Low Temperature Emission Control to Enable Fuel-Efficient Engine Commercialization

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Advanced Combustion Engines Program
U.S. Department of Energy

ACE085
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Project Overview

Timeline

- Year 1 of 3-year program*
- Builds on previous R&D in FY13-FY15

Budget

- FY2016: $400k (Task 1*)

*Task 1: Low Temperature Emission Control

Part of large ORNL project "Enabling Fuel Efficient Engines by Controlling Emissions" (2015 VTO AOP Lab Call)

Partners

- Low Temperature Aftertreatment Sub-Team of US DRIVE Advanced Combustion and Emission Control Tech Team
- Johnson Matthey (Haiying Chen)
- BES-funded scientists
- NSF-funded scientists/students University of South Carolina
- Karlsruhe Institute of Technology

Barriers

- From DOE Vehicle Technologies Multi-Year Program Plan (2011-2015)
  - 2.3.1.B: Lack of cost-effective emission control
  - 2.3.1.D: Durability
- Overall, addressing emission compliance barrier to market for advanced fuel-efficient engine technologies

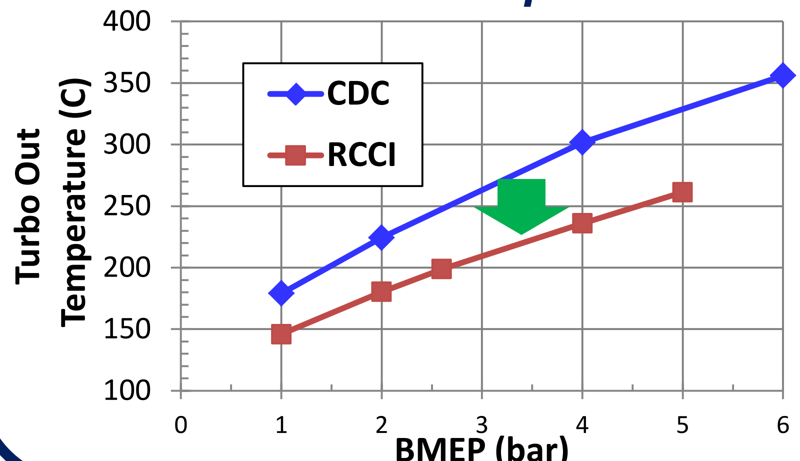
Objectives and Relevance

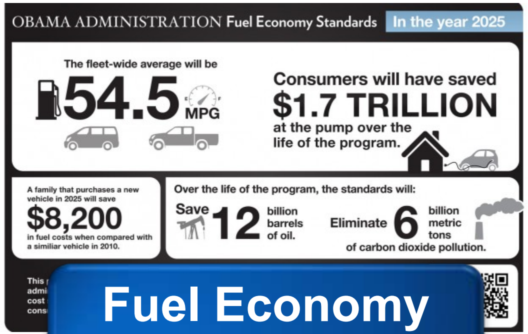
Develop new emission control technologies to enable fuel-efficient engines with low exhaust temperatures (<150ºC) to meet emission regulations

Goal: 90% Conversion at 150ºC

- Greater combustion efficiency lowers exhaust temperature
- Catalysis is challenging at low temperatures
- Emissions standards getting more stringent

Higher efficiency engines have lower exhaust temperatures*





Fuel Economy Standards

Fuel Economy

54.5 mpg CAFE by 2025

Emissions

EPA Tier 3 Emission Regulations

2017-2025 (phased in)

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

Relevance: Guiding Documents Define Needs

2015 CLEERS Industry Priorities Survey

USDRIVE "The 150ºC Challenge" Workshop Report

USDRIVE ACEC Tech Team Roadmap (2013)

Identified Needs Addressed:

- Lower temperature CO and HC oxidation
- Low temperature NOx reduction
- Cold start emission trapping technologies
  - Especially passive NOx adsorbers
- Reduced PGM
- Better durability
- Promote innovative catalytic solutions via partnering with DOE BES programs

Relative to all combustion approaches cited in ACEC Tech Team Roadmap

Low Temperature Combustion (LTC)

Dilute Gasoline Combustion

Clean Diesel Combustion (CDC)

Approach: employ low temperature protocols to evaluate novel catalysts

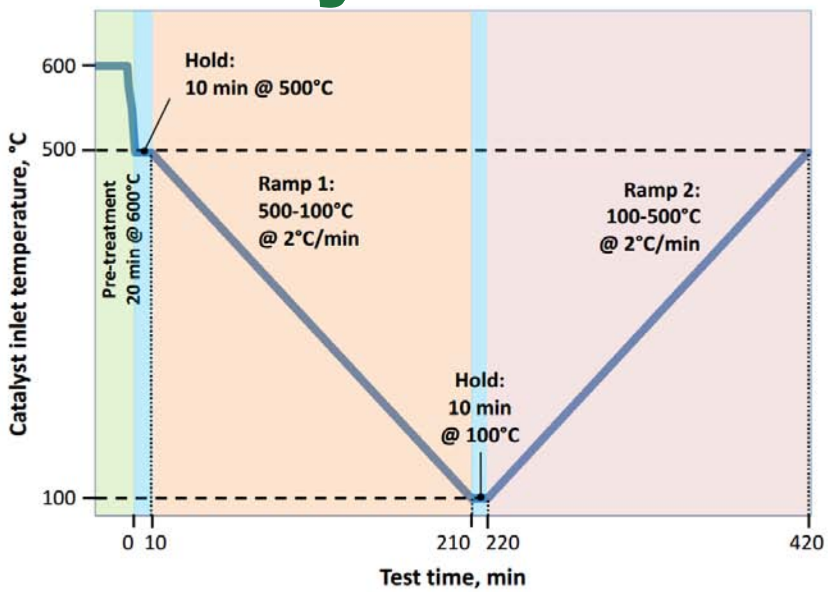
- Protocols finalized in June 2015 by the Low Temperature Aftertreatment Sub-Team of the US DRIVE Advanced Combustion and Emission Control Team
- Full file at: www.CLEERS.org

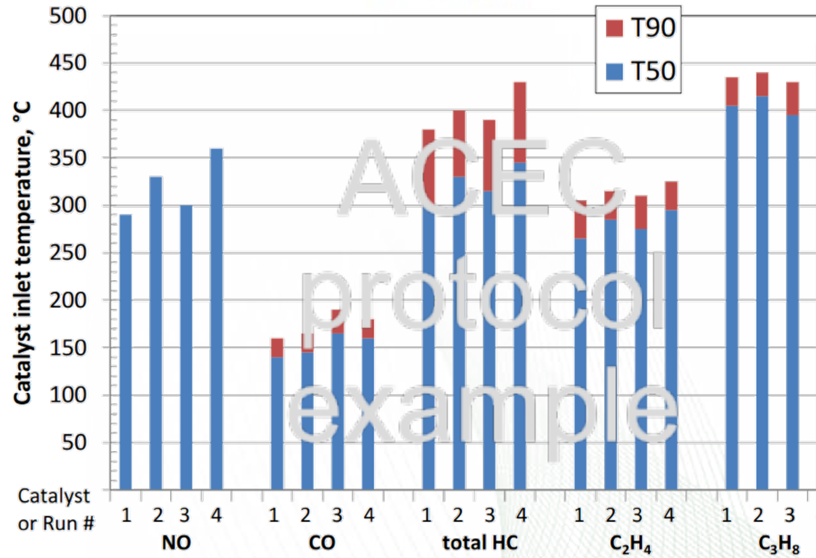
LTC-D: Low Temp. Combustion Diesel

Total HC:	3000 ppm
C_2H_4:	1667 ppm
C_3H_6:	1000 ppm
C_3H_8:	333 ppm
CO:	2000 ppm
NO:	100 ppm
H_2:	400 ppm
H_2O:	6 %
CO_2:	6 %
O_2:	12 %
Balance N_2	

Powder Catalyst Requirements

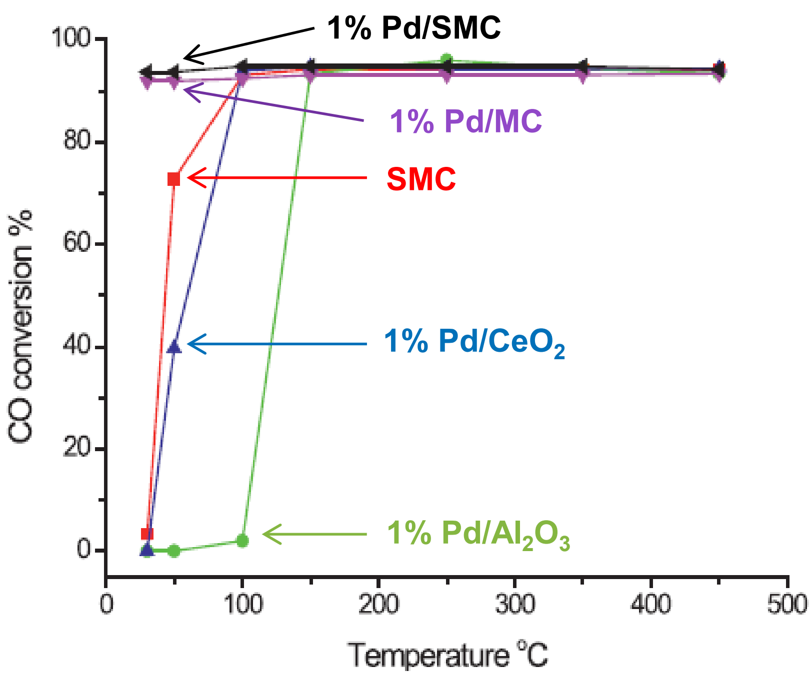
- Reactor ID 3-13 mm
- Catalyst particle size ≤ 0.25 mm (60 mesh)
- Catalyst bed L/D ≥ 1
- Space velocity
  - 200-400 L/g-hr
  - For 0.1 g sample, flow 333-666 sccm

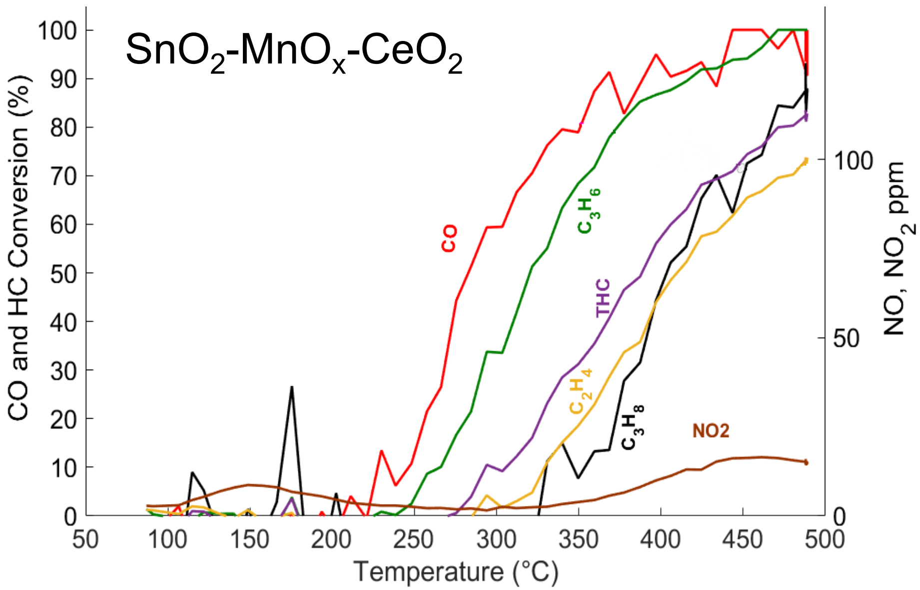




Approach: identify candidates through independent research and collaborations with NSF- and BES-funded scientists

- Initial data* from U. South Carolina shows good CO and propylene (not shown) activity
  - simple conditions, not full protocol
  - MC: MnO_x-CeO_2
  - SMC: SnO_2-MnO_x-CeO_2
  - Also evaluated with 1% Pd
- Through a collaboration, catalysts evaluated under LTC-D protocol





* - C. Wang et al. Catalysis Today 258 (2015) 481–486

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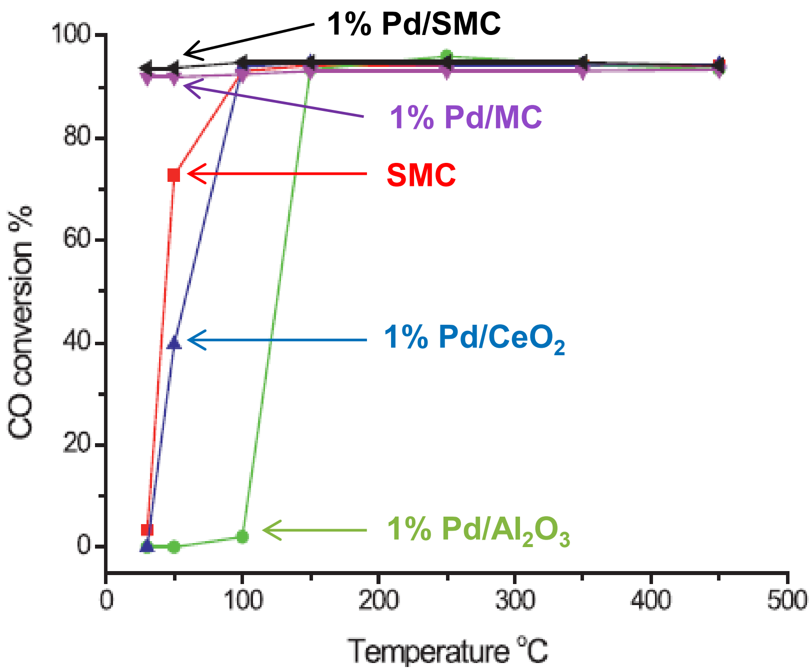
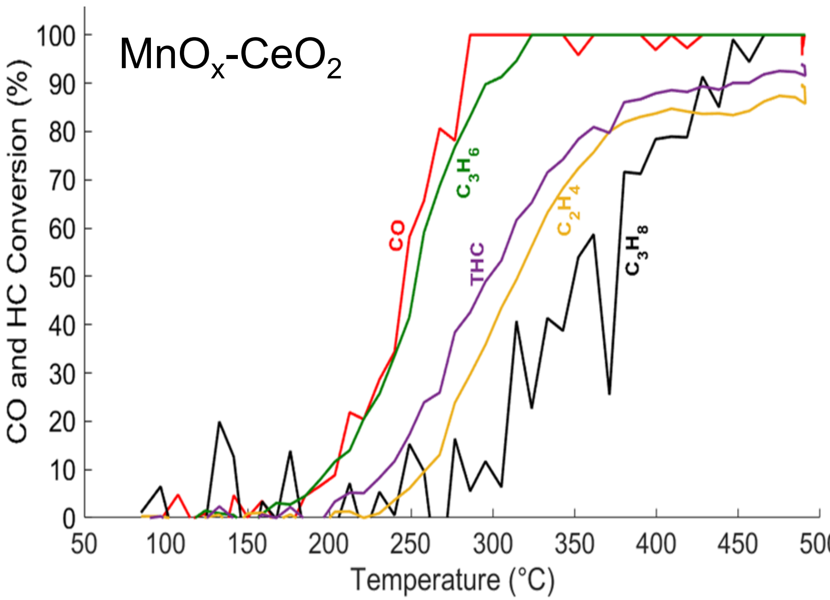
  - In general, hydrocarbon activity is promising





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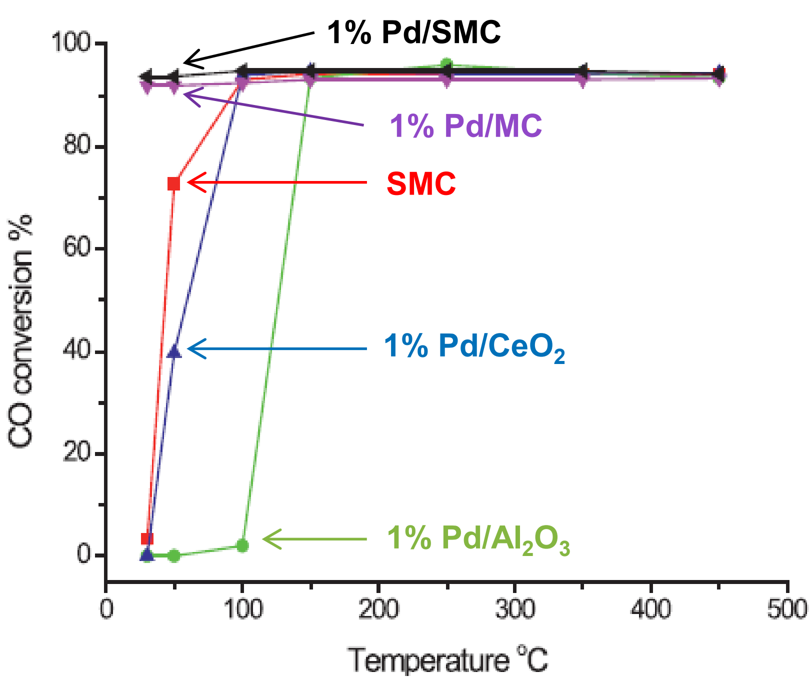
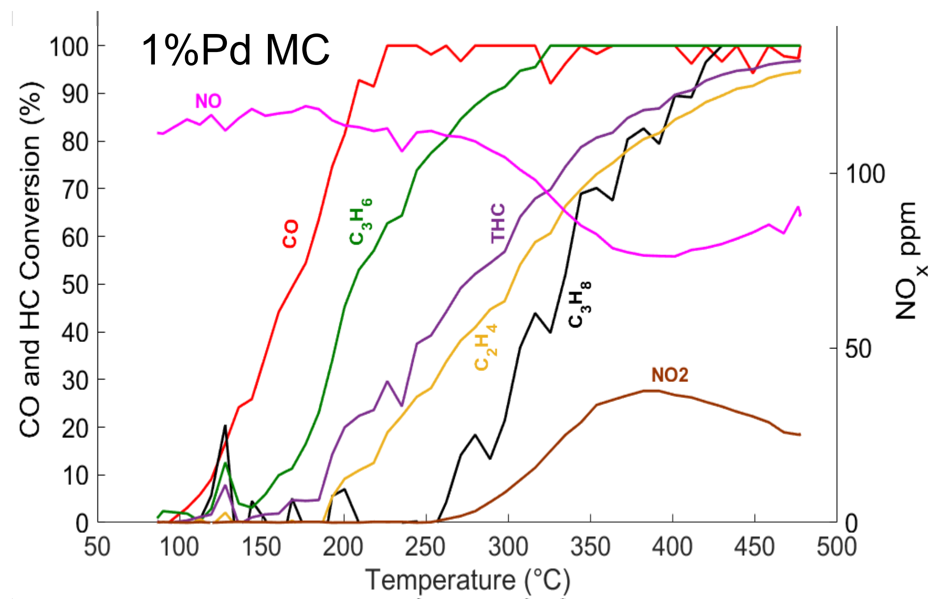


- Through a collaboration, catalysts evaluated under LTC-D protocol
  - For MC, CO and C_3H_6 reactivity muted, but good for a PGM-free catalyst
  - In general, hydrocarbon activity is promising
    - Improves further with Pd addition
- Protocols helping to elucidate strengths and weaknesses of catalysts being evaluated



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Collaborations

- **DOE Basic Energy Sciences Program**
  - Sheng Dai and Steve Overbury (ORNL), Center for Nanophase Material Science (ORNL)
- **CLEERS**
  - Dissemination of data; presentation at CLEERS workshop
- **Academia**
  - **University of South Carolina**
    - Professors John Regalbuto, Jochen Lauterbach and Erdem Sasmaz
  - **International collaborations**
    - UPMC, France (Dr. Cyril Thomas) & CNU, Korea (Prof. Sang-Wook Han), Karlsruhe Institute of Technology
- **Industry**
  - **USCAR/USDRIVE ACEC Tech Team Catalyst Sub-Team**
    - low temperature evaluation protocols
  - **Catalyst and washcoat suppliers**
    - **Johnson Matthey:** Industry input from Haiying Chen
    - **Solvay:** alumina-based supports provided for PGM support studies at USC (Barry Southward)
- **Other DOE-funded FOA Projects**
  - **Ford**-led project: Next Generation Three-Way Catalysts for Future, Highly Efficient Gasoline Engines
    - Catalysts being investigated for stoichiometric applications
  - **UCONN**-led project: Metal Oxide Nano-Array Catalysts for Low Temperature Diesel Oxidation

Milestones

- **FY15 Milestones:**
  - {Key SMART milestone} Investigate individual roles of the components in the CuCoCe ternary oxide and potential synergies with standard emissions control components (12/31/2014) ***complete***
  - Identify candidate materials for NH_3 SCR catalysts that are active at low temperatures (9/30/2015) ***complete***
    - Intended as an identification of catalysts being studied in the literature and through fundamental studies, not as an experimental campaign
    - Identified MnOx-based catalysts to be the only materials to show significant activity below 150°C…as low as 110-120°C [1,2]; concerns regarding thermal durability.
- **FY16 Milestones:** ***on track***
  - Report on evaluation of CCC+PGM emissions control studies including implementation of full ACEC low temperature protocol (9/30/2016).

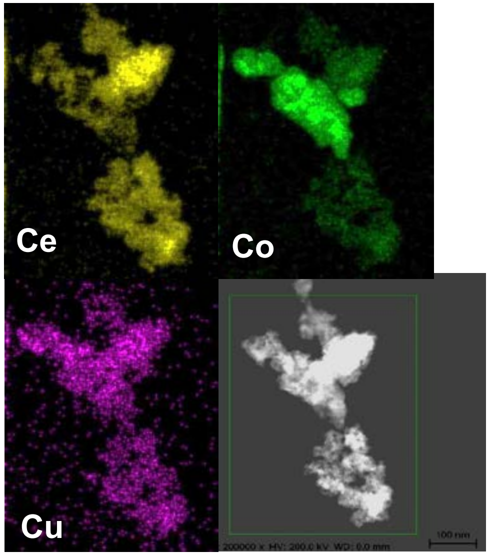
[1] G. Qi, R.T. Yang, "Performance and kinetics study for low-temperature SCR of NO with NH_3 over MnO_x-CeO_2 catalyst," Journal of Catalysis 217 (2003) 434-441.
[2] P.G. Smirniotis, P.M. Sreekanth, D.A. Peña, R.G. Jenkins, "Manganese Oxide Catalysts Supported on TiO_2, Al_2O_3, and SiO_2: A comparison for Low-Temperature SCR of NO with NH_3," Industrial & Engineering Chemistry Research 45 (2006) 6436-6443.

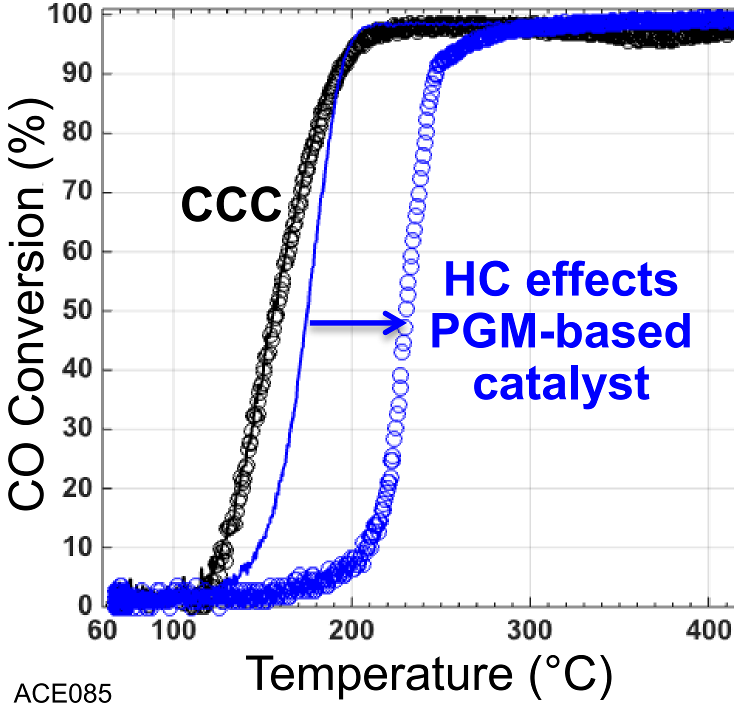
Technical Accomplishments

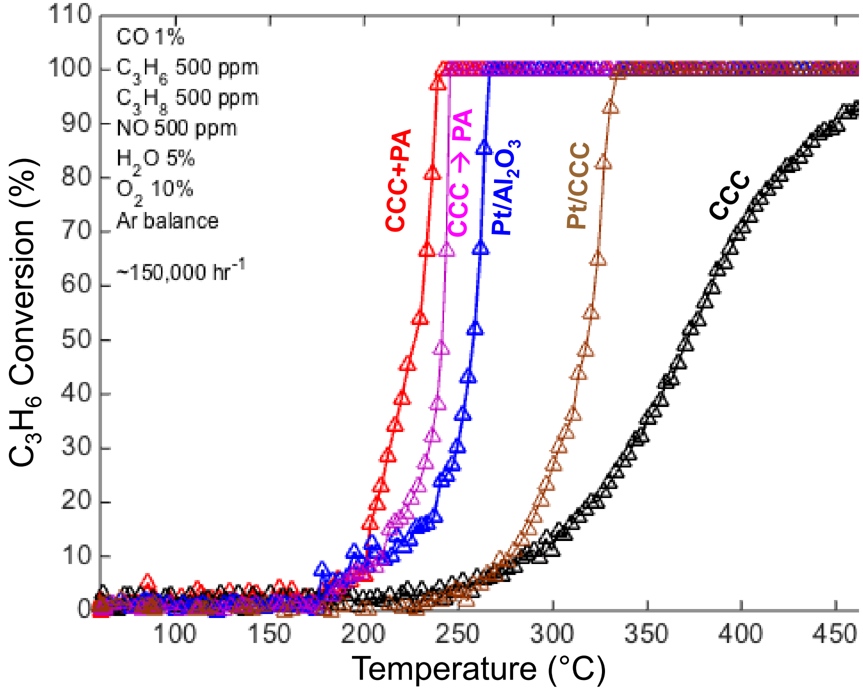
- PGM-free mixed metal oxides
  - Identified new mixed metal oxide candidate (USC) that has improved HC activity (Sn-Mn-Ce and Mn-Ce)
  - Measured sulfur tolerance of CCC while also exploring mitigation strategies with PGM
- Support modifications for enhanced PGM activity
  - New core@shell technique employed to maximize ZrO_2 surface for PGM catalysis shown to yield improved activity especially for THC
  - Successfully implemented nano-on-nano technique with Pd dispersed on nanoparticles of Ce-Zr dispersed on Al_2O_3; high activity observed, approaching targets for some gases
- Trapping materials
  - Determined key attributes of silver-alumina HC trap; deep ion exchange and low Si:Al
  - Demonstrated NO adsorption on Pd/ZSM-5; impact of pretreatment temperature

Mixed metal oxide has shown interesting chemistry and some promise without PGM

- CuO_x-CoO_y-CeO_z (CCC) promising for CO oxidation
  - Interfacing crystalline regions of Co_3O_4 and CeO_2
  - Cu in lattices of both Co_3O_4 and CeO_2 evenly
  - CO oxidation unaffected by HC
- Need additional catalyst for low-temp. HC oxidation
  - Aids HC oxidation over Pt/Al_2O_3 in physical mixture

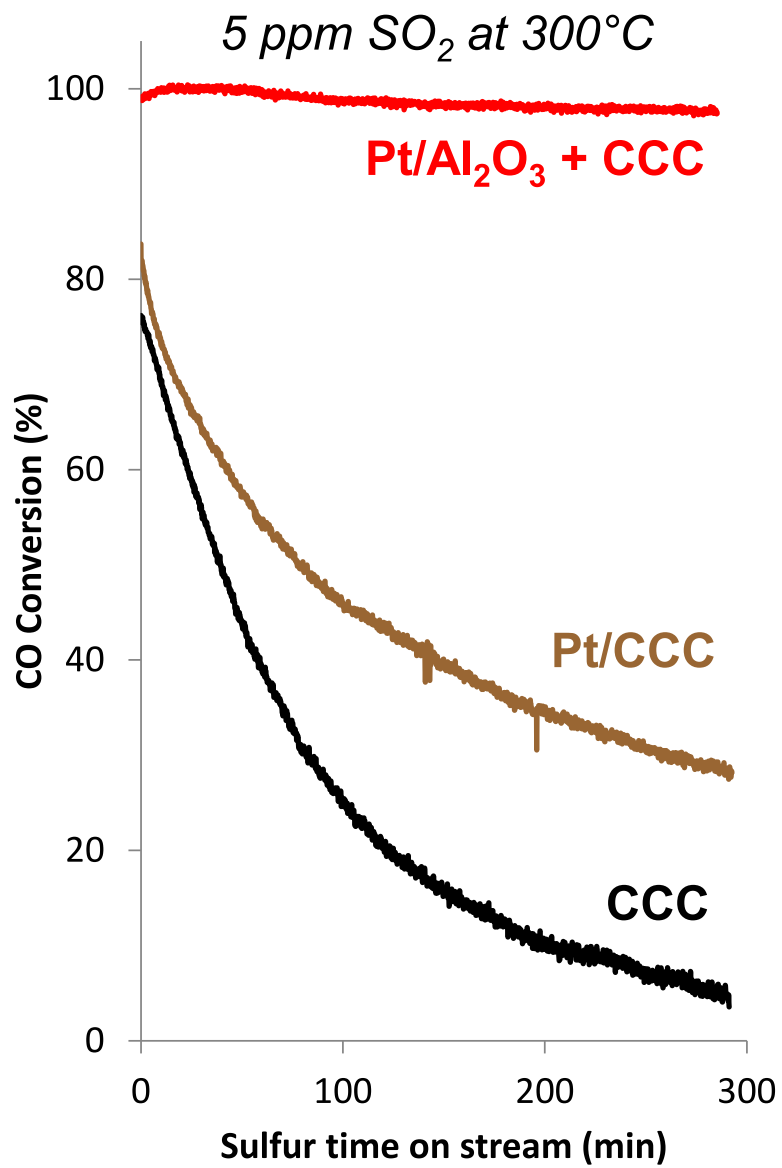






Inclusion of PGM improves sulfur tolerance and sulfur removal of CCC

- Employed ACEC protocol for sulfur poisoning
  - Flow 5 ppm SO_2 at 300°C for 5 hours
  - 200 L/g-hr (GHSV ~300,000 h^{-1})
    - Dense catalyst results in small volume
- Significant deactivation observed if Pt/Al_2O_3 not included



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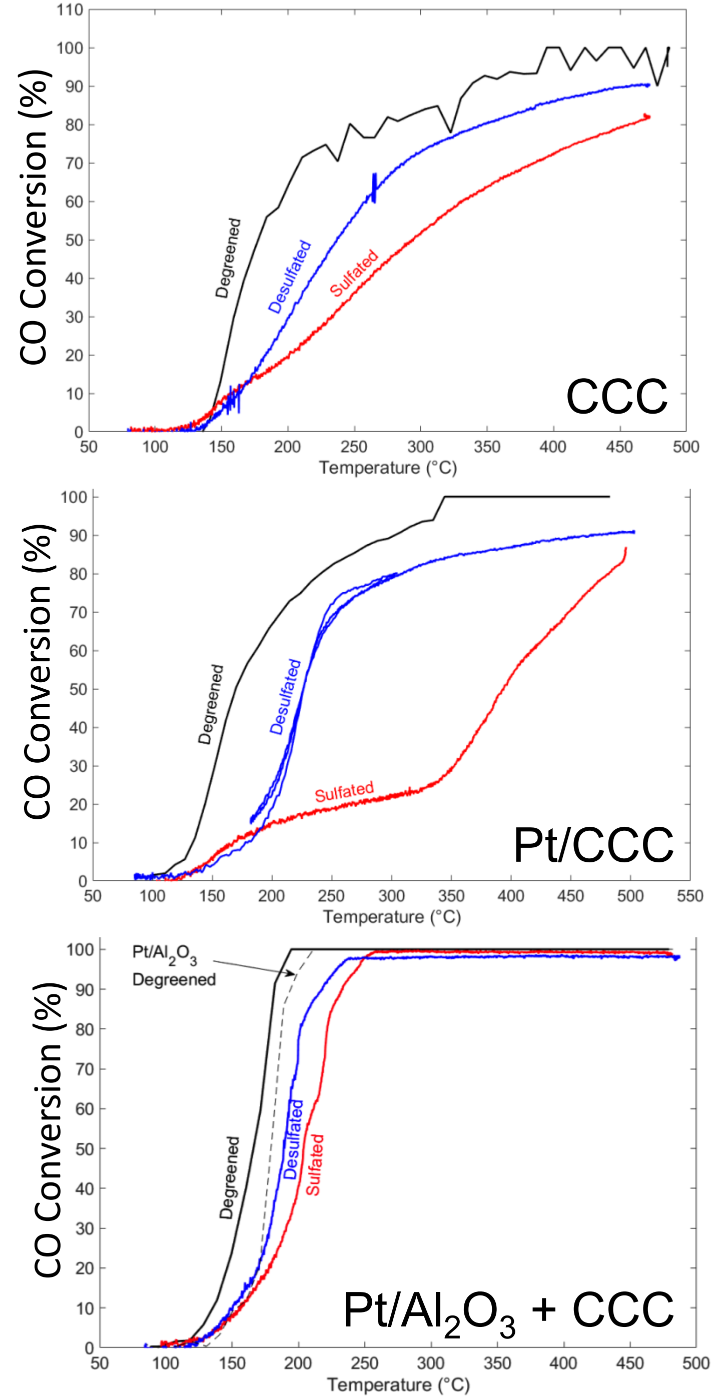
- After sulfation, ramp under LTC-D conditions to investigate full reactivity
- Desulfation attempted at 600°C under cycling lean and rich conditions
  - 10% O_2 and 1% H_2
  - 30 seconds each, 30 minutes total
- Results show the presence of Pt help protect/recover activity of the catalysts
  - Unclear if CCC has role as desulfated evaluation behaves similar to Pt/Al_2O_3



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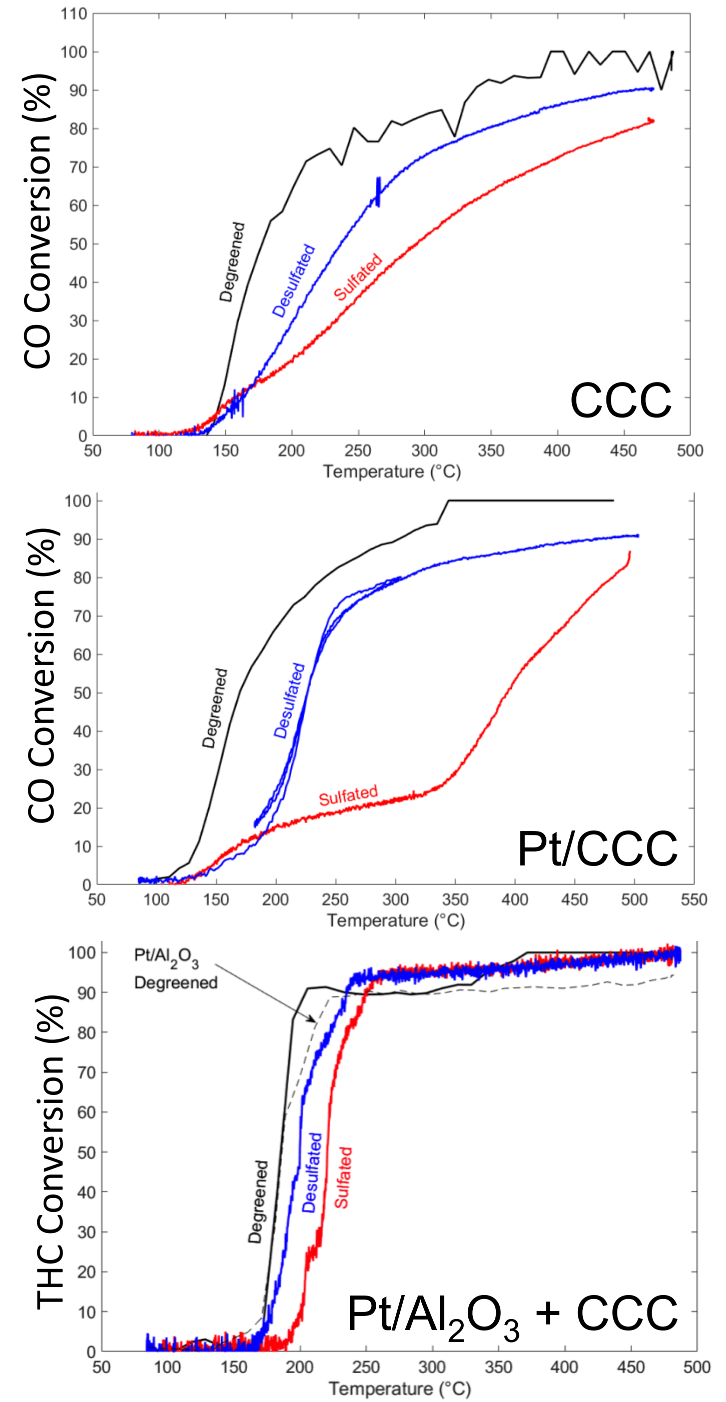

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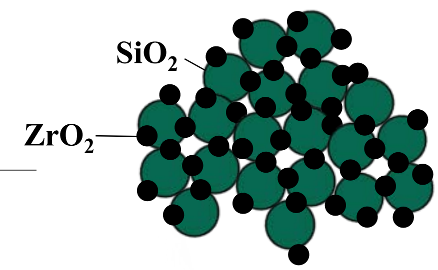
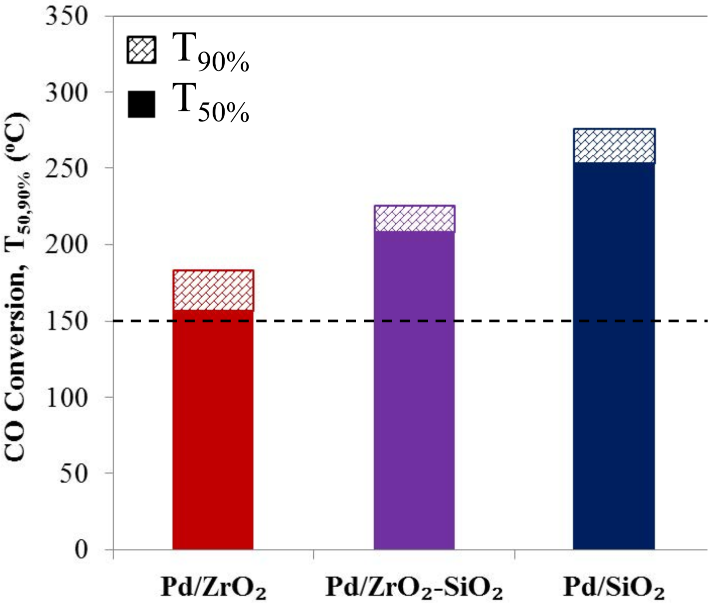
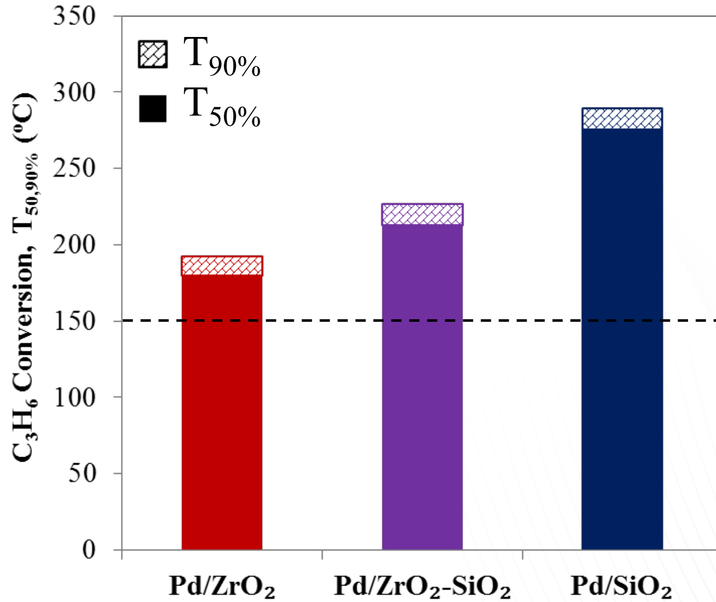
ZrO_2 support has shown excellent activity with Pd catalyst; efforts to improve ongoing

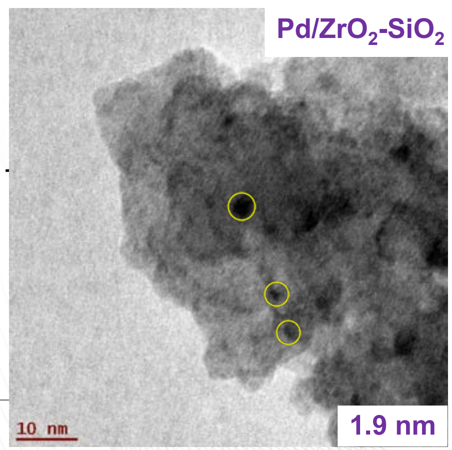
- Pd/ZrO_2 has good activity, excellent thermal durability, good S tolerance
- Goal: further improve activity and sulfur tolerance
  - Support ZrO_2 on high surface area SiO_2
- Initial effort not successful as Pd/ZrO_2 still more active
  - not a monolayer; 15% coverage of SiO_2 surface
  - Pd dispersed on both ZrO_2 and SiO_2

ZrO_2-SiO_2 mixed oxide









Kim et al. Applied Catalysis B: Environmental 187 (2016) 181–194.

New synthesis technique successfully creates ZrO_2 shell around SiO_2 core

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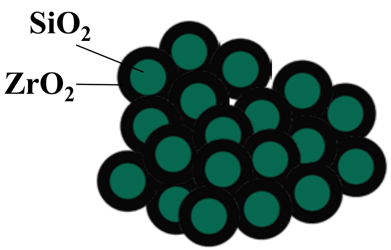
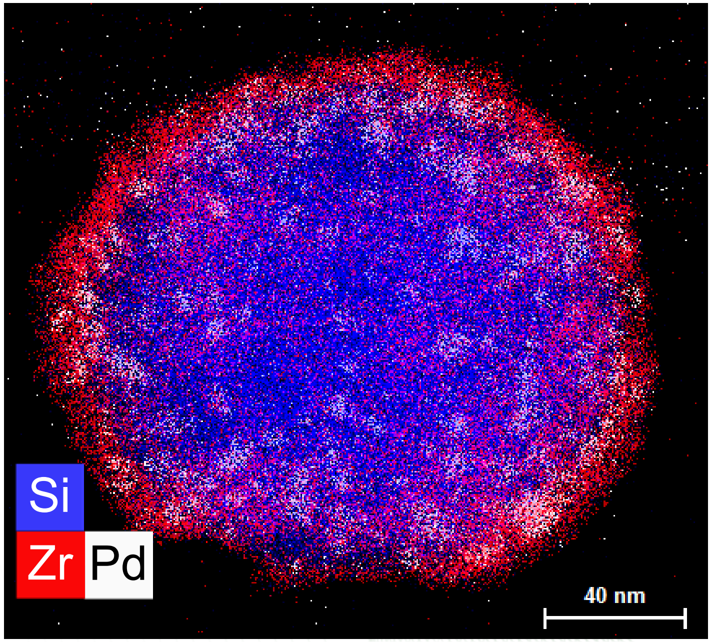
ZrO_2-SiO_2 mixed oxide





This research was performed, in part, using instrumentation (FEI Talos F200X S/TEM) provided by the Department of Energy, Office of Nuclear Energy, Fuel Cycle R&D Program and the Nuclear Science User Facilities.

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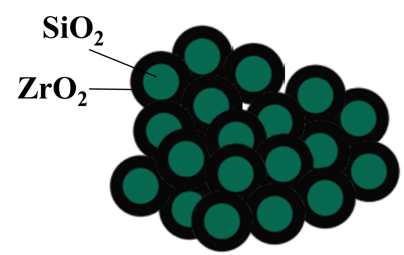

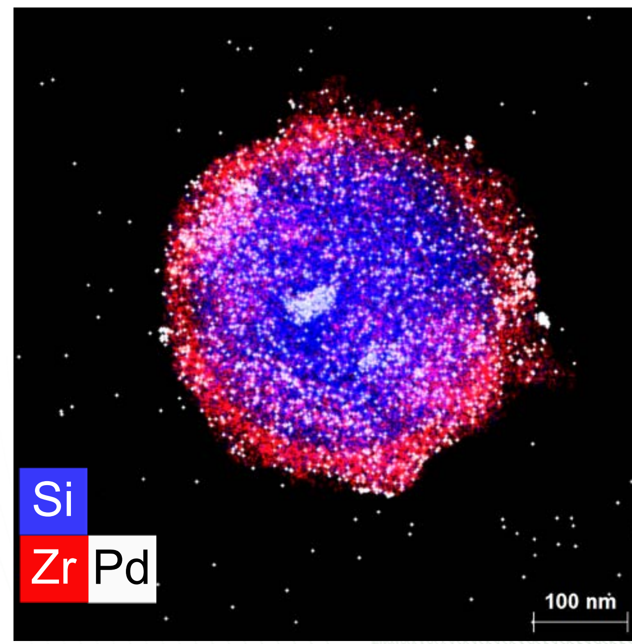

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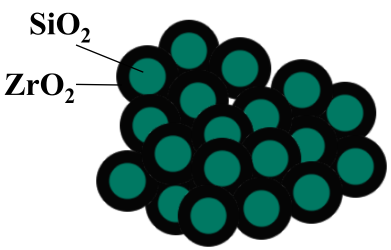

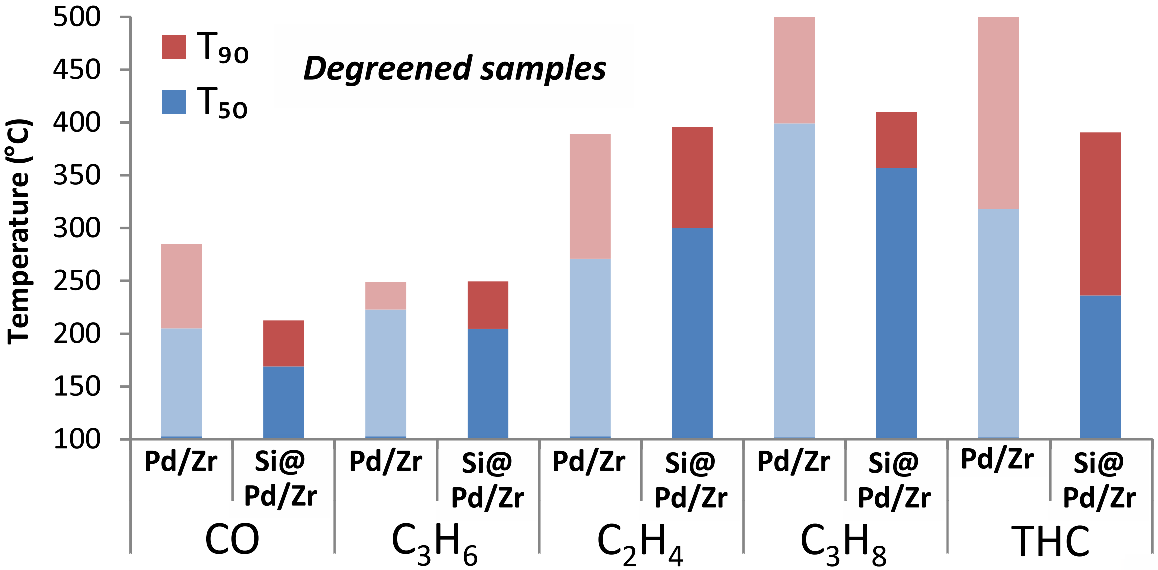

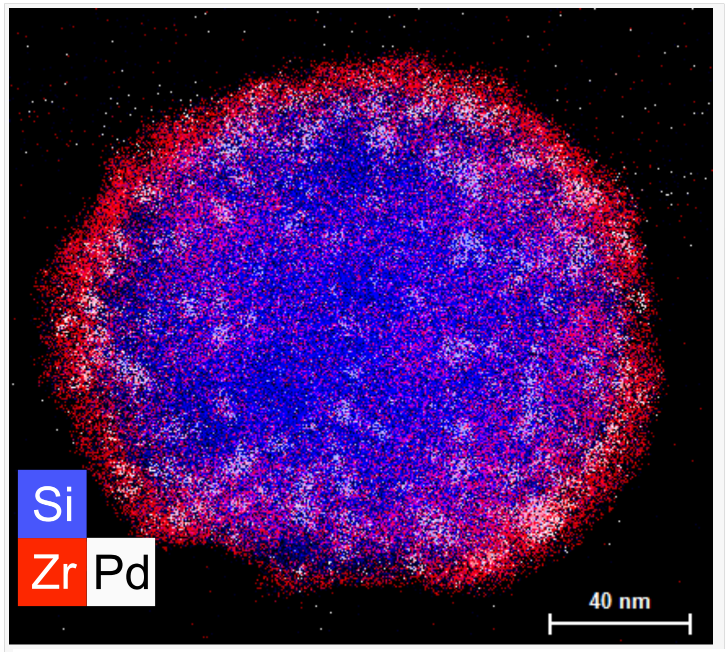

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  - Pd (1 wt%) deposition solely on ZrO_2 outer shell
- While employing ACEC low temperature protocols improved activity shown with this technique
- Robust after aging at 900°C for 10h
  - Improved initial dispersion technique still needed

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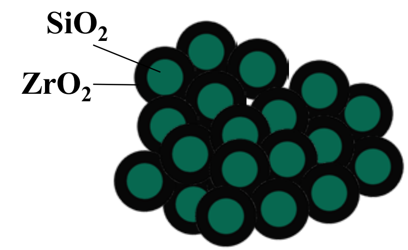
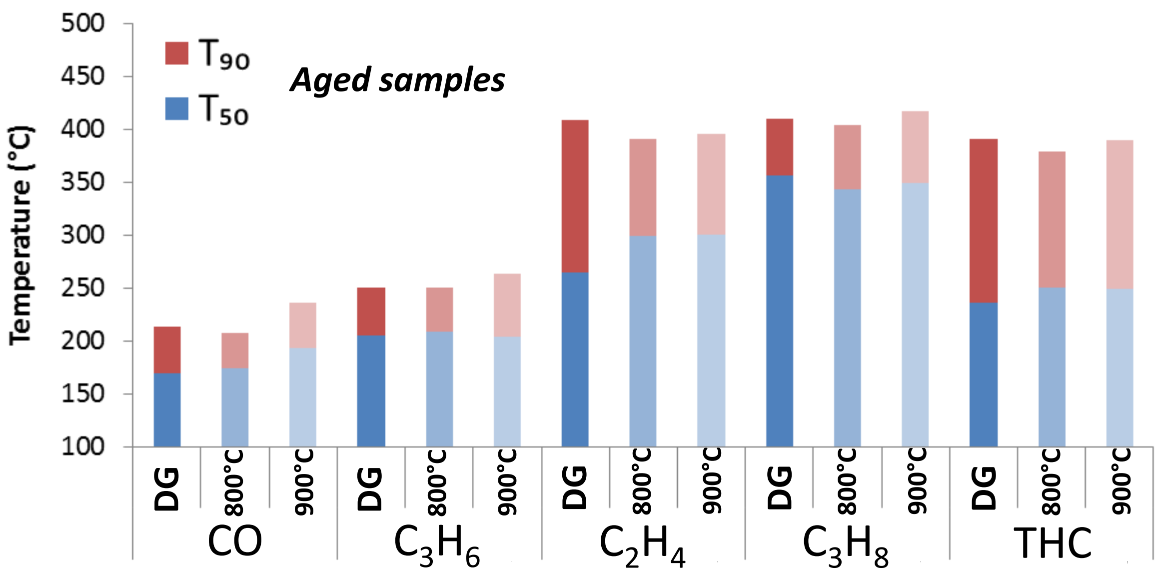
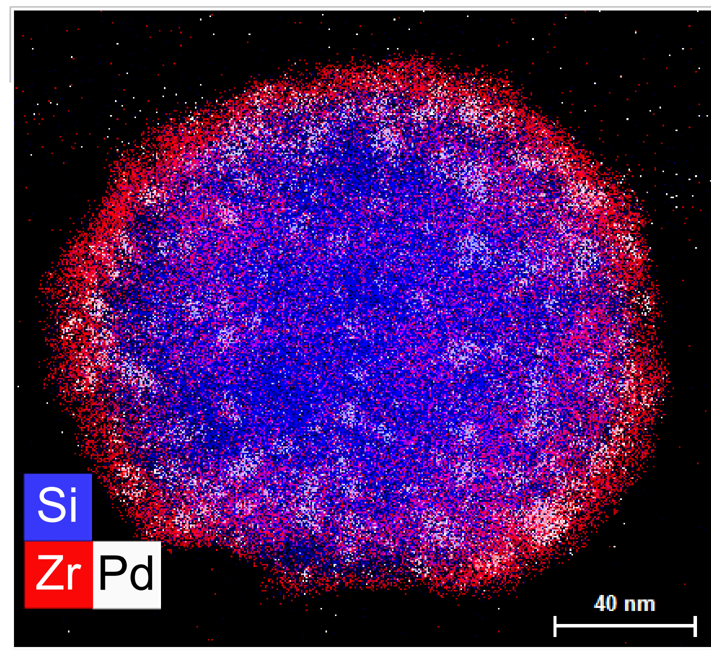




DG = Degreened



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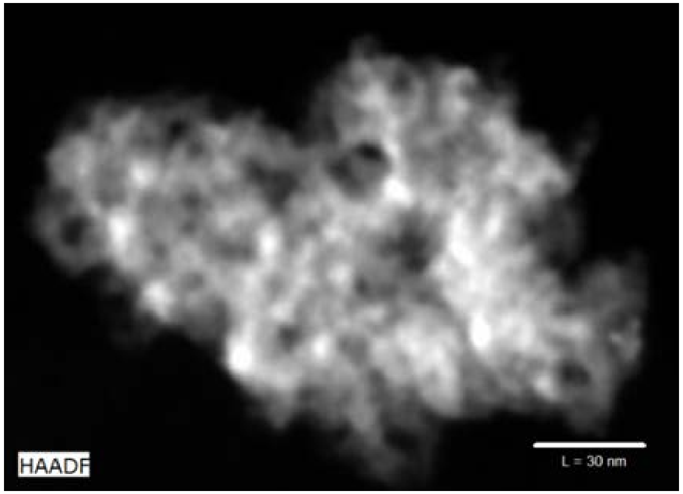
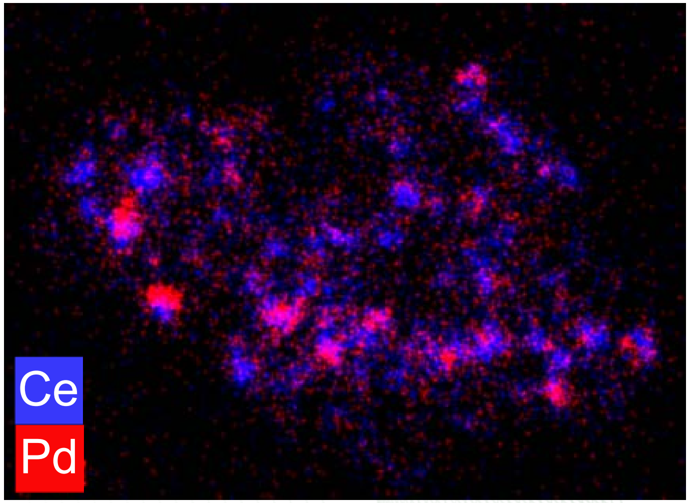
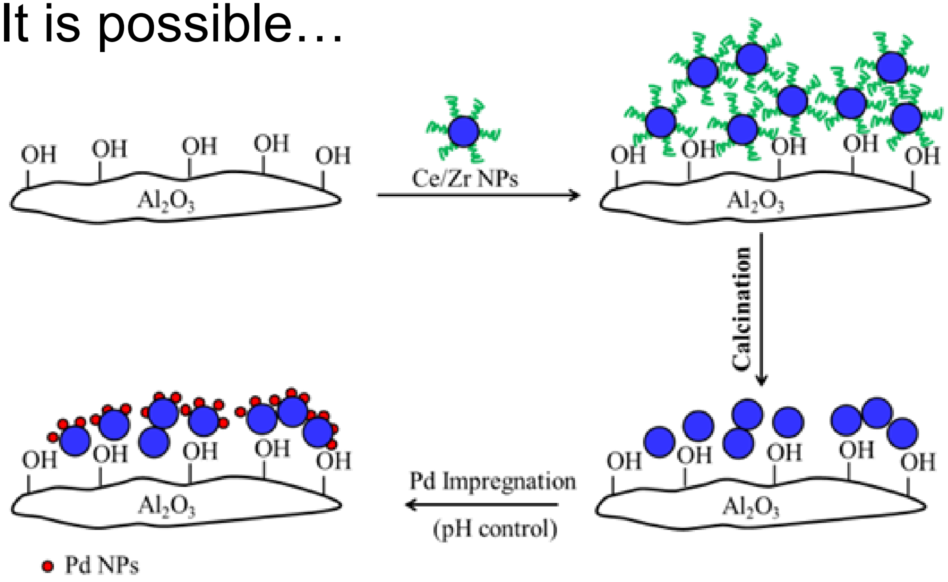
Targeted PGM deposition on Ce-Zr nanoparticles also investigated

- Starting with CeZr nanoparticles, ~5 nm, anchor them to high surface area supports
  - In this instance Al_2O_3, but SiO_2 also possible
- Target Pd deposition on preferred supported metal oxide
  - nano-particles of PGM on nano-particles of Ce-Zr
  - Controlling pH enables targeted deposition
- It is possible…







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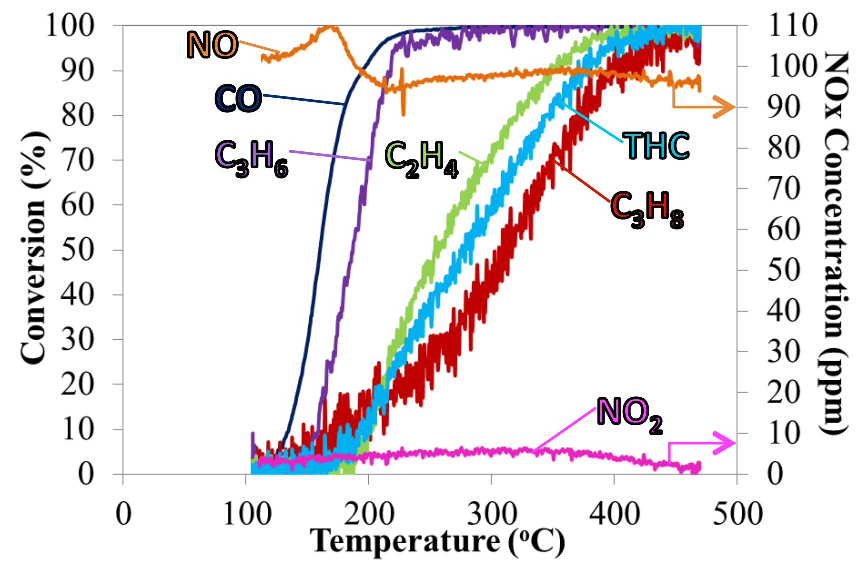
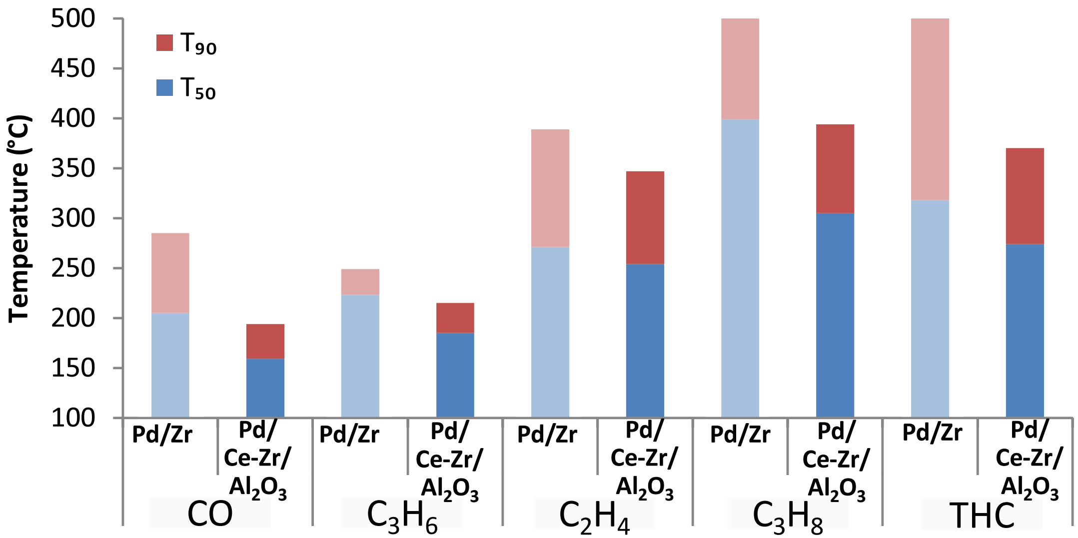
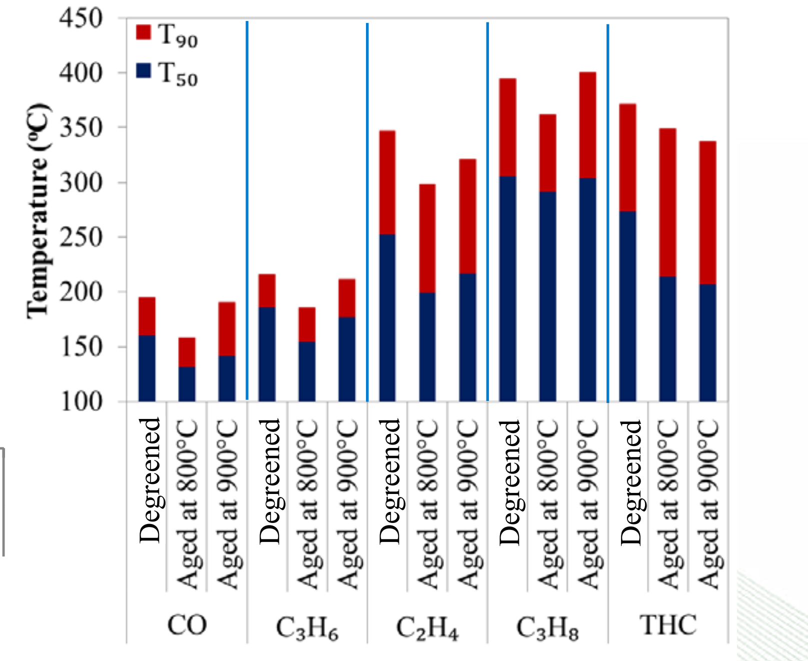
Pd/Ce-Zr/Al_2O_3 catalysts show promise

- Good activity being observed
  - Degreened, 4wt.% Pd/Ce-Zr/Al_2O_3
    - Pd nano-particles on Ce-Zr nano-particles
  - Also, tolerant to hydrothermal aging
    - THC oxidation improves after 900°C
- However, meeting 150°C target still challenging, especially for C_2H_4 & C_3H_8







Pd/ Zr only has 1% Pd

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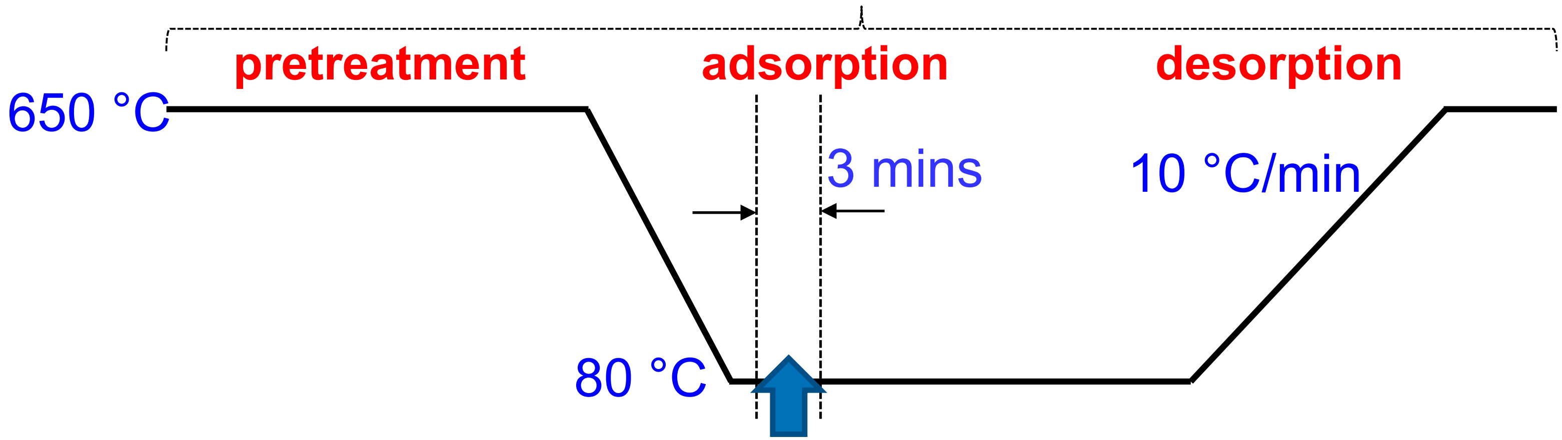
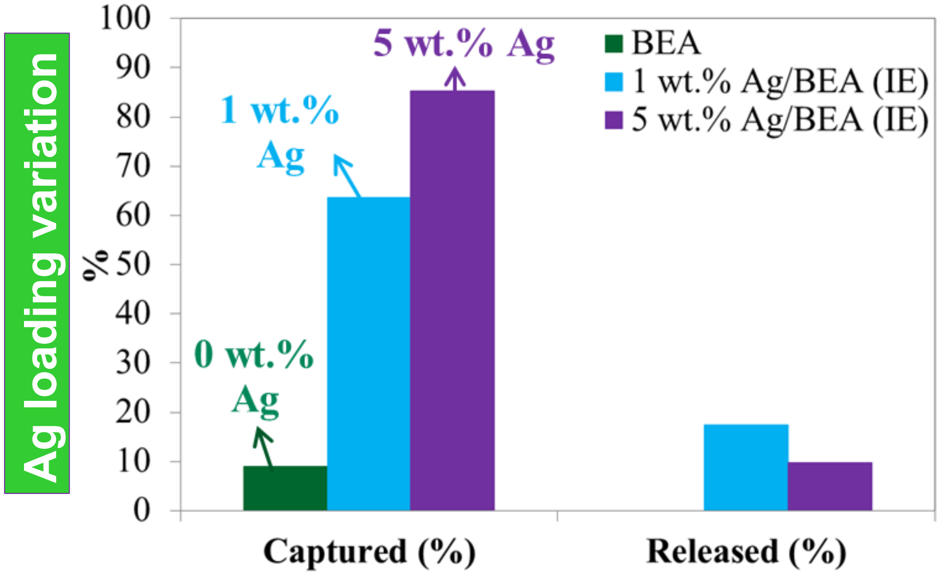
Ion-exchanging and Ag loading key factors in HC adsorption in the presence of H_2O

Base gas: 10% O_2 and 5% H_2O

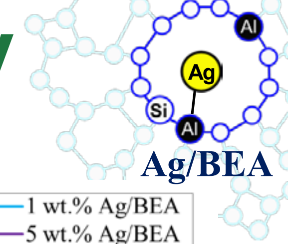


500 ppm HC (C_1 basis), 200 ppm NO, 200 ppm CO



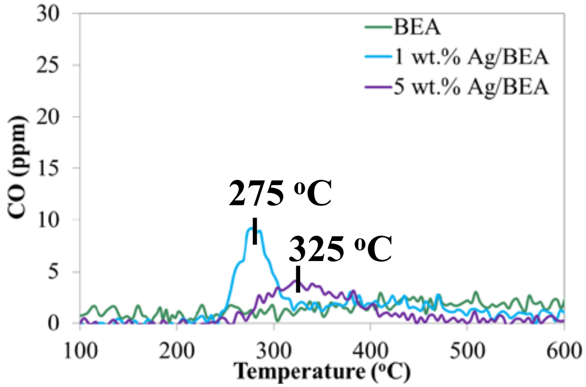
- NO does not adsorb significantly
- C_3H_6 adsorption requires **ion-exchanged sites** in the zeolite
- **Higher Ag loading** results in higher C_3H_6 adsorption/ desorption
- Release is complicated

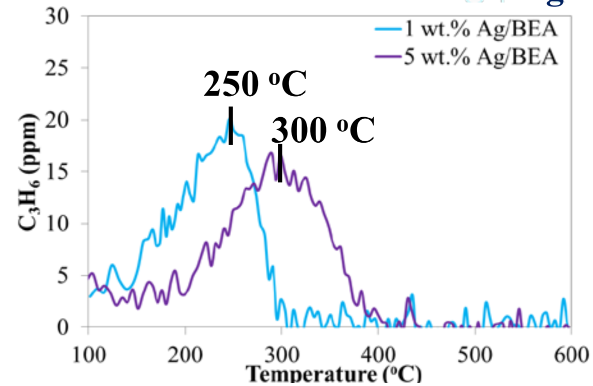
Release profile indicates significant reactivity of stored HC and varies with Ag loading

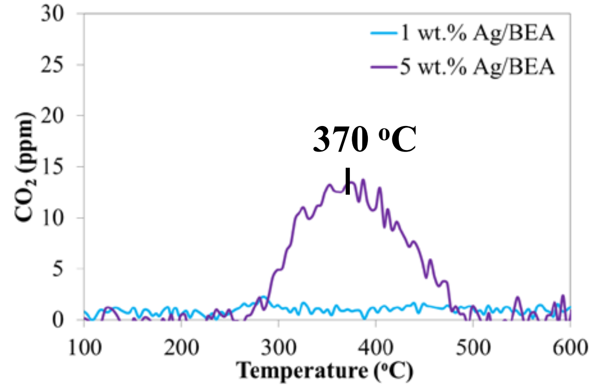


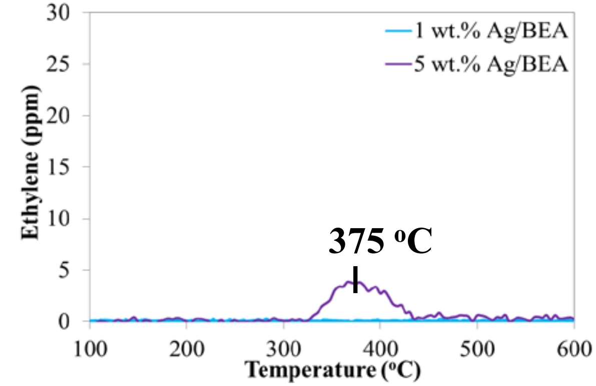
Stored C_3H_6 is released as:

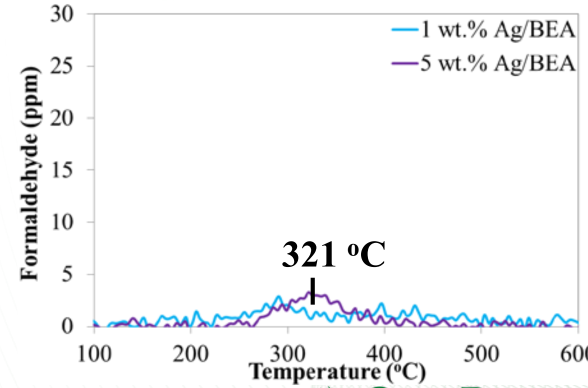
- CO → **BEA-zeolite**
- CO, C_3H_6 → **1 wt.% Ag/BEA**
- CO, C_3H_6, CO_2, ethylene, formaldehyde → **5 wt.% Ag/BEA**





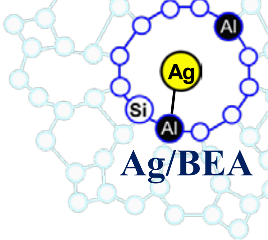


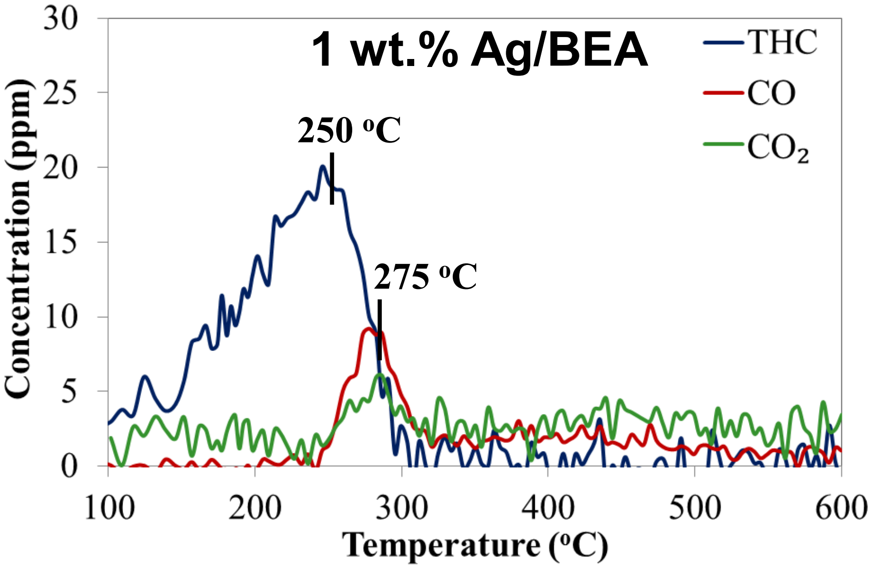




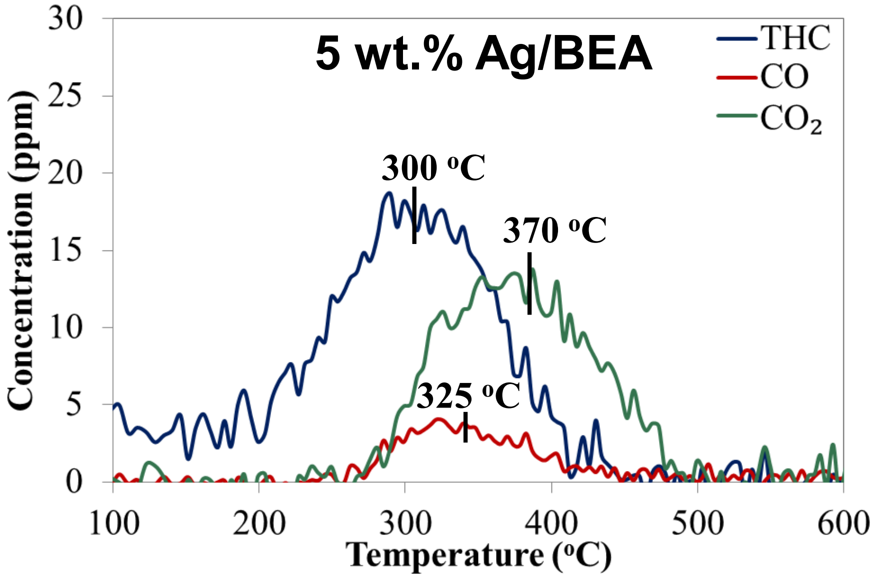
Adsorption Conditions:
C_3H_6: 167 ppm, O_2: 10%, H_2O: 5%, NO: 200 ppm, Total Flow: 300 sccm, SV: 90,000 h^{-1}
Desorption Conditions:
O_2: 10%, H_2O: 5%, Ar balance

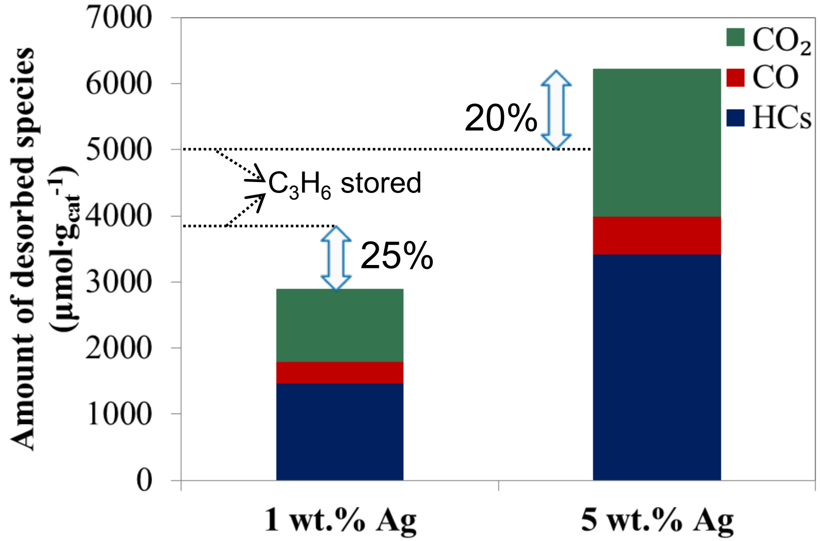
Release profile indicates significant reactivity of stored HC and varies with Ag loading





- C_3H_6 is released mainly as HCs followed by smaller amounts of CO_2 and CO.
- The desorption T of C_3H_6 is lower for lower Ag loading.





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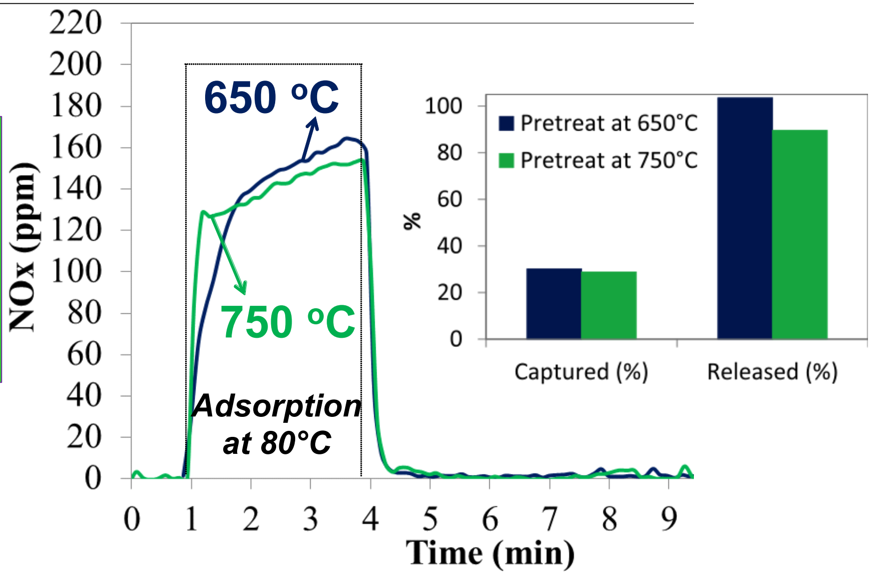
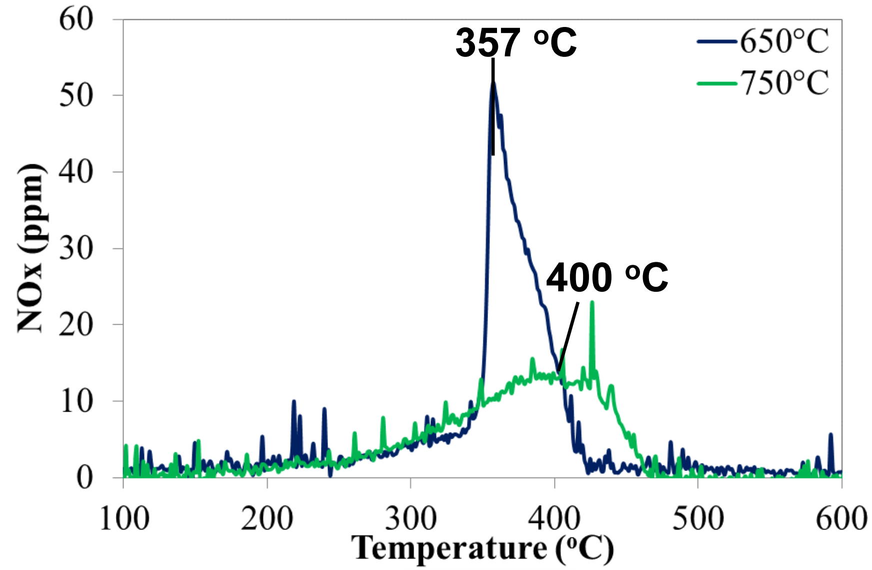
Pd/ZSM-5 stores both NO and HC; pretreatment temperature affects NO release

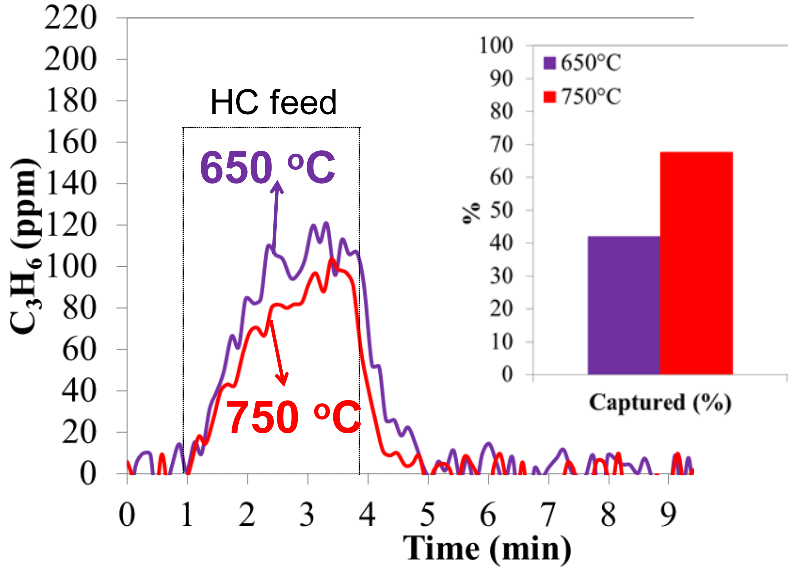
Adsorption



Desorption

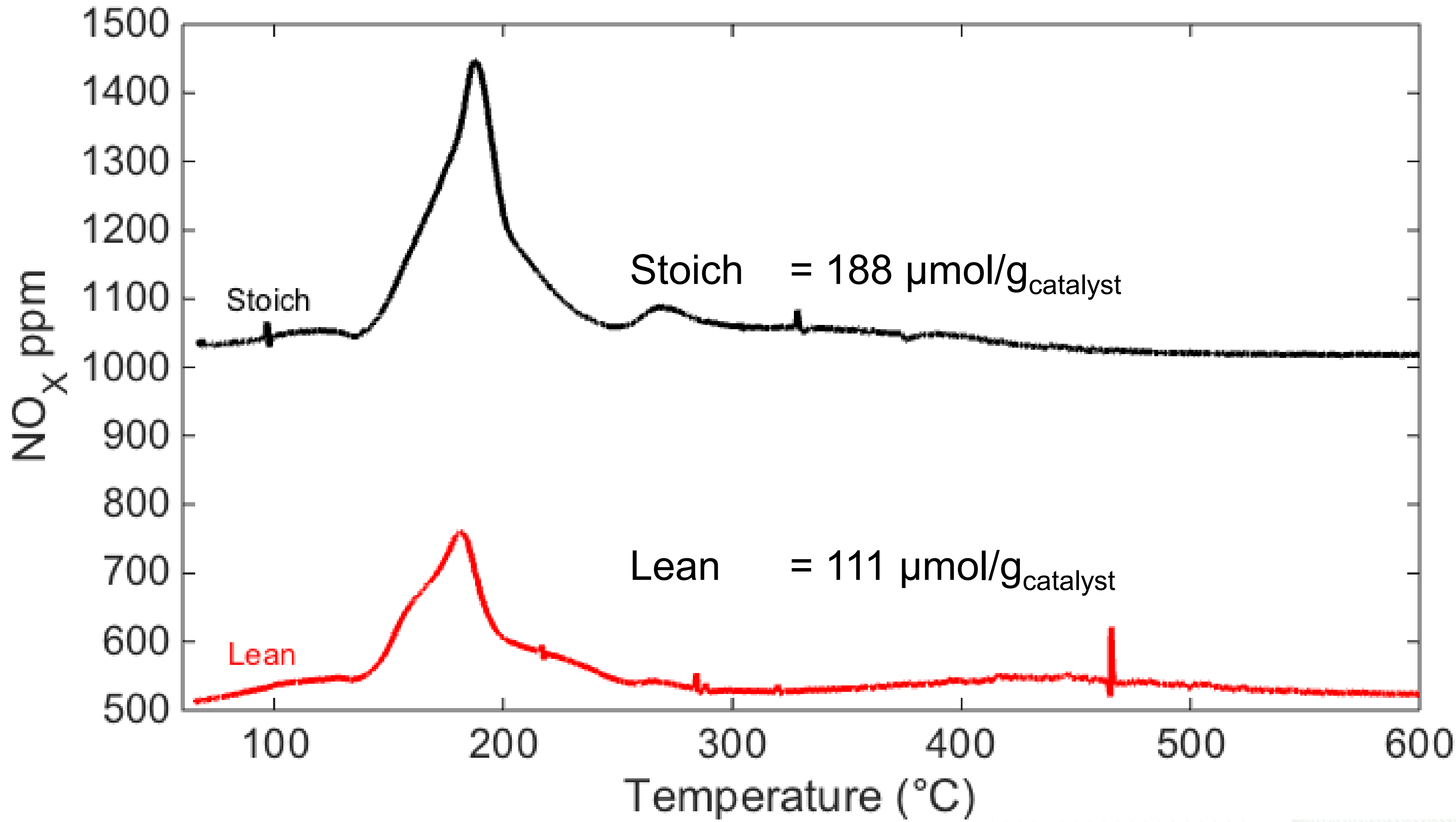


Adsorption



- Pd/ZSM-5 key attribute is the ability to store both NO and HCs
- NO release profile affected by pretreatment
  - Materials characterization needed to explain effect
- HC capture is similar to Ag-BEA
  - Release profile data incomplete

CCC also shows the ability to store and release NO at low temperatures while flowing full simulated exhaust streams



Preliminary data

Remaining Challenges

Future Directions

- **PGM-free mixed metal oxides**

Remaining Challenges	Future Directions
Overall activity needs to be improved, especially for hydrocarbons	Identify and increase active sites on CCC through systematic synthesis; expand collaboration w/USC (Sn-Mn-Ce oxide)
Sulfur tolerance needs to be improved and strategies for removal need to be identified	Investigate S interactions in physical mixture w/ PGM catalyst; find minimum PGM needed to mitigate S impact

- **Support modifications for enhanced PGM activity**

Remaining Challenges	Future Directions
Overall activity needs to be improved, especially for C_2H_4 and C_3H_8	Initial dispersion of PGM to be improved; new techniques (precursor, pH, reduction step); **Begin Pt + Pd + Rh studies**
Sulfur tolerance has not been demonstrated on new samples	Implement ACEC S protocol for new samples; initial samples showed good recovery at low temperatures

- **Trapping Materials**

Remaining Challenges	Future Directions
Trapping efficiency needs to be improved for both NO and HC	Increase active sites w/ higher loadings and more complete ion-exchange
Demonstration of effectiveness when mixed with oxidation catalysts has not been shown	Explore effectiveness with best catalysts from other areas; implement new ACEC trapping protocols (when published)

Responses to 2015 Reviewers (3)

- **Approach (3.67/4.0):** steps taken are logical …process and techniques of evaluating the material are excellent …[need to] **expose the candidate catalysts to hydrothermal aging and sulfur poisoning** … **exhaust approach and test protocol critical to move into practical application**
- **Technical Accomplishments (3.33/4.0):** very high caliber work … new approach delivering results, good start … **begun the SCR work but show no plans or data** … findings have been very insightful … **more involvement from catalyst suppliers would be sensible** … **sulfur exposure on the CCC catalysts**
- **Collaborations (3.33/4.0):** collaborators have the needs covered, excellent … **more regular technical interactions with industrial partners** … **reaching out to additional catalyst suppliers could be beneficial**
- **Future plans (3.33/4.0):** future work was clear and consistent with the remaining challenges and the overall target path…. sound technical path forward … **sulfur studies are very critical for CCC and long overdue** ... **effect of sulfur should be the top priority**…. **design of experiment technique should be considered to speed up the project**
- **Relevance (100%):** addresses a key enabling issue with regards to low-temperature combustion engine technology … low-temperature catalysts with high efficiencies and durability is a critical enabler for advanced engine technologies
- **Resources (33% Insufficient):** **resources sufficient for HC/CO oxidation work, but likely not enough for SCR work** … **much on HC remediation, unless more resources are added, the project will miss the NH_3 SCR goals**

Responsive Actions
1. ***Sulfur* exposure and hydrothermal aging being implemented** 2. ***New ACEC protocols have been fully integrated into project***
1. ***Effort on SCR last FY was literature review not experimental work*** 2. ***Will work to engage more suppliers, especially as promising technologies are identified for fully-formulated samples*** 3. ***Sulfur now studied on CCC***
1. ***Added more partners; will engage more*** 2. ***…and catalyst suppliers***
1. ***Aging studies being performed on CCC with sulfur*** 2. ***will introduce sulfur to adsorbers*** 3. ***will consider design of experiments***
1. ***Partnering with several universities, and are aligning their fundamental studies to address challenges of low temperature catalysts*** 2. ***NH_3-SCR evaluation not currently planned***

Summary

- Relevance: These studies are targeted towards providing data and predictive tools to address gaps in information needed to enable increased use of biofuels
- Approach: Targeted, engine-based and flow-reactor studies with in-depth characterization of PM, HCs, and emissions control devices to better understand fuel and lubricant effects
- Collaborations: Wide-ranging collaboration with industry, academia, and national labs maximizes breadth of study and guides research from other funding sources
- Technical Accomplishments:
  - Identified new mixed metal oxide candidates (USC) that have improved HC activity
  - Measured sulfur tolerance of CCC while also exploring mitigation strategies with PGM
  - New core@shell technique employed to maximize ZrO_2 surface for PGM catalysis shown to yield improved activity especially for THC
  - Successfully implemented nano-on-nano technique with Pd dispersed on nanoparticles of Ce-Zr dispersed on Al_2O_3; high activity observed, approaching targets for some gases
  - Determined key attributes of silver-alumina HC trap; deep ion exchange and low Si:Al
  - Demonstrated NO adsorption on Pd/ZSM-5; impact of pretreatment temperature
- Future Work: expanding effort with new materials to increase active sites and understand interactions with sulfur; increased implementation of multi-component beds and Pt+Pd catalysts

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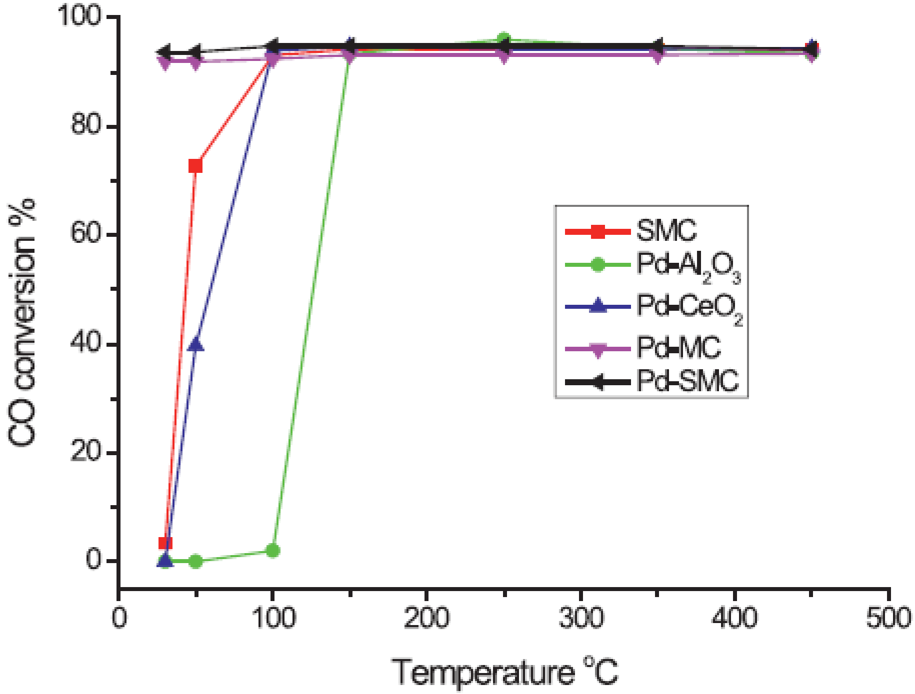
Technical Backup Slides

Evaluating Mn, Ce and Sn with good durability and HC oxidation

- Collaboration with U. South Carolina (USC)
  - MC: MnO_x-CeO_2
  - SMC: SnO_2-MnO_x-CeO_2
  - Also evaluated with 1% Pd
- Catalysts show good HC activity and durability
  - C. Wang et al. Catalysis Today 258 (2015) 481–486



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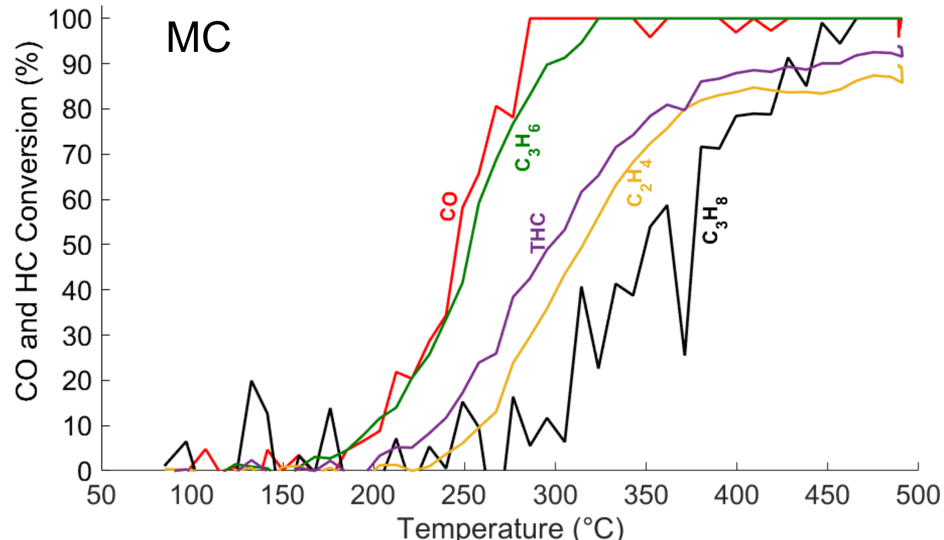
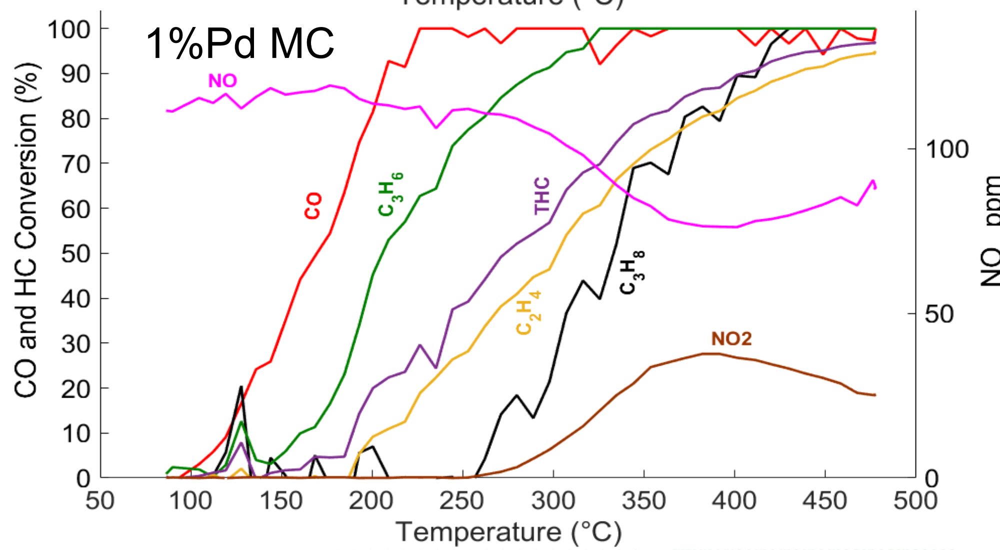
  - Conditions more challenging, but improved HC reactivity observed w/o Pd
  - Efforts for improvement continuing at USC





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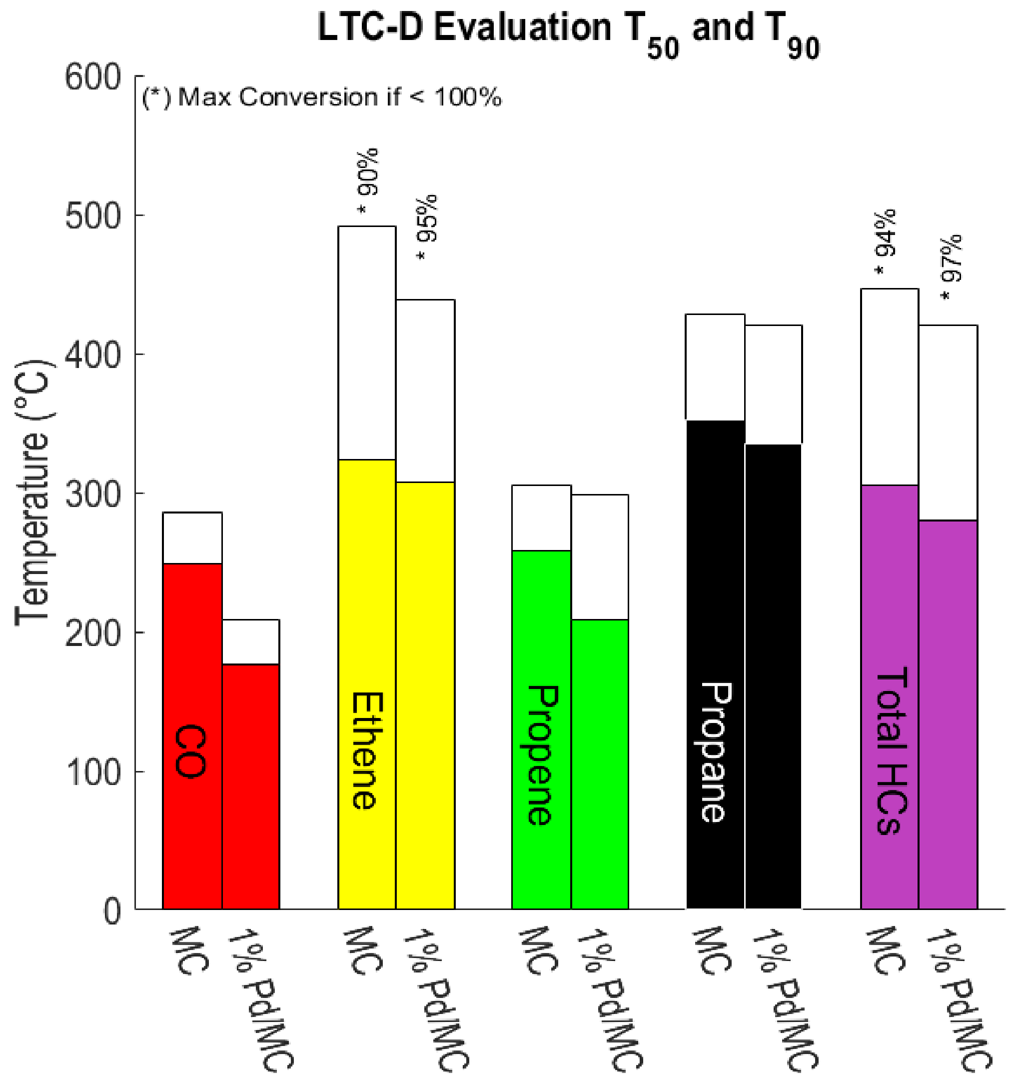
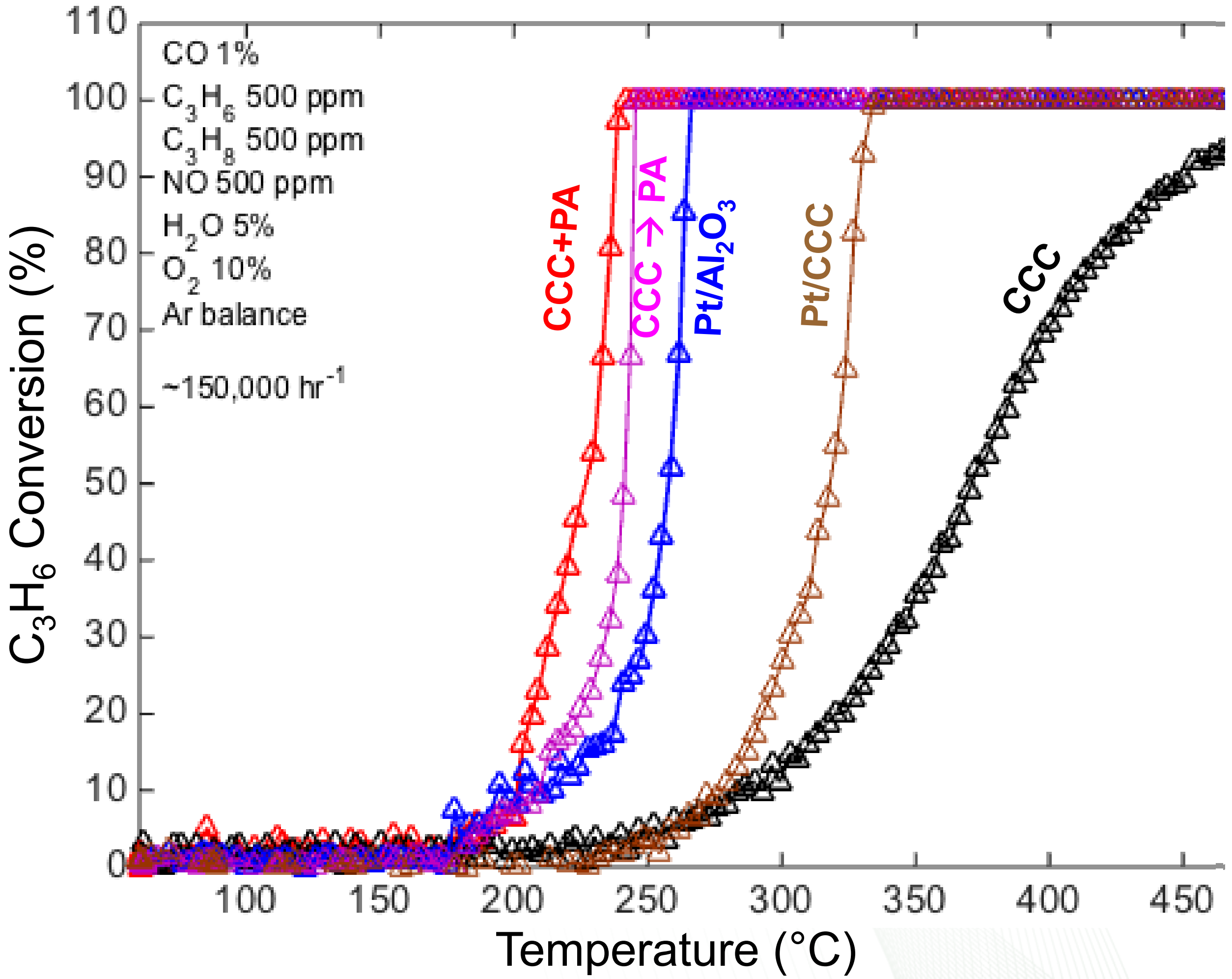


CCC as a component in a PGM-containing system lowers the HC light-off temperature

- Pt deposited on CCC shows less activity than Pt/Al_2O_3
  - But better than CCC
- CCC in front of Pt/Al_2O_3 improves C_3H_6 oxidation
- Mixing CCC with Pt/Al_2O_3 gives best C_3H_6 activity
- Still need additional improvements to get to lower light off temperatures



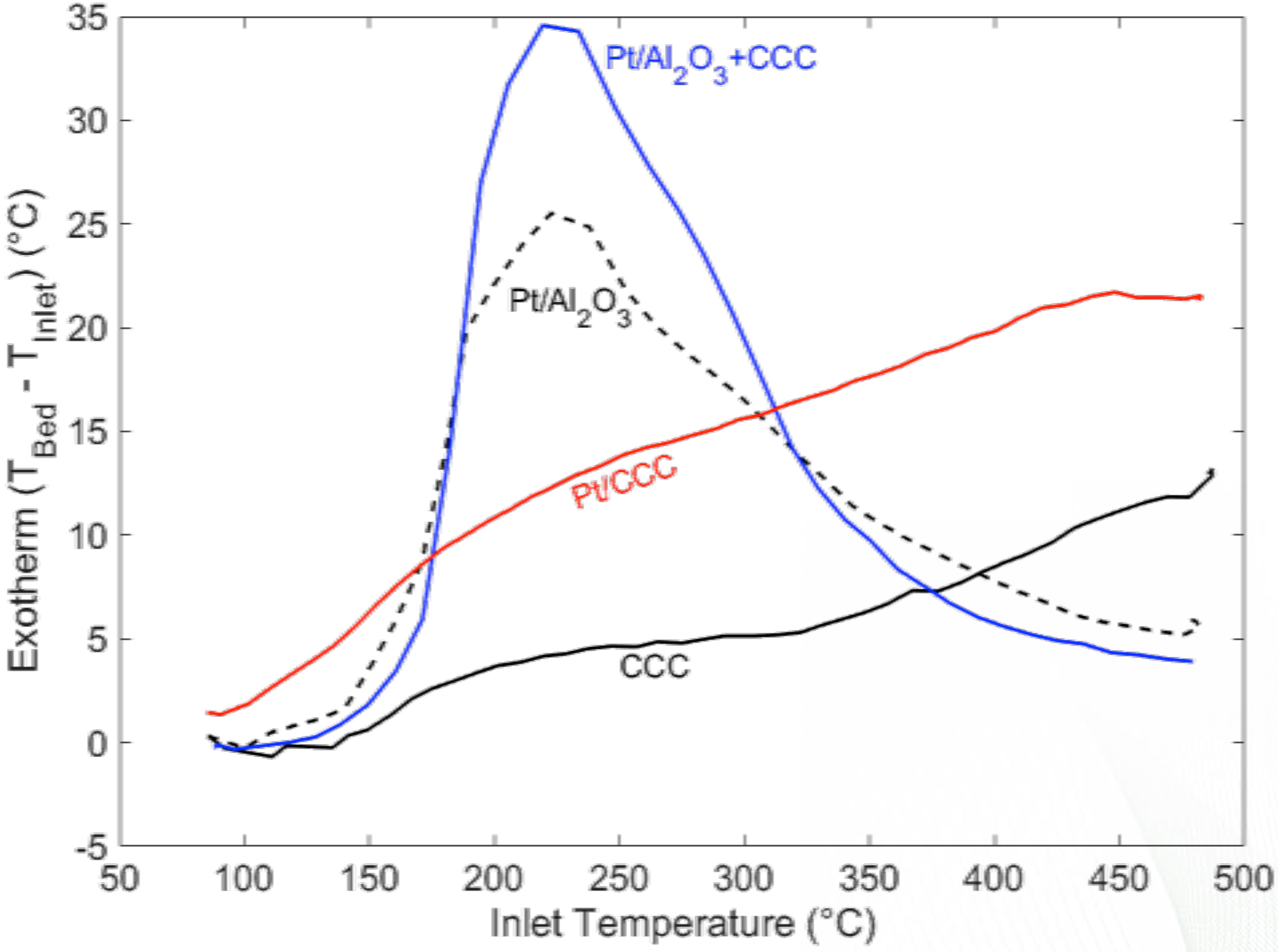
Pt/Al_2O_3 = 1% wt. (nominal) Pt/Al_2O_3

Pt/CCC = 0.5% wt Pt on CCC

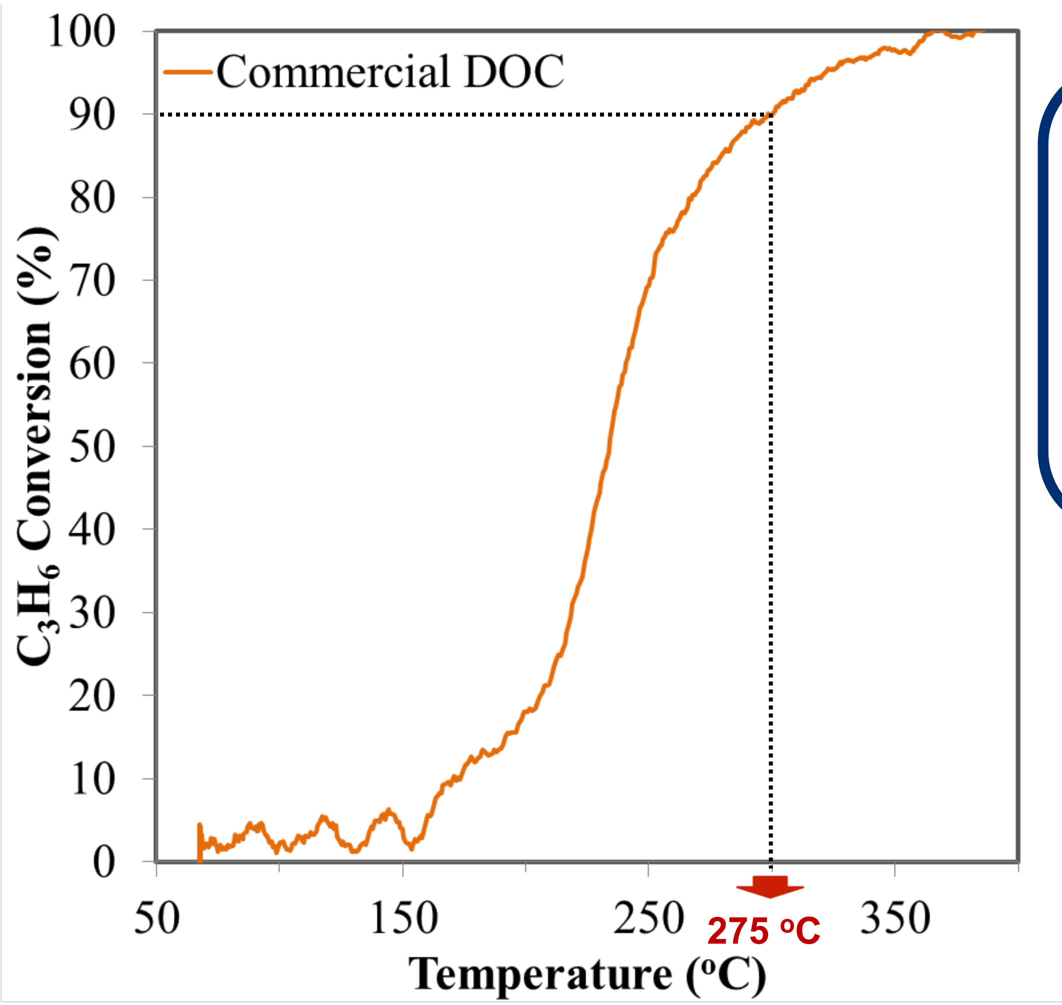
CCC+PA = 50:50 physical mixture (wt)

CCC→PA = Split bed

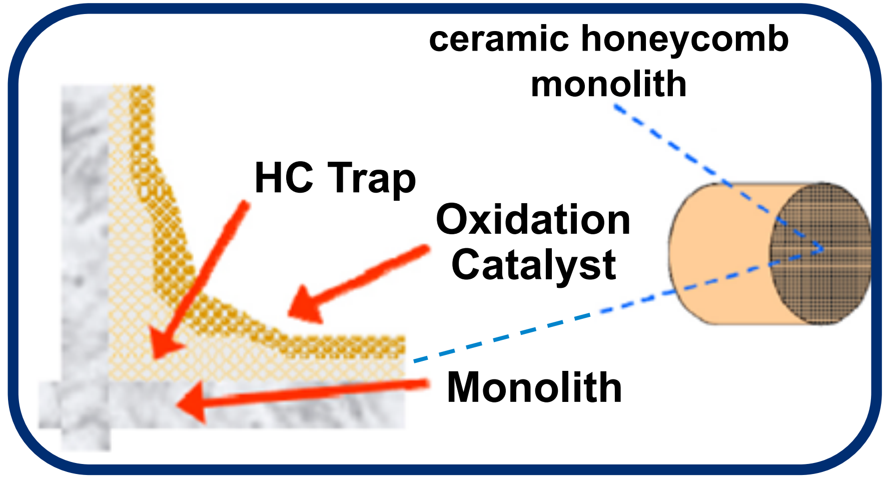
Observed exotherm is highest with Pt/Al_2O_3 + CCC



Trapping for low temperature emissions control



Example of a Catalyzed HC Trap.



- DOCs able to oxidize HCs and CO at ~ 275 °C;
  - SCR: active at ~175°C for NO
- Ideal process:
  - Trap HC+NO during cold start and low temperature operation
  - At higher temperatures, desorb from the surface when catalysts are active

Kim, M.-Y., Kyriakidou, E.A., Choi, J.-S., Toops, T.J., Binder, A.J., Thomas, C., Parks, J.E., Schwartz, V., Chen, J., Hensley, D.K., Submitted to Appl. Catal. B: Environ. (09/2015).

Nunan, J., Lupescu, J., Denison, G., Ball, D., Moser, D., SAE Int. J. Fuels Lubr., 6 (2013) 430.

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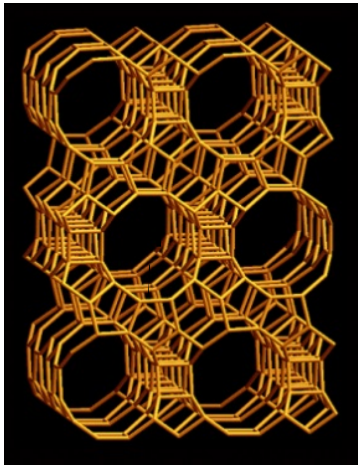
Zeolites can be effective traps that have variable material properties

- Understand zeolites in HC and NO adsorption and desorption study to help optimize processes
- Systematic variation of key zeolite properties:
  - **Cation type** (H^+ vs. Ag^+)
  - H_2O, CO_2, NO
  - **Acidity** (low vs. high SiO_2/Al_2O_3)
  - Metal loading

- **Retain** olefins and aromatics at low T.
- **Resistance** to water adsorption.

Loading: 0, 1, 5 wt.%
Calcination: 500-750°C (2 h)

Ion-Exchanged Zeolites.



BEA

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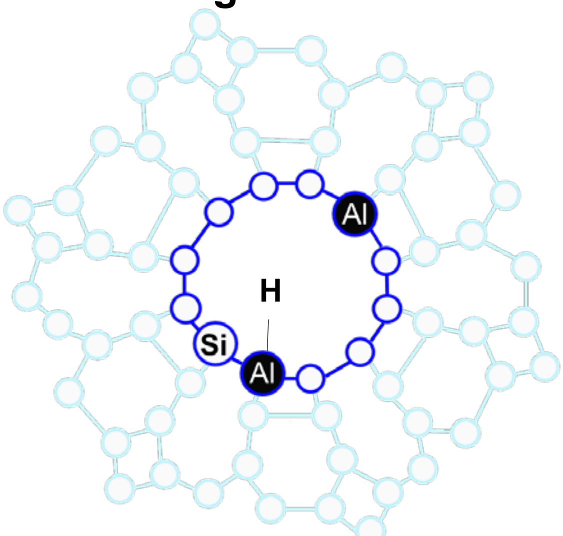

BEA

Liu, X., Lambert, J.K., Arendarskiia, D.A., Farrauto, R.J., Appl. Catal. B 35 (2001) 125.
Lambert, J.K., Deeba, M., Farrauto, R.J, US Patent 6,074,973 (2000).
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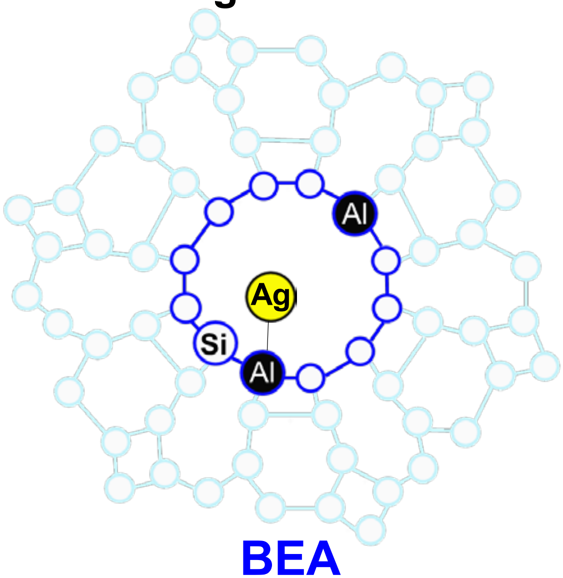

Zeolite type	SiO_2/Al_2O_3 molar ratio	Nominal cation form	Surface Area (m^2/g)
Beta	25	H^+	680
Beta	25	Ag^+	NM
ZSM-5	30	Pd^{2+}	NM

Liu, X., Lambert, J.K., Arendarskiia, D.A., Farrauto, R.J., Appl. Catal. B 35 (2001) 125.
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