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# CLEERS: Aftertreatment Modeling and Analysis

FENG GAO, JAMIE HOLLADAY, KEN RAPPE, MARK STEWART, JANOS SZANYI, DIANA TRAN, DONGHAI MEI, YILIN WANG, YONG WANG (P.I.)

PACIFIC NORTHWEST NATIONAL LABORATORY

JUNE 7, 2017

ACS023

# Overview

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## Timeline

- Status: On-going core R&D
- Particulate/filtration activity originated in FY03
- Now also includes LNT (and PNA), SCR, and LTAT technologies

## Budget

- FY17 funding - $770K
- FY18 funding - $865K
  - SCR task - $220K
  - PNA task - $310K
  - Particulate/Filtration task - $135K
  - LTAT activities - $200K

## Barriers

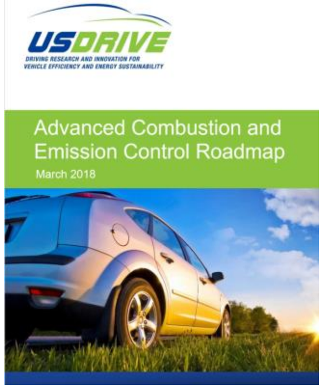
- Emission controls contribute to durability, cost and fuel penalties
  - Low-temp performance is now of particular concern
- Improvements limited by:
  - Available modeling tools
  - Chemistry fundamentals
  - Knowledge of material behavior
- Effective dissemination of information

## Partners

- DOE Advanced Engine Crosscut Team
- CLEERS Focus Group
- 21CTP partners
- USCAR/USDRIVE ACEC team
- Oak Ridge National Lab
- Kymanetics, Inc.
- NSF/DOE-funded program with partners at Purdue, Notre Dame, WSU, Cummins, and ANL

# Relevance






- Increasing the efficiency of internal combustion engines is a technologically-proven and cost-effective approach to dramatically improving the fuel economy of the nation's fleet of vehicles in the near- to mid-term, with the corresponding benefits of reducing our dependence on foreign oil and reducing carbon emissions.
- The overarching emissions goal is the U.S. EPA Tier 3 Bin 30 emission standard.
- Compliance with exhaust emission regulations will be mandated and requires aftertreatment technologies integrated with the engine combustion approaches.
- Achieve greater than 90% conversion of criteria pollutants ($NO_x$, CO, HCs) at 150°C for the full useful life of the vehicle (defined as the longer of 150,000 miles or 15 years).
- Need to develop models and simulation tools ranging from the molecular level to the system level to predict performance and better understand catalytic processes.
- Require the research and development of new and novel material combinations that will enable lower temperature catalytic performance, increased selectivity to inert species, and optimal storage of pollutant and reductant species.

# Relevance (and Goals)



- "CLEERS is a R&D focus project of the Diesel Cross-Cut Team. The overall objective is to promote development of improved computational tools for simulating realistic full-system performance of lean-burn engines and the associated emissions control systems."

> CLEERS PNNL Subprogram Goal
>
> Working closely with our National Lab partners, the CLEERS industrial/academic team and in coordination with our CRADA portfolio, PNNL will…
>
> …provide the practical & scientific understanding and analytical base required to enable the development of efficient, commercially viable emissions control solutions and modeling tools for ultra high efficiency vehicles.

- VT program goals are achieved through these project objectives:
  - interact with technical community to identify relevant technological gaps
  - understand fundamental underlying mechanisms and material behavior
  - develop analytical and modeling tools, methodologies, and best practices
  - apply knowledge and tools to advance technologies leading to reducing vehicle emissions while improving efficiency
- Specific work tasks in support of the objectives are arrived at through:
  - focus group industrial monthly teleconferences, diesel cross-cut meetings
  - yearly workshops and surveys
  - ongoing discussions on program priorities with the VT office

# Approach/Strategy

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## Approach - "Science to Solutions"

- Build on our strong base in fundamental sciences and academic collaborations
  - Institute for Integrated Catalysis (IIC)
  - Environmental Molecular Sciences Laboratory (EMSL)
- Orient strongly towards applications and commercialization
  - OEMs
  - TIER 1 suppliers
- Work closely with our partners and sponsors
  - ORNL (coordination of website, workshops, etc.)
  - DOE Advanced Engine Cross-Cut Team

**Foundational (CLEERS)** ⟷ **CRADA Activities**

**Foundational (CLEERS)**
- SCR
- PNA
- Multi-functional devices
- LTAT

**CRADA Activities**
- Standard LT SCR (FCA)
  Last year, not reviewed
- Advanced emission controls (Cummins/JMI))
  ACS118, 12pm June 20, Wang
- SCR dosing system (USCAR)
  ACS027, 2pm June 20, KarKamkar
- Fuel neutral particulate studies (GM)
  ACS56, 3pm June 19, Stewart
- SCR-DPF (PACCAR)
  ACS119, 2:30pm June 20, Rappe

## Strategy – "Balanced portfolio"

- Utilize open CLEERS work to support industry CRADA activities, e.g., fundamental SCR studies led to the new CRADAs with FCA and Cummins
- Maintain clear separation between CLEERS and CRADA activities

(only CLEERS project scope covered in this presentation)

# Technical Milestones and Go/No-Go Decisions

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**Milestones:**

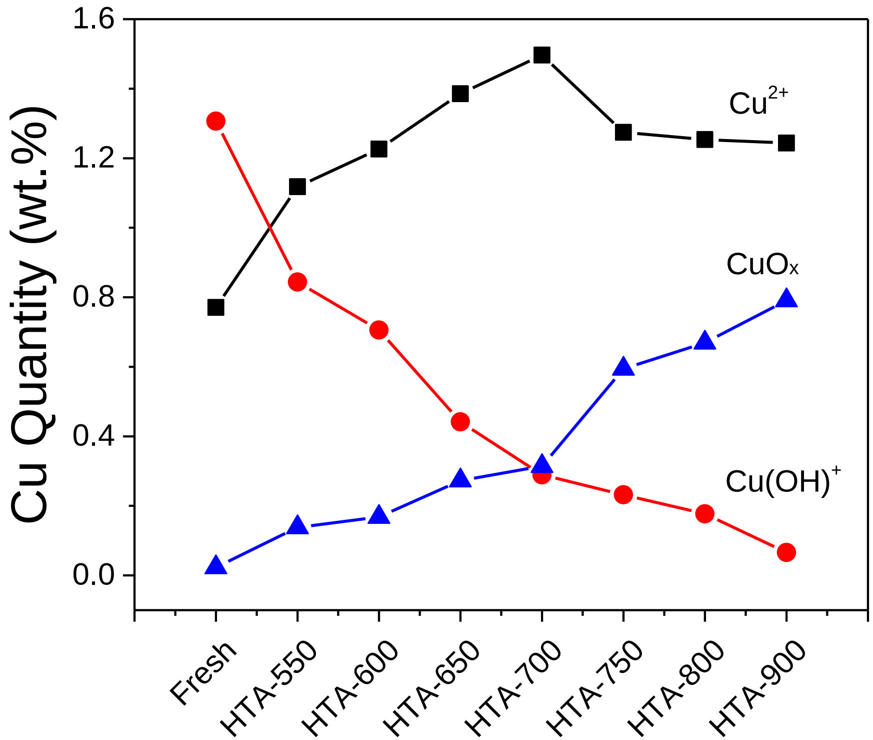
| | | |
|---|---|---|
| Provide fundamental understanding of zeolite supported Pd PNA materials | 12/31/2017 | √ |
| Understand the mechanisms of low-temperature SCR on Cu/SSZ-13 | 3/30/2017 | √ |
| Elucidate the deactivation of Cu/SSZ-13 under hydrothermal aging | 6/30/2017 | √ |
| Analyze X-Ray CT data and attempt to identify catalyst location in a commercial SCR-filter | 3/30/2017 | √ |
| Complete PNA hydrothermal stability and sulfur tolerance studies | 6/30/2018 | initiated |

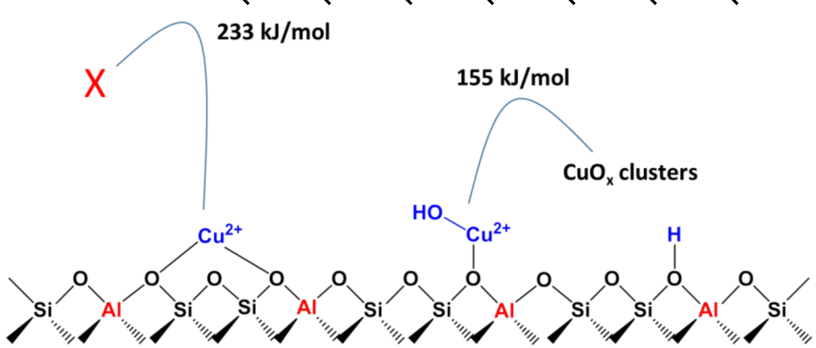
**Go/No-Go Decisions:**

| | | |
|---|---|---|
| Demonstrate sufficient catalyst activity at 175˚C | 3/30/2017 | √ |
| Identify key barriers to overcoming the "150˚C Challenge", and demonstrate a clear path to achieve sufficient catalyst activity at 150˚C | 9/30/2018 | on track |

# Accomplishments – SCR: Provided Molecular Level Understanding of Cu/SSZ-13 by Hydrothermal Aging






- For the first time, $Cu^{2+}$-2Z, $[Cu(OH)]^{+}$-Z and CuOx cluster species in Cu/SSZ-13 catalysts were quantified by EPR at any stage of aging.
- This quantification demonstrates the exceptional stability of $Cu^{2+}$-2Z, and gradual conversion of $[Cu(OH)]^{+}$-Z to CuOx clusters during aging.
- Activation energy barriers for the departure of both isolated ions from their cationic positions by DFT provide a rationale for their difference in hydrothermal stability.
- Harsh hydrothermal aging temperatures (e.g., 800 ºC) led to micropore damage due to CuOx cluster migration.

| Sample | Micro Pore Volume ($cm^3/g$) | Meso Pore Volume ($cm^3/g$) | Total Pore Volume ($cm^3/g$) |
|---|---|---|---|
| Fresh | 0.23 | 0.047 | 0.277 |
| HTA-700 | 0.23 | 0.159 | 0.389 |
| HTA-800 | 0.18 | 0.202 | 0.382 |

Song *et al.*, ***ACS Catal***. 2017, 7, 8214-8227

# Accomplishments – SCR: Proper Selection of Co-Cation Improves the Low Temperature Activity and High Temperature Durability of Cu/SSZ-13

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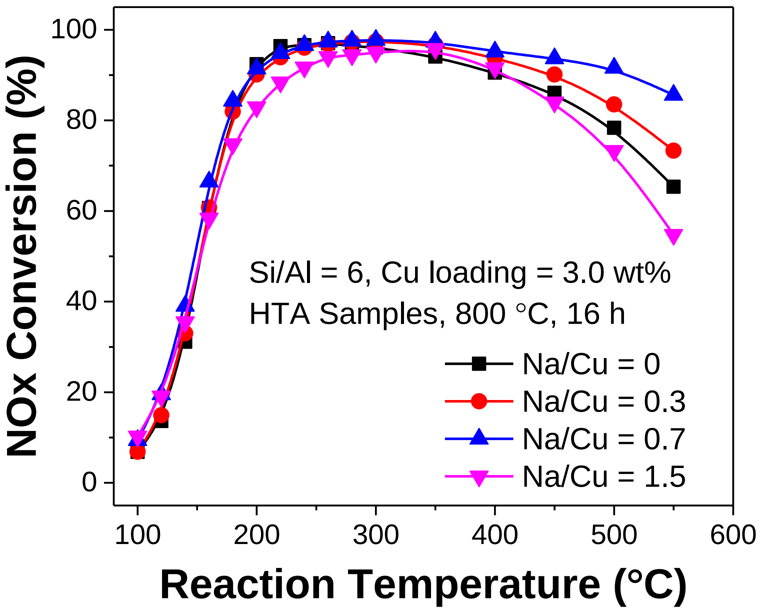


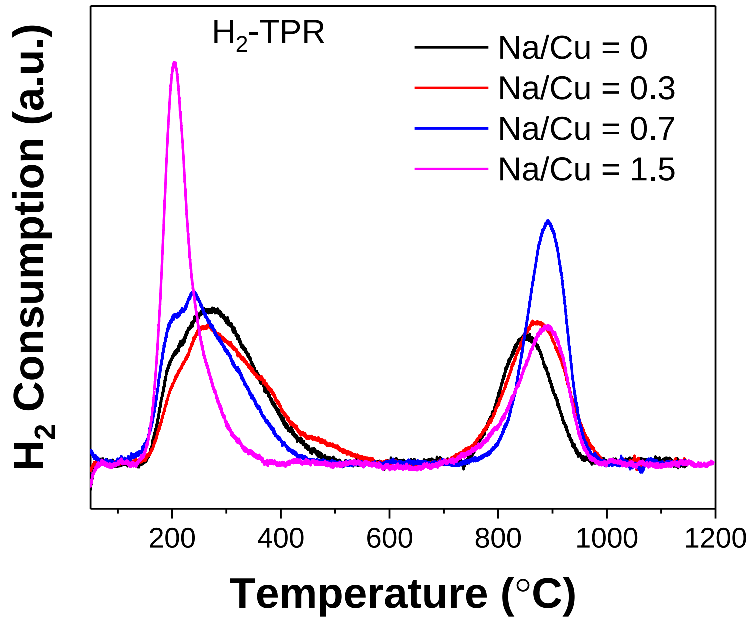


- For the first time, Cu/SSZ-13 catalysts with practical compositions are further optimized with co-cation addition.
- At optimized loadings, $Na^{+}$ and $K^{+}$ promote both low temperature $NO_x$ conversion rates and high temperature SCR selectivity simultaneously, while $Ca^{2+}$ co-cation shows no such beneficial effects, which is consistent with theoretic predictions.

# Accomplishments – SCR: Improved Low Temperature Activity and High Temperature Durability of Cu/SSZ-13

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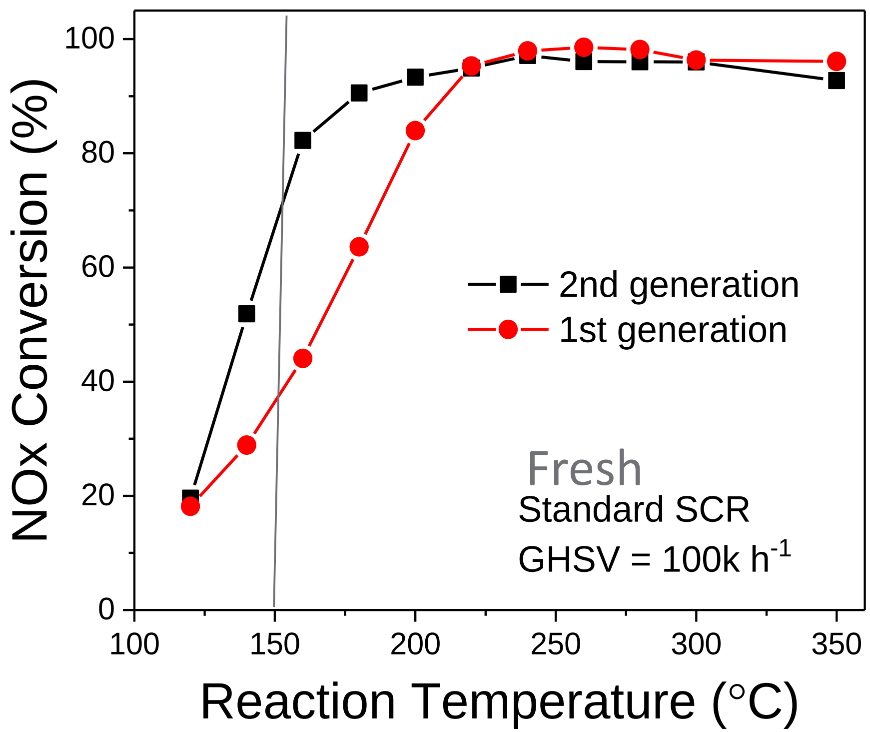
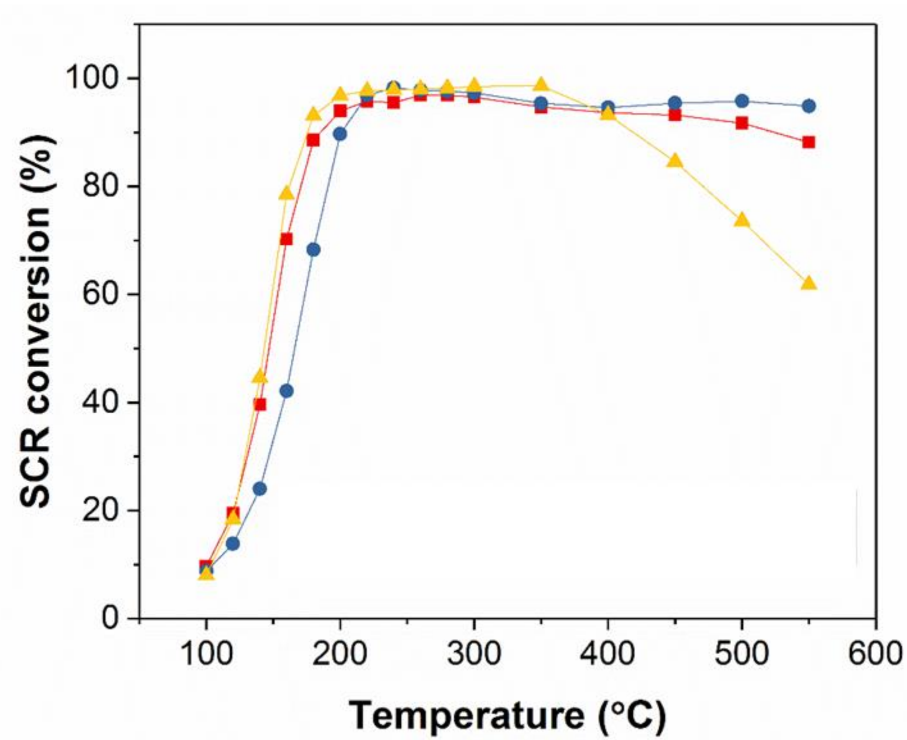
Fresh




Degreened and HTA

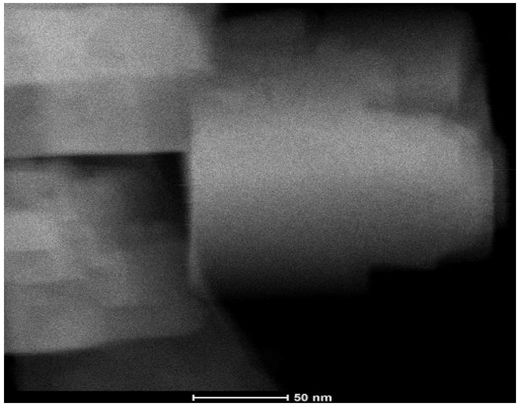


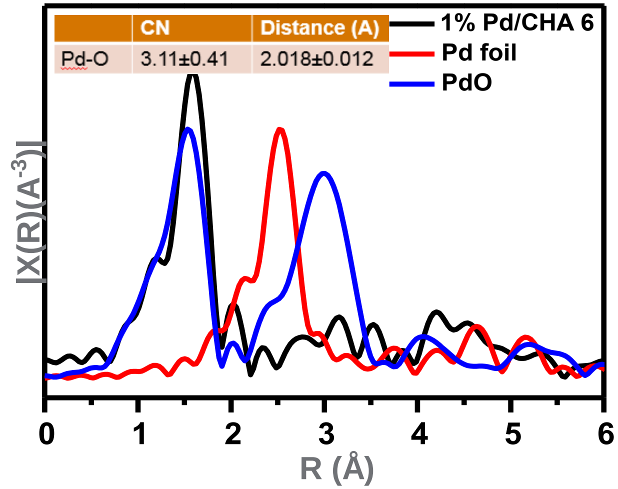

- Molecular level understanding of the barriers associated with low temperature activity and high temperature durability provide the guidance to improved SCR catalysts jointly with FCA.
- New insight is provided into more accurate assumptions of active site requirements and degradation in simulations under CLEERS.

# Accomplishments – PNA: Prepared Lead PNA Materials (1wt%Pd/SSZ-13 with Si/Al Ration of 6) with Well-defined Structures to Provide Molecular Level Insight Into PNA mechanism



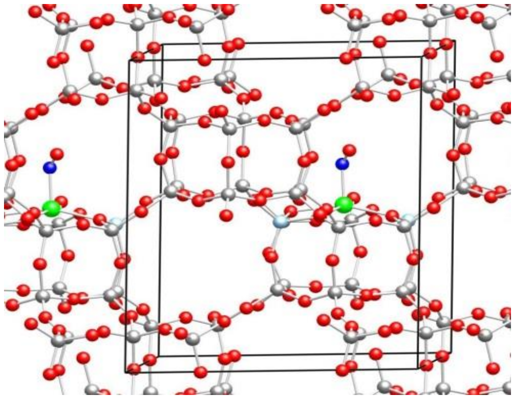
## HAADF-STEM and EXAFS: Pd(II) atomically dispersed



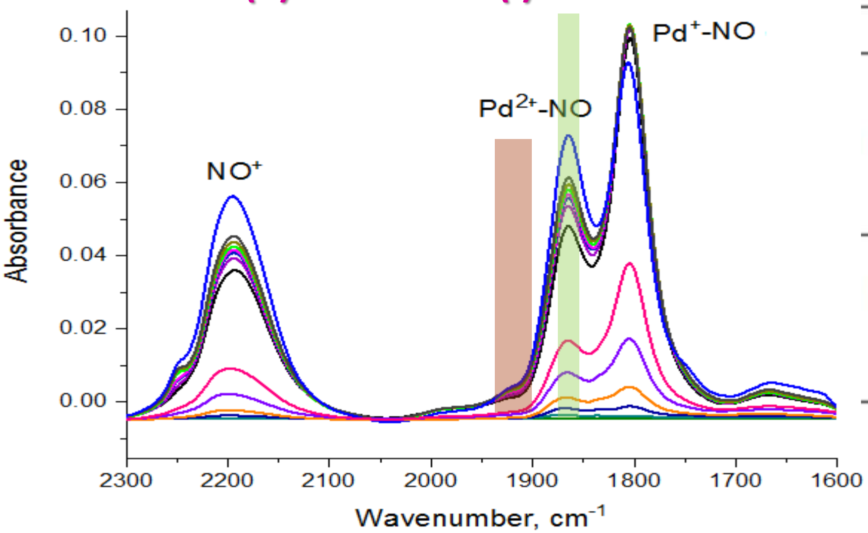

## DFT modeling

## Pd(II)-NO/SSZ13



## FTIR of adsorbed NO:

**Pd(II) + NO → Pd(I) + $NO^+$**




| Str. | υ(L)[a] | d(Pd-L)[a] | d(Pd-$O_{zeo}$) | $N_s$ |
|---|---|---|---|---|
| $Pd^+$ | | | 221;222;225 | 1 |
| $Pd^+H_{zeo}$ | | | 215;218;224;228 | 1 |
| $Pd^+(NO)$ | 1806 | 180 | 219;230 | 0 |
| $Pd^+(NO)_2$ | 1823;1748 | 196; 201 | 223;236 | 1 |
| $Pd^+(NO)_3$ | 1818;1739;1717 | 201;202;207 | 238;240 | 0 |
| $Pd^{2+}$ | | | 206.206.214.214 | 0 |
| $Pd^{2+}(NO)$ | 1845 | 194 | 218;219;232;233 | 1 |
| $Pd^{2+}(NO)_2$ | 1880;1824 | 197;199 | 226;226 | 0 |
| $Pd^{2+}(NO)_3$ | 1872;1820;1797 | 202;206;218 | 228;231 | 1 |

# Accomplishments – PNA: Presence of $O_2$ Promotes PNA of Pd/SSZ-13 via Nitrosyl Formation

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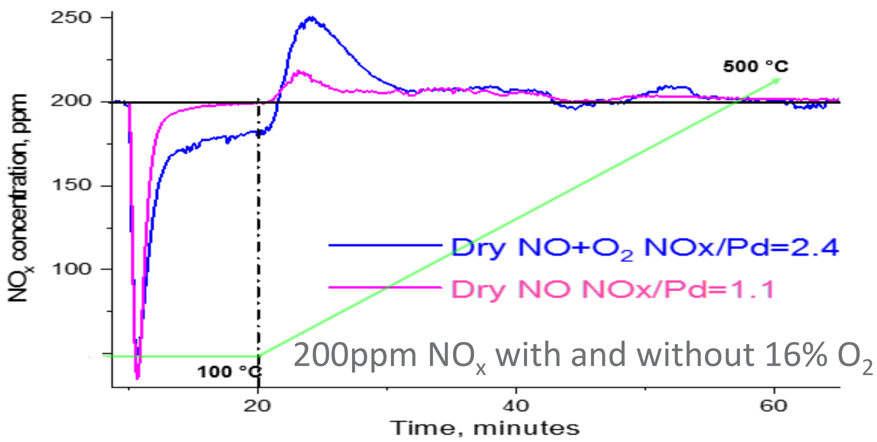
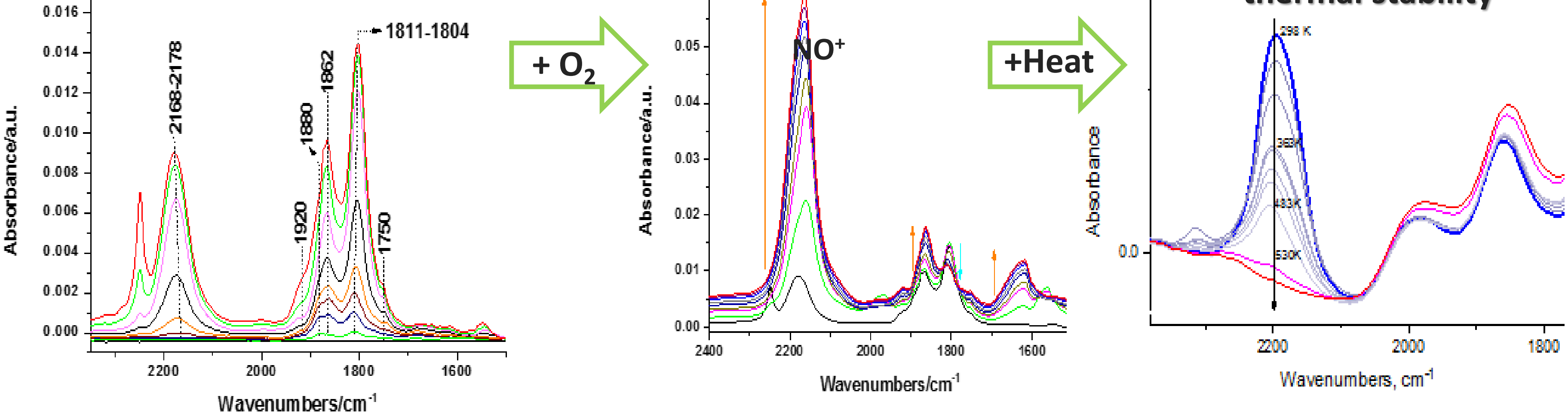



- Addition of $O_2$ to NO improves the uptake of NO on Pd/SSZ-13 due to nitrosyl $NO^+$ formation in cationic positions in addition to Pd(I/II)-NO complexes.
- As we reported last year, PNA performance decreases in the presence of water due to the fact that water competes with NO for the first coordination sphere of Pd.

## $O_2$ addition to Pd(I/II)-NO/SSZ-13 improves PNA via $NO^+$ formation

## FTIR evidence of $NO^+$/SSZ-13 thermal stability




Khivantsev *et al.*, ***J.Phy.Chem.C***. 2018, **DOI:**10.1021/acs.jpcc.8b01007

# Accomplishments – PNA: CO Improves PNA Performance of Pd/SSZ-13 in the Presence of $H_2O$ due to the Formation of Pd(II)(NO)(CO) Complex

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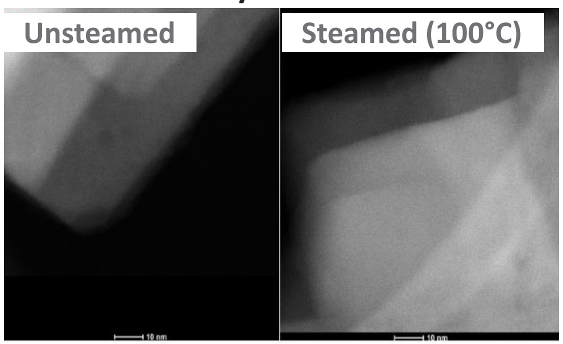
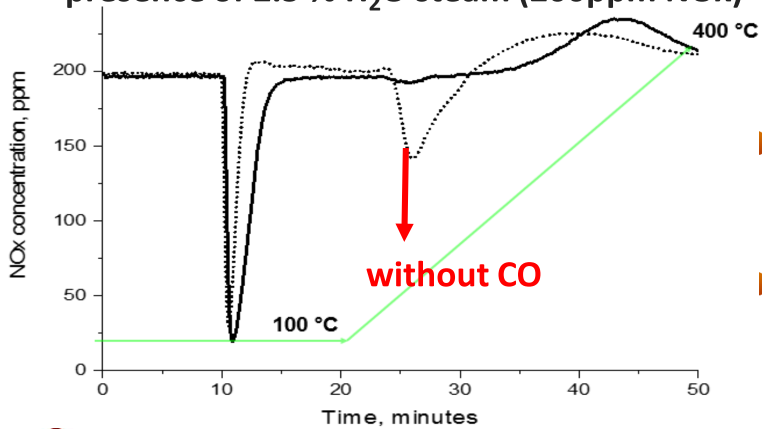
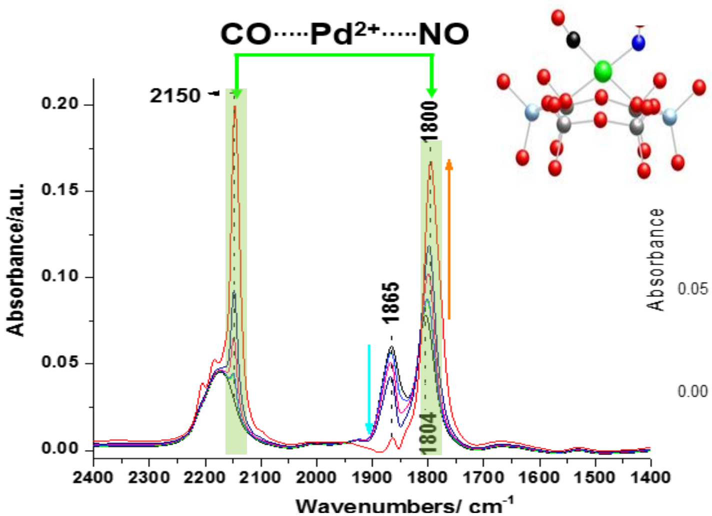
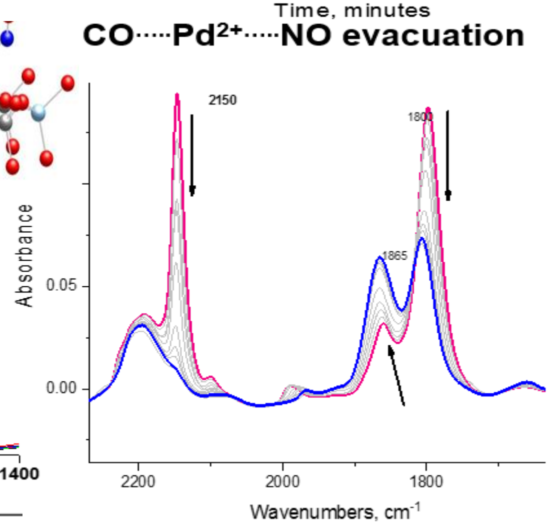
**Cryo HAADF-STEM images for Pd/SSZ-13**




**PNA with and without 200 ppm CO in the presence of 2.5 % $H_2O$ steam (200ppm NOx)**




| Str. | $\upsilon(L)^a$ | $d(Pd\text{-}L)^a$ | $d(Pd\text{-}O_{zeo})$ |
|---|---|---|---|
| $Pd^{2+}(CO)(NO)$ | 2145/1822 | 193/199 | 213;218 |
| $Pd^{2+}(CO)_2(NO)$ | 2129;2109/1825 | 198;198/231 | 219;220 |
| $Pd^{2+}(CO)(NO)_2$ | 2145/1865;1811 | 199/214;214 | 240;240 |

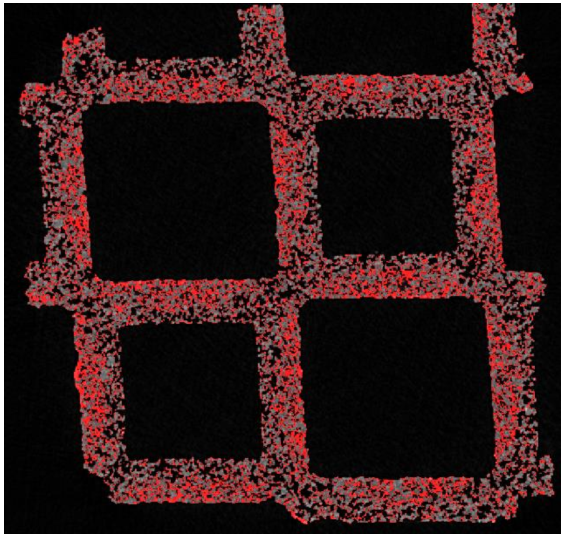
- Water inhibition is not due to the agglomeration of Pd as confirmed by cryo HAADF-STEM.
- Presence of CO increases $NO_x$ uptake and shifts $NO_x$ desorption to >320°C.
- FTIR and DFT provides evidence for selective formation of only Pd(II)(NO)(CO) complex: Pd(II)-NO + CO → OC-Pd(II)-NO
- NO binds much stronger than CO to Pd(I/II) due to a different coordination mode: CO binds linearly, NO binds in a bent fashion
- Pd(I)-NO does not bind CO
- New insight is provided into more accurate descriptions of PNA mechanisms in simulations under CLEERS.

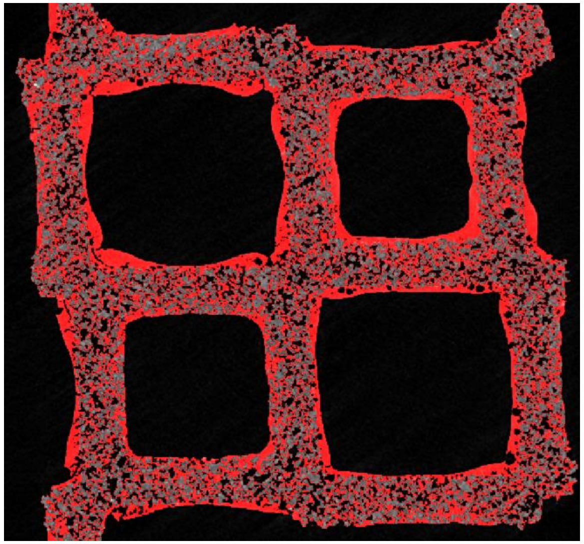
Khivantsev *et al.*, ***J.Phy.Chem.C***. 2018, **DOI:**10.1021/acs.jpcc.8b01007

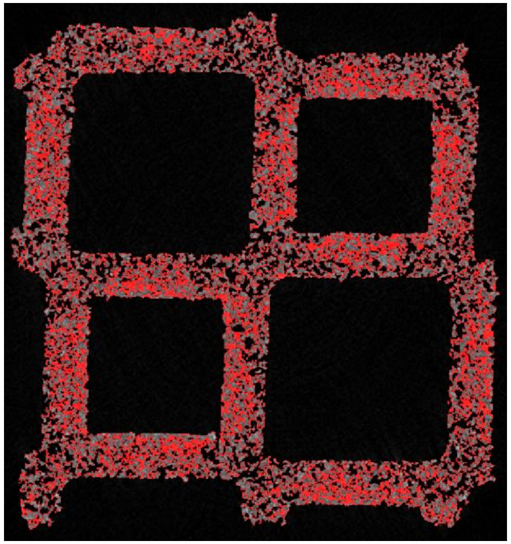
# Accomplishments - Multi-functional Devices: A Commercial SCR-filter Is Characterized by Micro-X Ray CT



- Three distinct axial coating regions observed in commercial SCR-filter
- Micro-Xray CT cross-sections shown with catalyst in false red color







- Region 2
  - Next 14-20% of axial length
  - Relatively heavy coating from both sides of filter walls
- Region 2
  - Next 14-20% of axial length
  - Relatively heavy coating from both sides of filter walls
- Region 3
  - Last 65-70% of axial length near outlet
  - Intermediate coating from downstream side of filter walls

# Accomplishments - Multi-functional Devices: A Commercial SCR-filter Is Characterized by Mercury Porosimetry, and SEM

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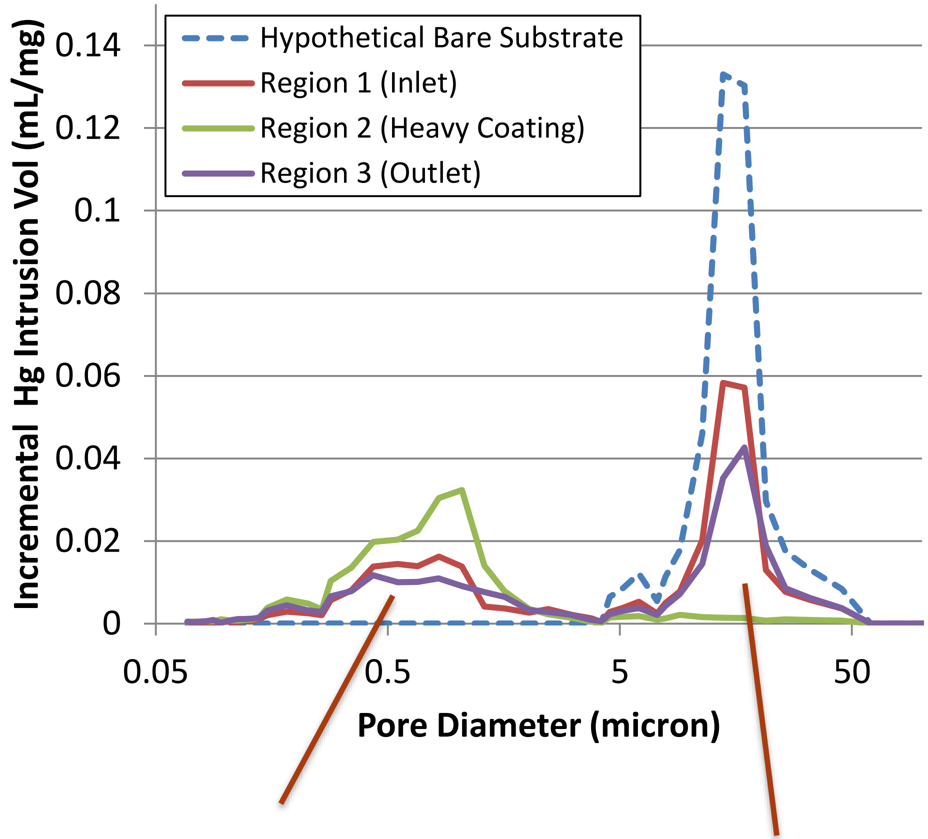
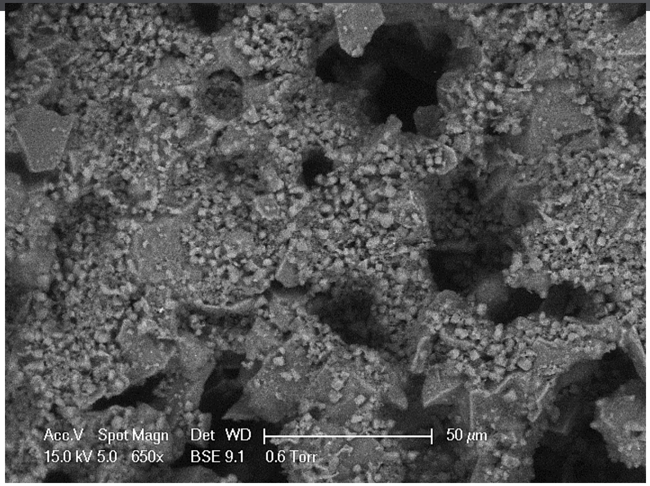
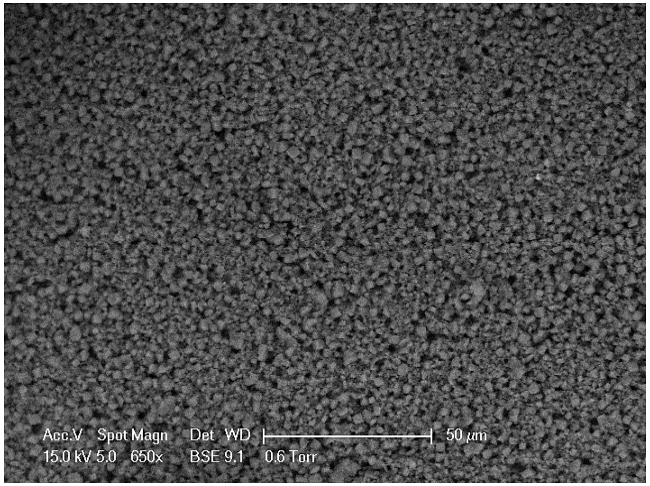



Smaller pores in SCR catalyst coating

Larger pores in original high-porosity filter substrate




Electron micrograph of upstream filter wall surface near outlet end (Region3)




Upstream filter wall surface in heavily coated Region 2 near inlet end

# Accomplishments - LTAT: Low Catalyst Test Protocol Development

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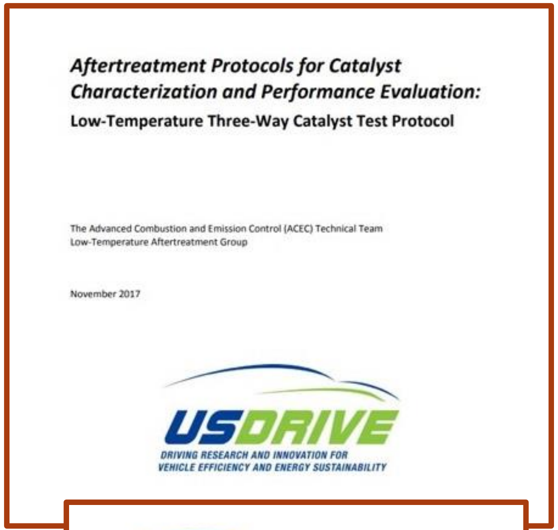
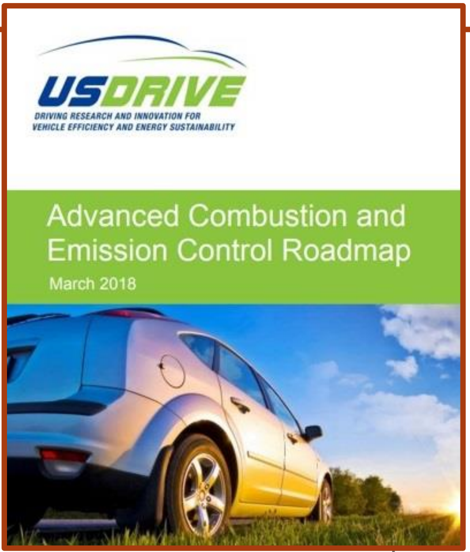
- Low-Temperature Storage Catalyst Test Protocol
  - Complete – released to the technical community on the CLEERS website https://cleers.org/wp-content/uploads/2018/03/2018_LTAT_Low-Temperature-Storage-Protocol.pdf
- Low-Temperature Three-Way Catalyst Test Protocol
  - Complete – released to the technical community on the CLEERS website https://cleers.org/wp-content/uploads/2018/01/2017_LTAT-TWC-test-protocol.pdf
- Support provided to update the US DRIVE ACEC Tech Team Roadmap
  - Complete – available on the DOE website https://www.energy.gov/sites/prod/files/2018/03/f49/ACEC_TT_Roadmap_2018.pdf
- On-going interaction with LTAT sub-group of the ACEC Tech Team
  - Bi-monthly ACEC and AE Crosscut participation
  - Bi-weekly LTAT sub-group participation
  - Prioritization of activities moving forward



# Accomplishments - LTAT: A New Type of Active Site Meets the Dual Challenge of Achieving High Activity and Thermal Stability in Single Atom Catalysts for CO Oxidation

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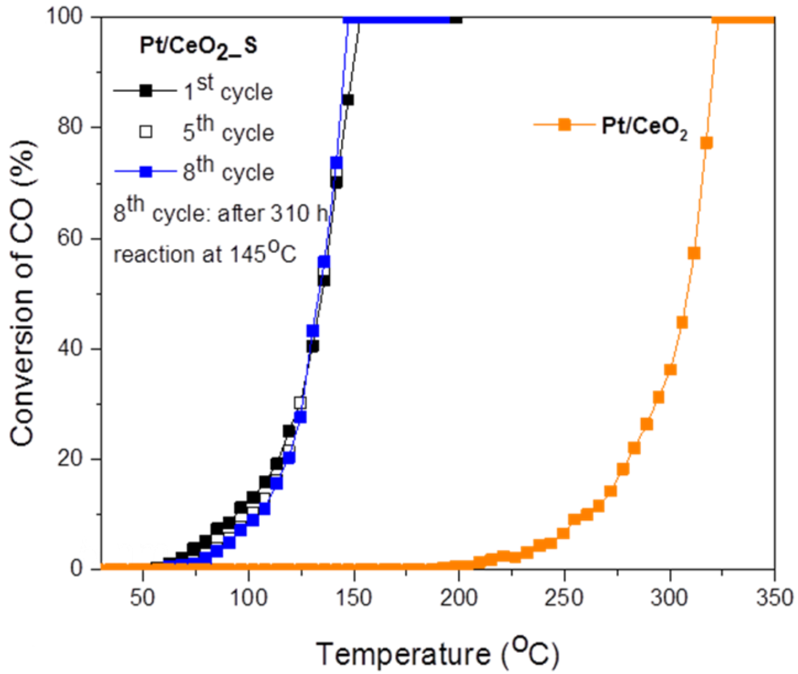


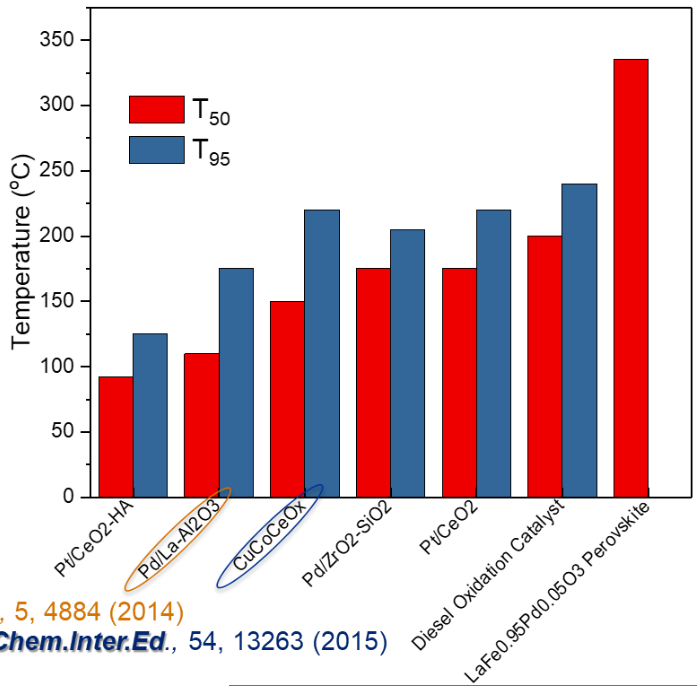


***Nature Comm***., 5, 4884 (2014)
***Angew.Chem.Inter.Ed***., 54, 13263 (2015)

$[O_2]$=10%, [CO] = 0.4% balanced with Ar , GHSV: 200,000 ml/(gcat.hr)

- Hydrothermal aging (750°C, 10% $H_2O$ for 9 hrs) of single atom Pt1/$CeO_2$ synthesized by atom trapping led to high active CO oxidation catalyst, achieving 100% CO conversion at 148°C.
- Best performer among all catalysts reported in open literature after hydrothermal aging (750°C, 10% $H_2O$ for 9 hrs).


Nie, Datye, Wang *et al.*, ***Science***. 2017, 358, 1419-1423 (Dec. 15, 2017 issue)

# Accomplishments - LTAT: Negligible Effect of Sulfur on CO and Propylene Oxidation After Exposing to 5ppm $SO_2$ Following the Low-Temperature Oxidation Catalyst Test Protocol

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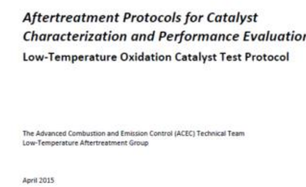
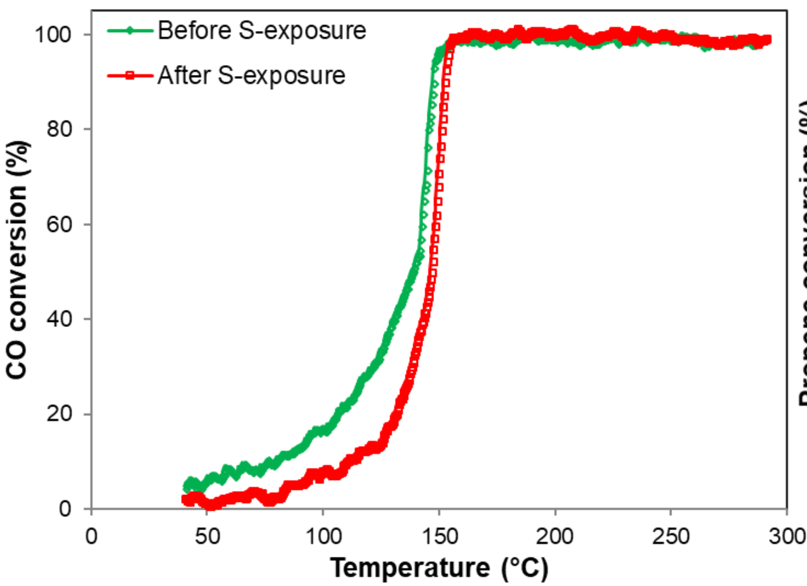

*Aftertreatment Protocols for Catalyst Characterization and Performance Evaluation:*
Low-Temperature Oxidation Catalyst Test Protocol

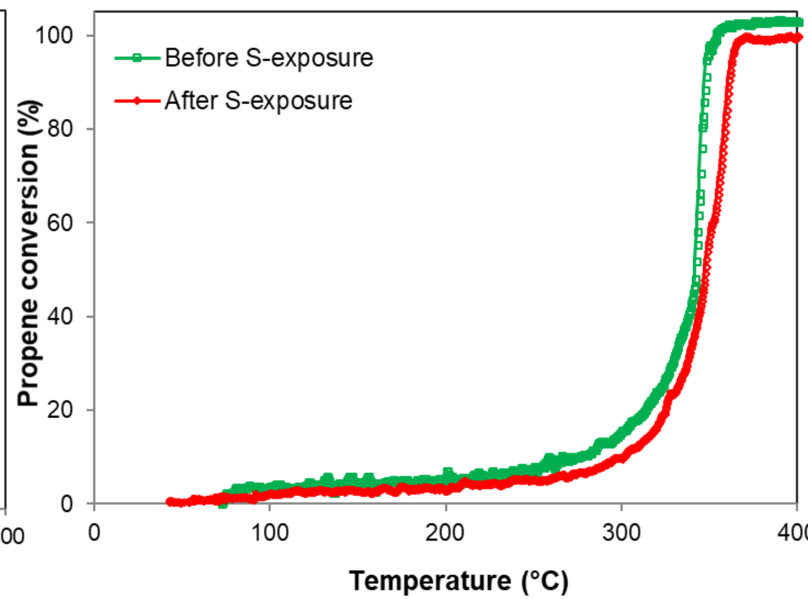
The Advanced Combustion and Emission Control (ACEC) Technical Team
Low-Temperature Aftertreatment Group

April 2015

## CO Oxidation




## Propylene Oxidation




[CO]=0.4% , $[C_3H_6]$=0.1%, [NO]=0.05%, $[O_2]$=10%, $[H_2O]$=5%, balanced by $N_2$

- Even after S-treatment, 100% CO conversion is reached at ~ 150 °C

# Accomplishments – Responses to Previous Years Reviewers' Comments

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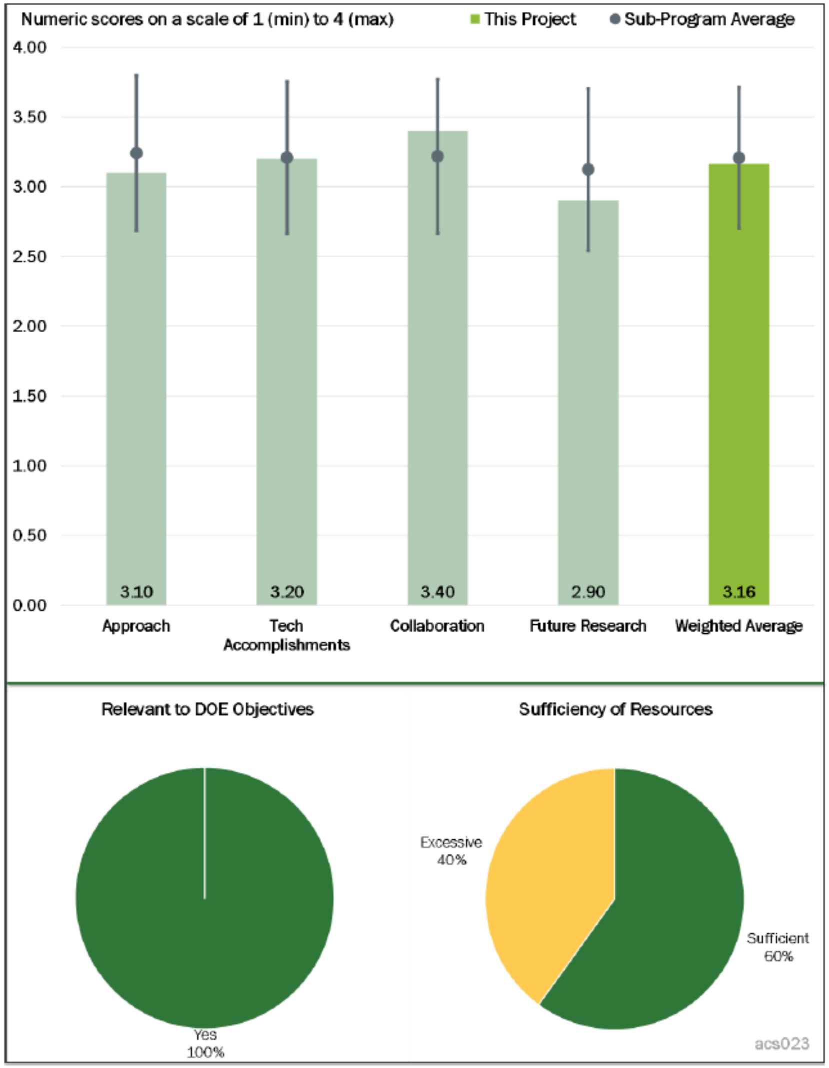
- Nearly all the comments from the reviewers last year were very supportive and complimentary.
- Some comments/recommendations included:
  1. ..it would be good to know what portions were used successfully by the companies involved in the project…
  2. ….S tolerance and reactivation….. The reviewer cautioned that this ought to be addressed sooner rather than later because the proposed project directions may make the matter worse.
  3. … CLEERS has more work to do to improve aftertreatment performance and durability..
- PNNL response:
  1. Improved low temperature activity and high temperature durability of Cu/SSZ-13 jointly developed with FCA is illustrated as an example (slide 9).
  2. Sulfur tolerance of single atom Pt1/CeO2 was evaluated at the early stage (slide 17).
  3. Focus SCR, PNA, and LTAT on performances (e.g., Pd utilization for PNA) and durability (e.g., both SCR and PNA)



# Collaboration and Coordination with Other Institutions

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**Collaborators/Coordination**

- DOE Advanced Engine Crosscut Team (this group is the primary sponsor and overseer of all activities)
- CLEERS Focus Groups
- USCAR/USDRIVE ACEC team
- 21CTP partners
- Oak Ridge National Lab
- Kymanetics, Inc.
- Very active collaboration with an NSF/DOE-funded program with partners at Purdue, Notre Dame, WSU, Cummins and ANL

**Acknowledgements**

- PNNL: Haiying Chen (Johnson Matthey), Laura Righini (Politechnico Milano), John Luo (Cummins), Alla Zelenyuk, Carl Justin Kamp (MIT, Kymanetics), Craig DiMaggio (FCA), Wei Li (GM), Se Oh (GM), Hristiyan A. Aleksandrov and Georgi N.Vayssilov (Sofia University, Blgaria), Franklin Tao (University of Kansas), Abhaya Datye (University of New Mexico).
- ORNL: Stuart Daw, Jim Parks, Josh Pihl, John Storey, Vitaly Prikhodko, Samuel Lewis, Mary Eibl, and support from the ORNL team.
- DOE Vehicle Technologies Program: Gurpreet Singh and Ken Howden.

# Remaining Challenges and Barriers



**SCR**

- Low-temperature activity enhancement for standard SCR.
- Elimination of low-temperature ammonium nitrate poisoning for fast SCR, particularly for small pore zeolite catalysts.
- Enhancement of NO oxidation function via hybrid SCR catalysts containing zeolite and a second phase without sacrificing catalyst stability due to mutual interactions between phases.

**PNA**

- Understand the nature of all the adsorbed species formed on PNAs during their operation.
- Identify the spectroscopic characteristics of all the adsorbed species present.
- Test new PNA formulations (new structures, even non-zeolitic ones)

**Multi-functional devices**

- Detailed performance models are needed for production multi-functional exhaust filters, including SCR/DPF and TWC/GPF.
- There is a lack of fundamental understanding of interactions between advanced substrates, advanced catalyst coatings, and ash, and their effects on device performance as a function of time.

**LTAT**

- Developing a fundamental understanding of limitations to low-temperature catalysis in exhaust environments and identification of thermally-durable pathways to mitigate or circumvent.
- Development of catalysts with superior low-temperature activity that retain high temperature durability.
- The need for consistent and realistic metrics for low-temperature testing and reporting that sufficiently captures catalyst performance.

# Proposed Future Work

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**SCR**

- Establish structure-function correlations for the fast SCR reaction on Cu and Fe exchanged small pore zeolites.
- Provide fundamental understanding of exchanged zeolite + metal oxide hybrid materials to guide the further improvement of low-temperature SCR and overall durability of the SCR component of the exhaust aftertreatment system.
- Develop operando EPR system for standard and fast SCR, to further gain insights into reaction mechanisms and site requirements.

**PNA**

- Identify all PNA intermediates formed through co-adsorption of different gas molecules present in PNA streams by spectroscopy methods
- Perform advanced spectroscopic and DFT characterization of species thus formed and correlate the structure-PNA storage performance
- Sulfur and HC tolerance for the PNA catalysts.

**Multi-functional devices**

- Use modeling and fundamental experiments to explore the effects of catalyst distribution on the performance of commercial multi-functional filters.

**LTAT**

- Continue addressing the issues for practical applications of promising emerging catalysts, including HCs and S effects.
- Work with ACEC to identify LTAT Group focus beyond protocol development, e.g., modeling needs and priority identification.

Any proposed future work is subject to change based on funding levels

# Summary

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**SCR**

- Provided detailed atomic-level understanding on the transformation of Cu active sites during hydrothermal aging of Cu/SSZ-13 SCR catalysts, via a combined experimental and theoretical approach.
- Identified migration of CuOx clusters during hydrothermal aging as the primary reason for structural degradation.
- Detailed atomic-level understanding on the beneficial or detrimental roles of alkali and alkaline co-cations.
- Provided the guidance for further activity and durability improvement.

**PNA**

- Prepared Pd/SSZ-13 PNA materials with well-defined structure to provide molecular level insight into PNA chemistry using combined spectroscopic and DFT approach.
- Fundamentally understood the inhibiting role of $H_2O$ and promotion role of CO on PNA, even in the presence of $H_2O$, and identified that the maximum NO/Pd ratio of Pd/SSZ-13 is 1 due to stoichiometry of Pd(I/II)-NO and Pd(II)(NO)(CO) complexes.
- Provided more accurate descriptions of PNA mechanisms in simulations under CLEERS.

**Multi-functional devices**

- A number of techniques were used to examine catalyst distribution in a commercial SCR-filter; including micro X-Ray CT, electron microscopy, and mercury porosimetry
- Three distinct axial regions were observed with varying loading and catalyst placement relative to wall orientation.

**LTAT**

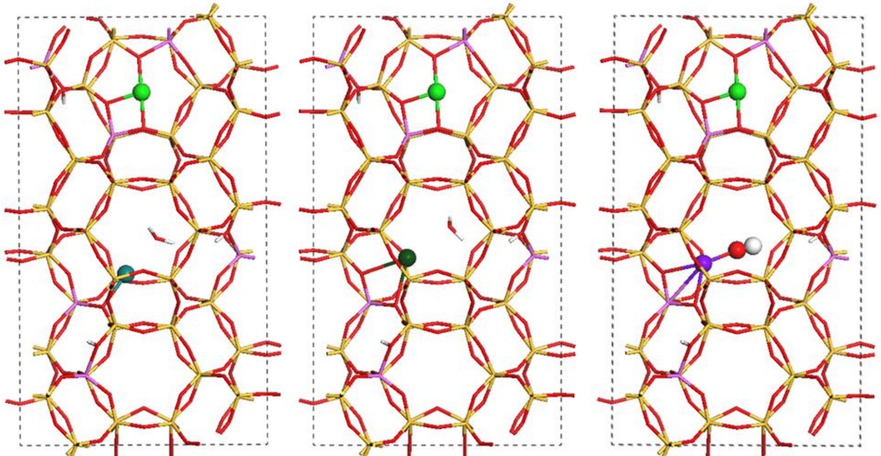
- On-going interaction with LTAT sub-group of the ACEC Tech Team to prioritize activities moving forward.
- Longer term activity testing of single atom Pt1/$CeO_2$ for CO oxidation.

14 peer-reviewed publications in *Science, Nature Catalysis, ACS Catalysis, J.Catal.*

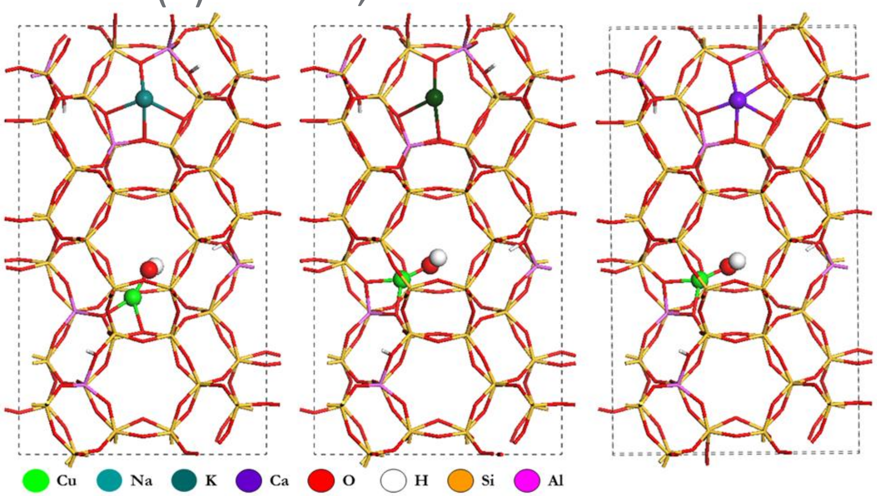
# Technical Backup Slides

# Understanding of Co-cation Effects on Cu/SSZ-13 by DFT Simulations



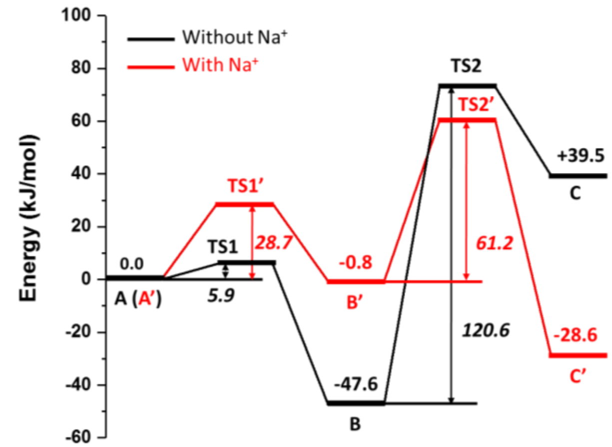


Cu(II) in 6MR, cocation in 8MR




Cu(II) in 8MR, cocation in 6MR

| | $Na^+/Cu^{2+}$ | $K^+/Cu^{2+}$ | $Ca^{2+}/Cu^{2+}$ |
|---|---|---|---|
| ΔE ($kJ\ mol^{-1}$) | +43.0 | +20.6 | -101.6 |




- $Na^+$ and $K^+$ delay dealumination, but they do not prevent $Cu^{2+}$ from occupying windows of 6MR. However, they also destabilize $Cu(OH)^+$, causing $CuO_x$ cluster formation much more readily. Their presence can promote maximization of $Cu^{2+}$-2Z sites when their contents are properly chosen.
- $Ca^{2+}$ compete with $Cu^{2+}$ for the thermodynamically most stable sites. They do not show beneficial co-cation effects.

# Sulfur Tolerance Testing of Single Atom $Pt1/CeO_2$ for CO Oxidation

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***Aftertreatment Protocols for Catalyst Characterization and Performance Evaluation:***

**Low-Temperature Oxidation Catalyst Test Protocol**

The Advanced Combustion and Emission Control (ACEC) Technical Team
Low-Temperature Aftertreatment Group

April 2015

USDRIVE
DRIVING RESEARCH AND INNOVATION FOR VEHICLE EFFICIENCY AND ENERGY SUSTAINABILITY

**Measure CO or Propylene Lightoff**

↓

**Exposure to 5ppm $SO_2$, 6% $H_2O$, balanced with air, 300°C, 200,000 ml/(gcat hr), 2hrs**

↓

**Re-measure CO or Propylene Lightoff Measurement**

https://cleers.org/wp-content/uploads/2015_LTAT-Oxidation-Catalyst-Characterization-Protocol.pdf

# Generation of $O_{lattice}H$ by Steam Treatment

Pacific Northwest NATIONAL LABORATORY
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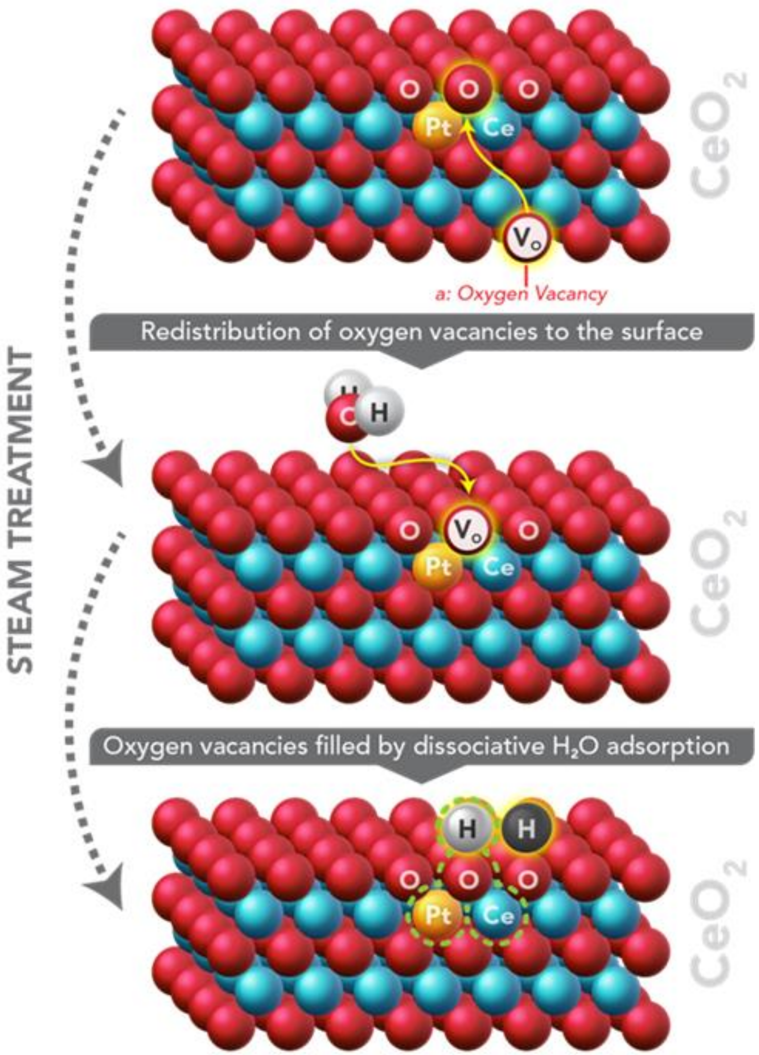
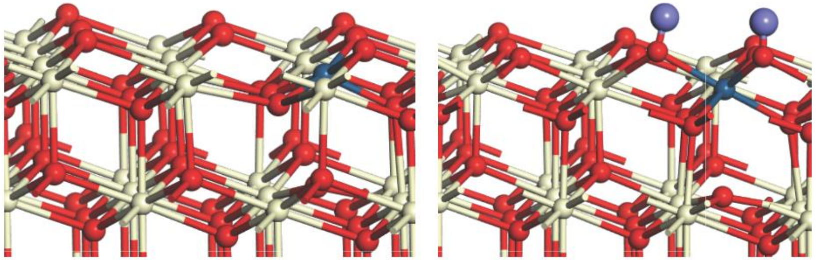
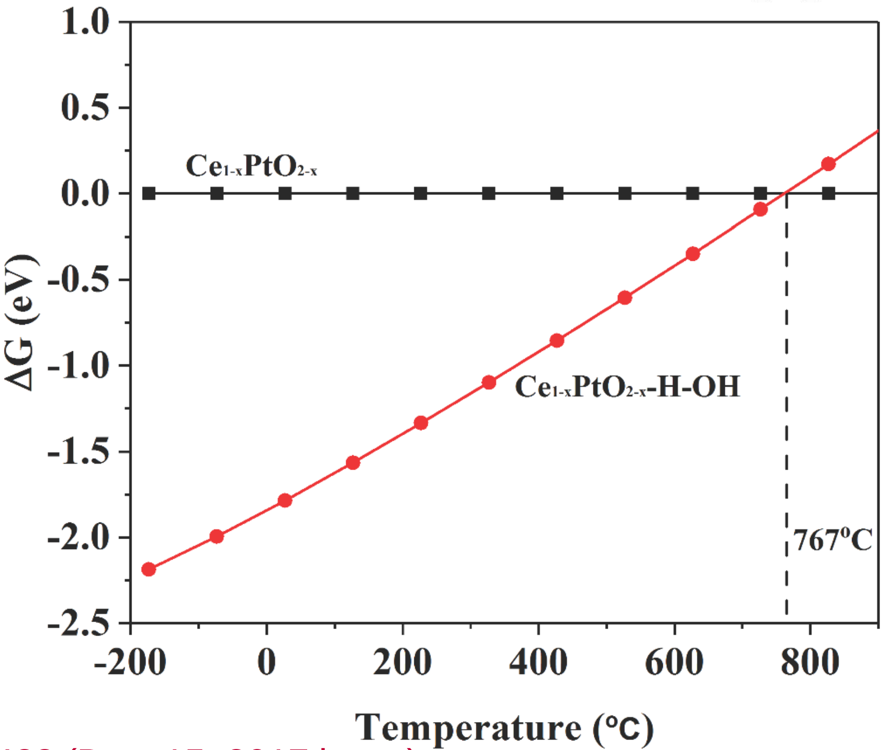
C.H.F.Peden *et al.*, *Surface Science* 526, 1-18 (2003)



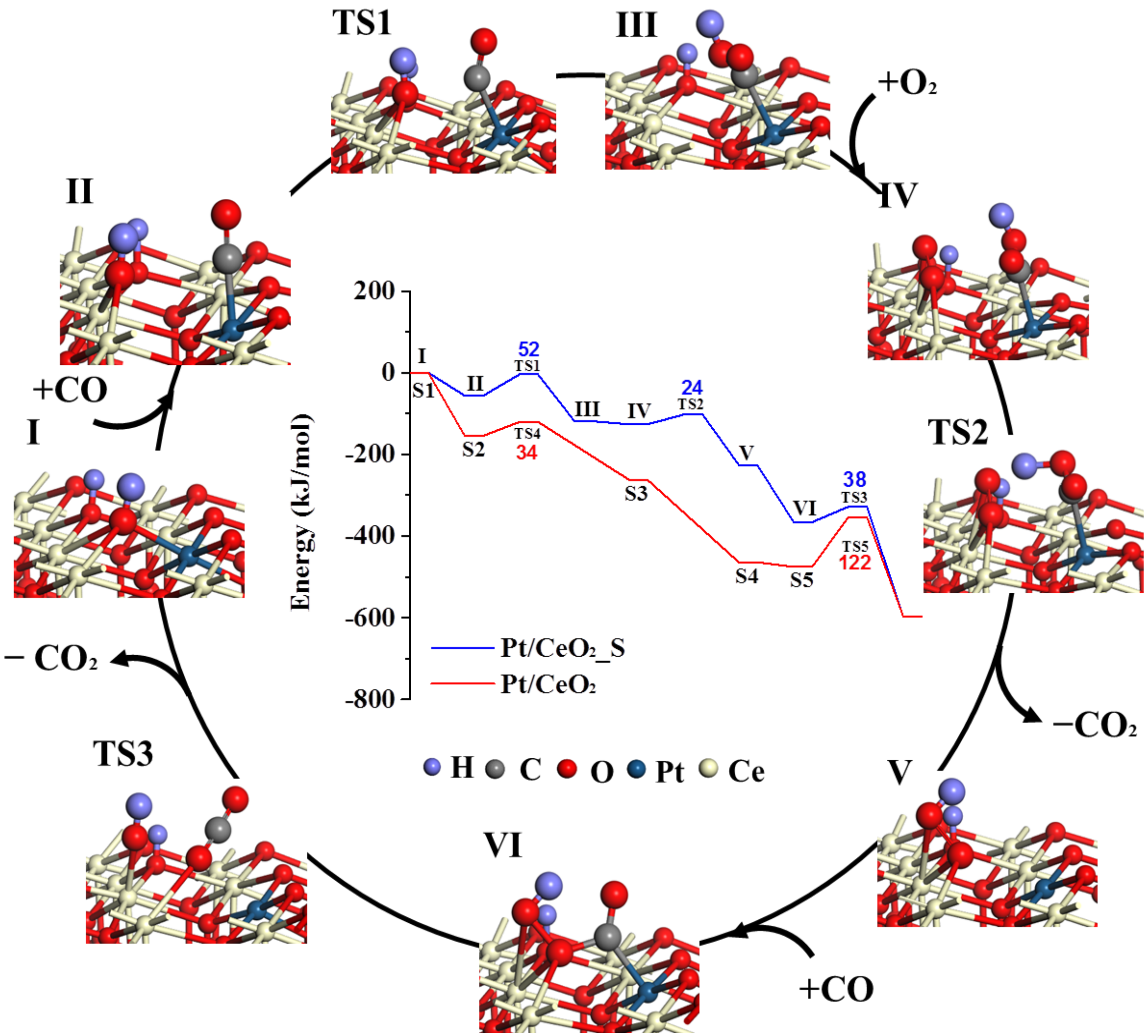
$$Ce_{35}PtO_{71} + H_2O \rightarrow Ce_{35}PtO_{72} + 2[H]$$




Nie, Datye, Wang *et al.*, ***Science***. 2017, 358, 1419-1423 (Dec. 15, 2017 issue)

# A Facile Pathway for CO oxidation Involving A Carboxyl Intermediate Significantly Improves CO Oxidation

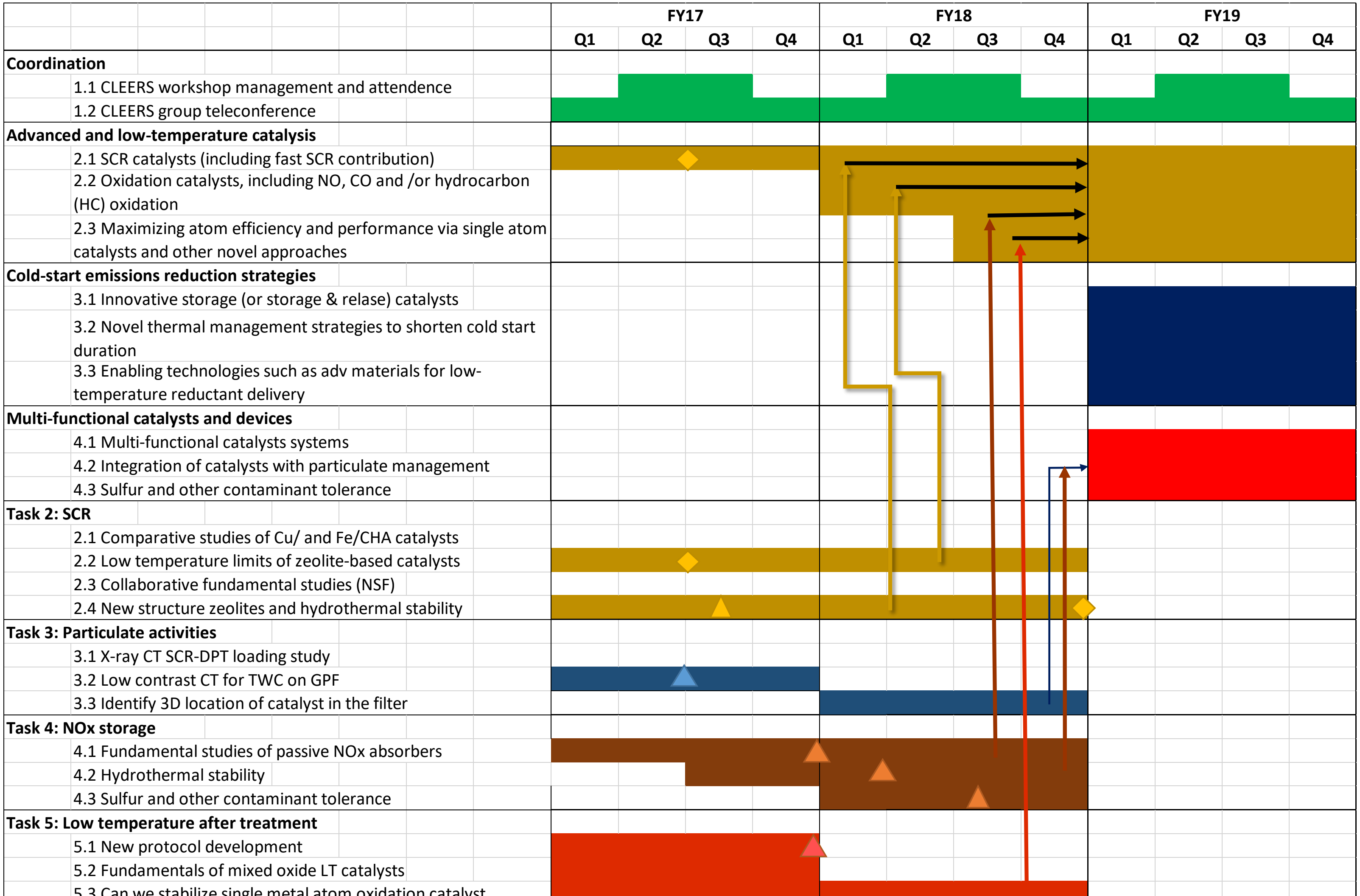





Nie, Datye, Wang *et al.*, ***Science***. 2017, 358, 1419-1423 (Dec. 15, 2017 issue)

# Proposed Schedule for PNNL CLEERS Activities Shifts Focus to Advanced Low-Temperature Catalysis, Cold-Start Emissions Reduction Strategies, and Multi-functional Catalysts/Devices






▲ Milestones
♦ Go/No-Go Decision