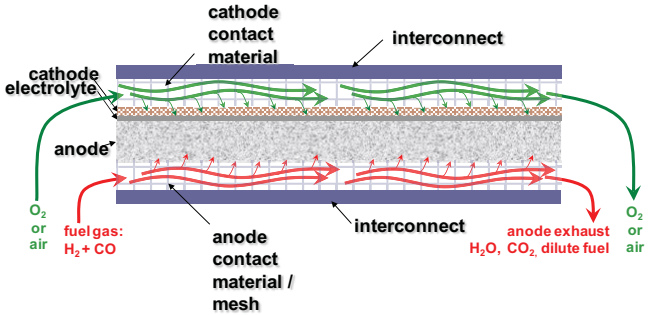
- Automotive exhaust catalysts—alumina stabilization
  - Lanthana is added to stabilize the alumina catalyst support against loss of surface area through conversion to an alternate (more stable) alumina phase
  - Typically, ~2wt.% rare earth is used to accomplish this stabilization, through a strong interaction between the added rare earth and specific Al^{3+} cations on the surface
- Three-way exhaust catalyst for control of CO, HC, and NOx
  - Precise control of air/fuel ratio is required for optimal performance of three-way catalyst
  - Ceria, generally combined with zirconia, is added to “3-way” emissions catalyst to provide “buffering” oxygen storage, assisting in maintaining air/fuel ratio for optimal converter performance
  - Significant levels of ceria are added to the formulation (as high as 10-50 mol%) to provide necessary oxygen storage performance





Rare Earths in Automotive Catalysis – Potential Research Directions

- Develop operating understanding of structure and mode of interaction of CeO_2-ZrO_2 catalytic materials in three way exhaust application
- Tabulate and quantify oxygen storage and redox properties of candidate metal oxides using techniques such as temperature programmed oxidation and reduction
- Develop high throughput testing for rapid redox cycling of alternative oxides and mixed oxides under simulated reaction conditions
- Develop characterization methods to examine long term efficacy of alternate compositions
- Identify materials that can improve efficacy of CeOx without complete replacement
- Develop computational methods to improve theory of oxygen storage
- Develop dynamic model to simulate transient behavior over three-way catalysts



Learn from solid oxide fuel cells that show ability to dissociate and transport oxygen

Rare Earths in Fuel Cells and Oxygen Membrane Generators

Presenter: Suresh Baskaran

Contributors: Vince Sprenkle and Jeff Stevenson (vince.sprenkle@pnl.gov)

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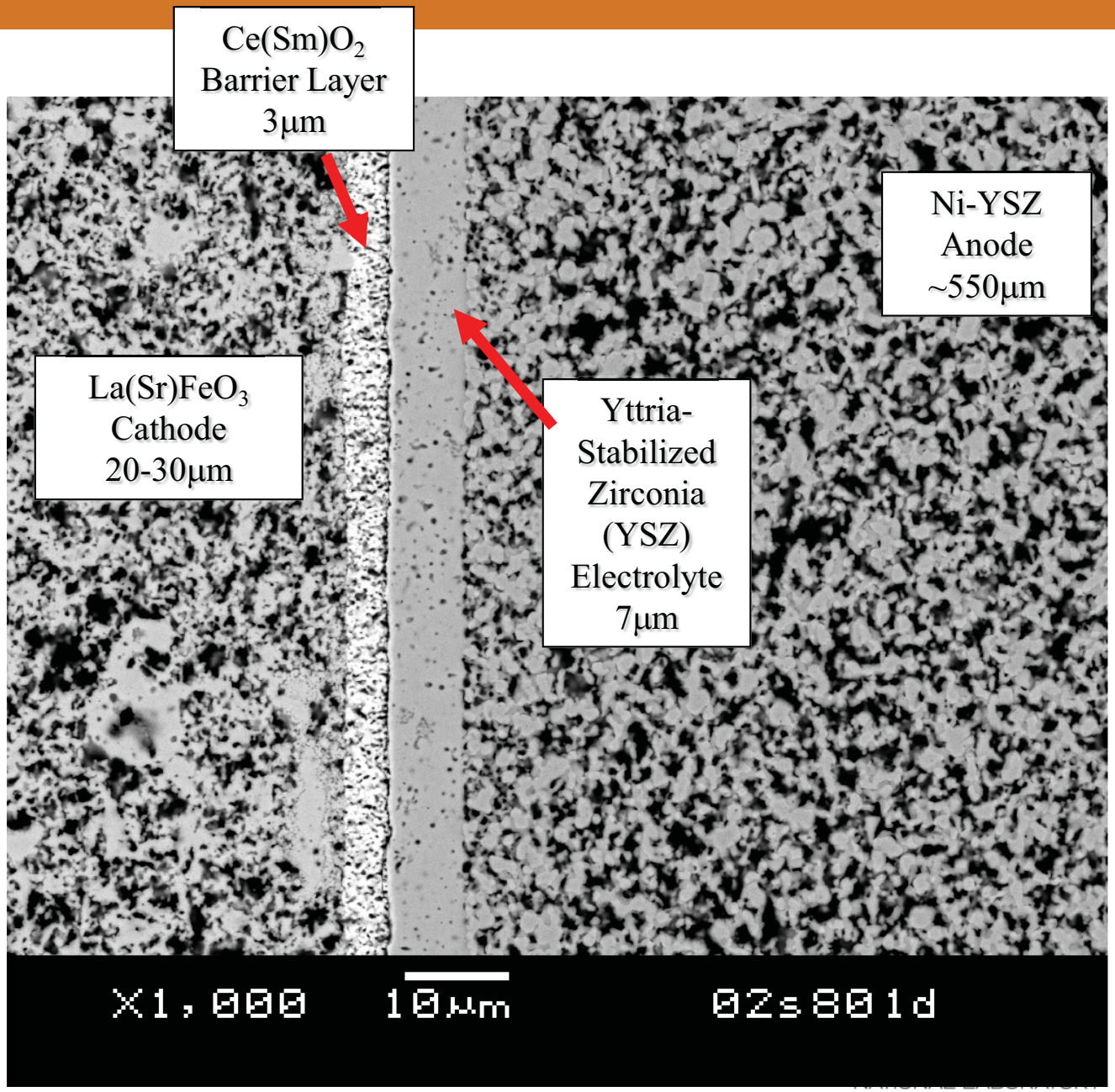
Solid Oxide Fuel Cells and Oxygen Generators

- Solid Oxide Fuel Cells
  - Rare earths in electrolyte, cathodes, anodes and interlayers

$$H_2 + O^{2-} \Rightarrow 2e^- + 2H_2O$$
$$CO + O^{2-} \Rightarrow 2e^- + CO_2$$

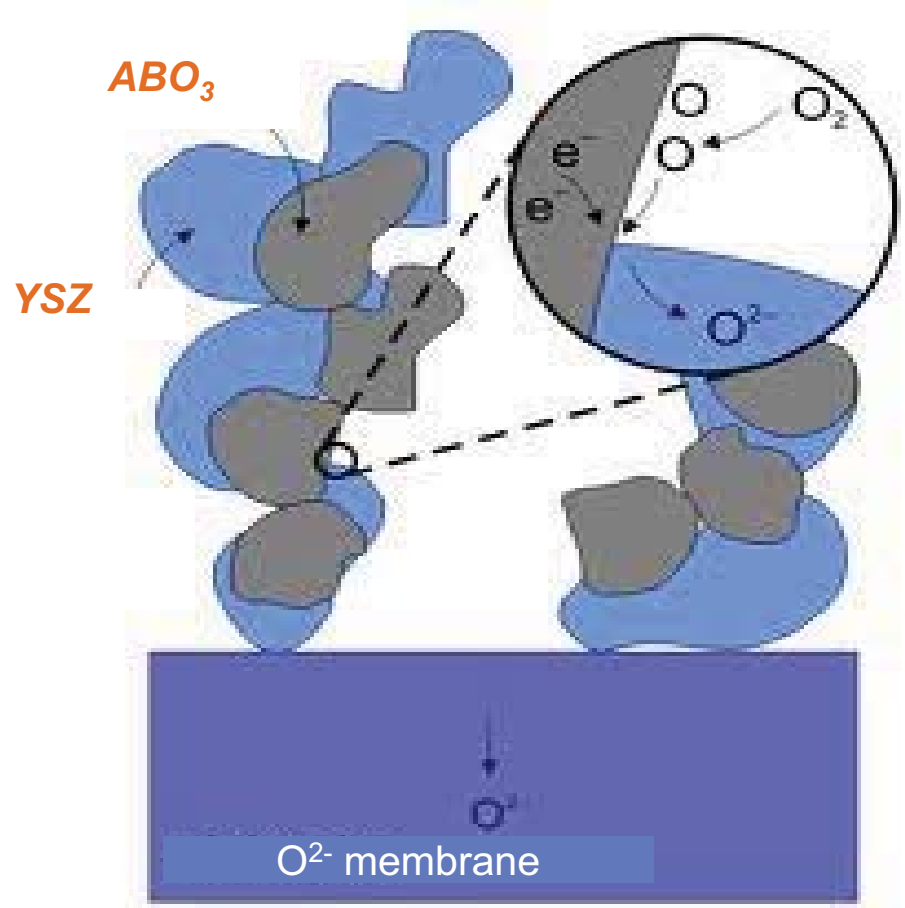
- Membranes for oxygen production (for oxy-combustion coal generation):
  - Rare earths in oxygen ion and electronic conductors, or within mixed ion conductors

$$CH_x + 2O_2 \Rightarrow CO_2 + 2H_2O + heat$$



Potential research needs/directions for electrolytes, electrodes and membranes

- Alternative stabilizers and dopants with comparable ionic, electronic conductivity
- New electrocatalysts that facilitate reactions at multi-phase boundary
- New mixed ion conductors
- Advanced scalable synthesis methods for new materials
- Fabrication technology for low dimension structures
- Manufacturing process development



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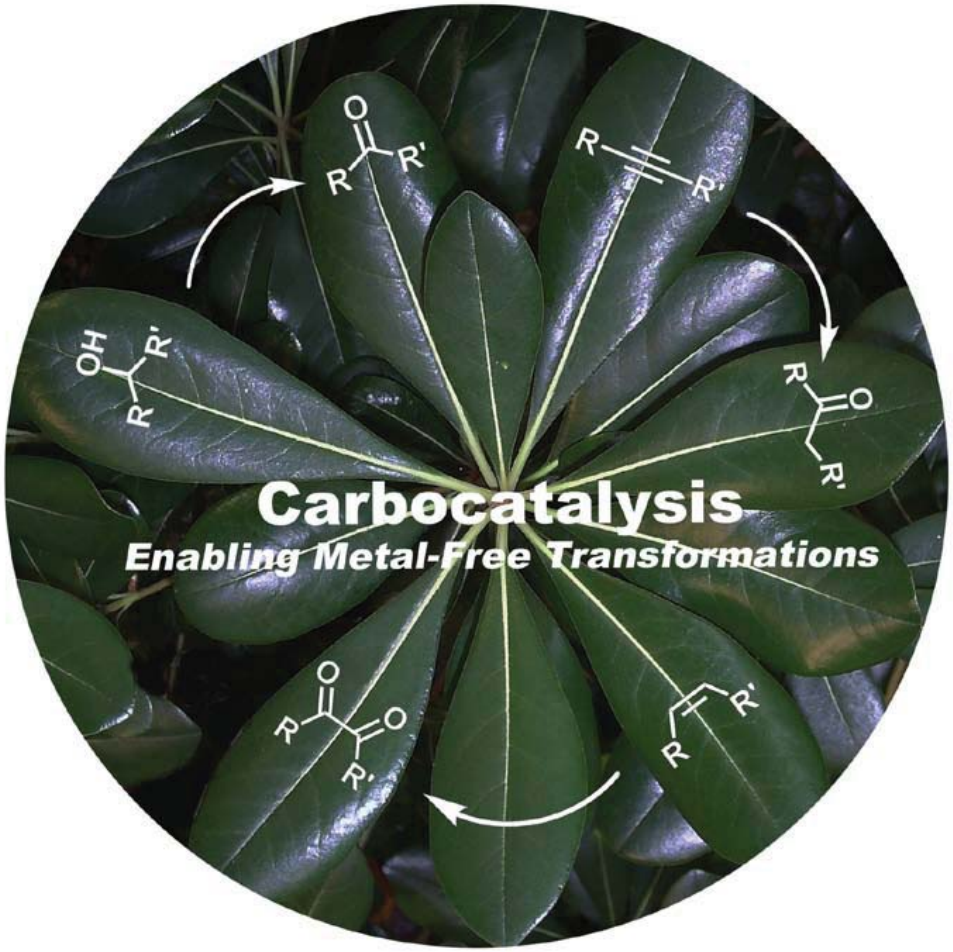

Graphite Oxide as a Metal-Free Catalyst: Forays into "Carbocatalysis"

Christopher W. Bielawski
Department of Chemistry and Biochemistry
The University of Texas at Austin

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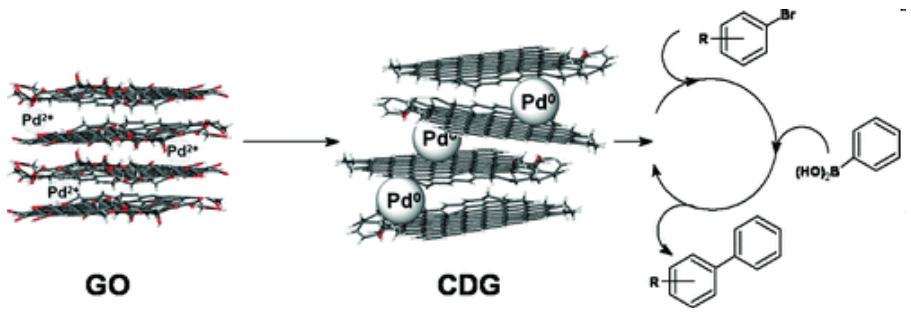
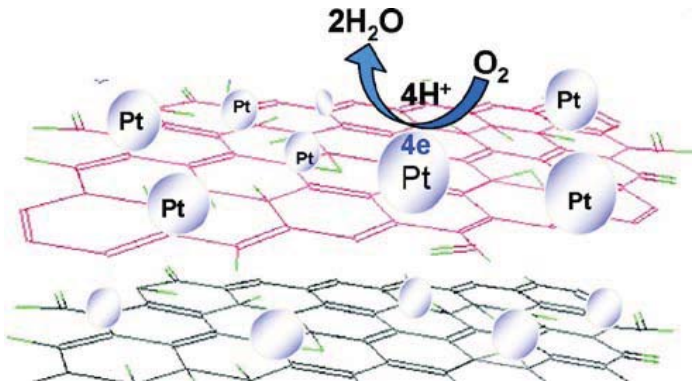
Carbon-Based Materials as Catalysts and Cat. Supports

Graphene:



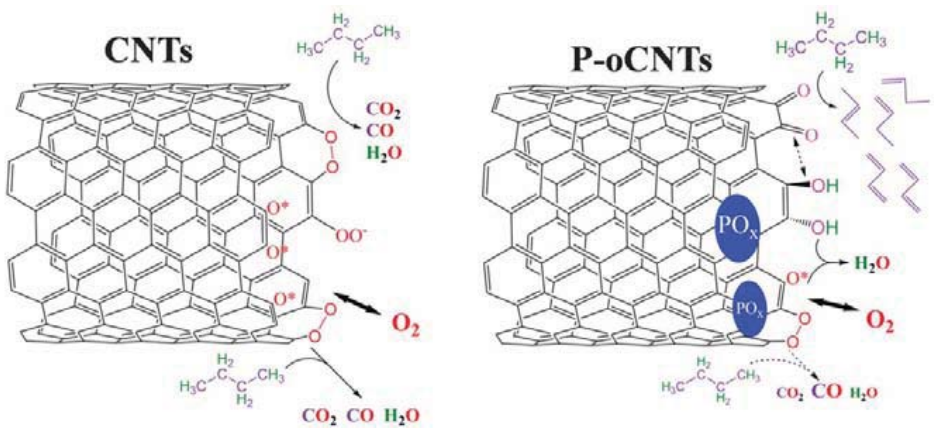


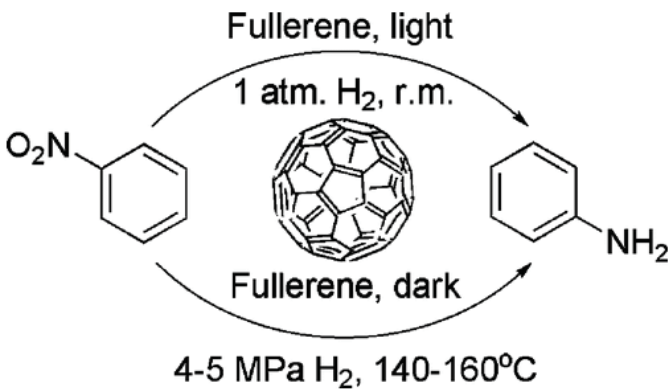
These systems utilize the carbon as a high surface area support to increase the activity of the metal; ***the metal is the active species****.*

J. Am. Chem. Soc. **2009**, *131*, 8262-8270

J. Phys. Chem. C **2009**, *113*, 7990-7995

Other Carbon Allotropes:





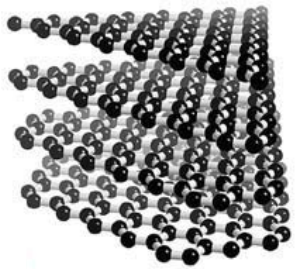
Reactions are relatively low yielding (<20%); doping may be required.

Unless performed under light, high temperatures and high pressures of hydrogen are required.

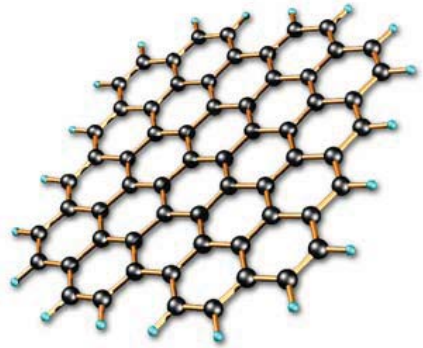
Science **2008**, *322*, 73-77

J. Am. Chem. Soc. **2009**, *131*, 16380-16382

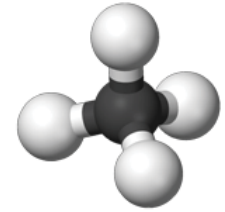
A Closer Look at Graphene and Graphite Oxide



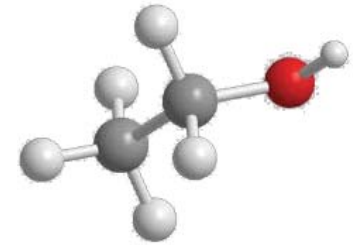
Top-Down →



← *Bottom-Up*



Methane



Ethanol

Acetylene

Graphite Oxide

Graphene Oxide (~ 1 mg mL^{-1} dispersion)

What kinds of reactivity might such a structure exhibit?

Graphite Oxide (GO) as a Metal-Free Catalyst

Alcohol Oxidations

Alkene Oxidations

Alkyne Hydrations

C-C Bond Forming Reactions

Typical reaction conditions:

5-100 wt% GO, 25-100 °C, 6-24 h; simple filtration workup procedure

Questions:

1.) What is the mechanism?

2.) Fate of the catalyst?

3.) Catalyst optimization?

Angew. Chem. Int. Ed. **2010**, *49*, 6813; *Adv. Syn. Catal.*, **2010**, in press

Rare Earths in Catalysis

Presenter: Glen Fryxell

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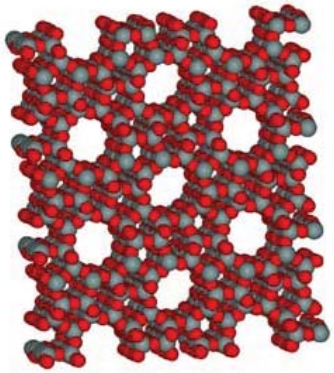
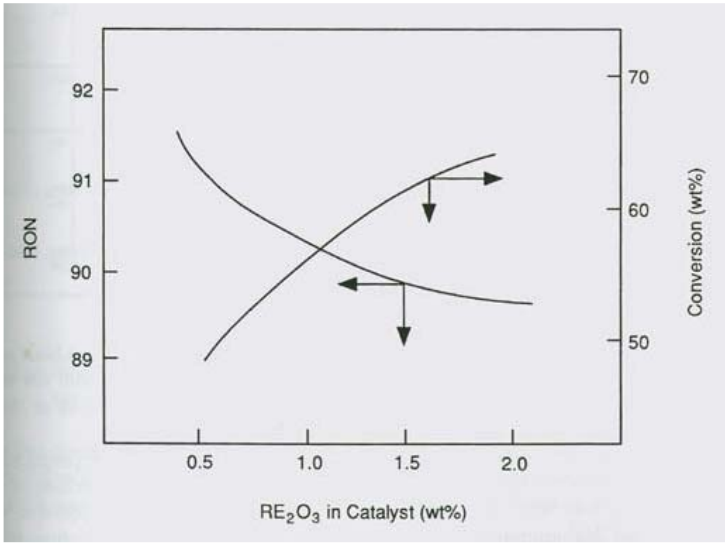


Zeolite cracking catalyst



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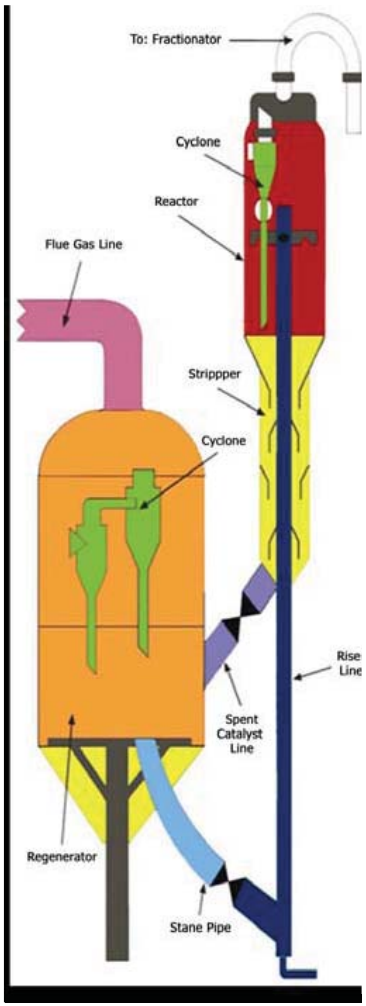
  - Quantify strength and nature of the interaction between rare earth and Al using techniques such as solid state NMR, EXAFS, infrared spectroscopy

Evaluation of Alternative Cations

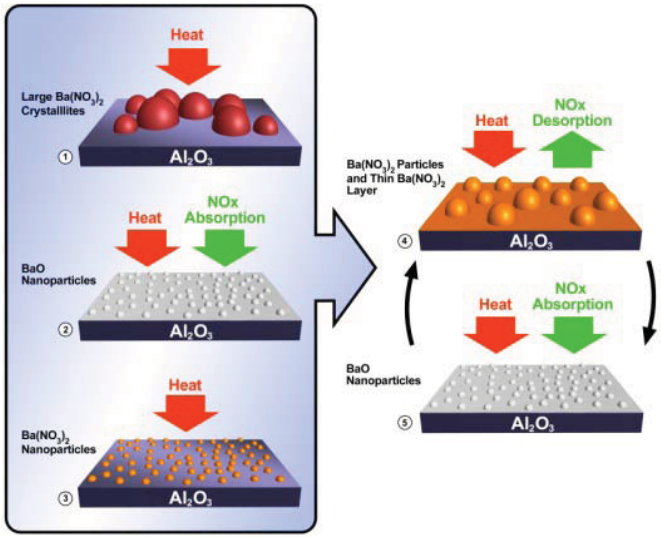
- Characterize the interaction of alternative cations with Al within the zeolite framework and compare with La or Ce interactions
  - Use molecular modeling techniques to gain additional quantitative insights
- Quantify the acidity generated by addition of alternative irreducible cations and down-select acceptable candidates
- Carry out extensive steam stability studies to compare effect of alternate exchanged cations with rare earths
- Examine effect of alternate stabilizing cations on product distribution from cracking reactions with selected model compounds

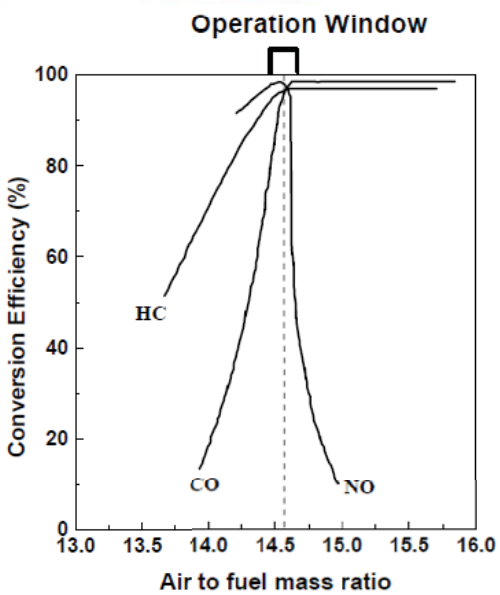


Fluid catalytic cracking unit

Rare Earths in Automotive Catalysts

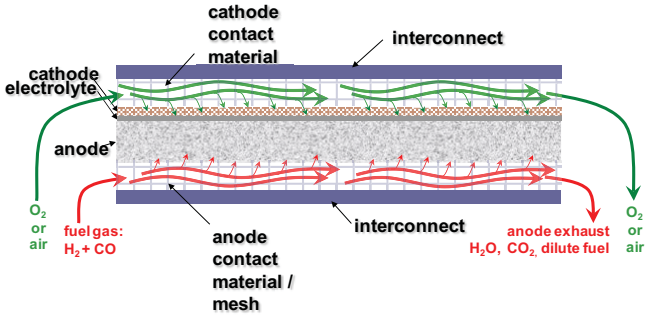
- Automotive exhaust catalysts—alumina stabilization
  - Lanthana is added to stabilize the alumina catalyst support against loss of surface area through conversion to an alternate (more stable) alumina phase
  - Typically, ~2wt.% rare earth is used to accomplish this stabilization, through a strong interaction between the added rare earth and specific Al^{3+} cations on the surface
- Three-way exhaust catalyst for control of CO, HC, and NOx
  - Precise control of air/fuel ratio is required for optimal performance of three-way catalyst
  - Ceria, generally combined with zirconia, is added to “3-way” emissions catalyst to provide “buffering” oxygen storage, assisting in maintaining air/fuel ratio for optimal converter performance
  - Significant levels of ceria are added to the formulation (as high as 10-50 mol%) to provide necessary oxygen storage performance





Rare Earths in Automotive Catalysis – Potential Research Directions

- Develop operating understanding of structure and mode of interaction of CeO_2-ZrO_2 catalytic materials in three way exhaust application
- Tabulate and quantify oxygen storage and redox properties of candidate metal oxides using techniques such as temperature programmed oxidation and reduction
- Develop high throughput testing for rapid redox cycling of alternative oxides and mixed oxides under simulated reaction conditions
- Develop characterization methods to examine long term efficacy of alternate compositions
- Identify materials that can improve efficacy of CeOx without complete replacement
- Develop computational methods to improve theory of oxygen storage
- Develop dynamic model to simulate transient behavior over three-way catalysts



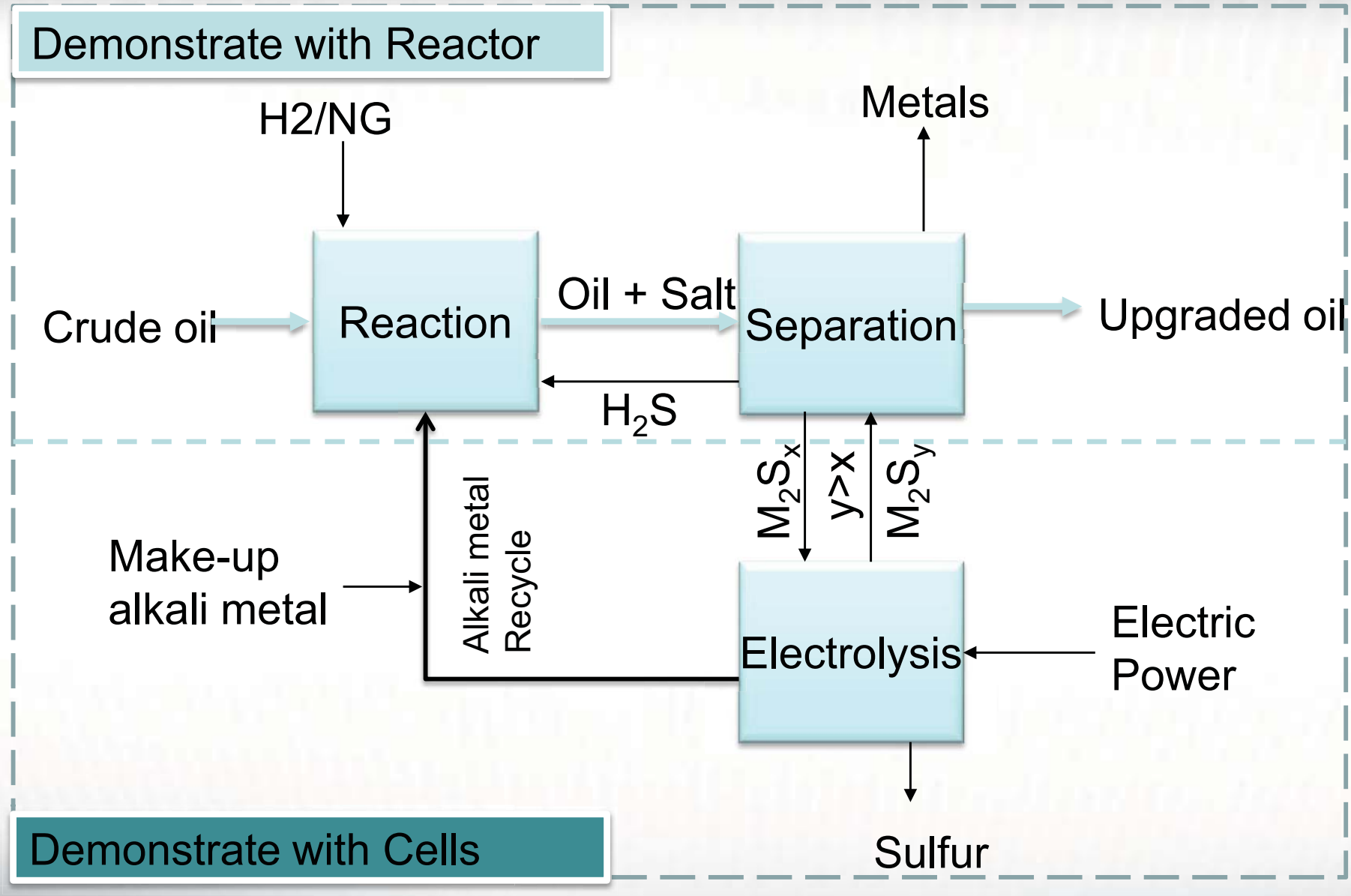
Learn from solid oxide fuel cells that show ability to dissociate and transport oxygen

Processing of Petroleum Crude prior to FCC

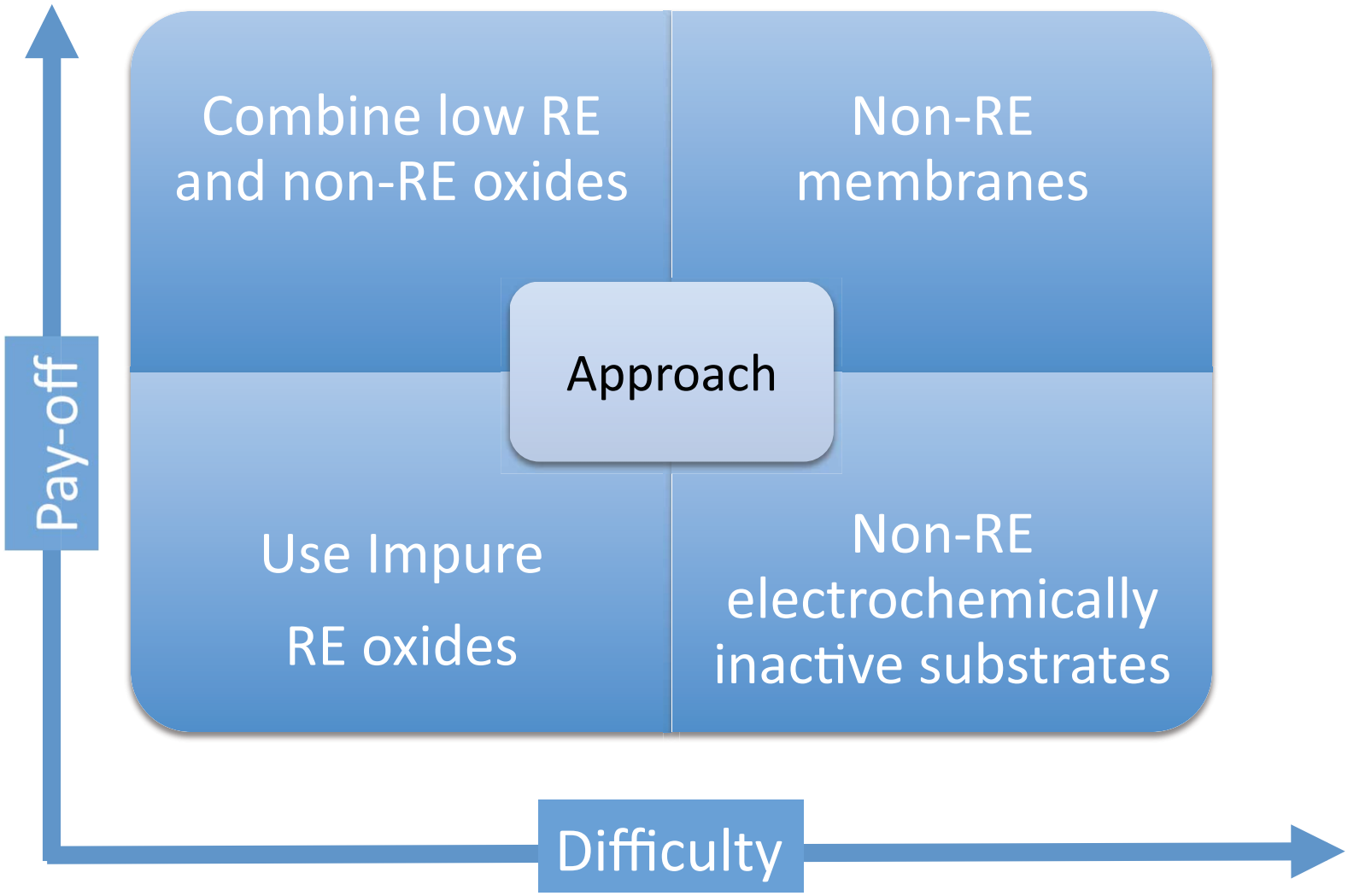
- Approximately 5 millions barrels /day are processed via FCC (~37% of crude)
- FCC constitutes use of catalysts that contain rare earth elements (Ce and La)
- Metals contained in petroleum crude (Ni, V, Fe) poison FCC catalysts
  - Reducing life
  - Higher utilization of rare earths

- Alkali metal process in presence of hydrogen or natural gas (no catalyst)
- The process serves several purposes:
  - Heteroatoms, sulfur and nitrogen are extracted.
  - The feedstock becomes lighter with higher API gravity.
  - Heavy metals including nickel, vanadium, iron are removed.
  - **Usage of Rare Earths is reduced**

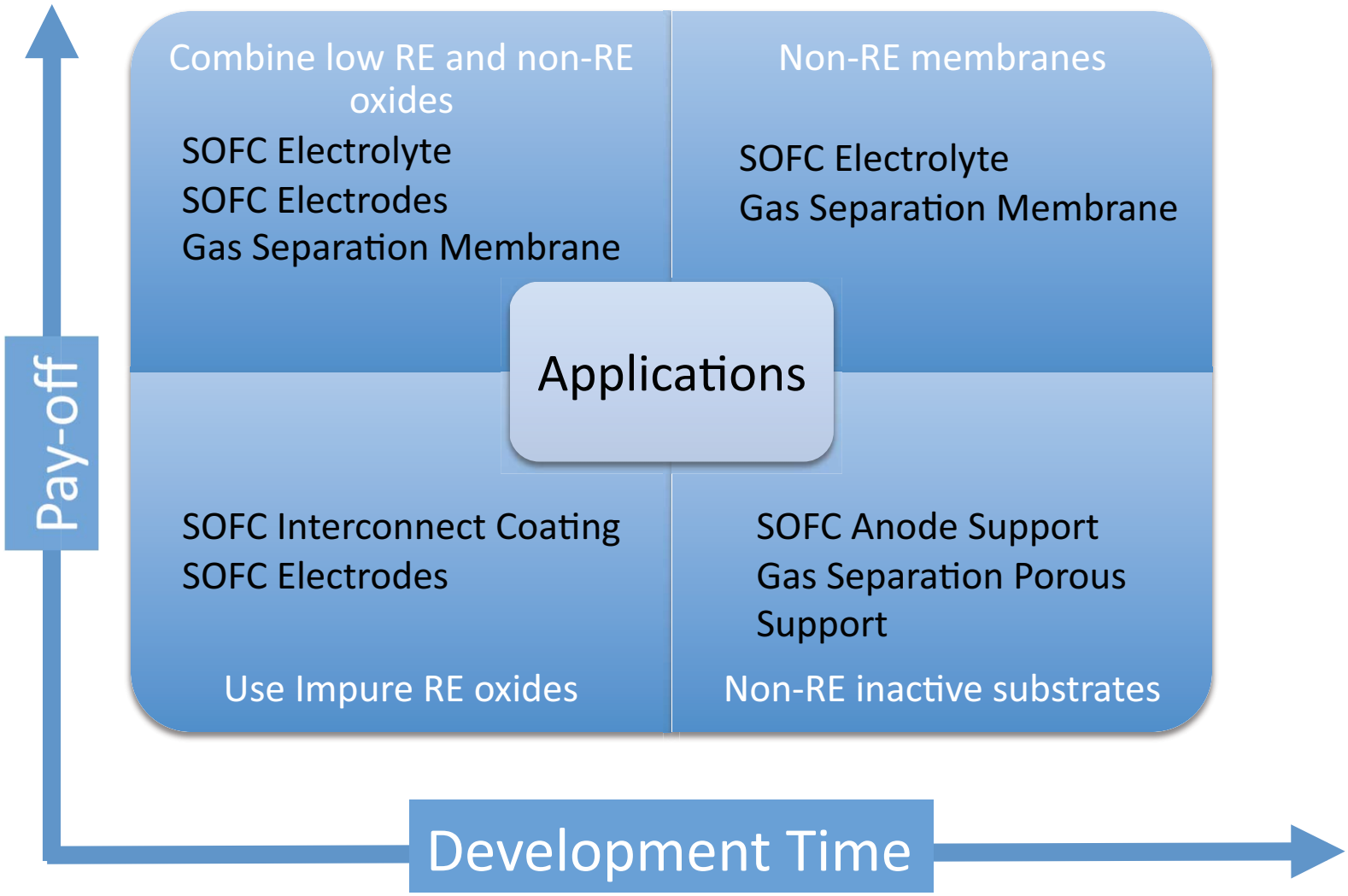
Overall Process



Rare Earth Dilemma



Rare Earth Dilemma

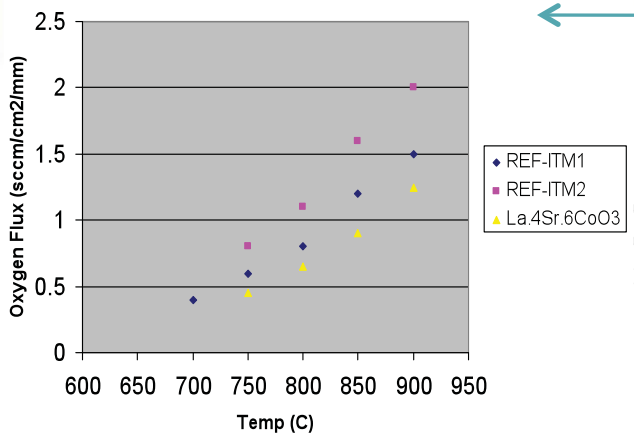


Process alternatives with RE implications

- Sodium super-ionic conductor (NASICON) ceramic membrane
  - Salt splitting to regenerate acid & caustic in RE separations
  - Current industrial scale uses
    - NaMeO for biodiesel, Rad-waste cleanup at Hanford
- Mixed RE use in SOFC
- Alkali metal pre-processing of crude oil
  - Remove S, N, V, Fe from heavy oils
  - Longer FCC catalyst life, reduced RE use in refining
- Ion Transport Membrane (ITM) $La_{0.4}Sr_{0.6}CoO_3$ – Prius La comparison
  - Oxygen generation for IGCC & oxy-fired combustion, 24x7 operation
  - 6.9kg La for 1.38 tpd CO_2 avoidance, 200kg CO_2/day /kg La
  - Prius 15 kg La, 2.76kg/day CO_2 avoidance, 0.184 kg CO2/day /kg La
- Non-thermal plasma catalyzed reactions
  - Use continuously regenerated plasma in place of RE containing catalyst
    - Reforming of tars & oils from biomass gasifier, reforming of logistic fuels, weapons destruction

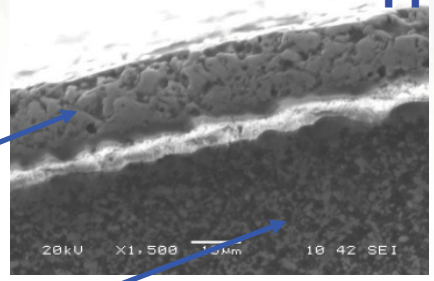
RE free O_2 Separation membrane for CCS

Rare Earth Free Membrane

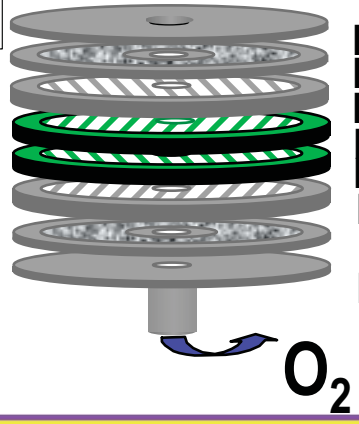


Far Term | *Near Term*

Rare Earth Free Support



membrane component



Membrane
Porous support
Microchannel support
Microchannel support
Microchannel support
Microchannel support
Porous support
Membrane

scalable, multi-component module

Use of rare earth materials

	Current	Near Term	Far Term
Membrane	Y	Y	N
Porous support	Y	N	N
Microchannel support	Y	N	N

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ARPA-E Workshop:
Rare Earths and Critical Materials

Catalysis Breakout Session – contribution

John Hryn

Arlington Hilton, Arlington Virginia

December 6, 2010

R&D opportunities: Alternatives to the high use of rare-earths in fluid catalytic cracking

- One of the major uses of REE is stabilization of zeolites in FCC
- REE imparts greater stability to the zeolite allowing the zeolite to withstand higher temperatures and high levels of steam without loss in activity
- REE used in FCC is mixture (not separated by RE element)
- Cerium alone has been demonstrated to stabilize one such zeolite (ZSM-5) to the destructive effects of high temperature steam
  - concept could be applied to the Y zeolites utilized in FCC applications
  - If Ce (the most abundant of the REE) could be substituted for the mixed REE currently used if FCC, then the less abundant heavier REE would be available for more high tech applications (magnets, phosphors, etc.)

- **Opportunity**: Efficient separation of Ce from remaining REE for FCC use

Mesoporous zeolites can increase the efficiency and mass transfer rates for fluid catalytic cracking

- Mesoporous materials (e.g. SBA-15 and MCM-41) hold much promise for the cracking of heavy oils such as those coming out of Alberta, Canada (the largest source of imported crude oil in the US)
  - Low stability at elevated temperatures
- Small (monolayer) coatings of certain transition metals (Nb has been demonstrated) in the pores of SBA-15 dramatically improves the stability
  - Could have transformational effect on refining industry if mesoporous zeolites without REE are adopted in FCC, since REE (Ce) may become supply-limited
  - Could extend use of these transition metal catalysts to Y-zeolites, or other FCC zeolites

- **Opportunity:** Development of commercially-viable coating technology for depositing transition metal monolayer coatings on to mesoporous zeolites
  - Demonstrate efficiency benefit in FCC with these coated mesoporous zeolites

High diffusivity oxygen separators - SOFC

- La-based perovskites presently used in separators and SOFC cathodes
  - No viable alternative for either separators or SOFC
- Requirement is to use less

- **Opportunity:** Anode must become support for SOFC
  - Allow for thinner subsequent layers of electrolyte and cathode
    - Electrolyte = YSZ (yttria stabilized zirconia)
    - Cathode = La-based perovsike

- SOFC could replace batteries for off-grid electricity supply
  - hydrogen production/supply issued resolved
  - Current La content in Nickel-Metal-Hydride batteries is not a long term issue
    - NMH batteries will be replaced by Li-ion batteries in the near term
      - **no R&D needed** to find La alternative for NMH batteries

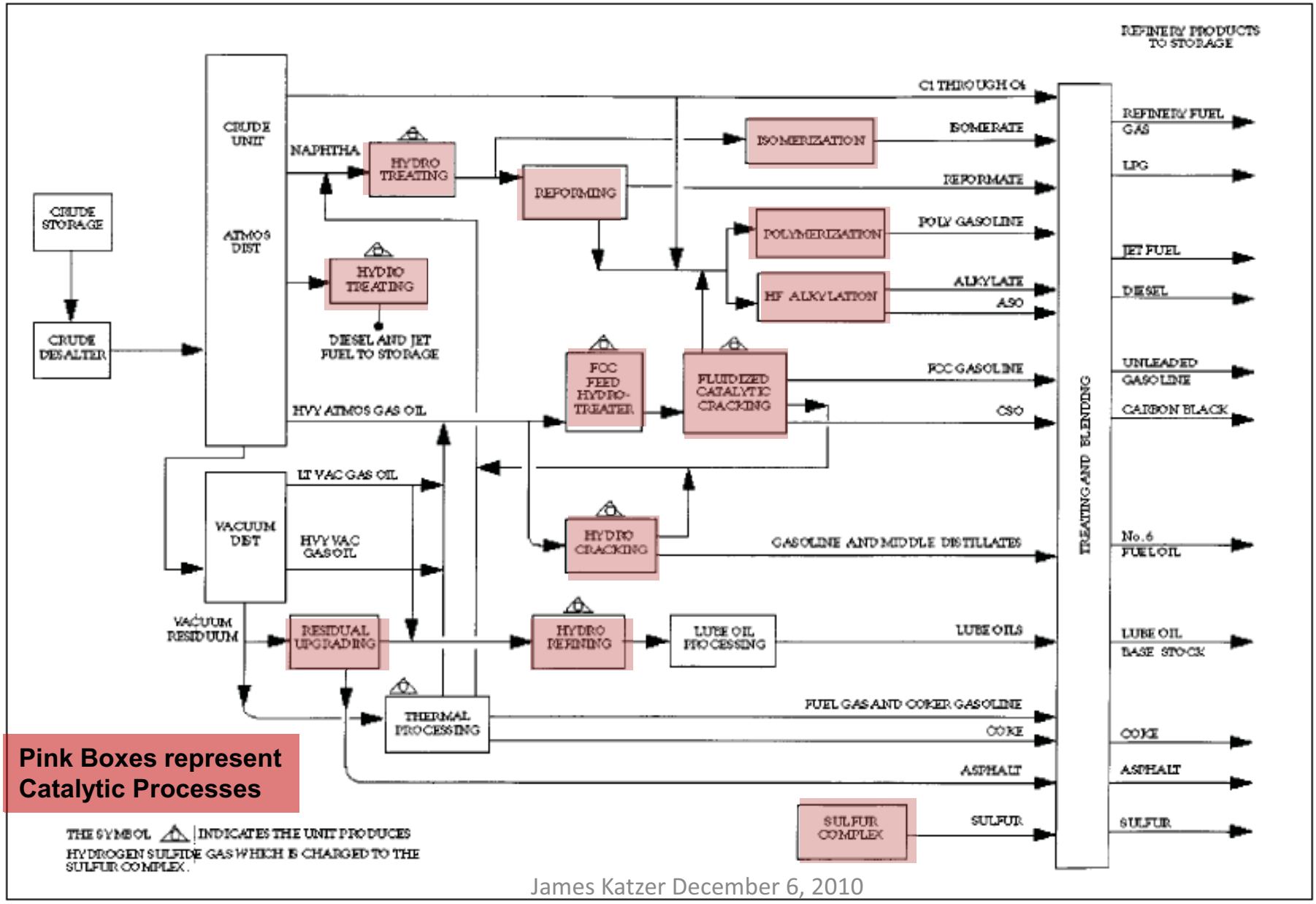
Aspects of Catalysis in Refining

James Katzer

DOE ARPA-E

December 6, 2010

Schematic of Typical Refinery

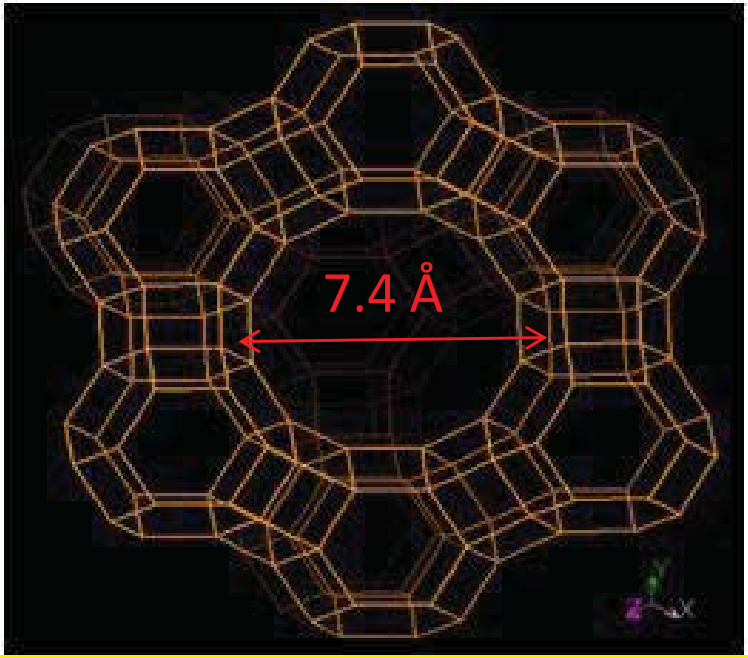


Pink Boxes represent Catalytic Processes

Refining Catalytic Chemistry

- One primary reaction type involves C=C bond hydrogenation to change the character of the molecule or to make the molecule reactive.
- The second primary reaction type involves C-C bond rupture involving carbenium-ion chemistry. These reactions include cracking to reduce molecular size and isomerization to change molecular structure.
- All refining catalysts have one or both of these functions; catalytic cracking is one of the most important refining reactions and involves acid-site cracking.
- Acid catalysts are extremely important. Zeolites are a critical component in providing the cracking function.
- Catalysts are not a fixed entity but undergo changes in use; stability is critical

Structure of Zeolites Faujasite (X & Y) and A



Faujasite X or Y; zeolite Y is primary component of cracking catalysts

NaX:

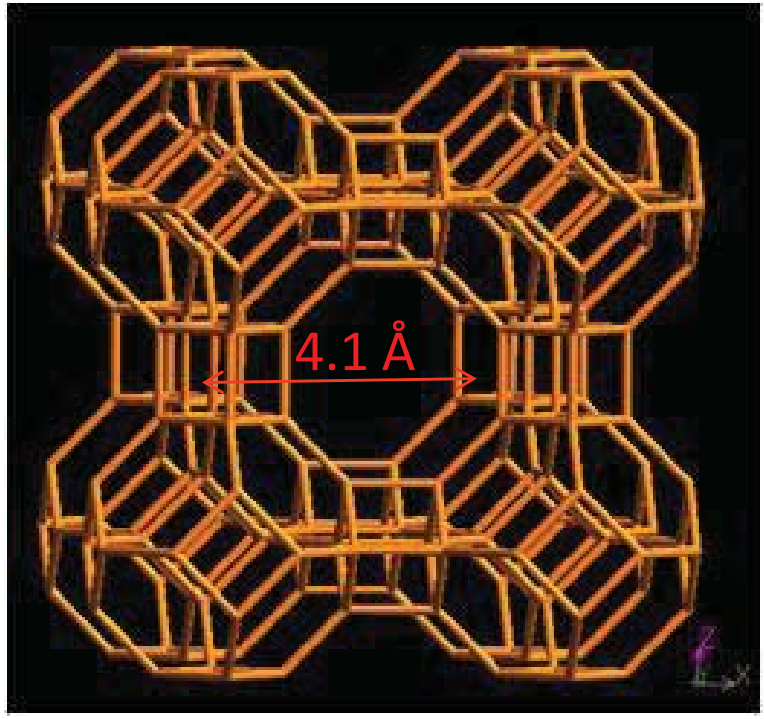
Si/Al = 1.2

NaY:

Si/Al = 2.5

USY:

Si/Al = ~6 or larger



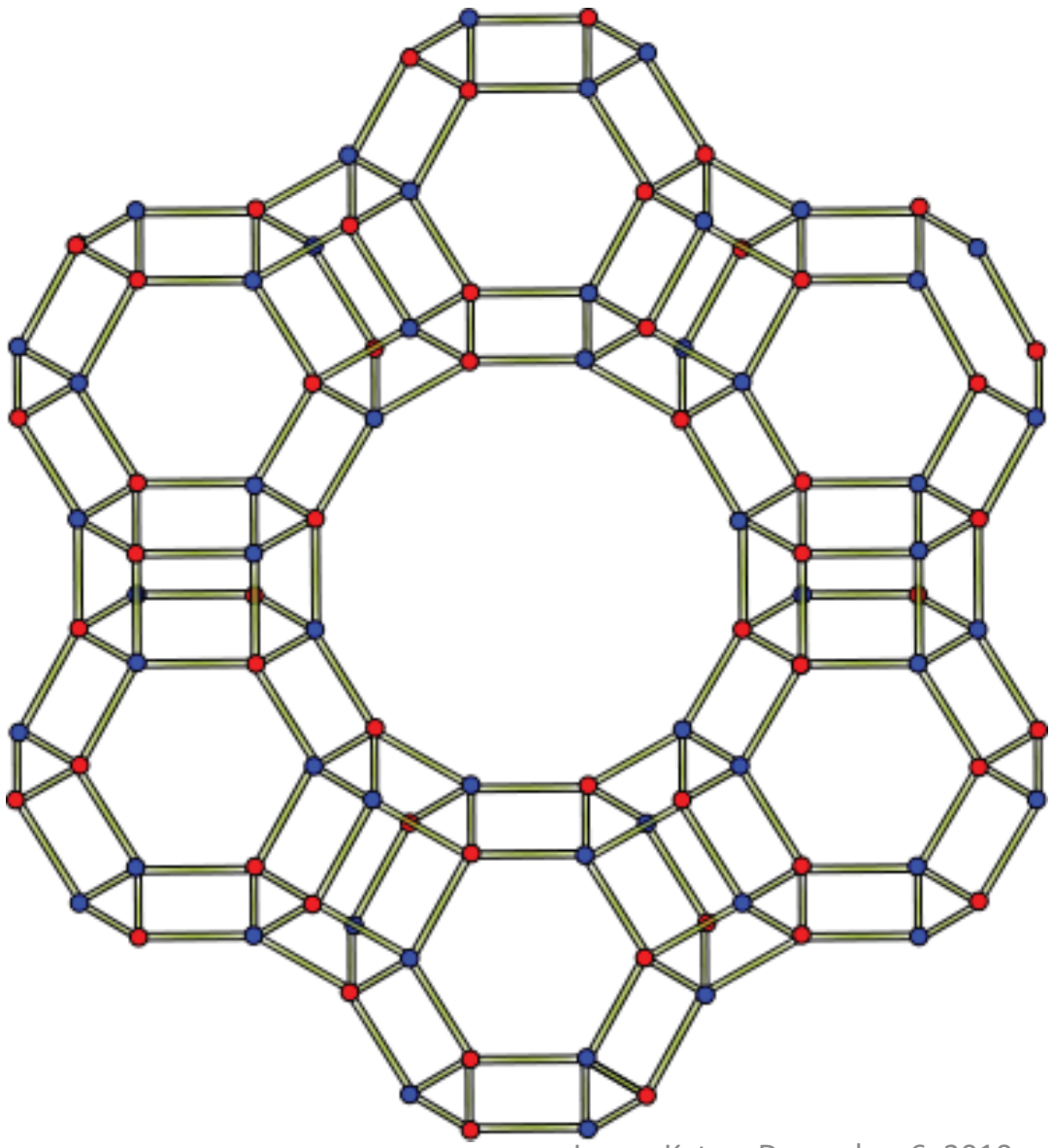
Zeolite A

NaA:

Si/Al = ~1.0

- In Na form, there is one Na cation per Al tetrahedra
- In acid form, H^+ cations replace Na cations originally present and represent the acid sites

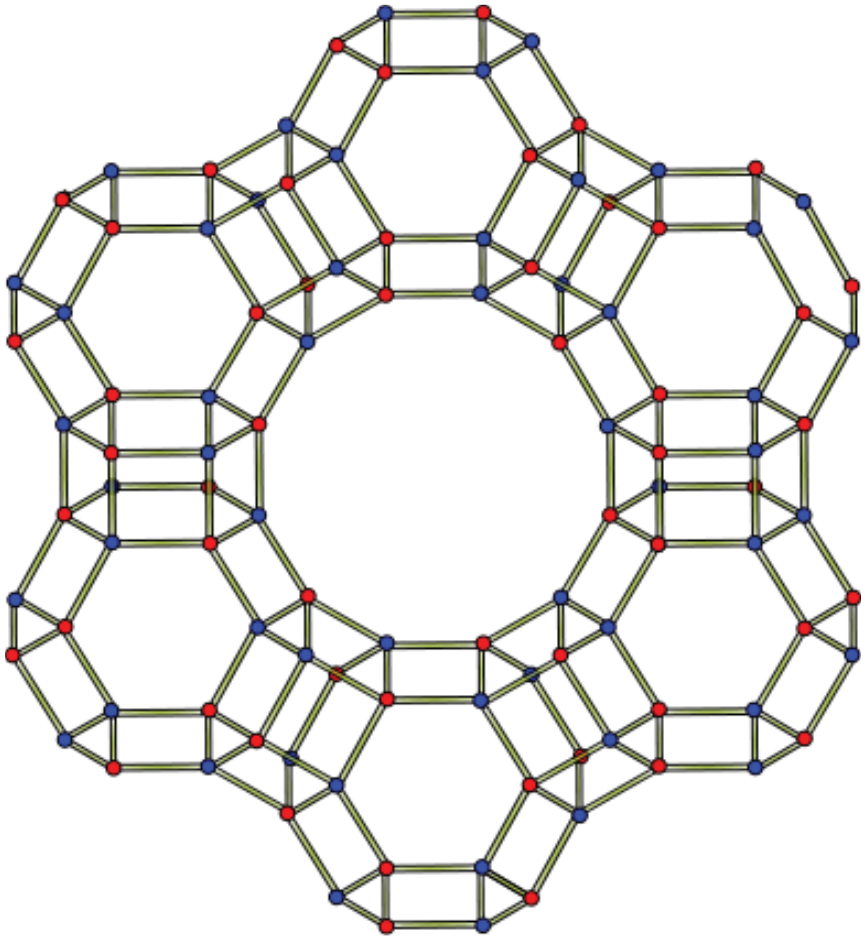
Y Zeolite For-Use Modifications



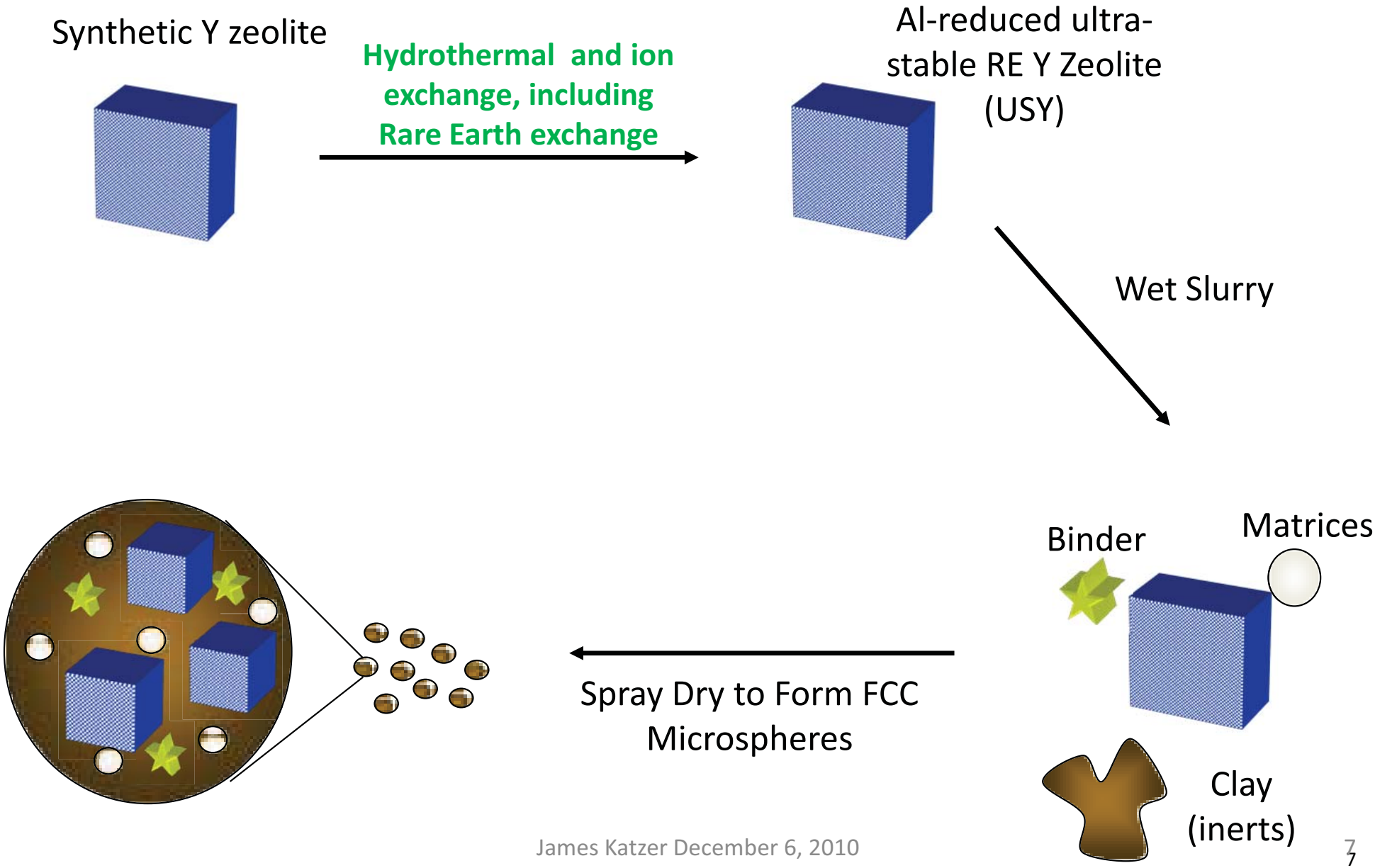
- Y as synthesized, one Na for each Al, Si/Al = 2.5
- Ammonium exchange and steam to dealuminize some of the Al tetrahedron
- Want some migration of Si into the vacant tetrahedron for enhanced stability
- USY results, with SI/Al ratio > 10, in H-form there is ~one acid site H^+ per tetrahedral Al
- Rare Earth may then be exchanged into the structure

Rare Earths in Catalytic Cracking

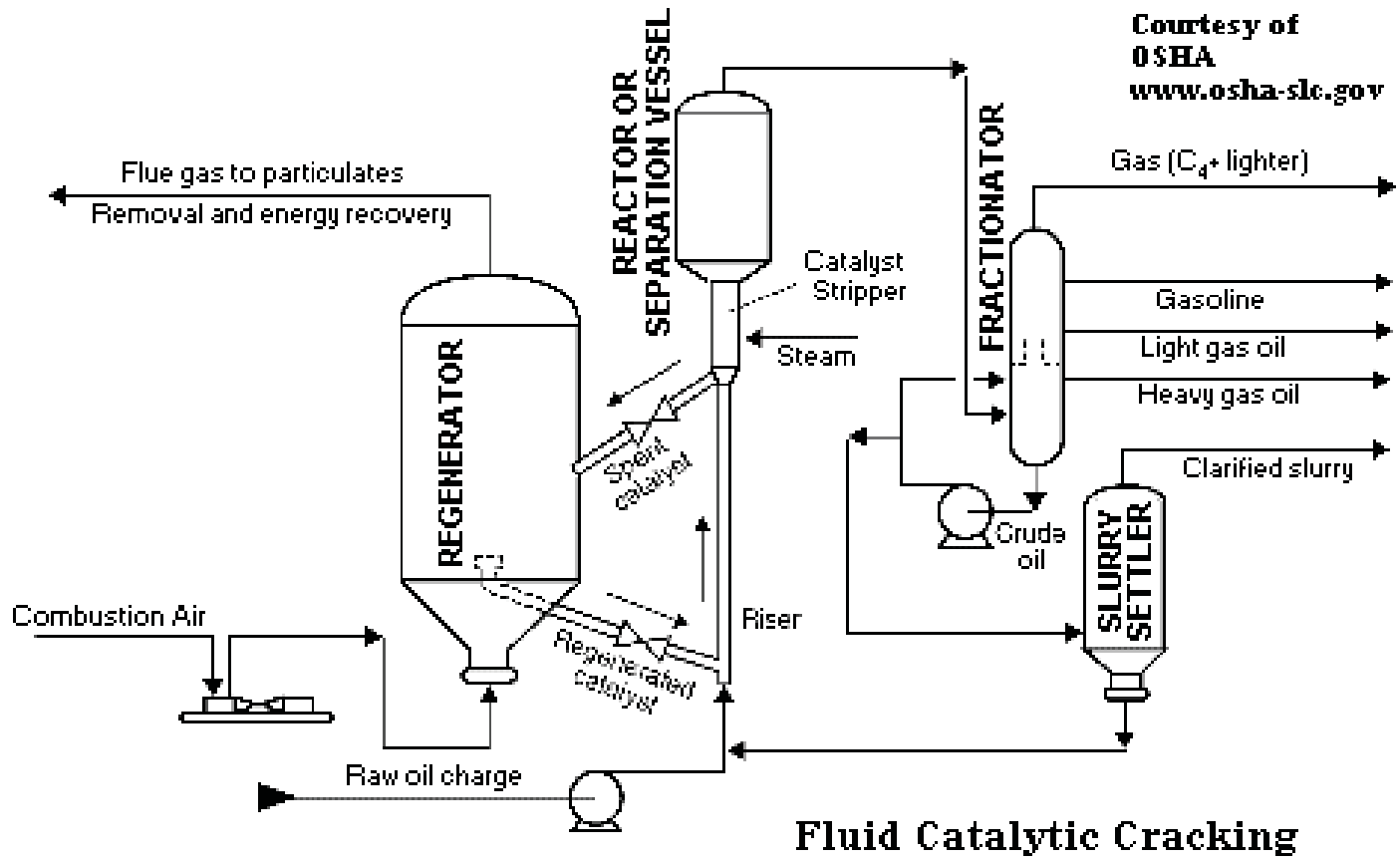
- Rare Earth cations initially reside in supercages, upon dehydration they move into the sodalite units
- Here they stabilize the zeolite to reduce the rate of further dealumination in service, maintaining activity
- Also impact hydrogen transfer reactions and impact gasoline properties.



Steps Included in Making Commercial FCC Catalyst

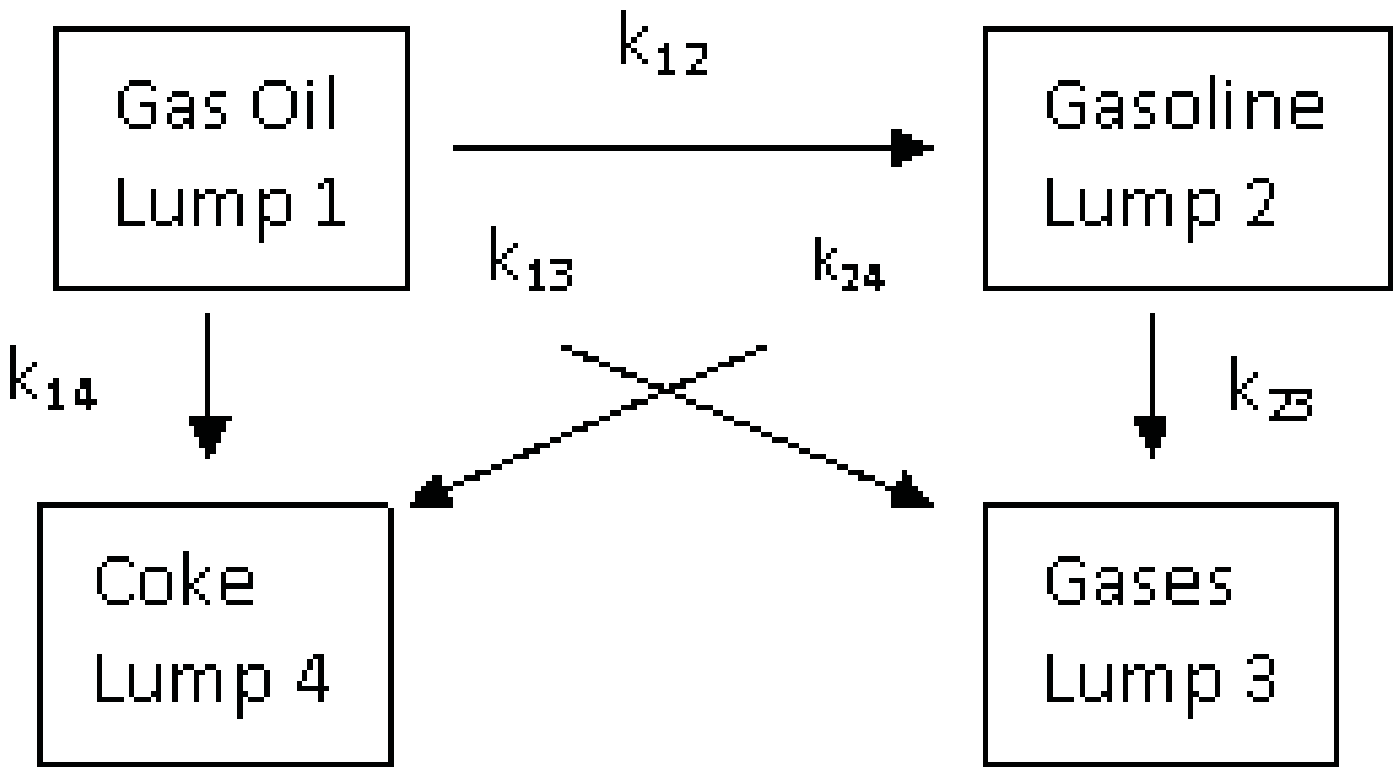


The Fluid Catalytic Cracking (FCC) is a Complex Unit



In-unit catalyst use results in slow deactivation and changes in other catalyst properties, RE is used to reduce the rate of this deactivation.

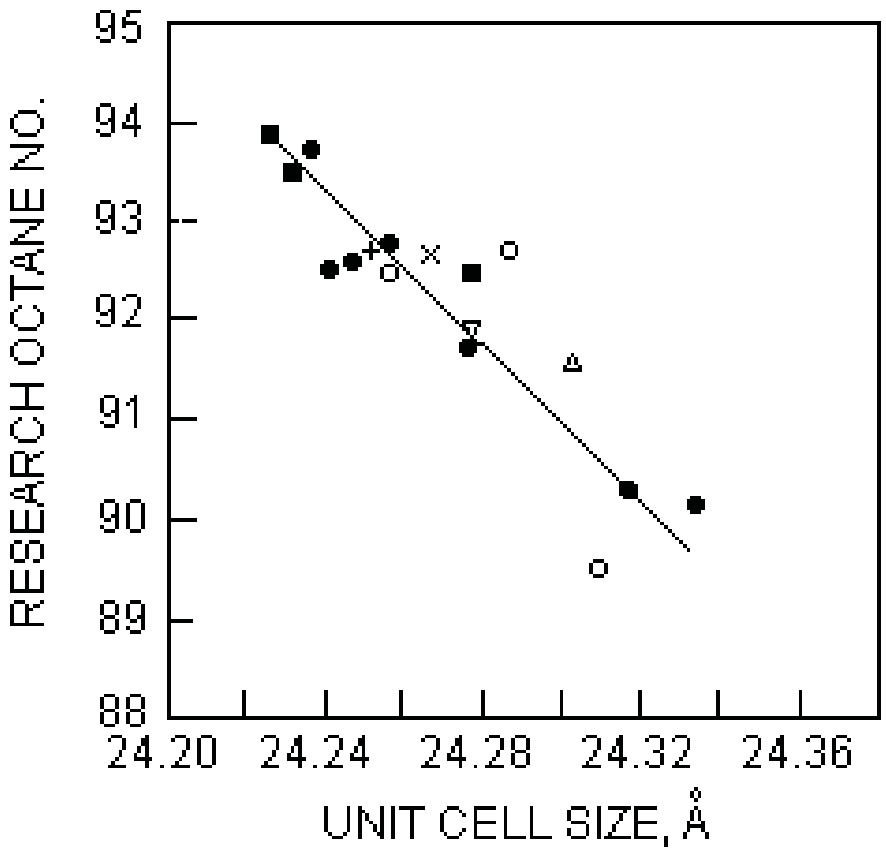
Gas Oil Cracking; Four Lump Model



- **Reaction system is complex and is often represented by simplified, lumped model**
- **Primarily desired reaction is gas oil to gasoline, the desired product**
- **Conversion of gasoline to other materials is to be minimized**
- **Complex interactions affect yield structure but maximum accessibility of reaction sites is desired to maximize gasoline yield**

Impact of Dealumination on Octane

FIGURE 1



DEPENDENCE OF NAPHTHA RESEARCH OCTANE NUMBER ON ZEOLITE UNIT CELL SIZE. NAPHTHA BOILING RANGE IS 18 TO 221°C AND VALUES REPORTED ARE UNLEADED OCTANE NUMBERS.

Cracking activity decreases as the zeolite unit cell size decreases

Questions

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U.S. DEPARTMENT OF ENERGY

Catalysis Breakout Session

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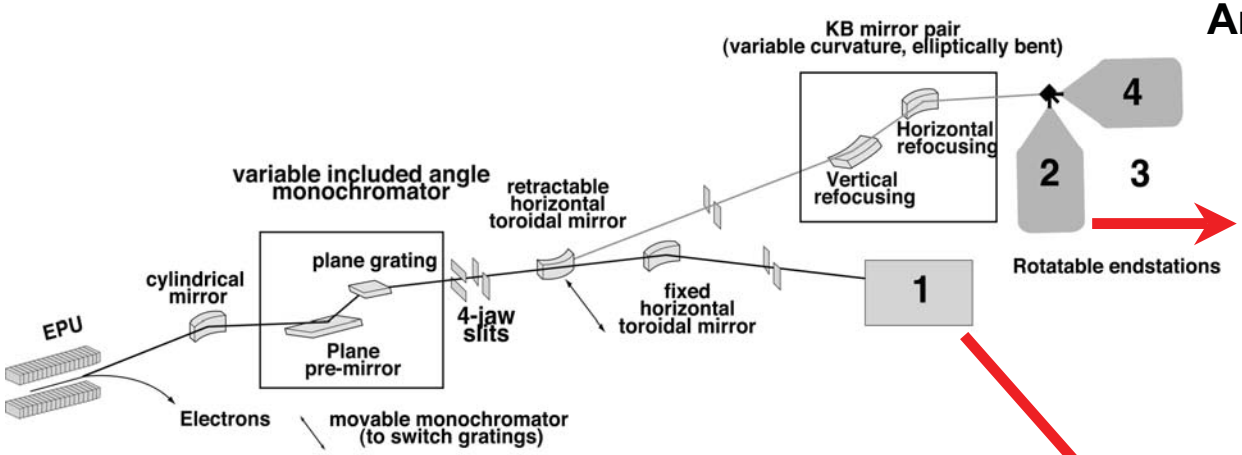
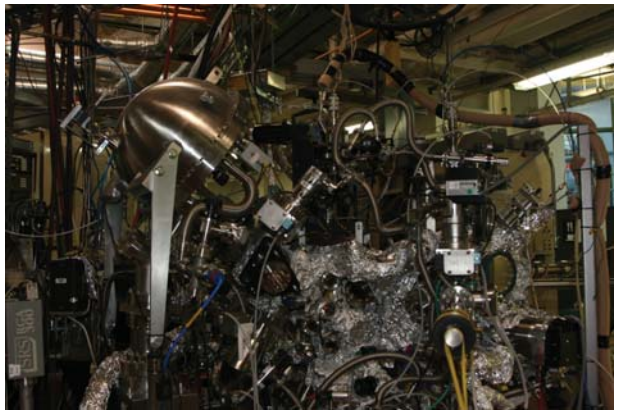
ARPA E Workshop
Arlington, VA
6 Dec. 2010

UNIVERSITY OF CALIFORNIA

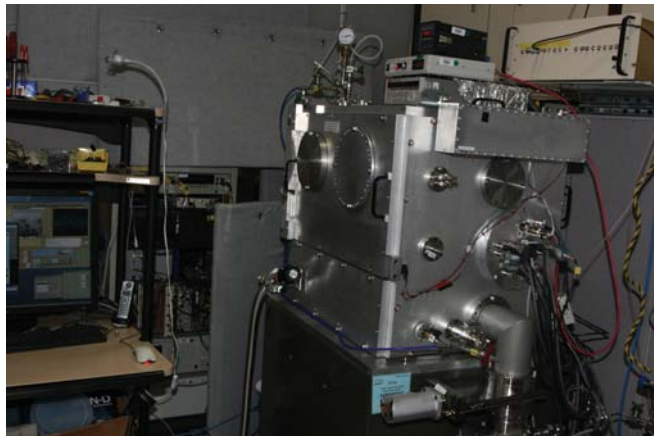
Advanced Light Source Molecular Environmental Science Beamline 11.0.2 - Realistic Catalysis



Ambient Pressure Photoelectron Spectrometer (APPES)

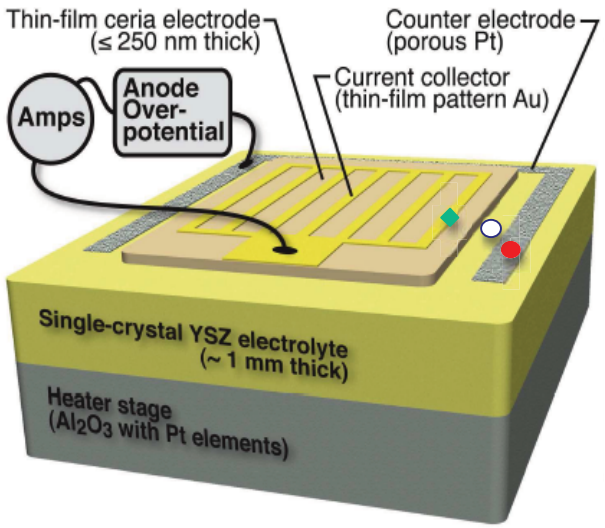


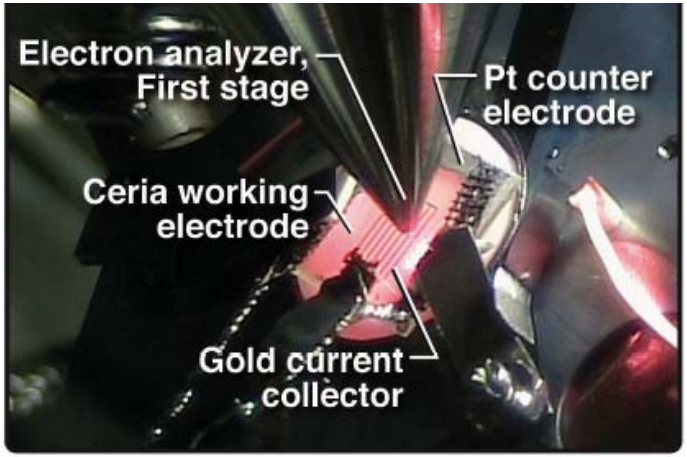
Scanning Transmission X-ray Microscope (STXM)



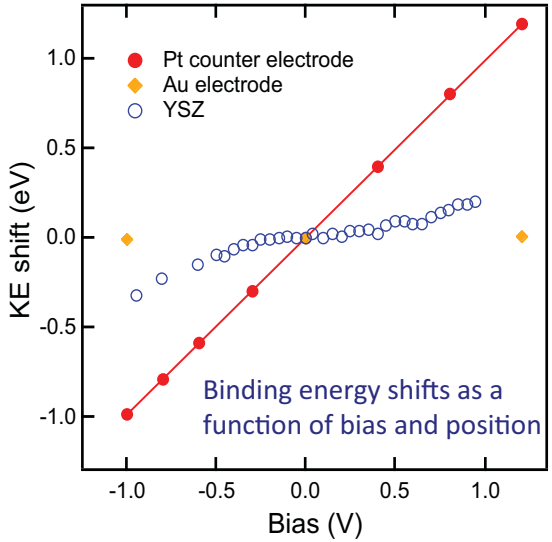
Over-subscribed by a factor of >7, ~7 years new

XPS on Fuel Cell Electrodes



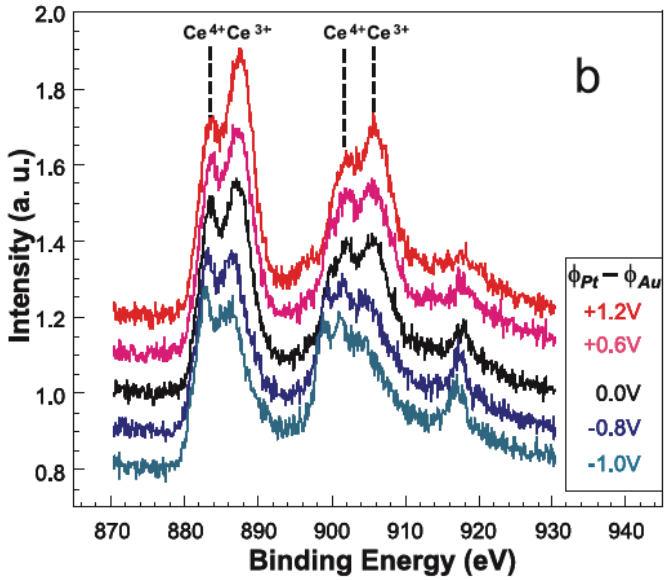


0.5 Torr H_2O+H_2, 700 °C



LBNL (CSD, ALS)
U. Maryland Sandia Nat'l Lab

Local potentials are probed by XPS KE shifts



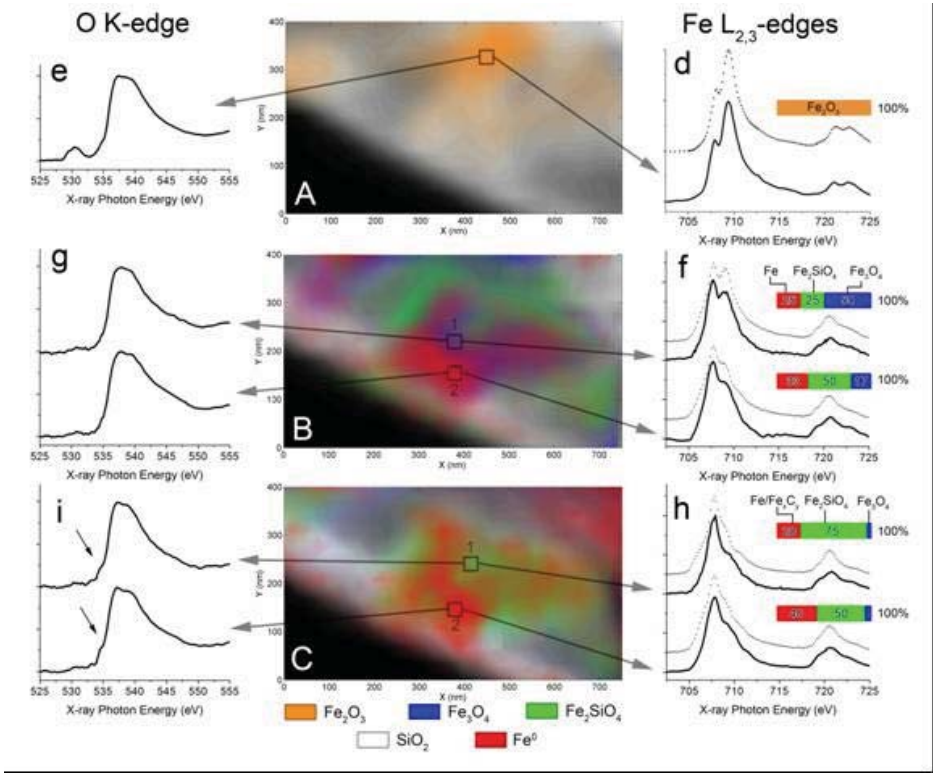
Oxidation state of CeO_x probed as a function of bias

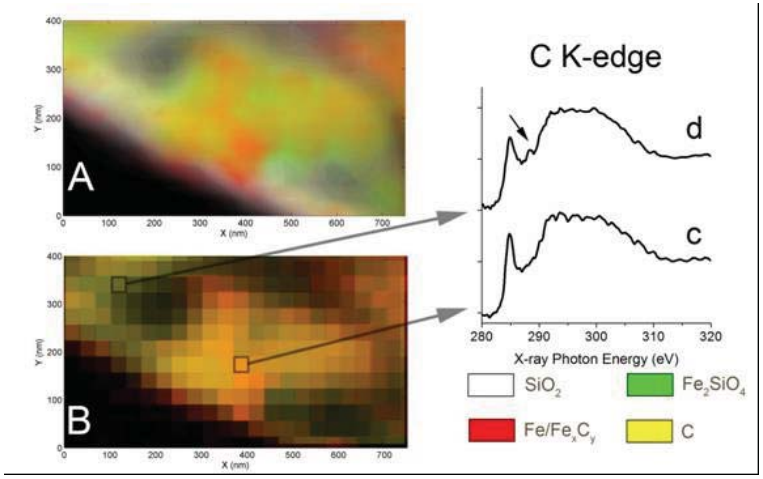
H. Bluhm et al. (LBNL)

In-situ Catalytic Reaction Observed on the Nanometer Scale

Nanoscale chemical imaging of a working catalyst by STXM

A complex iron oxide based Fischer-Tropsch catalyst





E. de Smit, I. Swart, J. Creemer, G. H. Hoveling, M. K. Gilles, T. Tyliszczak, P. J. Kooyman, H. W. Zandbergen, C. Morin, B. M. Weckhuysen and F. M. F. de Groot, Nature **456**, 222 (2008).