Minimizing low temperature emissions through advances in metal oxide catalysts, supports and traps

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Oak Ridge National Laboratory

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

ORNL is managed by UT-Battelle
for the US Department of Energy

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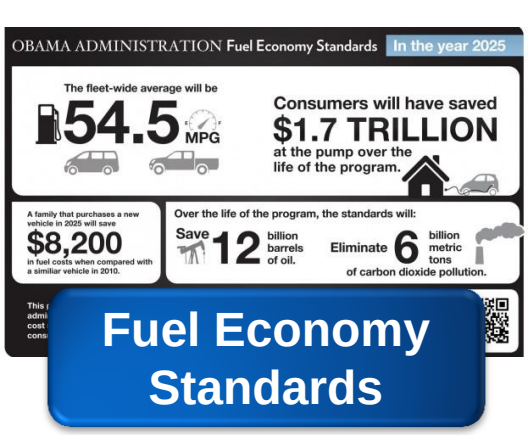
Objectives and Relevance

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

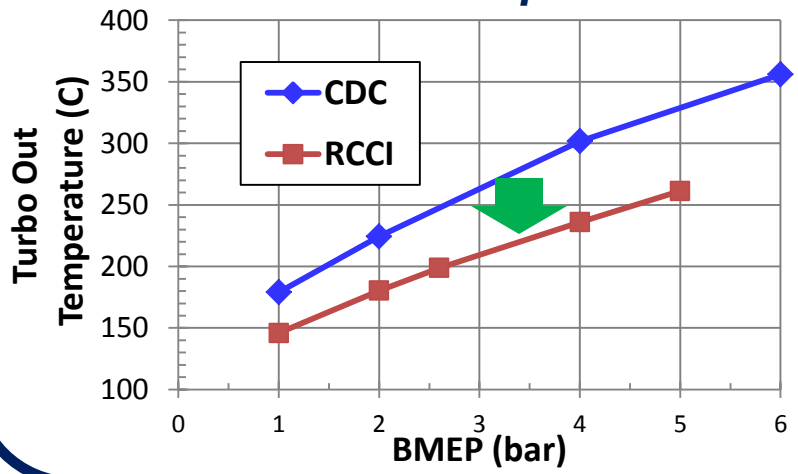
Goal: 90% Conversion at 150ºC

- Advance catalysts being studied to enable commercialization of advanced combustion engines
  - 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



54.5 mpg CAFE by 2025

Higher efficiency engines have lower exhaust temperatures*



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)

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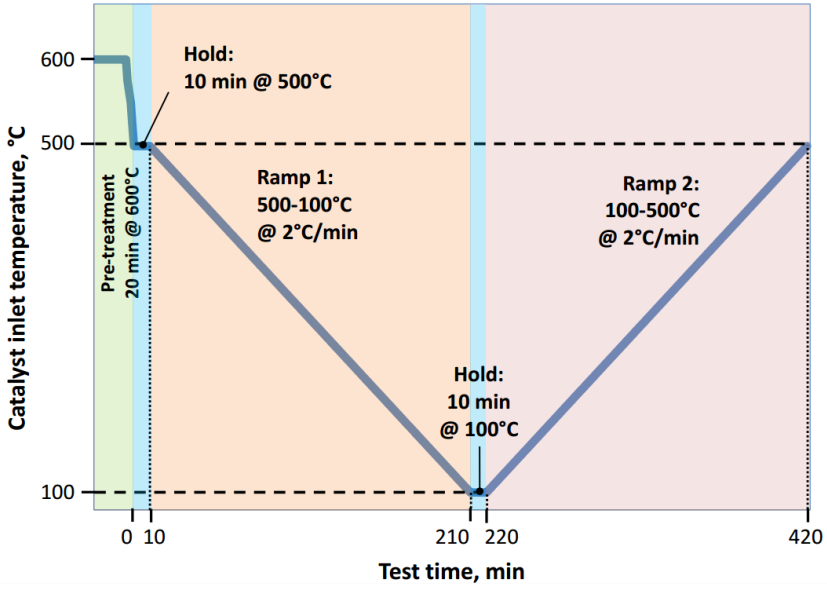
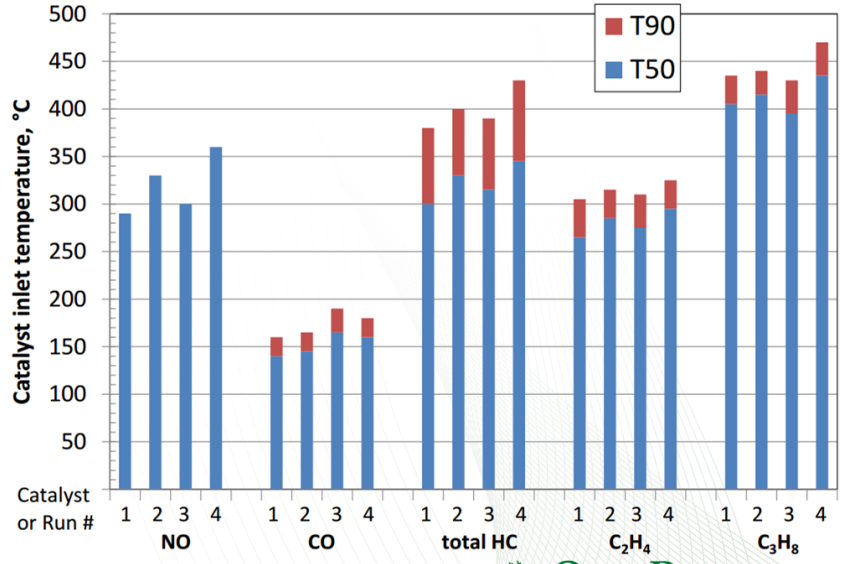
Low Temperature Protocols recently established by automotive manufacturers

- Protocol 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

CDC Conventional Diesel Combustion		LTC-D: Low Temp. Combustion Diesel	
Total HC:	1400 ppm	Total HC:	3000 ppm
C_2H_4:	778 ppm	C_2H_4:	1667 ppm
C_3H_6:	467 ppm	C_3H_6:	1000 ppm
C_3H_8:	155 ppm	C_3H_8:	333 ppm
CO:	500 ppm	CO:	2000 ppm
NO:	200 ppm	NO:	100 ppm
H_2:	100 ppm	H_2:	400 ppm
H_2O:	6 %	H_2O:	6 %
CO_2:	6 %	CO_2:	6 %
O_2:	12 %	O_2:	12 %
Balance N_2		Balance N_2	
GHSV:	30-60k h^{-1}	GHSV:	30-60k h^{-1}





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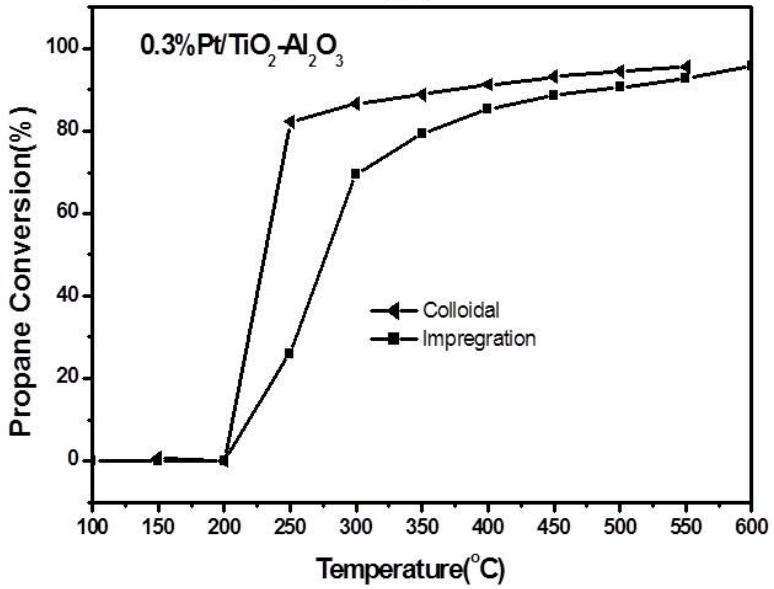
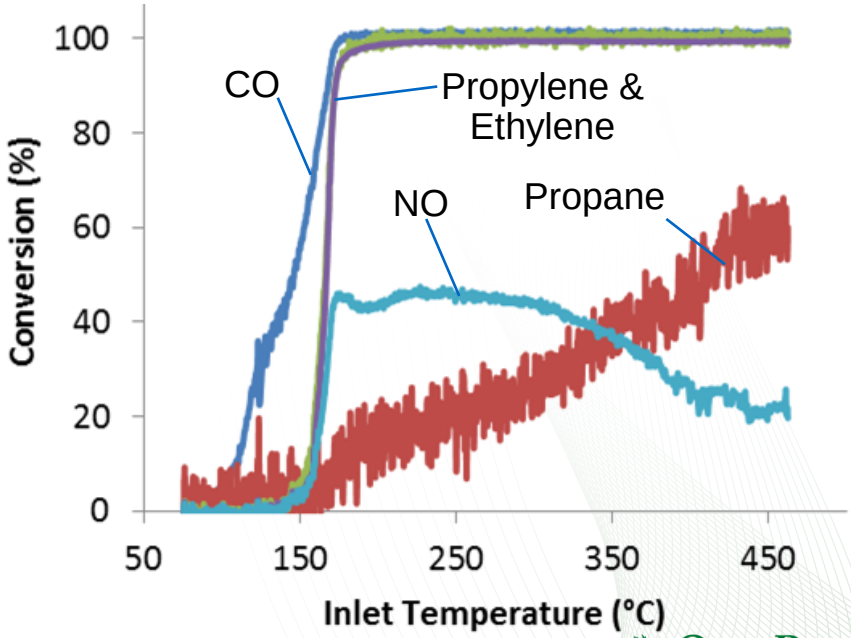
Protocols help define baseline and give common ground for comparisons

- Initial data in collaboration with UCONN data shows very good propane activity
  - simple conditions, not full protocol
  - 3-D array technology
  - Low PGM loading: 0.3%Pt



Gao et al. 2015 DOE AMR

- When Pt/TiO_2 catalyst evaluated under CDC protocol, a more realistic evaluation is seen
  - propane conversion not as promising
  - HOWEVER, illustrates excellent propylene/ethylene activity
- Protocols helping to elucidate strengths and weaknesses of catalysts being evaluated



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Approaches being investigated

- PGM-free mixed metal oxides

- Support modifications for enhanced PGM activity

- Trapping materials

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

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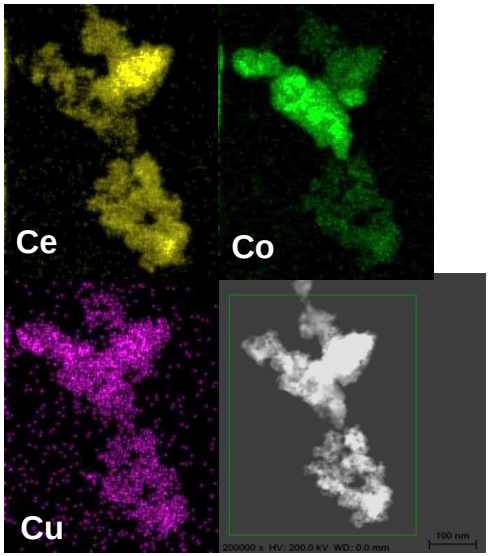
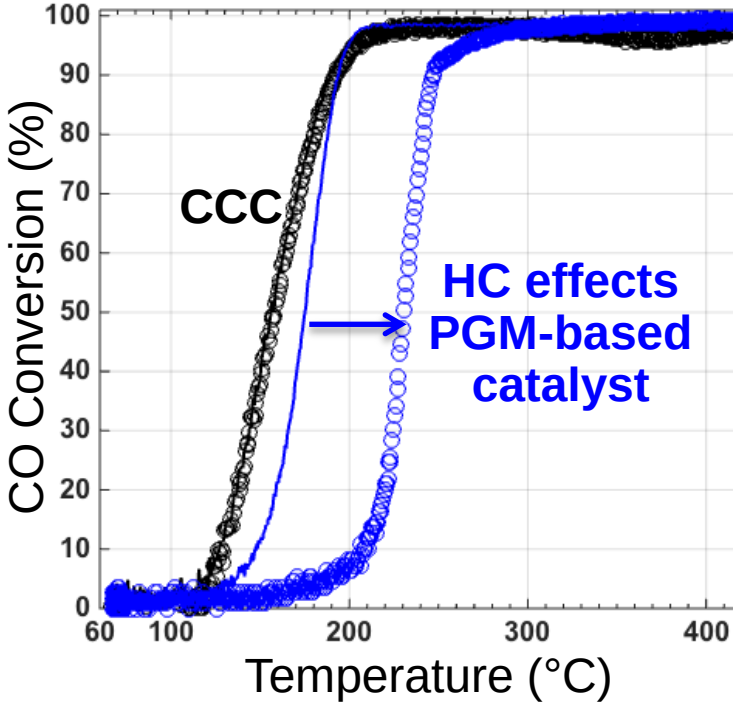
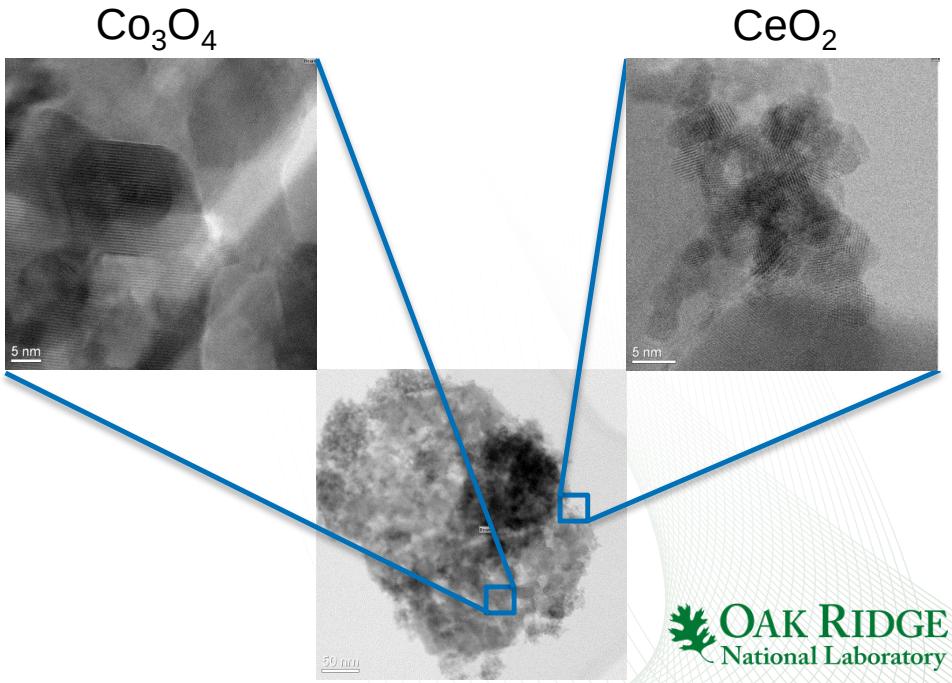
Mixed metal oxides showing interesting chemistry and some promise without PGM

- CuO_x-CoO_y-CeO_z (CCC) promising for CO oxidation
  - Interfacing crystalline regions of Co_3O_4 and CeO_2
  - Cu integrated into the lattices of both Co_3O_4 and CeO_2 evenly
  - Unaffected by HC, but not active for HC oxidation
- Need additional catalyst for low HC oxidation







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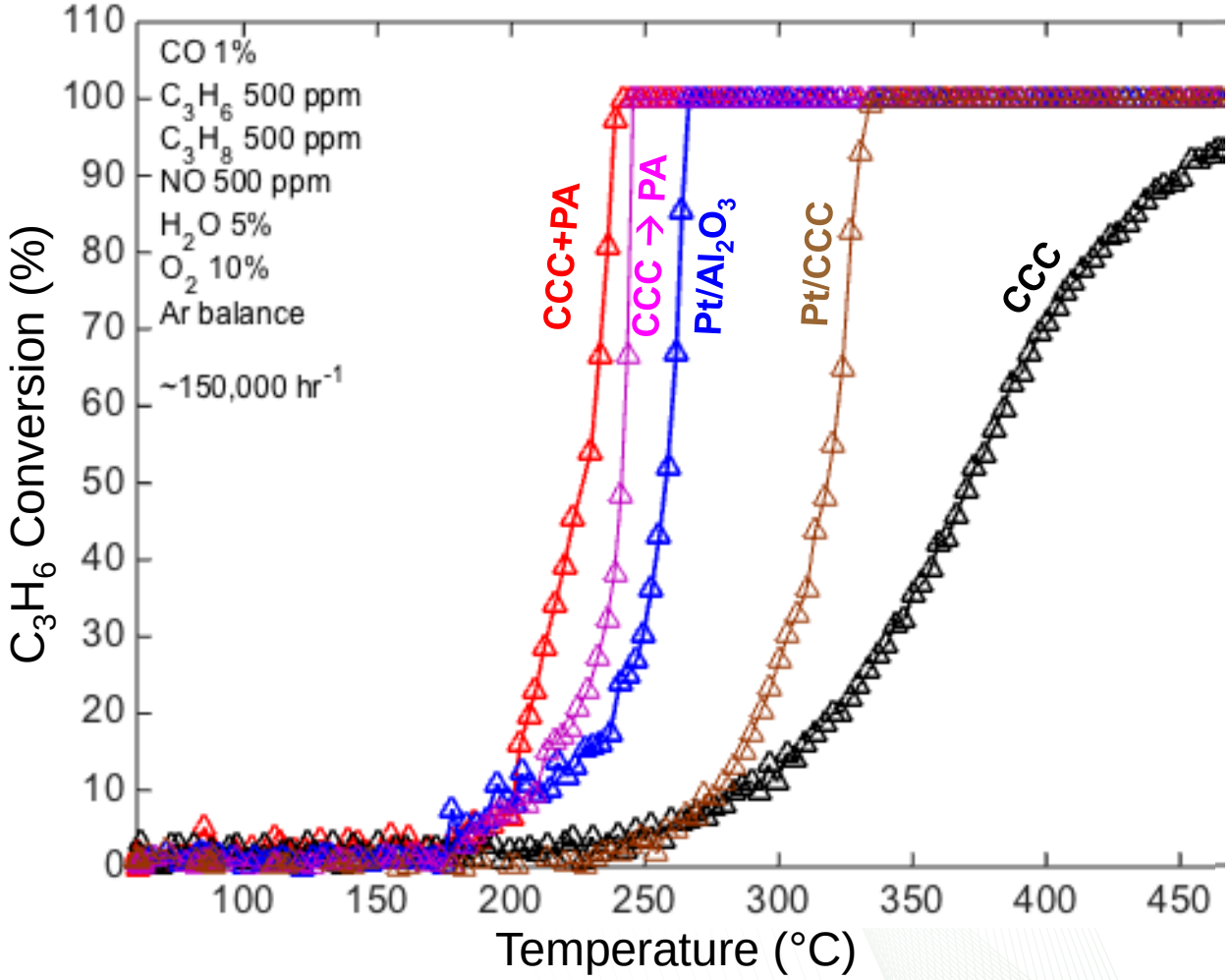
CCC as a component in a PGM-containing system lowers the HC light-off temperature

- 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

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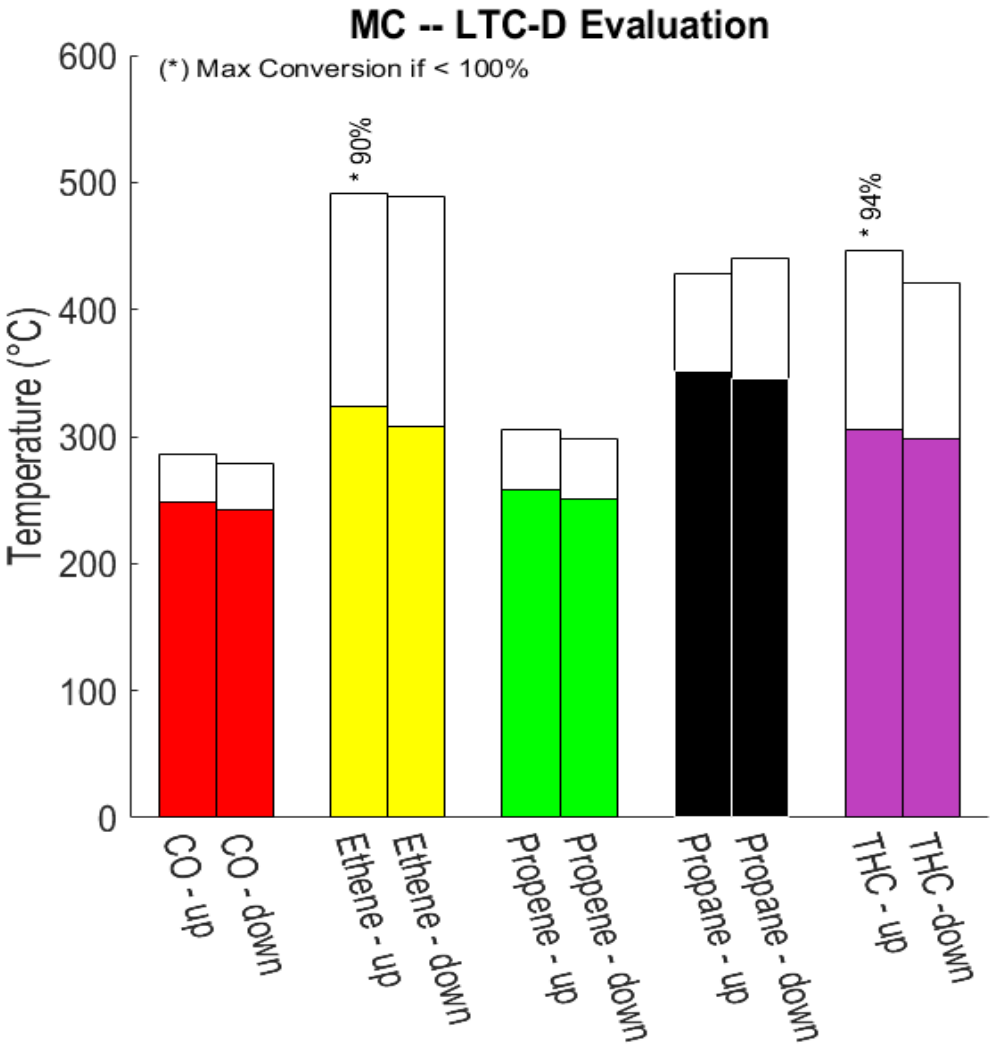
Evaluating Mn, Ce and Sn with good durability and HC oxidation

- 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
- Evaluated at ORNL with LTC-D protocol
  - Conditions more challenging, but improved HC reactivity observed w/o Pd
  - Efforts for improvement continuing at USC



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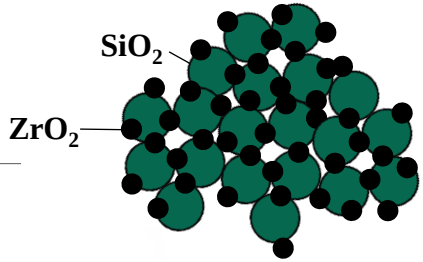
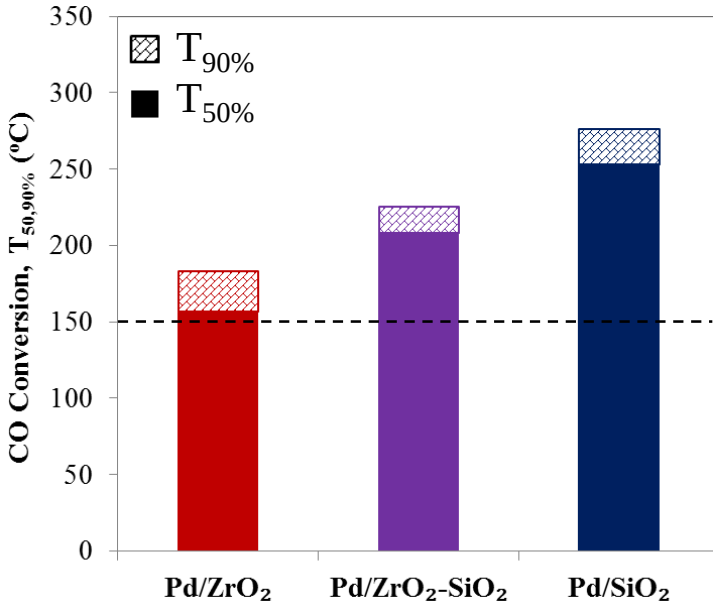
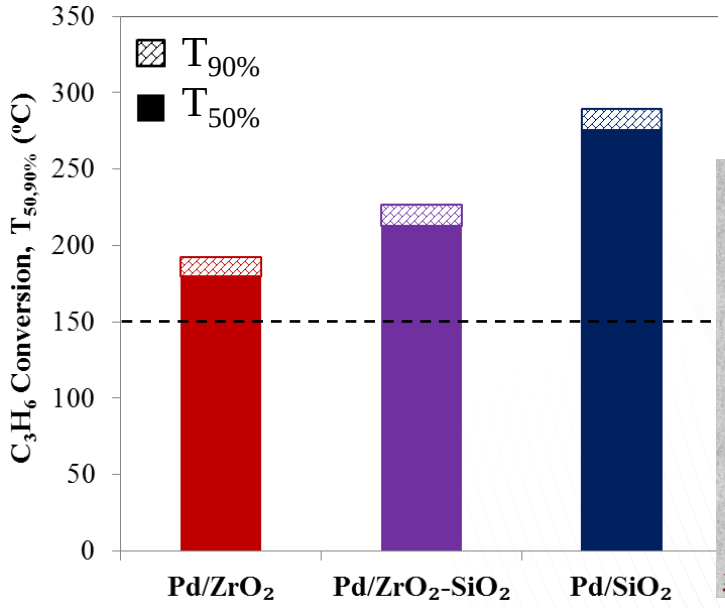
ZrO_2 support has shown excellent activity with Pd catalyst; efforts to improve ongoing

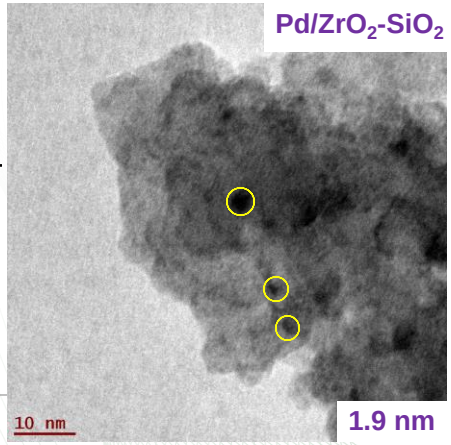
- Pd/ZrO_2 results in high activity, excellent Pd anchor for thermal durability
- Goal: further improve activity and sulfur tolerance
  - Support ZrO_2 on high surface area SiO_2
- Initial effort not successful as Pd/ZrO_2 still more active
  - not a monolayer; 15% coverage of SiO_2 surface
  - Pd dispersed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

ZrO_2-SiO_2 mixed oxide









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

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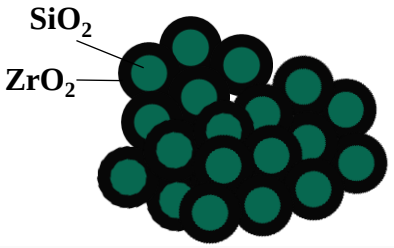
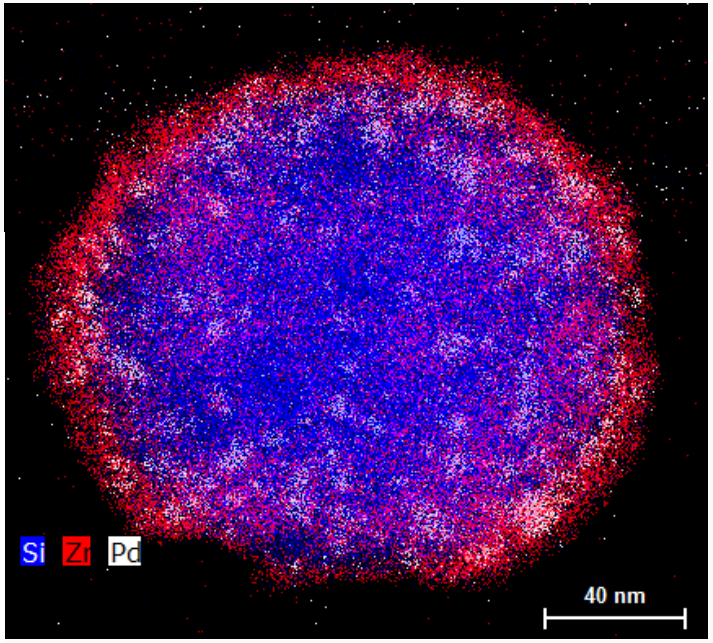
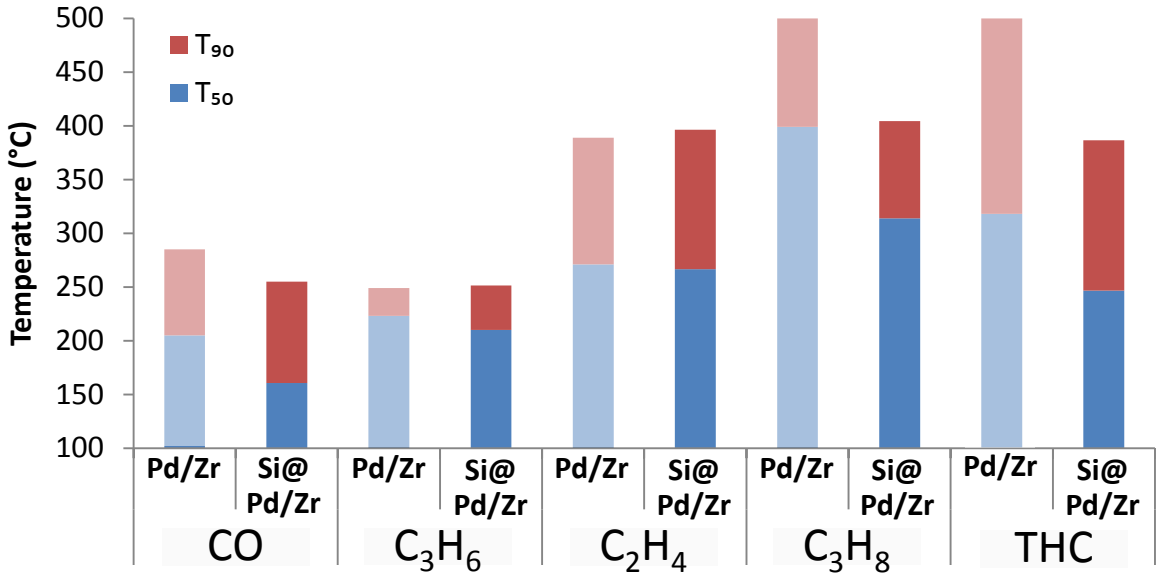
New synthesis technique successfully creates ZrO_2 shell around SiO_2 core

- Able to synthesize a complete shell around SiO_2 core using new technique SiO_2@Pd/ZrO_2
  - Pd deposition solely on ZrO_2 outer shell
- Activity improves, but Pd/ZrO_2 still showing best reactivity with simple oxidation conditions (not full protocol)
- While employing ACEC low temperature protocols improved activity shown with technique
  - Improved dispersion technique employed; higher Pd loading

ZrO_2-SiO_2 mixed oxide







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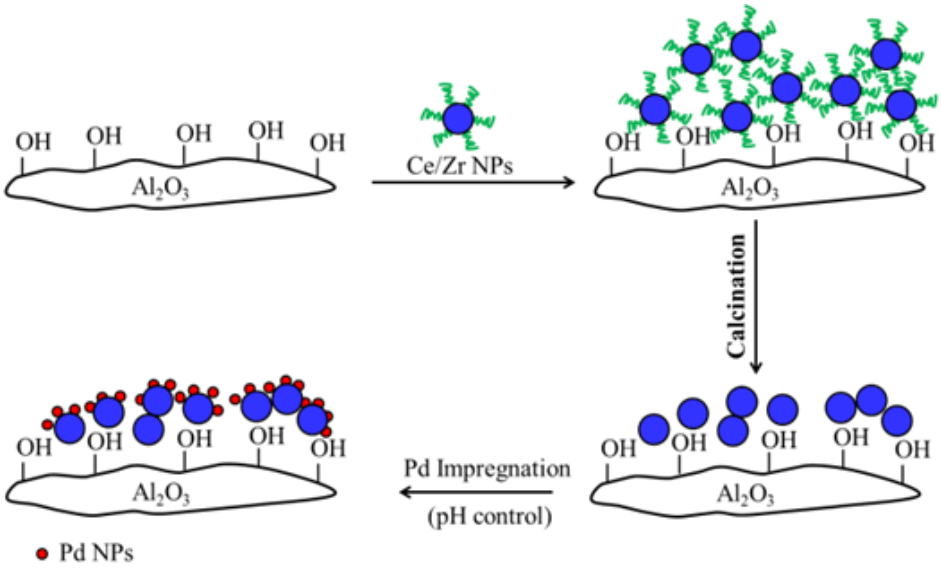
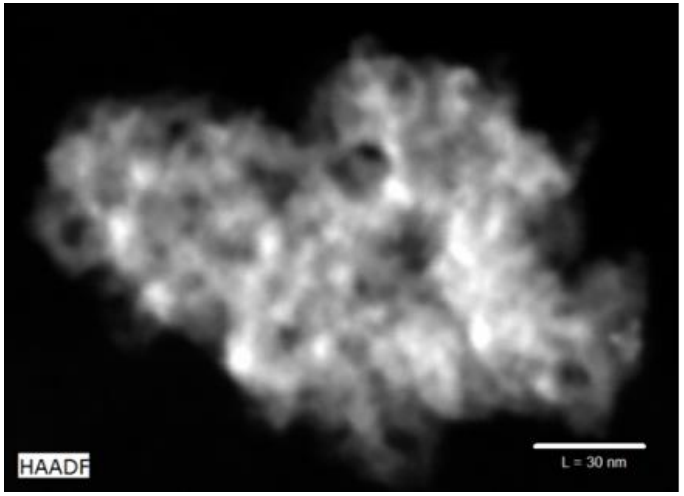
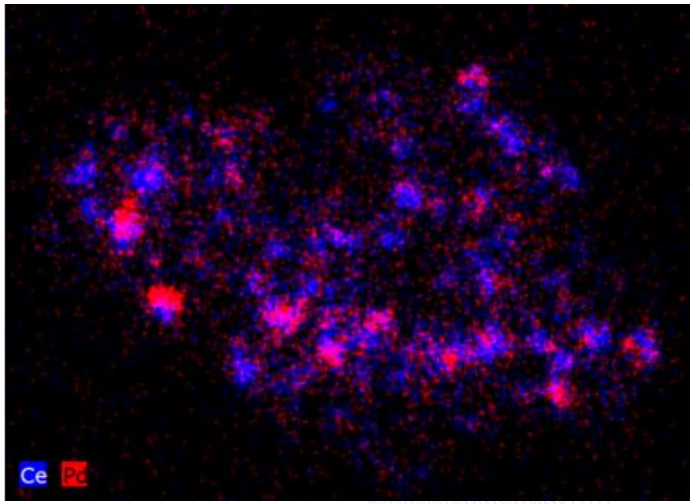
Targeted PGM deposition on Ce-Zr nanoparticles also investigated

- 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
  - Controlling pH enables targeted deposition
- It is possible…







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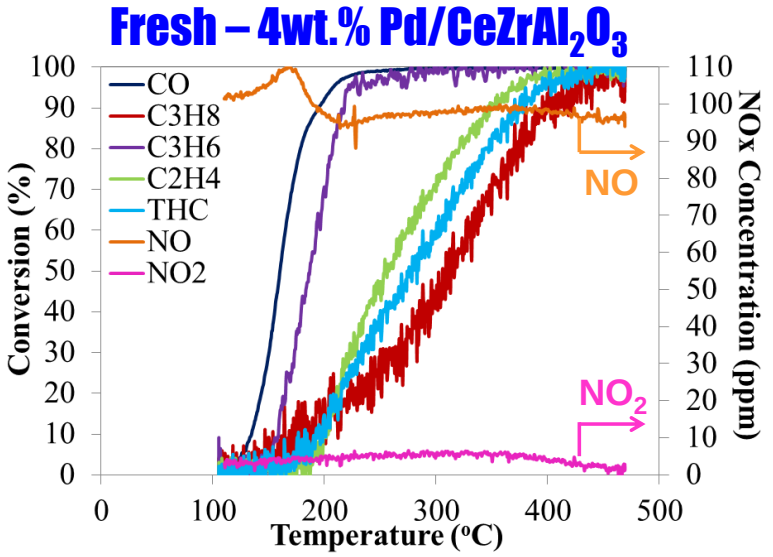
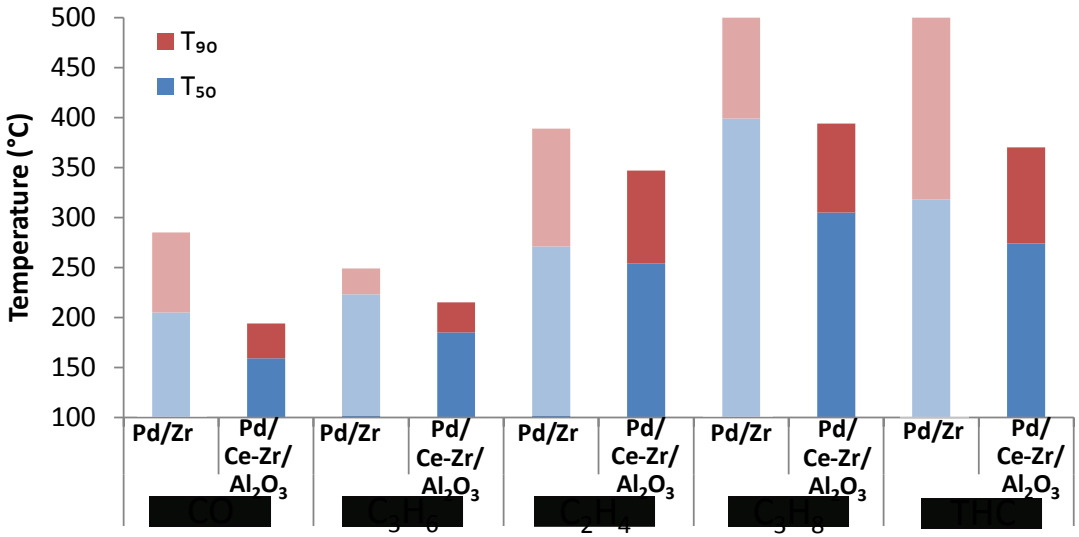
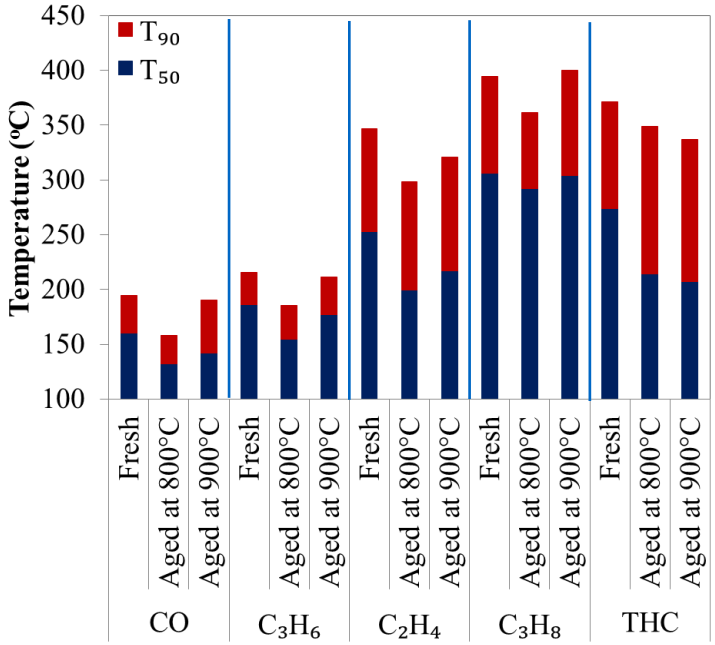
Pd/Ce-Zr/Al_2O_3 catalysts show promise, but far from target

- Good activity being observed
  - Also, tolerant to hydrothermal aging
    - HC oxidation actually improves
- …however meeting 150°C target still challenging, especially for C_2H_4 and C_3H_8





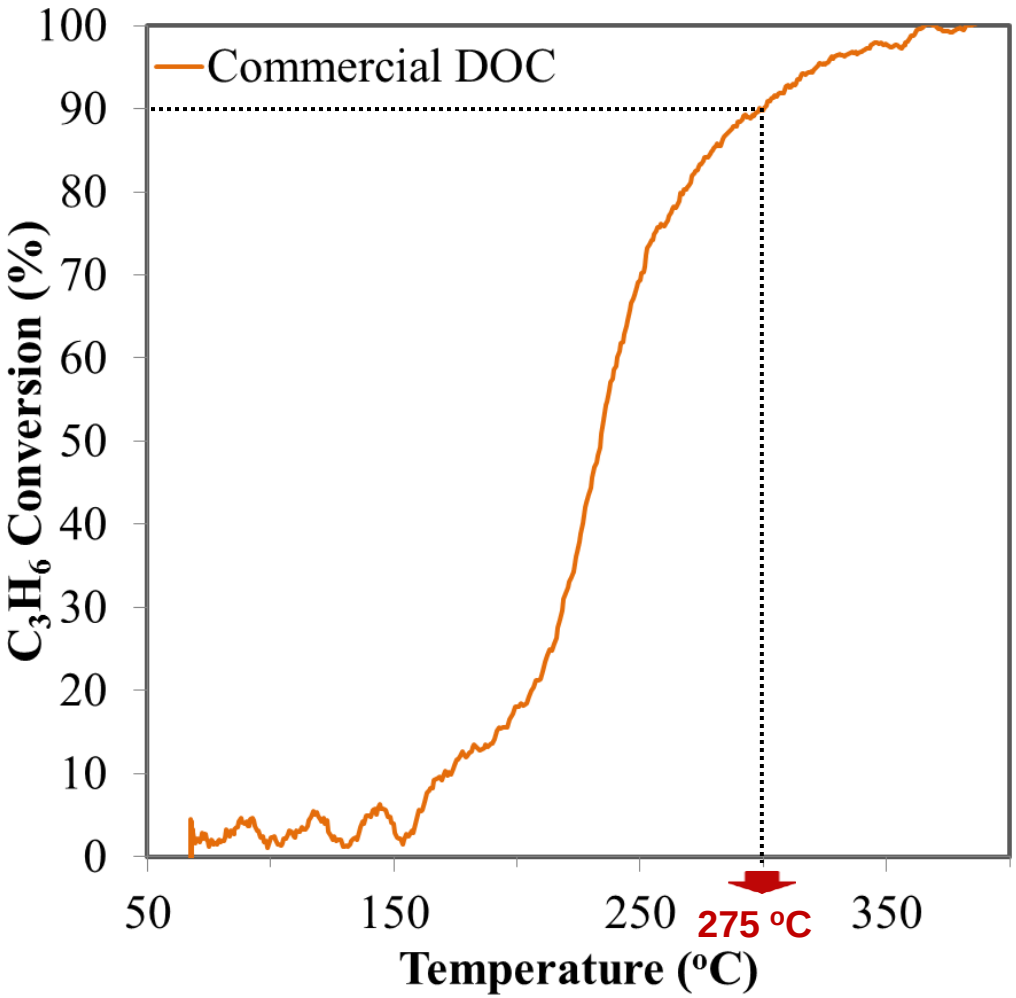


Approaches being investigated

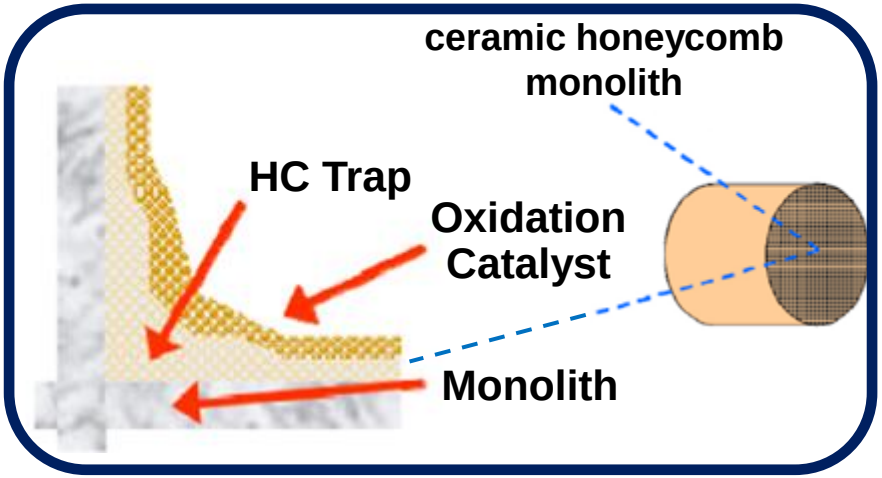
- PGM-free mixed metal oxides
- Support modifications for enhanced PGM activity
- Trapping materials

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

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.

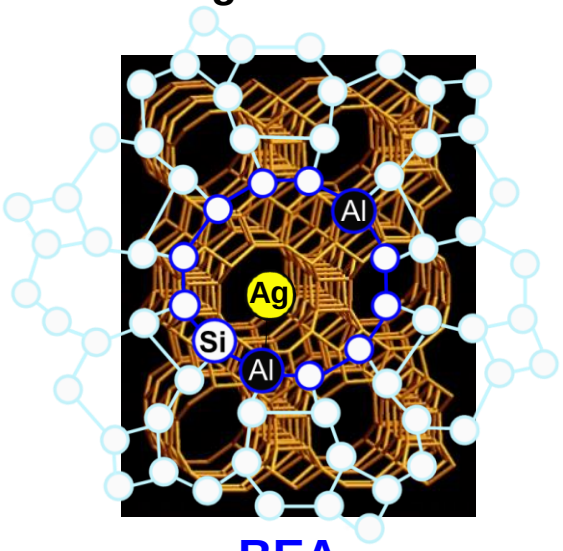
Zeolites can be effective traps that have variable material properties

- 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.

Ion-Exchanged Zeolites.



BEA

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

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.
Lambert, J.K., Deeba, M., Farrauto, R.J, US Patent 6,074,973 (2000).
Nunan, J., Lupescu, J., Denison, G., Ball, D., Moser, D., SAE Int. J. Fuels Lubr. 6 (2013) 430.

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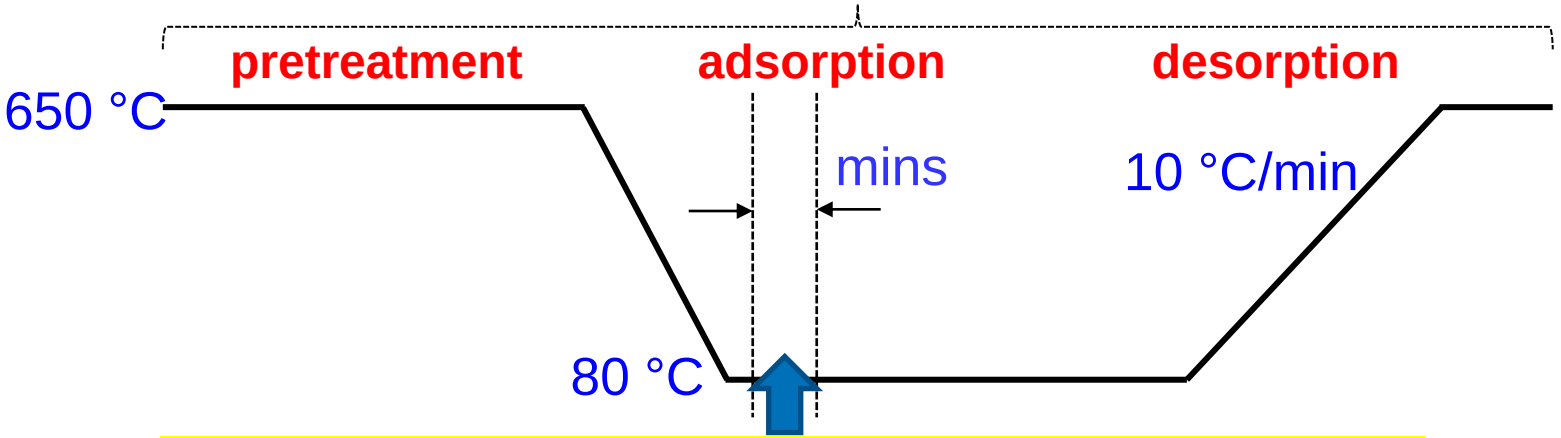
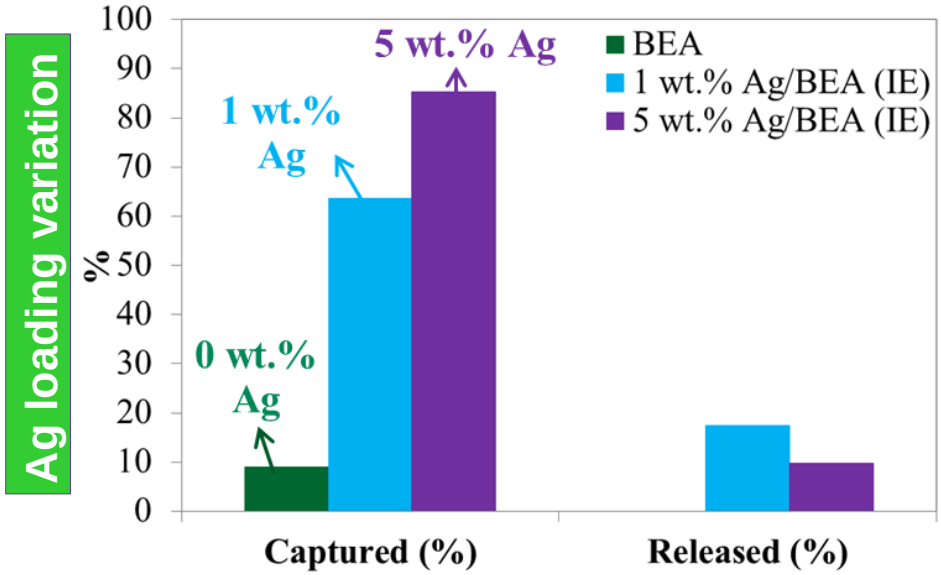
Ion-exchanging and Ag loading key factors in HC adsorption in the presence of H_2O

Base gas: 10% O_2, 5% H_2O, 5% CO_2



500 ppm HC (C1 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

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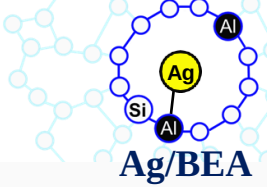
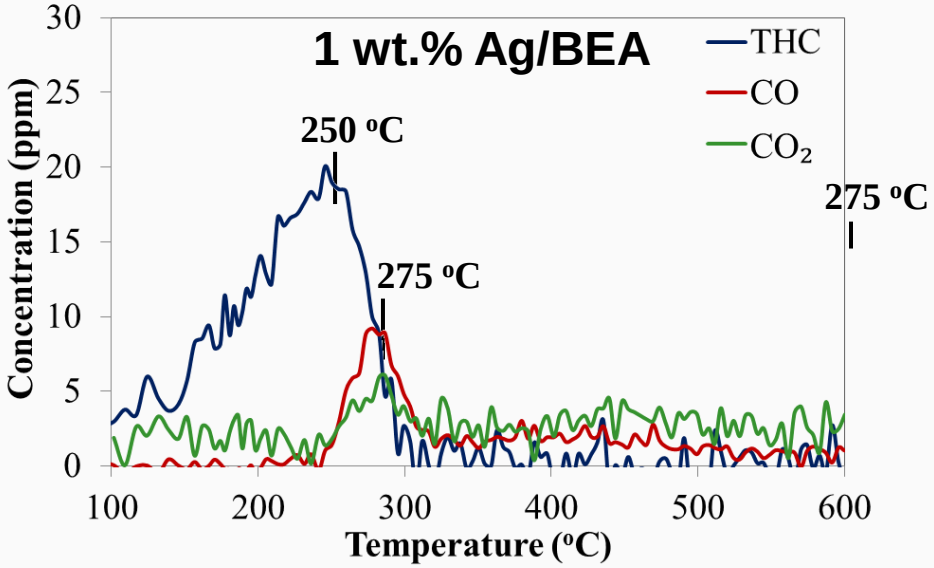
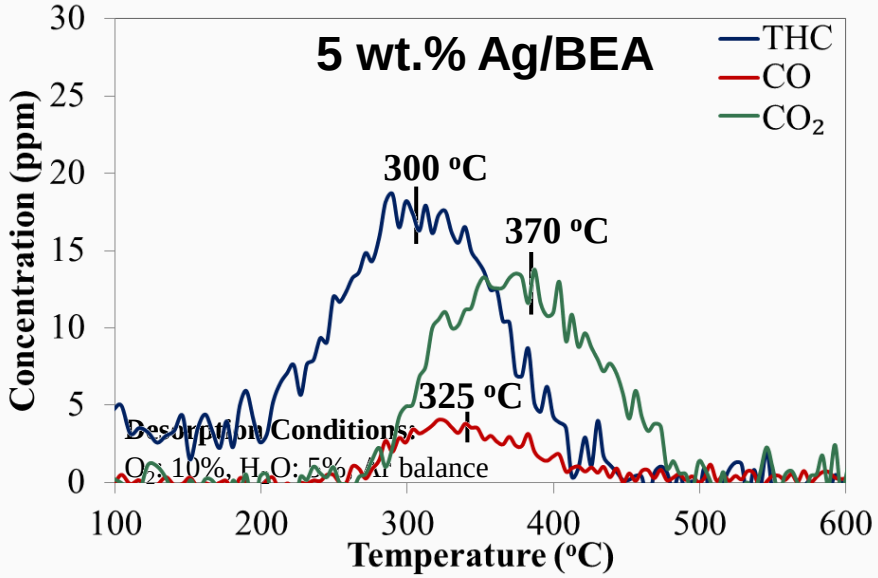
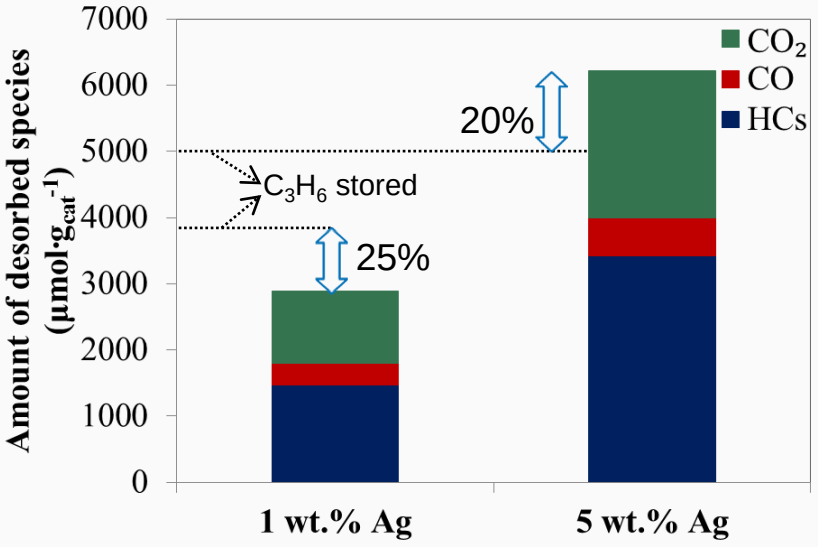
Release profile indicates significant reactivity of stored HC and varies with Ag loading







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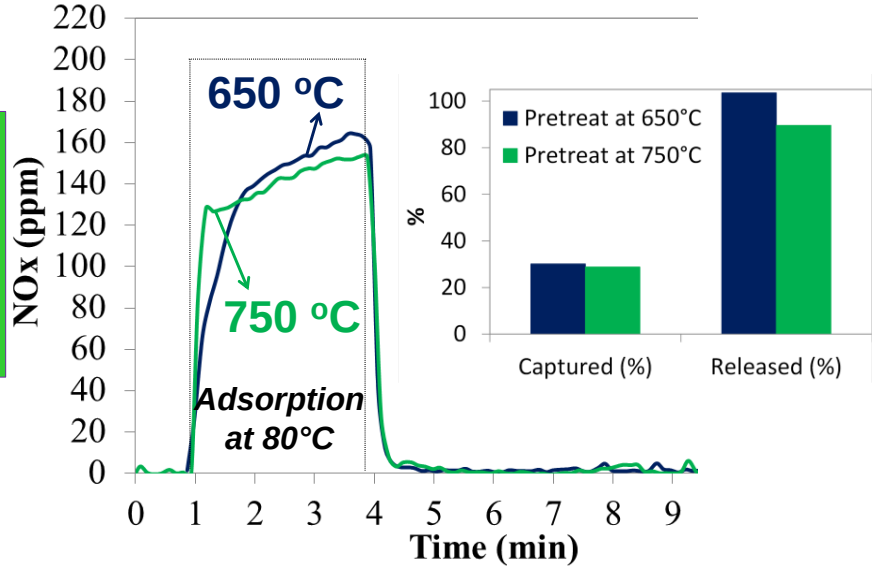
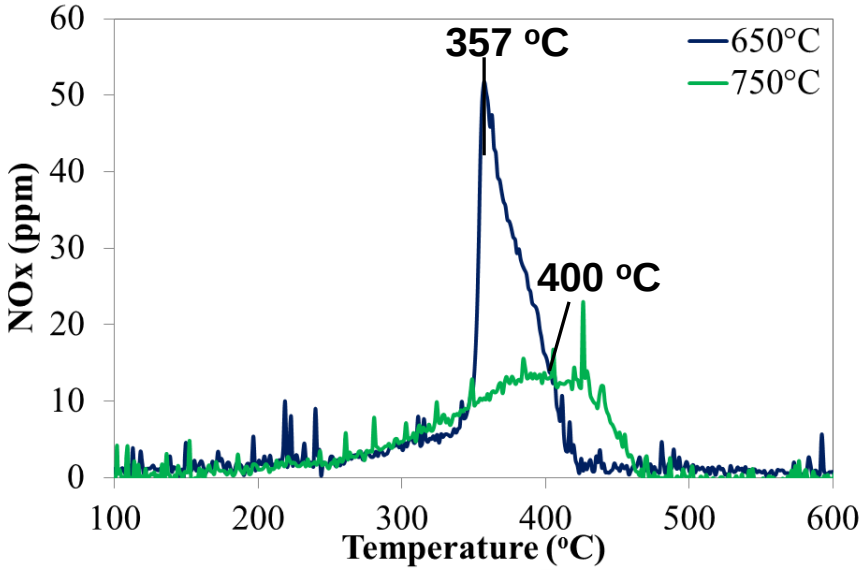
Pd/ZSM-5 stores both NO and HC; pretreatment temperature affects NO release

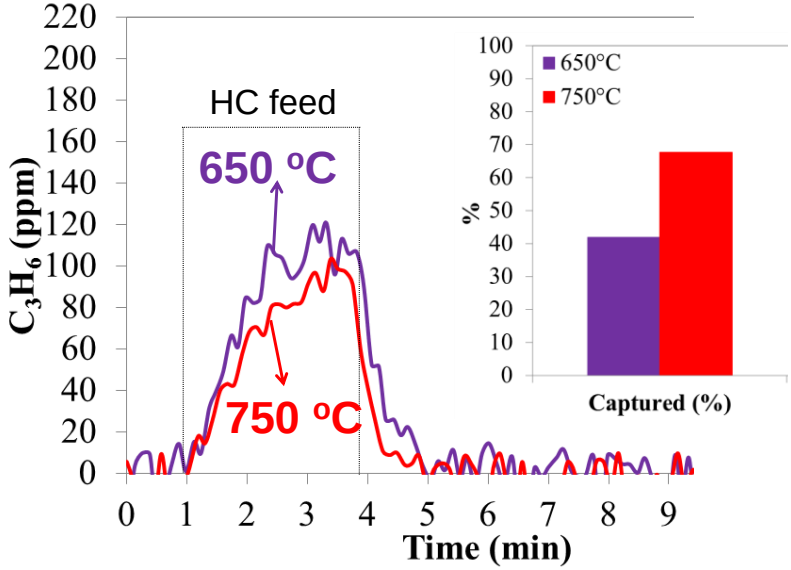
Adsorption



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

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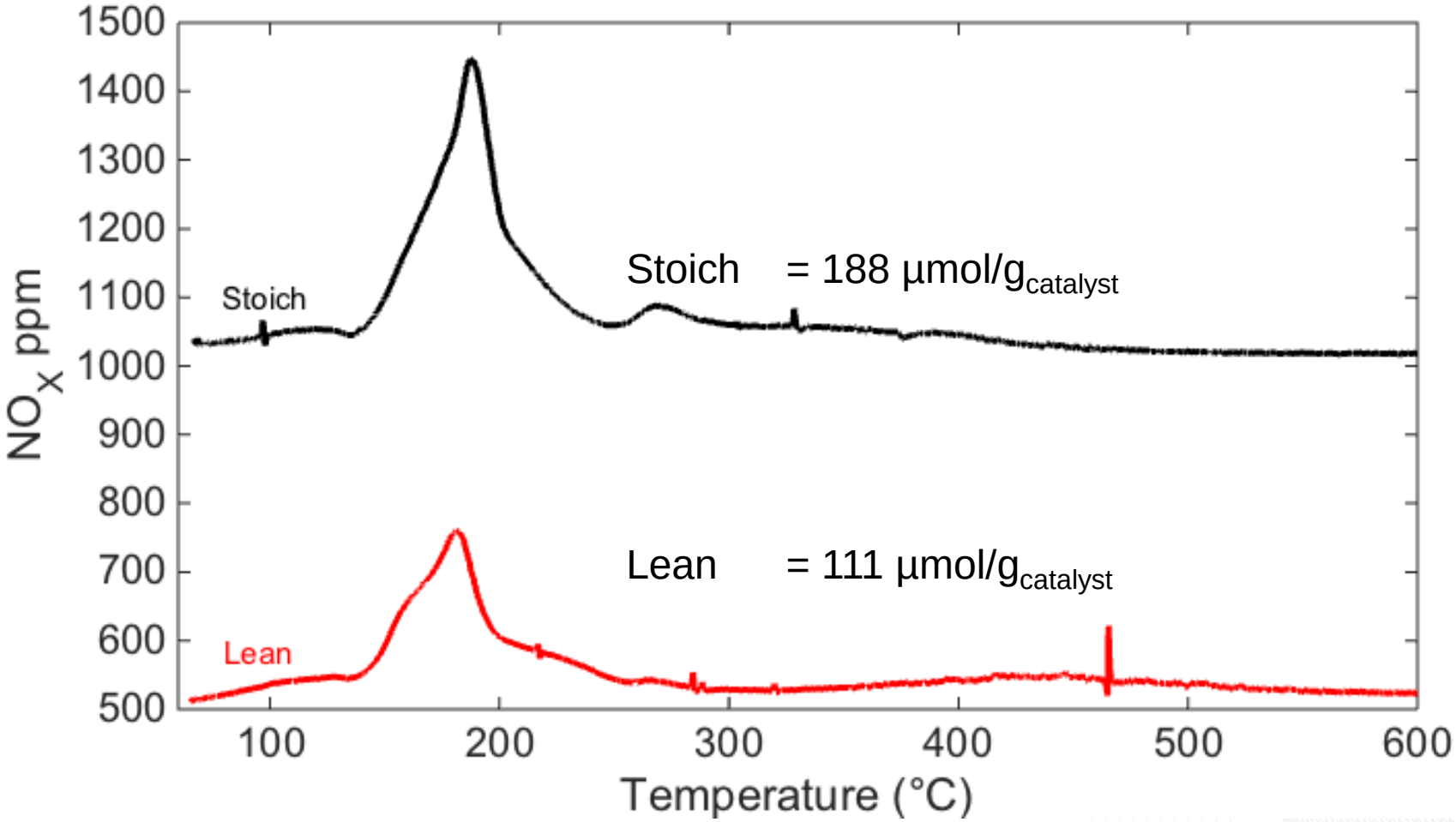
CCC also shows the ability to store and release NOx at low temperatures



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Summary

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

Approaches

PGM-Free Catalyst	**New mixed metal oxide formulations being evaluated; currently identified CO oxidation specialist; looking for HC improvements**
PGM Support	**Supports have significant effect on PGM reactivity and stability; improvements ongoing; will need to begin investigations on bi-metallics shortly**
Zeolite Traps	**Implementation of technology is continuing; understanding of potential benefits ongoing; connecting release to activity key**

- With full protocol published ability to compare catalysts in the most relevant conditions can now occur
- Conditions are very challenging and the bar is high, but some avenues are showing potential, and a single solution is very unlikely
  - Role of bi-metallic catalysts likely to be significant

Technical Backup Slides

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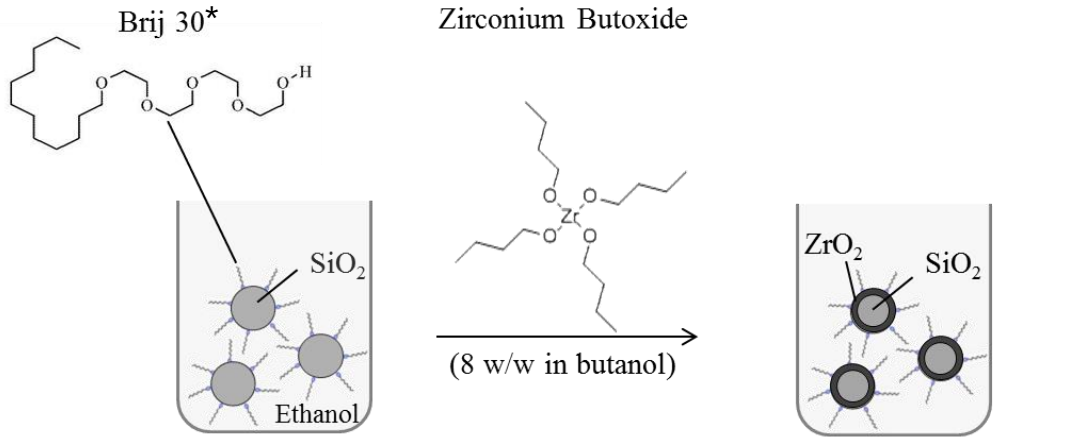
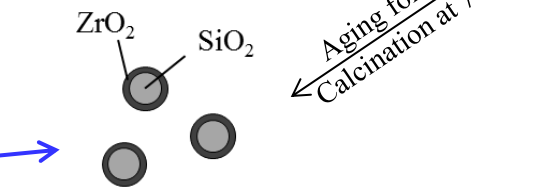
Experiment Detail: Synthesis of SiO_2@ZrO_2 core@shell Oxide Support



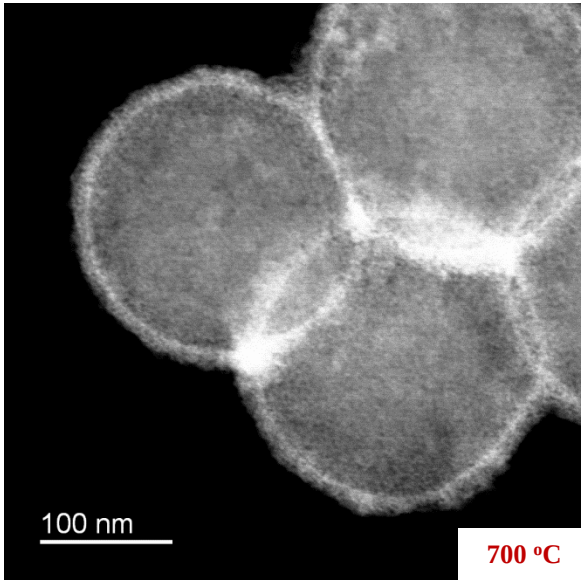
Synthesis of silica spheres

Silica core and amorphous shell with zirconium hydroxide

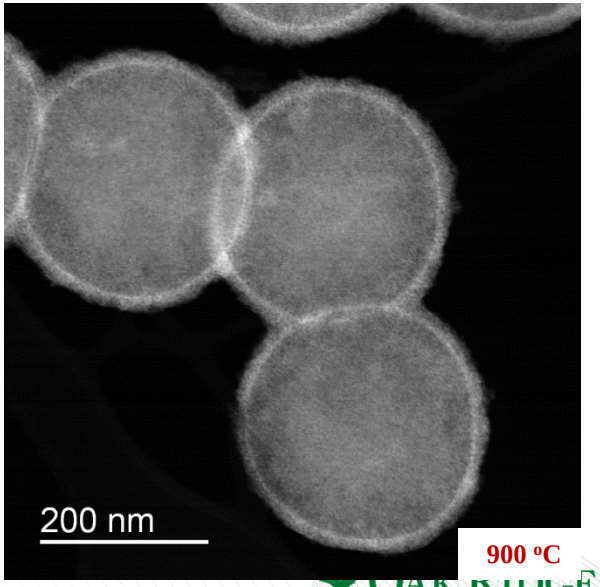
Material	Surface Area (m^2/g)
ZrO_2	97
ZrO_2-SiO_2	153
SiO_2@ZrO_2	**210**
@ZrO_2	**117**



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



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

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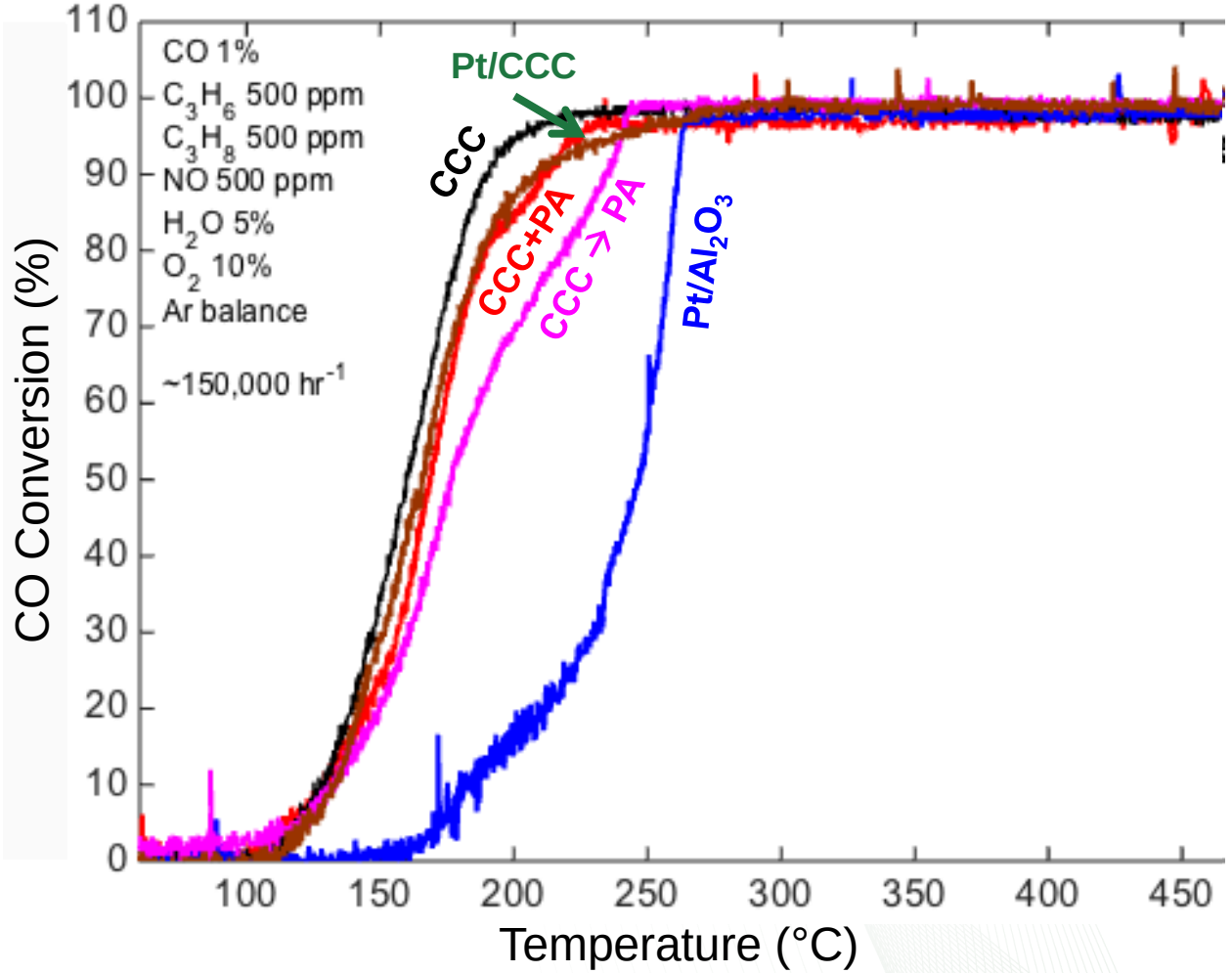
CCC as a component in a PGM-containing system lowers the HC light-off temperature

- 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

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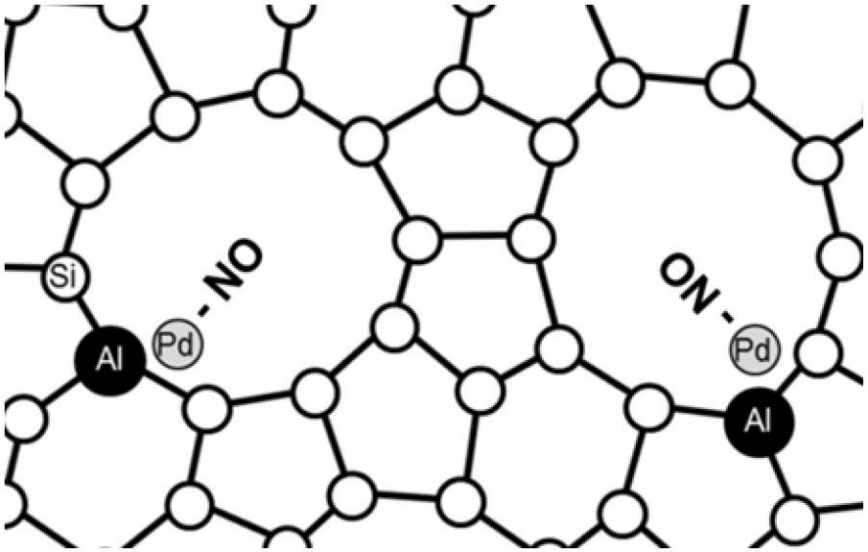
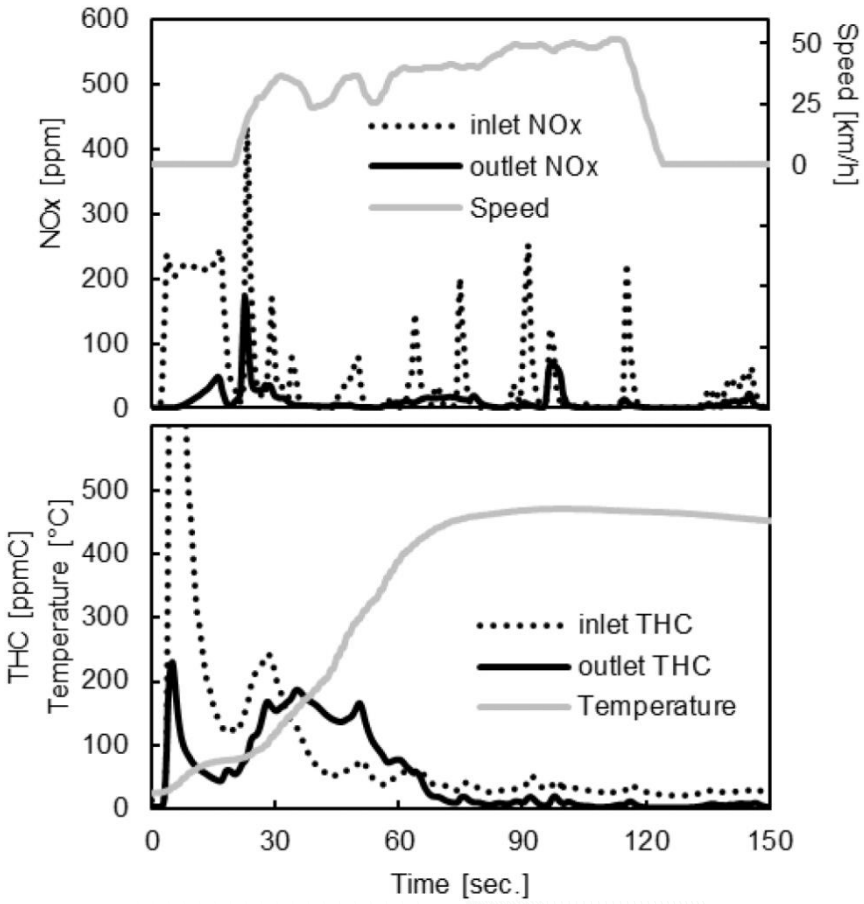
Recent report on NO + HC trap using Pd/ZSM-5 (Y. Murata et al. SAE 2015-01-1002, Honda*)

- Pd exchanged in zeolite at Al site in cage
- Pd/ZSM-5 able to trap NOx in the form of NO
  - Not necessary to oxidize to NO_2
  - HCs also trapped





- Significant emissions reduction observed during test cycle (~80%)
  - FTP-75

* images imported from SAE 2015-01-02

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