Approaches and advances to the challenges of treating emissions at low temperatures

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Oak Ridge National Laboratory

CLEERS Workshop
April 26, 2015

Sponsors: Gurpreet Singh, Ken Howden, and Leo Breton
Advanced Combustion Engines Program
U.S. Department of Energy

OAK RIDGE
National Laboratory

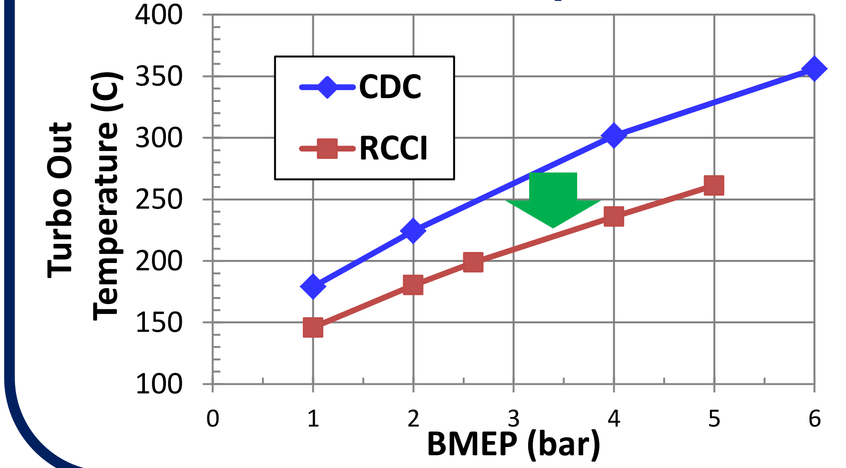
Objectives and Relevance

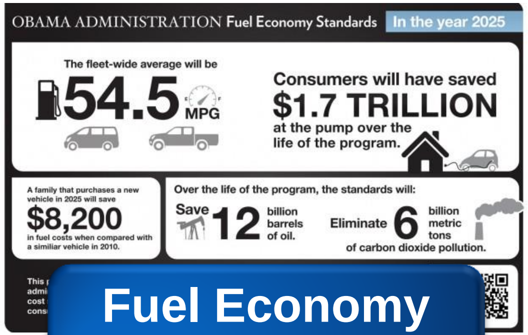
Develop emission control technologies that perform at low temperatures (<150ºC) to enable fuel-efficient engines with low exhaust temperatures to meet emission regulations

Goal: 90% Conversion at 150ºC

- Advance catalysts to enable commercialization of advanced combustion engine vehicles
  - Advanced combustion engines have greater efficiency and consequently lower exhaust temperature conditions
  - At low temperatures, catalysis is challenging and emissions standards harder to meet
  - Investigate “trap” material technologies that temporarily store emissions for later release and treatment

Higher efficiency engines have lower exhaust temperatures*




OBAMA ADMINISTRATION Fuel Economy Standards In the year 2025

The fleet-wide average will be 54.5 MPG

Consumers will have saved $1.7 TRILLION at the pump over the life of the program.

A family that purchases a new vehicle in 2025 will save $8,200 in fuel costs when compared with a similiar vehicle in 2010.

Over the life of the program, the standards will: Save 12 billion barrels of oil. Eliminate 6 billion metric tons of carbon dioxide pollution.

This
admi
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cons

Fuel Economy Standards

Fuel Economy

54.5 mpg CAFE by 2025

Emissions

>70% less NOx

>85% less NMOG

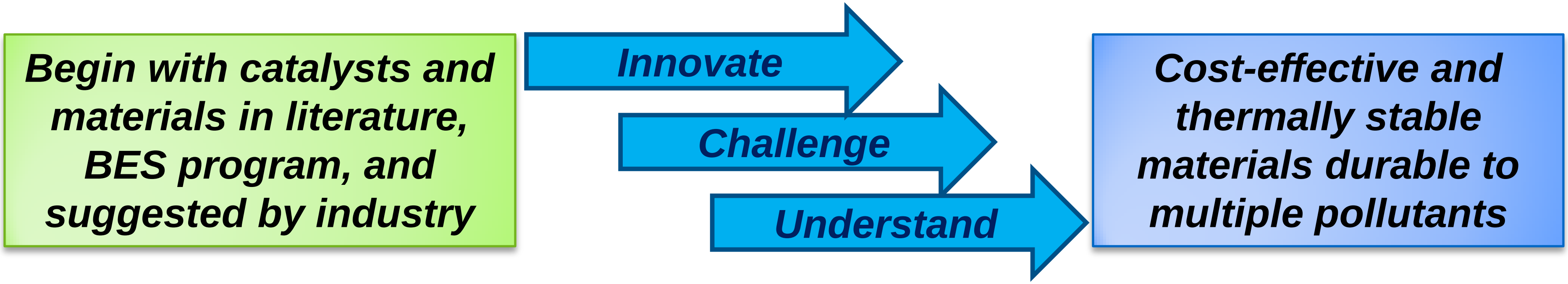
70% less PM

EPA Tier 3 Emission Regulations

2017-2025 (phased in)

*Reactivity Controlled Compression Ignition (RCCI) [a Low Temperature Combustion mode] vs. Conventional Diesel Combustion (CDC)

Approach: Challenge and advance novel approaches for low temperature emission control



Begin with catalysts and materials in literature, BES program, and suggested by industry

Innovate

Challenge

Understand

Cost-effective and thermally stable materials durable to multiple pollutants

This project is "high risk-high reward" by design

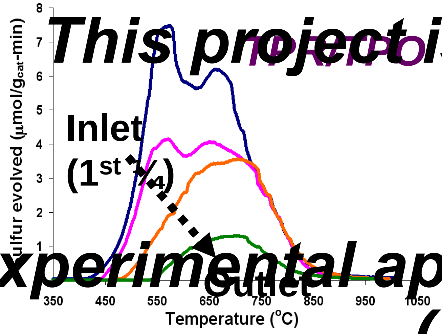
Experimental approach with emphasis on challenging…

(1) In full exhaust mixture

(2) After hydrothermal aging

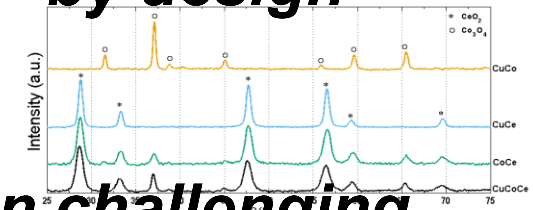
(3) After sulfur exposure

TPR/TPO

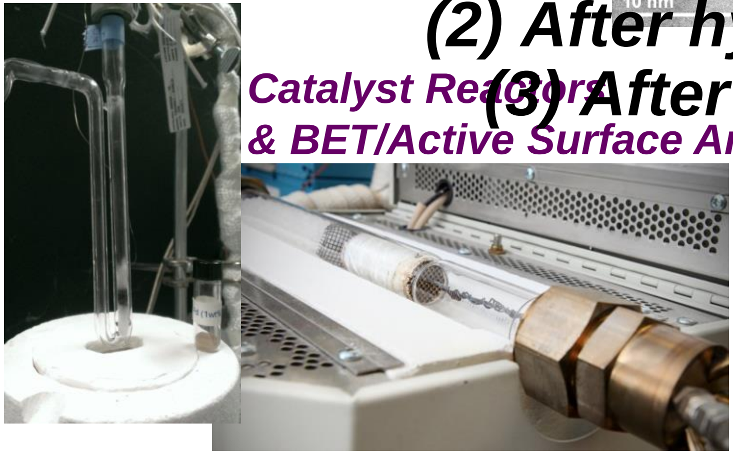


Electron Microscopy

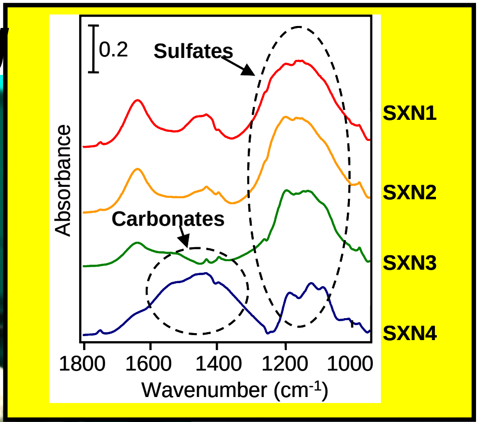
X-Ray Diffraction



Catalyst Reactors & BET/Active Surface Area



DRIFT Spectroscopy



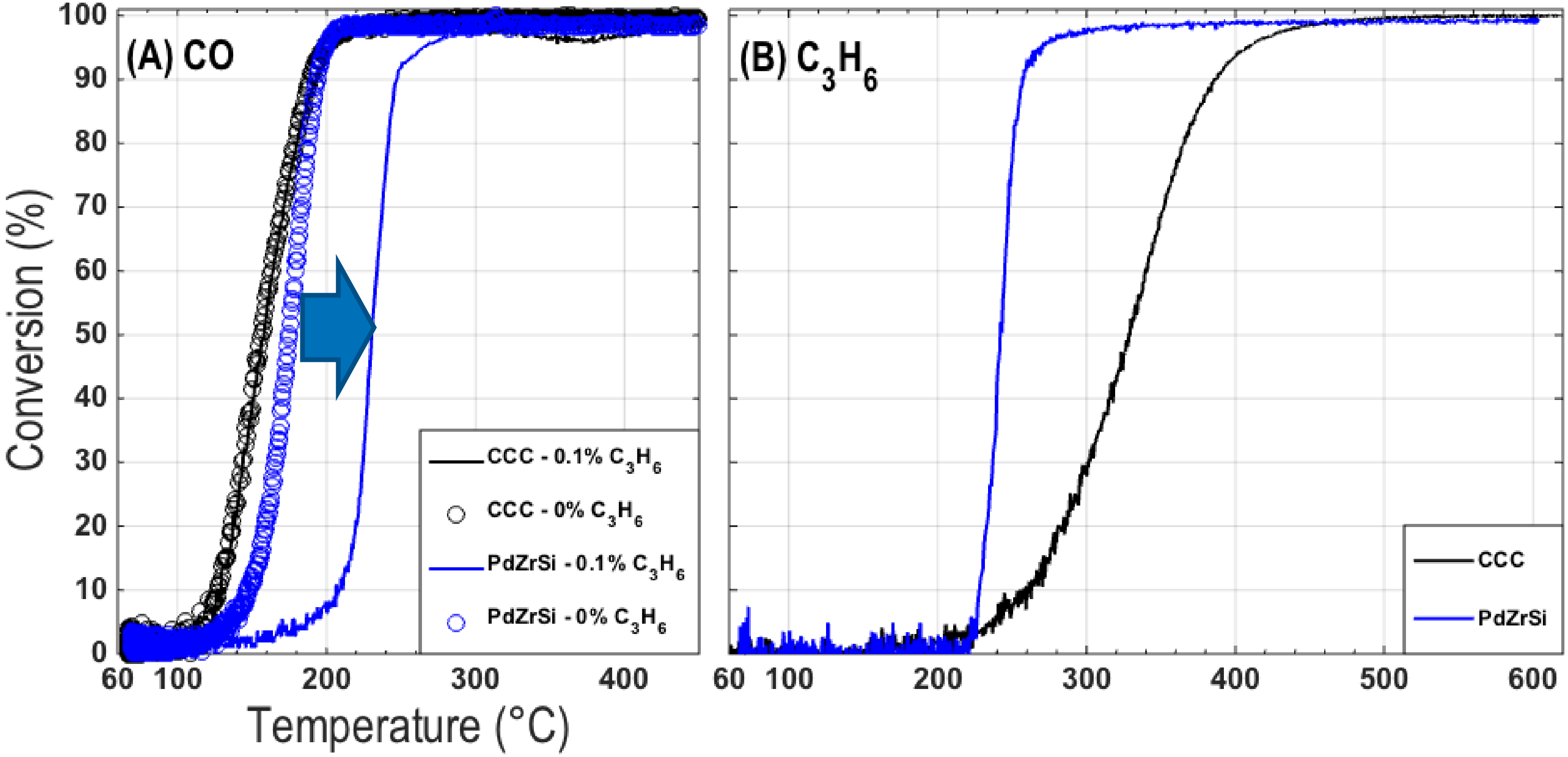
Areas of active research

- PGM-free mixed metal oxides
  - *Copper/Cerium/Cobalt oxide (CCC)
  - Collaboration with BES funded scientists
    - Sheng Dai and Steve Overbury (ORNL)
    - Center for Nanophase Material Science (ORNL)
- Support modifications for enhanced PGM activity
  - *Pd on zirconia modified silica and alumina
  - Nano-phase ceria and ceria/zirconia supported on silica and alumina
    - Target PGM addition to Cerium phases
  - SEA-approaches with highly stable Solvay supports
  - Collaborations with numerous organizations
    - UPMC (France); CNU (Korea); U. South Carolina; Solvay
- Trapping materials
  - *Currently investigating zeolites including ion-exchanged

* - also presented in more detail as posters by Andrew Binder and Eleni Kyriakidou

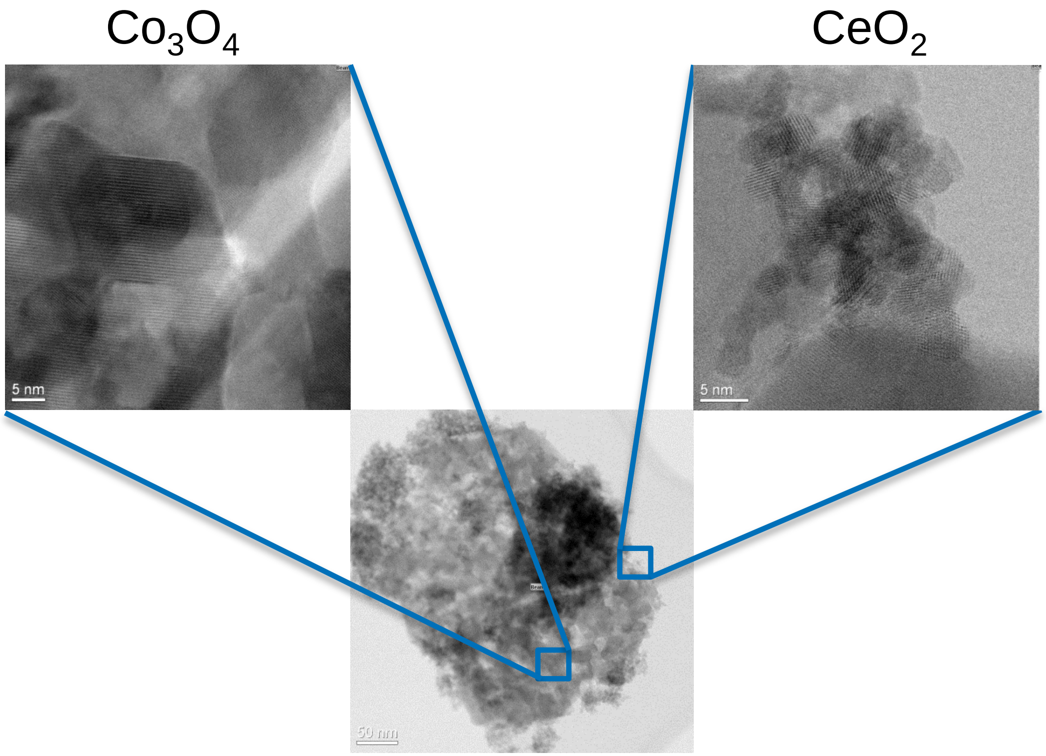
PGM-Free CuO_x-CoO_y-CeO_z Catalyst

Co-precipitated CuO_x, CoO_y, and CeO_2 (dubbed CCC catalyst) has shown to have both **high CO oxidation activity** and **exceptional tolerance for propylene.**

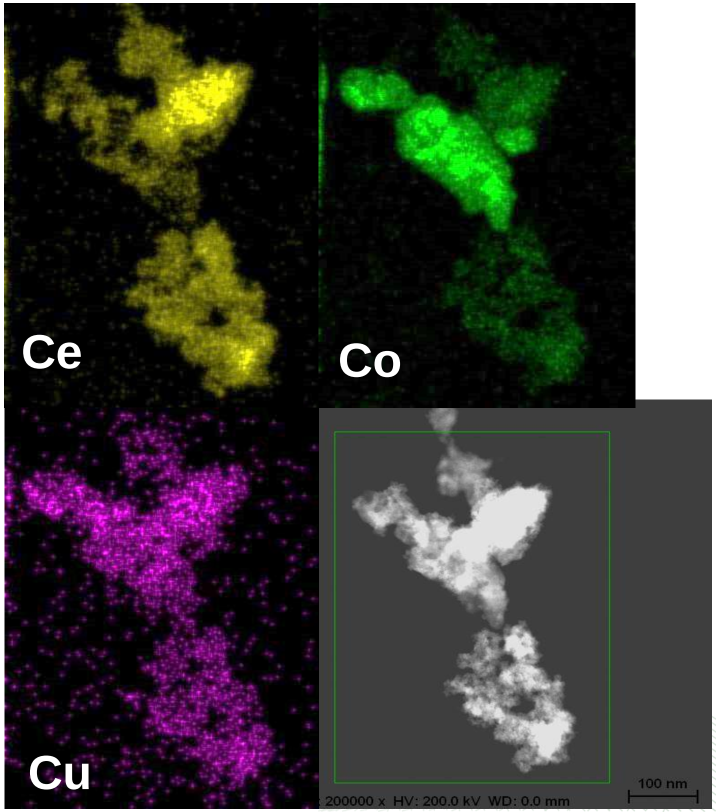


- PGM-Free CCC (**black**) shows unique lack of inhibition by HCs; for reference, Pd/ZrO_2-SiO_2 catalyst (**blue**) shows inhibition which shifts light-off to higher temps
- Hydrocarbon oxidation, however, is still relatively high for CCC catalyst

CCC structure and composition



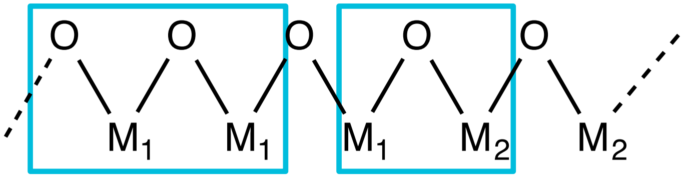
- STEM analysis confirms interfacing regions of Co_3O_4 and CeO_2 with high crystallinity for each phase.
- Ceria has a much smaller average particle size.



- XRD analysis and EDX mapping shows that the Cu species is integrated into the lattices of both Co_3O_4 and CeO_2 evenly.

Separated Active Sites?

Binary catalyst comparisons indicate different sites are important for CO or C_3H_6 activity under simulated exhaust.

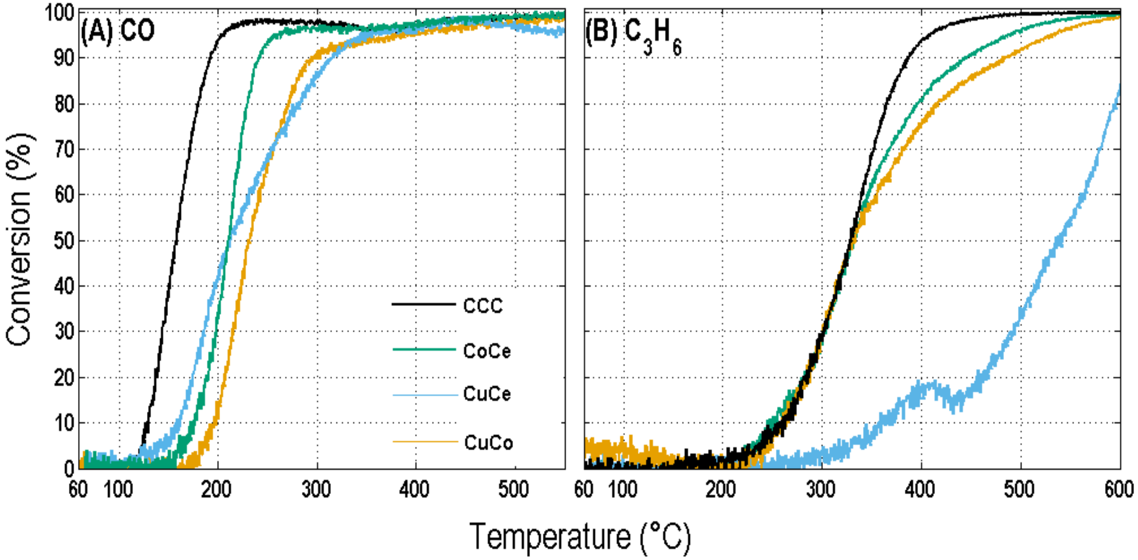


C_3H_6 ox.

CO ox.

M_1 = Co

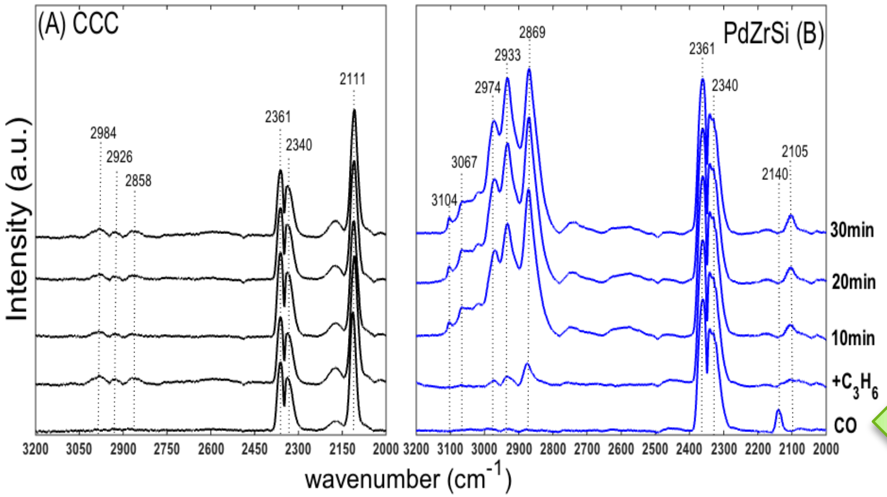
Preferably
M_1=Cu,Co M_2=Ce

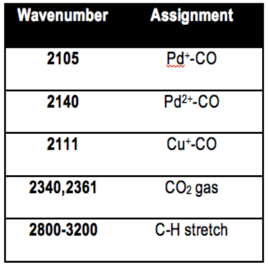


Low temperature CO ox. is significantly influenced by choice of oxide combination.
Interface sites are important for CO oxidation.

C_3H_6 is not significantly influenced by oxide combination or Co_3O_4 particle size.
Co_3O_4 surface is important for C_3H_6 conversion.

DRIFTS provides insights into CCC hydrocarbon inhibition resistance; initial aging results obtained





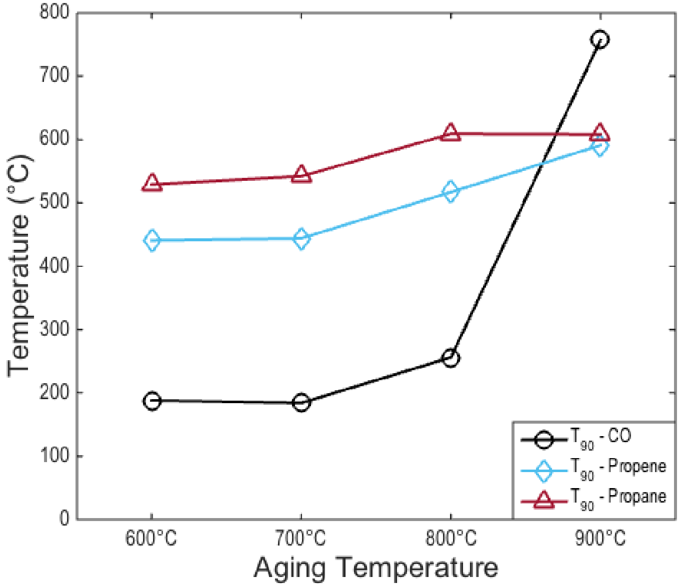
Wavenumber	Assignment
2105	Pd^{+}-CO
2140	Pd^{2+}-CO
2111	Cu^{+}-CO
2340,2361	CO_2 gas
2800-3200	C-H stretch

- DRIFTS data indicates a lower adsorption of C_3H_6 on CCC (compared to Pd/ZrO_2-SiO_2) and almost no effect on the Cu-carbonyl binding site due to introduction of propene

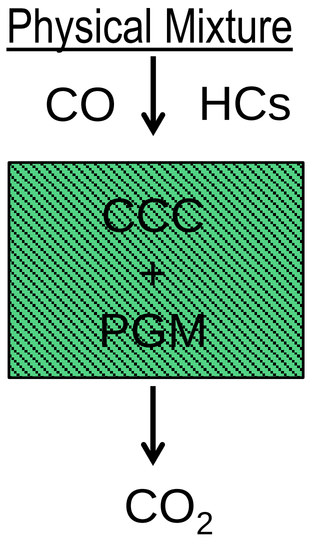
CO coverage to start; HC added

- Maintains low temperature CO oxidation even in the presence of multiple hydrocarbon species (propene + propane shown left)

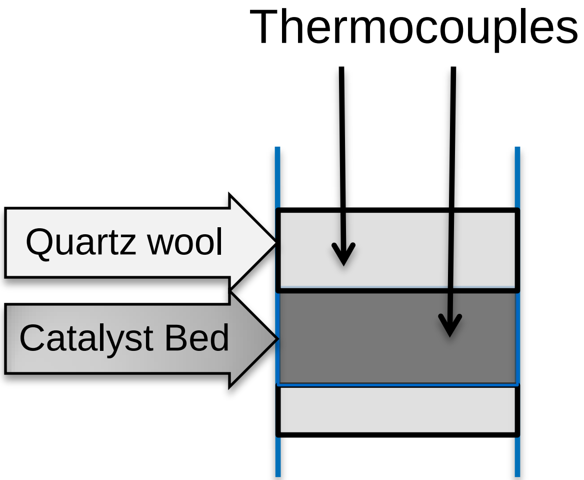
- Short term (2 hr) thermal aging shows CCC to be very stable up to 800°C with major deactivation at 900°C



CCC + Pt/Al_2O_3 combination investigated to find lowest combined CO and HC light-off temps

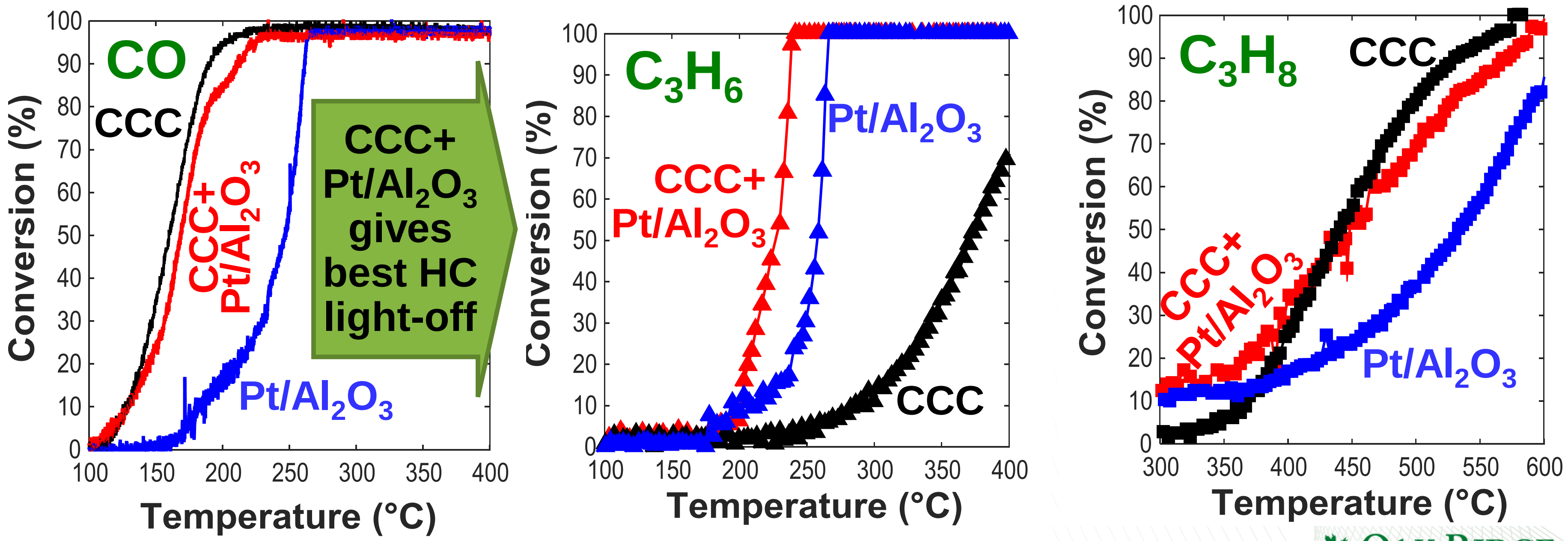


- Physical mixture of 50% CCC and 50% Pt(1% wt.)/Al_2O_3 allows for high CO and propene oxidation with half as much total Pt content vs. Pt/Al_2O_3
- C_3H_6 light-off greatly improved with CCC + Pt physical mixture



CO+HC+NOx Conditions:

CO (1%), C_3H_6 (500ppm), C_3H_8 (500ppm), NO (500ppm), O_2 (10%), H_2O (5%)



SV ~150k/hr

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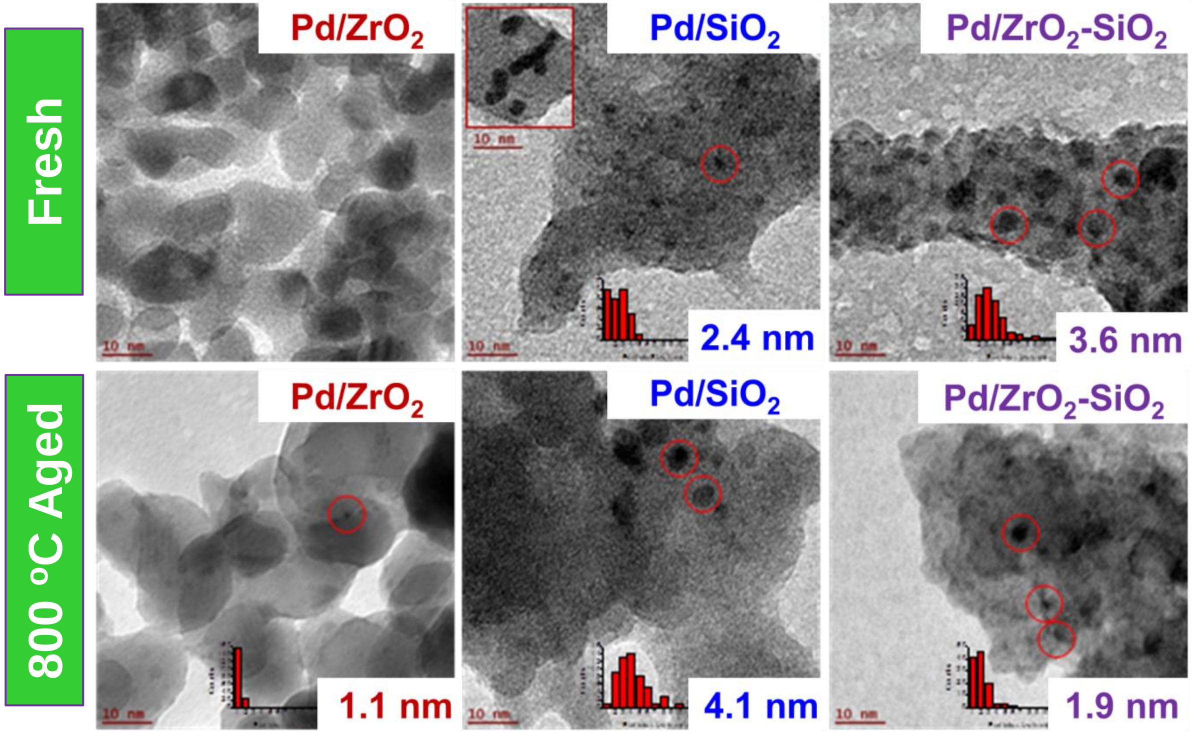
* - also presented in more detail as posters by Andrew Binder and Eleni Kyriakidou

PGM/support study focusing on improving durability through support modifications

- Pd/ZrO_2 is a good relatively stable catalyst
- Want to enhance activity/durability through modifications



Well dispersed Pd on ZrO_2 (fresh). Aggregation of Pd particles begins with aging (still small).

Pd/PdO particle growth with aging

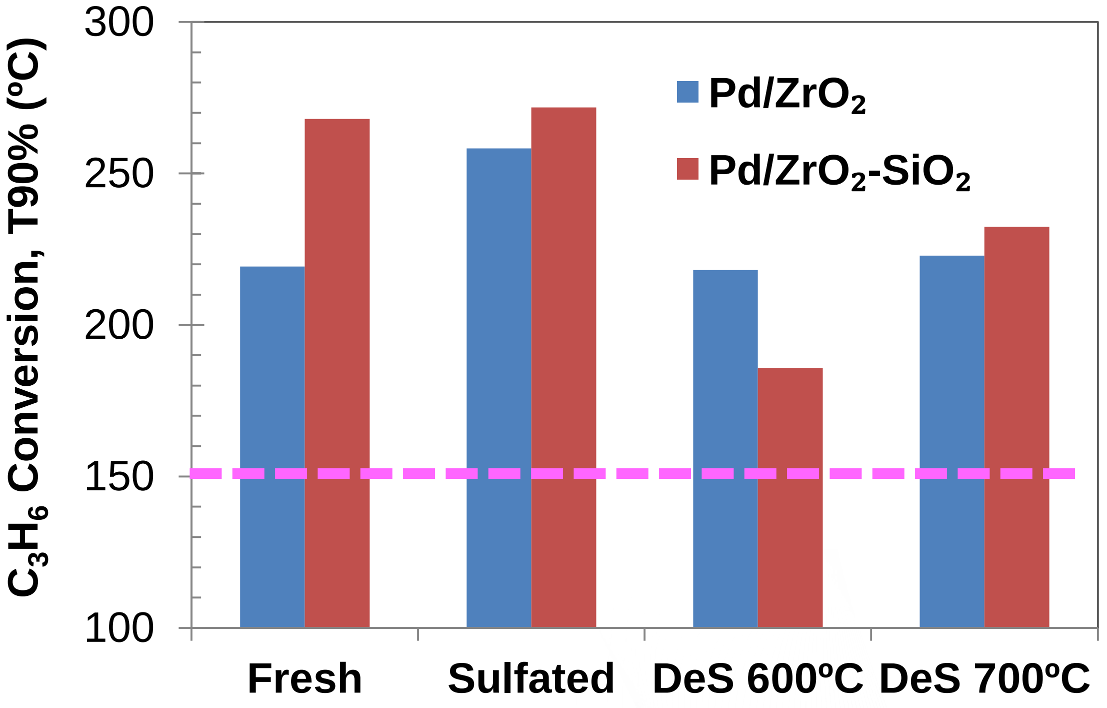
Presence of PdO particles with aging (XRD)

Sample	Surface Area (m^2/g)
Fresh **Pd/ZrO_2**	92.6
Aged **Pd/ZrO_2**	*24.3*
Fresh **Pd/SiO_2**	447.4
Aged **Pd/SiO_2**	*300.9*
Fresh **Pd/ZrO_2-SiO_2**	404.4
Aged **Pd/ZrO_2-SiO_2**	*325.3*

Incorporation of ZrO_2 on SiO_2 appears to enhance hydrothermal stability of Pd catalysts and silica SA

Sulfur tolerance of ZrO_2 coating on SiO_2 improved Pd catalysts after deS at 600ºC

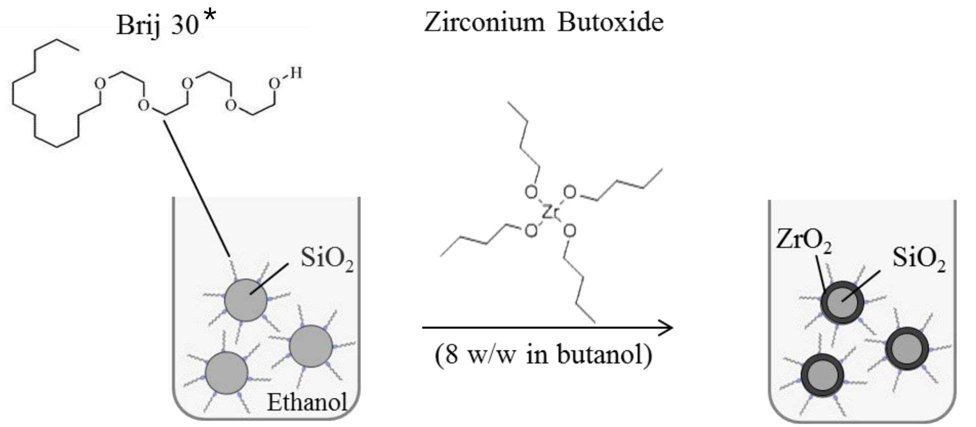
- **ZrO_2 coating introduces surface acidity**
  - High acidity: benefit on HC oxidation vs. high basicity: high sulfur adsorption
  - Pd/ZrO_2 has both strong acidic and basic sites, while Pt/Si has neither
  - Pd/ZrO_2-SiO_2 has acidic sites but negligible basic sites
  - Favorable for Pd dispersion, HC oxidation, and sulfur tolerance
- **Trying to understand 600°C DeS improvement for Pd/ZrO_2-SiO_2**



Reaction Conditions: 4000 ppm CO / 500 ppm NO / 1000 ppm C_3H_6 +4% O_2 + 5% H_2O in Ar, Total Flow: 200 sccm

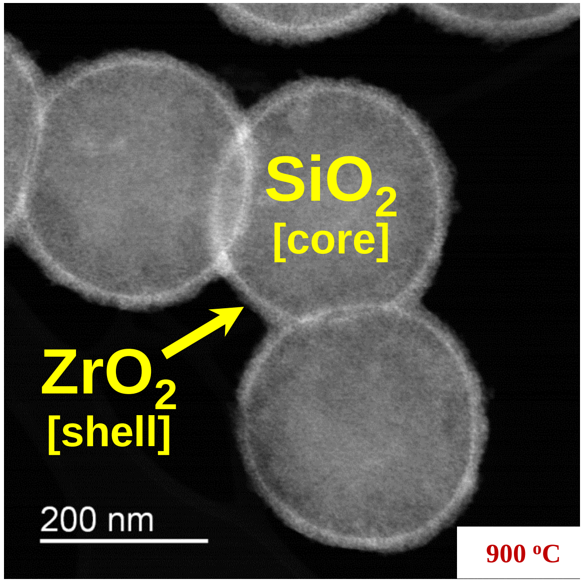
Sulfation Conditions: 50 ppm SO_2+4% O_2 +5% H_2O in Ar, Total Flow: 200 sccm at 400°C

New synthesis of $SiO_2@ZrO_2$ core@shell improves ZrO_2 coverage of SiO_2 (vs. FY2014 results)

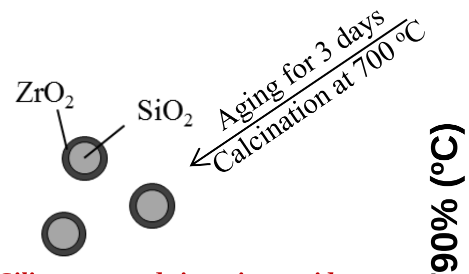


Synthesis of silica spheres

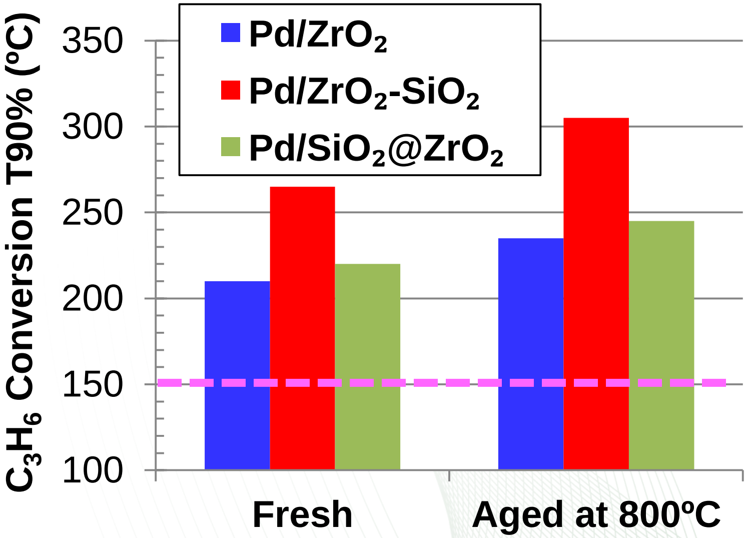
Silica core and amorphous shell with zirconium hydroxide



Material	Surface Area (m^2/g)	ZrO_2 S. A. (m^2/g)**
ZrO_2	97 ------>	(97)
ZrO_2-SiO_2	402	60
$SiO_2@ZrO_2$	**210**	**---**
@ZrO_2***	**117 ------>**	**(117)**



Silica core and zirconium oxide shell after calcination at 700 ºC



- Successfully synthesized **core@shell $SiO_2@ZrO_2$** with more uniform ZrO_2 coating than previous **amorphous SiO_2-ZrO_2** catalyst
- Initial hydrothermal aging results good, but more important evaluation of S tolerance (main objective) coming next

*(Brij 30): Polyoxyethylene(4) lauryl ether from P.M. Arnal, C. Weidenthaler, F. Schuth, Chem. Mater. 18, (2006) 2733.; **based on NOx TPD with UPMC method; ***with SiO_2 removed;

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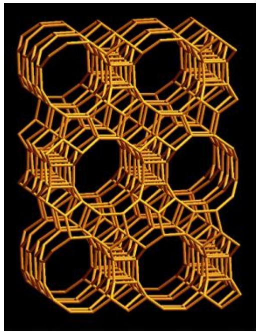
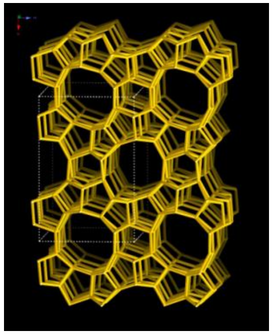
Baseline HC-trap materials selected to determine key controlling factors

- Zeolites chosen based on industry feedback and literature survey
  - Most studied materials in academic settings
  - Components of actual commercial technology (conventional ICEs)
- Investigating performance trends will give Information necessary for designing HC-traps tailored to advanced ICEs
- Systematic variation of key zeolite properties
  - Pore structure (Beta vs. ZSM-5)
  - Acidity (low vs. high SiO_2/Al_2O_3)
  - Cation type (H^+ vs. Ag^+)



Beta (12-ring pore)

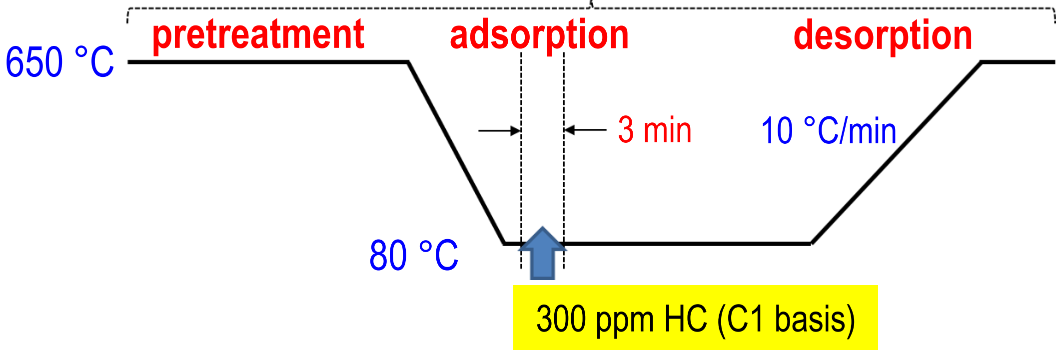


ZSM-5 (10-ring pore)

Large/medium pores allow easy HC

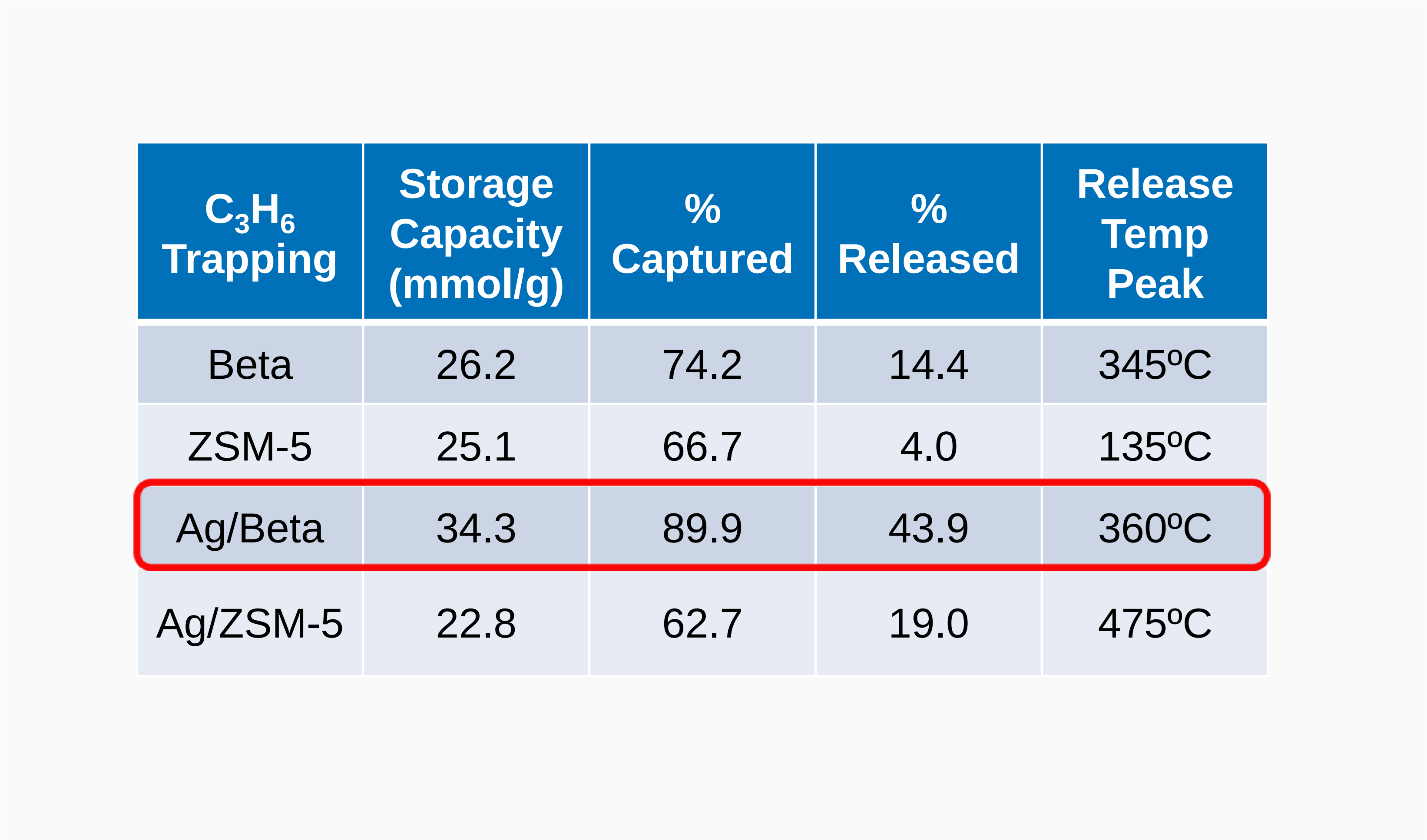
Zeolite type	SiO_2/Al_2O_3 molar ratio	Nominal cation form	Surface area (m^2/g)
Beta	25	H^+	680
Beta	25	Ag^+	NM
Beta	300	H^+	620
Beta	300	Ag^+	NM
ZSM-5	30	H^+	405
ZSM-5	30	Ag^+	NM
ZSM-5	280	H^+	400
ZSM-5	280	Ag^+	NM

Base gas: 10% O_2 + Ar balance (5% H_2O, 5% CO_2)



Trap loading: 25 mg/Total flow rate: 300 sccm

Ag added to zeolites improves C_3H_6 trapping desorption



C_3H_6 Trapping	Storage Capacity (mmol/g)	% Captured	% Released	Release Temp Peak
Beta	26.2	74.2	14.4	345ºC
ZSM-5	25.1	66.7	4.0	135ºC
Ag/Beta	34.3	89.9	43.9	360ºC
Ag/ZSM-5	22.8	62.7	19.0	475ºC

- Beta zeolite stores more C_3H_6 than ZSM-5
- Ag increases **both storage and desorption** for beta zeolite
- "Missing" C_3H_6 from TPD an important issue
  - strongly held cokes a potential cause

Conditions:
167 ppm C_3H_6 +10% O_2,
Total Flow: 300 sccm

(1) Takamitsu, Y., Ariga, K., Yoshida, S., Ogawa, H., Sano, T. Bull. Chem. Jpn. 85(8), 869 (2012)
(2) Moden, B., Donohue, J. M., Cormier, W. E., Li, H.-X. Top. Catal. 53, 1367 (2010)

Summary

Objective: Develop emission control technologies that perform at low temperatures (<150ºC) to enable fuel-efficient engines with low exhaust temperatures to meet emission regulations

Relevant To All ACEC Tech Team Combustion Techniques

Novel Concepts → *Innovate* → *Challenge* → *Understand* → *Real Conditions*

Accomplishments

PGM-Free Catalyst → Low cost catalyst with no CO-HC inhibition continuing promise: hydrothermal aging and PGM combos demonstrated

PGM Support → Improved SiO_2-ZrO_2 catalyst synthesized as core-shell; initial hydrothermal studies good – S will be challenge of focus

Zeolite Traps → Results for two zeolites with and without Ag obtained; more definition of study parameters continues – more materials too

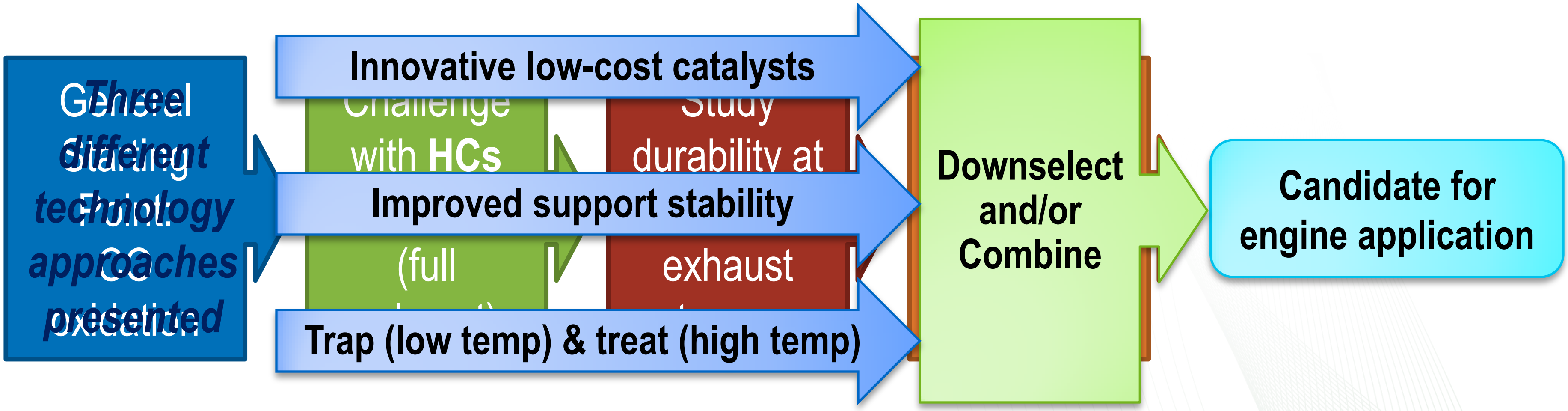
Future Work: **continue challenges of full exhaust mixture, aging, and S**

Technical Backup Slides

Approach: Specific Details

- ***Recent approach modification*** based on feedback from project review with ACEC Tech Team in FY2015Q1:
  - Research team reviewing literature* from notable catalysis, chemistry, and materials journals to ***(1) provide science support to applied efforts, (2) fine tune strategy for project material studies, (3) identify new ideas to pursue***
- ***Continuing approach*** to challenge materials in full exhaust with aging and poisons
  - CO oxidation is common metric in literature/BES program, but…***EPA Tier 3 requires dramatic reductions in HC & NOx [thus, we challenge materials in full conditions]***

Strategy ultimately aims to achieve EPA Tier 3 compliance



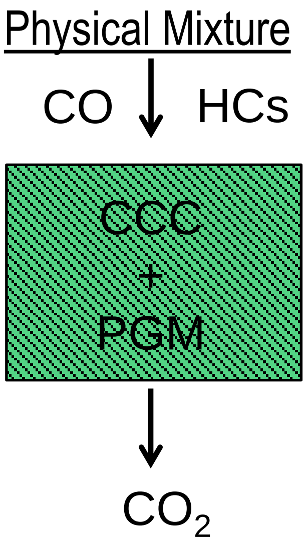
Low Temperature Protocols will be used for experiments

**backup slide has example list of journals reviewed*

Collaborations

- **DOE Basic Energy Sciences Program**
  - Sheng Dai and Steve Overbury (ORNL)
  - Center for Nanophase Material Science (ORNL)
- **University of South Carolina**
  - Professor John Regalbuto and student Andrew Wong
- **International collaborations**
  - UPMC, France (Dr. Cyril Thomas) & CNU, Korea (Prof. Sang-Wook Han)
- **Johnson Matthey**
  - Industry input from Haiying Chen
- **CLEERS**
  - Dissemination of data; presentation at CLEERS workshop
- **USCAR/USDRIVE ACEC Tech Team Catalyst Sub-Team**
  - Regarding low temperature protocols
- **DOE-funded FOA Project led by Ford: Next Generation Three-Way Catalysts for Future, Highly Efficient Gasoline Engines**
  - Catalysts being investigated for stoichiometric applications

Experiment Detail: added thermocouple in catalyst bed and using as temperature measurement



Physical Mixture

CO ↓ HCs

CCC + PGM

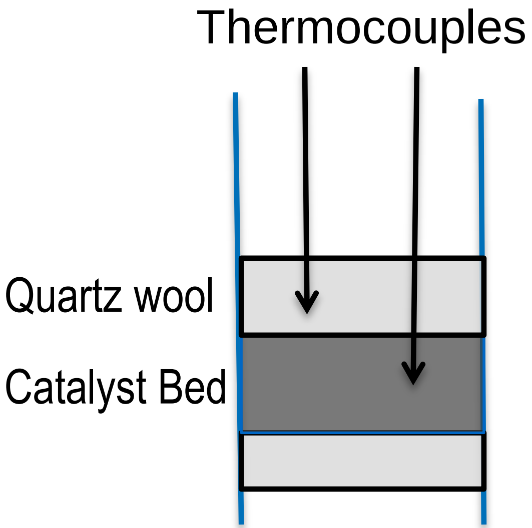
↓

CO_2

Experiment shown:

- Physical mixture of 50% CCC and 50% Pd(1% wt.)/ZrO_2 allows for high CO and propene oxidation with half as much total Pd content compared to pure Pd/ZrO_2.

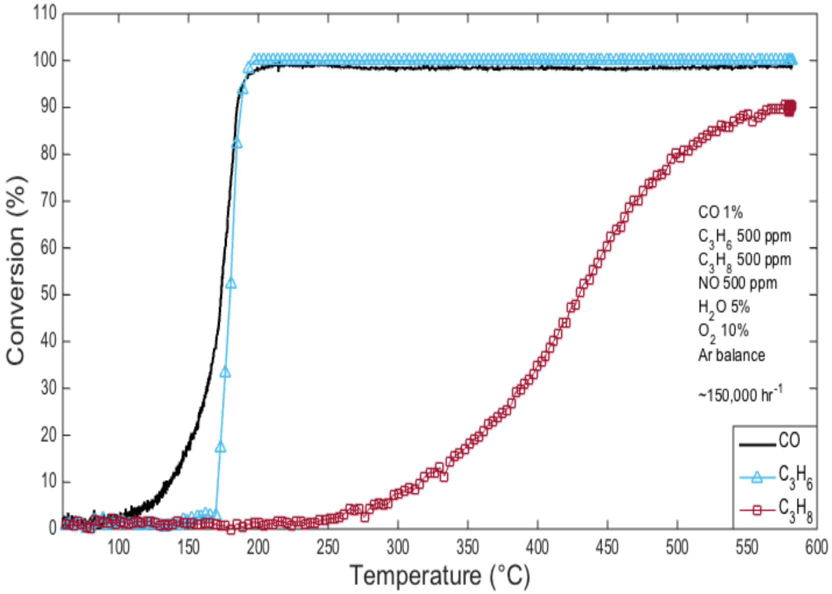
Distinct exotherm (lower right) can be seen in the catalyst bed which is being used as reference point for conversion data (lower left) – sharper light-off

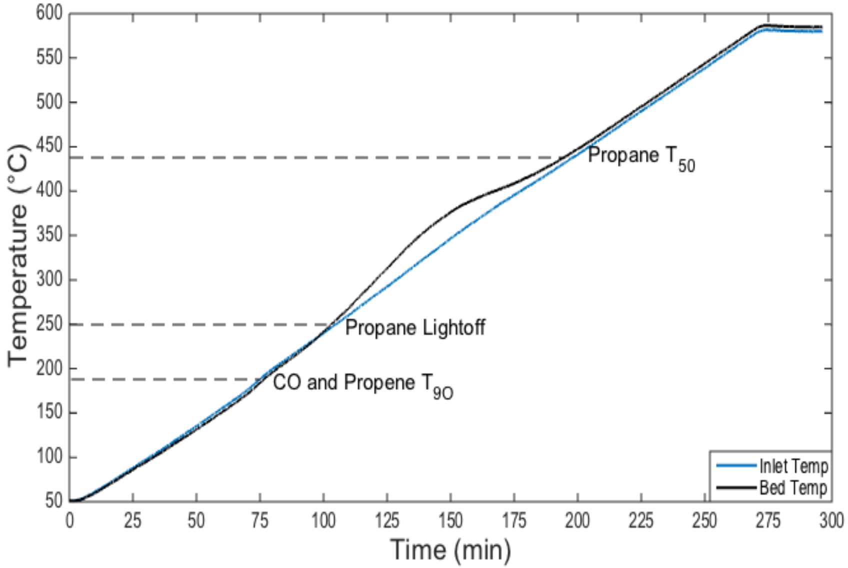


Thermocouples

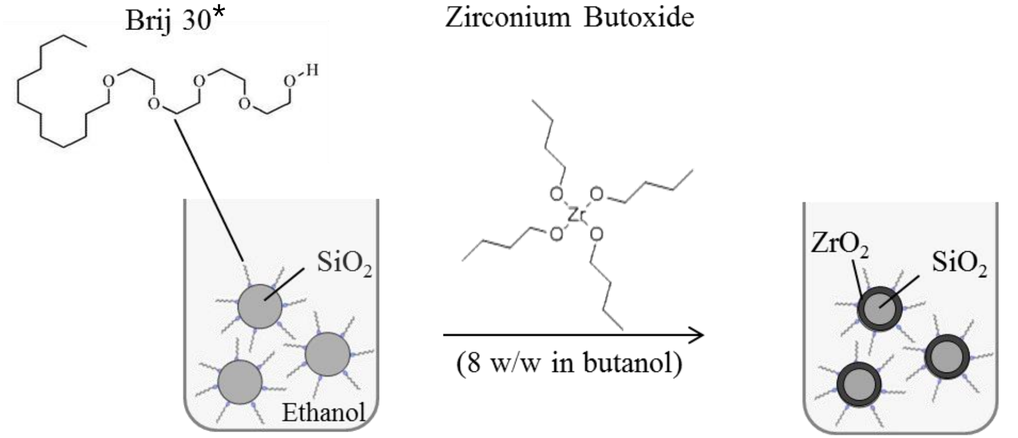
Quartz wool

Catalyst Bed



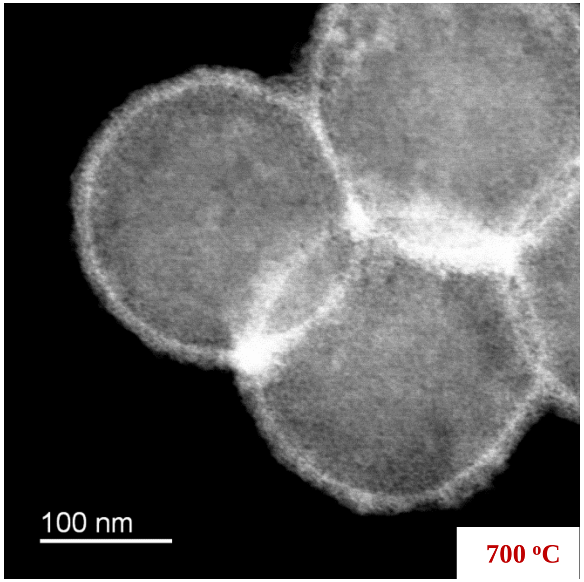


Experiment Detail: Synthesis of SiO_2@ZrO_2 core@shell Oxide Support



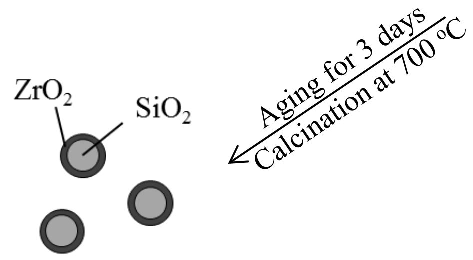
Synthesis of silica spheres

Silica core and amorphous shell with zirconium hydroxide

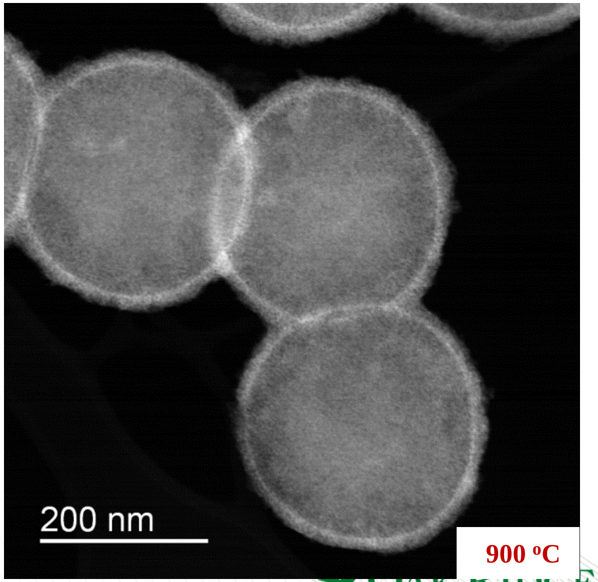


700 °C

Material	**Surface Area (m^2/g)**
ZrO_2	97
ZrO_2-SiO_2	153
SiO_2@ZrO_2	**210**
@ZrO_2	**117**



Silica core and zirconium oxide shell after calcination at 700 °C



900 °C

- **SiO_2** is located in the **core** (Si: 14 amu) and **ZrO_2** in the **shell** (Zr: 40 amu).
- The ZrO_2 **shell** seems to be **porous**.
- Growth of SiO_2@ZrO_2 spheres. Shell is maintained. Diameter at: **700 °C: ~220 nm**
  900 °C: ~250 nm

*(Brij 30): Polyoxyethylene(4) lauryl ether

Remaining Challenges and Future Work

	Accomplished	Remaining	Future Work
PGM-Free Catalyst	(1) Unique lack of inhibition demonstrated (2) Hydrothermally aged (3) Physical mixture advantage shown	(1) S exposure (2) In series and deposited Pd combination studies	(1) S studies (2) Pd combination studies (3) More fundamental studies
SiO_2-ZrO_2 Support	(1) Completed S studies of FY14 SiO_2-ZrO_2 support (2) New core-shell SiO_2@ZrO_2 catalyst made	(1) S exposure on core-shell catalyst (2) Hydrothermal aging (more) (3) Characterization (more)	(1) S studies (2) Hydrothermally aging studies (3) Characterization of core-shell
Zeolite Traps	(1) Two zeolites with and without Ag addition characterized (2) Initial mixture species effects studied	(1) Characterization of more materials (2) Hydrothermal aging (3) S exposure (4) Mixture species studies (more)	(1) Mixture species studies (2) Protocol development (3) Aging and S exposure (4) More materials