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# Advanced Emission Control for High-Efficiency Engines

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JOHNSON MATTHEY

ACS118

## Timeline

- ▶ 2009 – 2019
- ▶ 3-Year Renewal
  - Executed – March 2016
- ▶ Finish – March 2019

## Budget

- ▶ Matched 50/50 by Cummins as per CRADA agreement
- ▶ DOE funding for FY16 – FY19: \$300K each year

## Barriers

- ▶ Lack of cost-effective emission control
- ▶ Durability of emissions control devices
- ▶ Low temperature performances

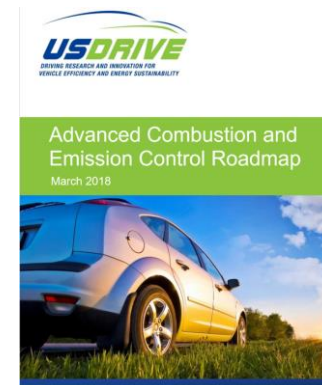
## Partners

- ▶ Pacific Northwest National Laboratory
- ▶ Cummins, Inc.
  - w/Johnson Matthey



# 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 ( $\text{NO}_x$ , CO, HCs) at  $150^\circ\text{C}$  for the full useful life of the vehicle (defined as the longer of 150,000 miles or 15 years)
- ▶  $\text{CH}_4$  emissions from natural gas engines are problematic, since the catalytic oxidation of  $\text{CH}_4$  is difficult and  $\text{CH}_4$  GHG emissions above the 30 mg/mi light duty vehicle cap, as measured over the Federal Test Procedure (FTP) drive cycle, count against fuel economy.





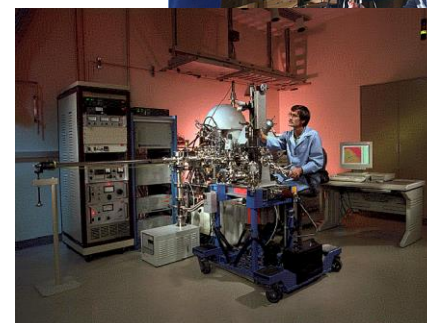
# Goals and Objectives

Focus on a broad and very important area of critical relevance to DOE and Cummins: Advanced emission control for high-efficiency engines

- ▶ Passive NO<sub>x</sub> absorbers - Develop next generation materials to address the cold-operation, as driven by improved engine efficiency.
- ▶ Oxidation of methane and short alkanes – Address cold-operation emissions arising from CNG vehicles.

# Approach

- ▶ Taking advantage of the strengths from the partners:
  - Johnson Matthey: Catalyst formulation and upgrading.
  - Cummins: catalysis laboratory with on-engine testing.
  - PNNL: state-of-the-art catalyst characterizations
- ▶ Revealing fundamental aspects of the chemistry and catalytic materials involved in PNA and small alkane catalytic oxidation.



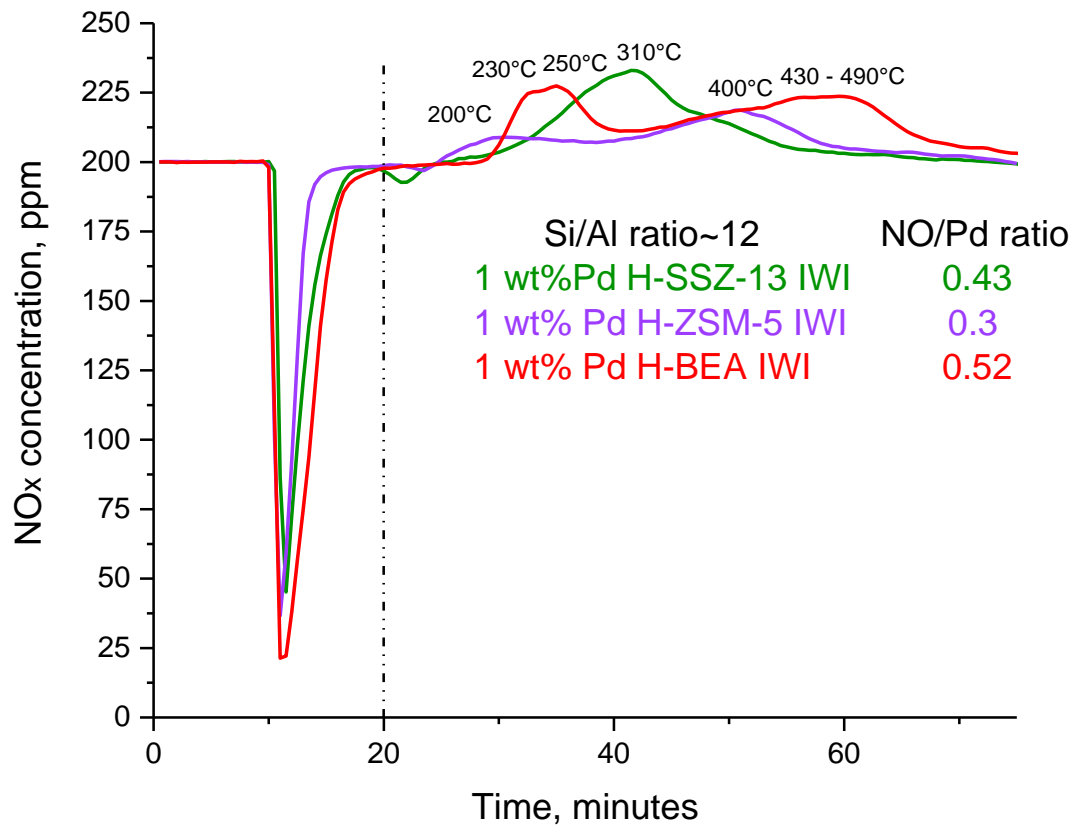
# Milestones

<b>1.0</b>	<b>Passive NOx Absorber</b>			
1.2	Determine PNA properties of all zeolites prepared (NOx uptake/release experiments).	PNNL/Cummins	Mar., 2017	√
1.3	Complete initial studies of NOx storage/release mechanisms in Pd-loaded zeolites (kinetic and spectroscopy studies).	PNNL	Mar., 2018	√
1.4	Evaluate thermal stability and resistance to poisons (S, HCs) of all Pd-loaded zeolites PNA materials.	PNNL	Mar., 2019	On track
<b>2.0</b>	<b>Methane and Ethane Oxidation at Low Temperature</b>			
2.1	Elucidate deactivation mechanisms of supported Pd catalysts	PNNL	June, 2017	√

# Accomplishments

## Identified 1wt% Pd H-SSZ-13 as Lead PNA Materials

### PNA NO<sub>x</sub> Profiles on 1 wt% Pd H-Zeolite Si/Al=12 prepared from Pd(II) and H-zeolite form



- ▶ NO<sub>x</sub> release T depends on framework type
- ▶ Pd is under utilized, e.g., NO/Pd < 1

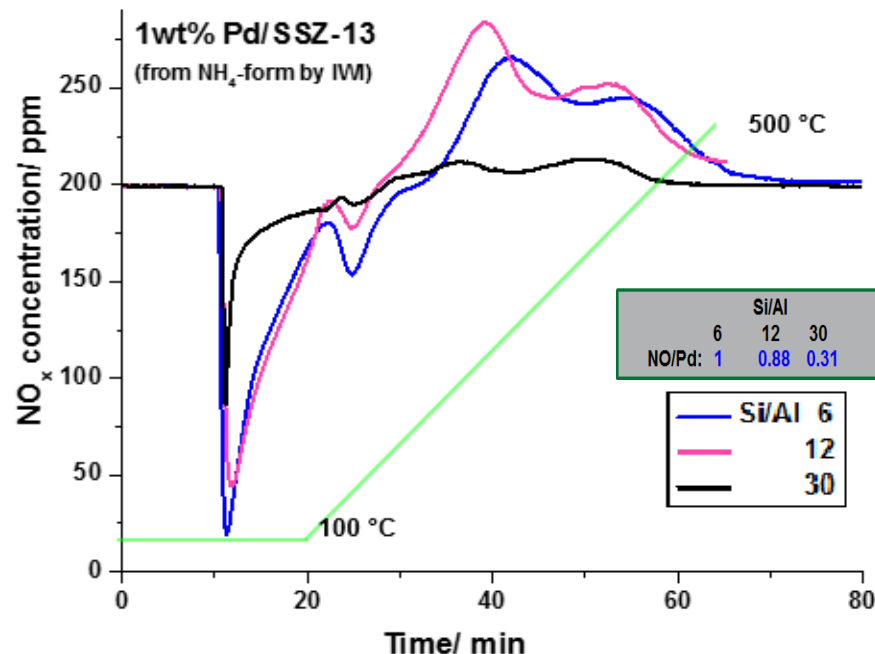
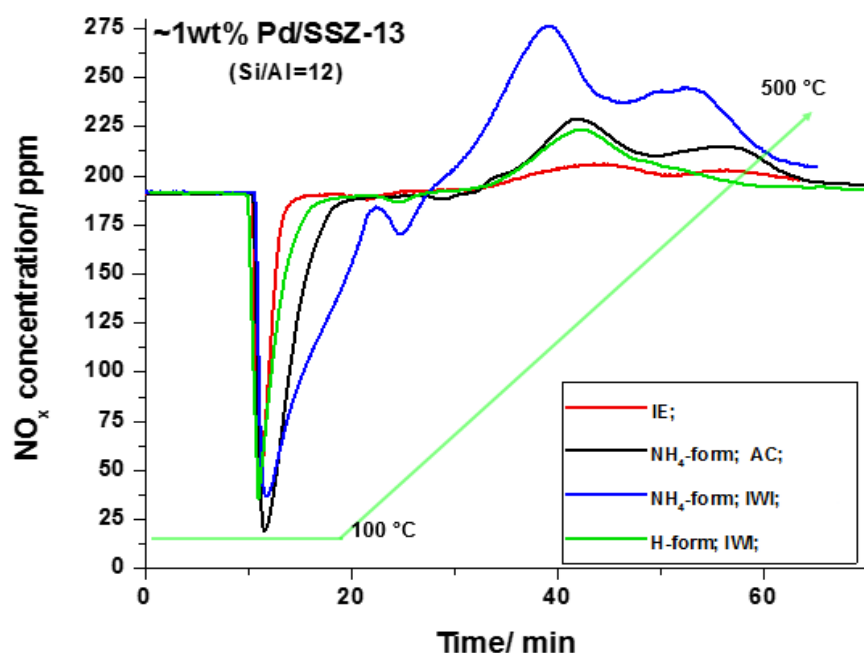
# Accomplishments

## Preparation Route and Si/Al Ratio Are Critical to the Performance of Pd/SSZ-13

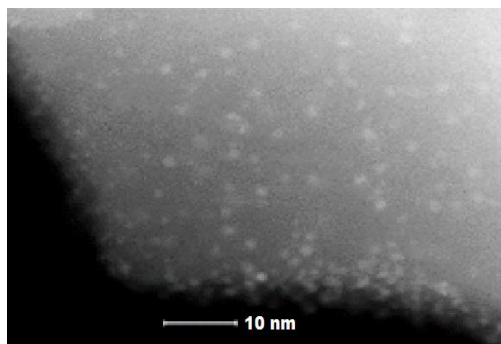


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**HAADF-STEM image of 1 wt%Pd H-SSZ13 prepared by IWI from Pd(II) NH<sub>4</sub>-SSZ13 with Si/Al=12**



- ▶ IWI with NH<sub>4</sub>-SSZ-13 is the route to better performing materials.
- ▶ At Si/Al=12, PdO<sub>x</sub> clusters are on external surface, and not all Pd are atomically dispersed and fully available for PNA.
- ▶ Varying Si/Al ratio leads to the best performing materials with full utilization of Pd at Si/Al ratio=6: NO/Pd ratio ~ 1.



# Accomplishments

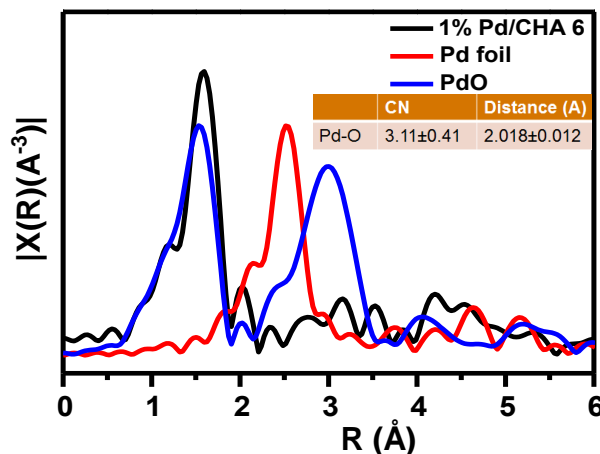
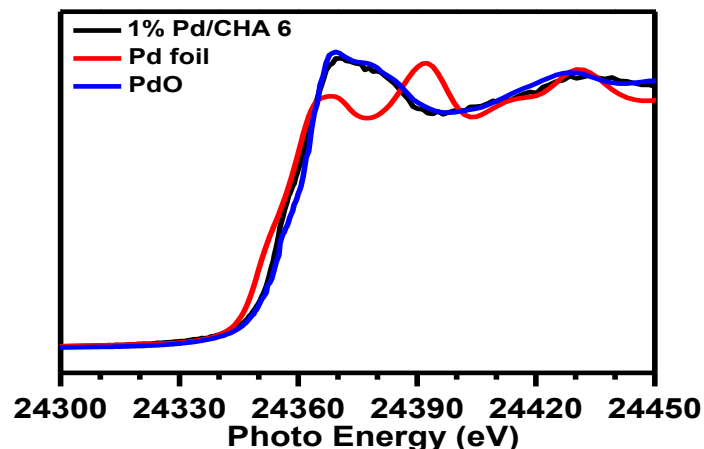
## EXAFS, XANES, HAADF-STEM, CO- and NO-FTIR Confirm Pd Is Atomically Dispersed with 2+ Oxidation State on 1wt%Pd NH<sub>4</sub>-SSZ-13 (Si/Al=6)



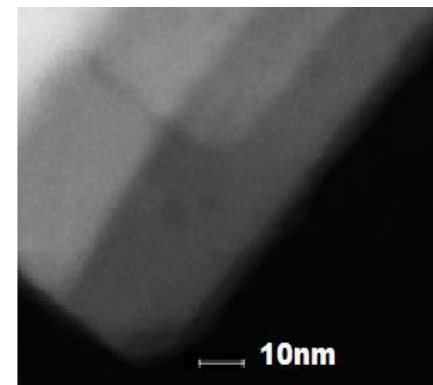
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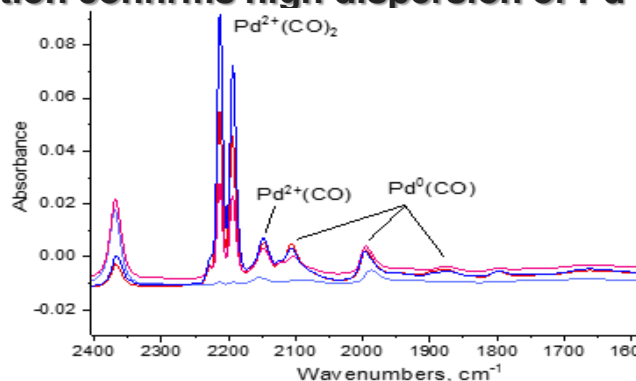
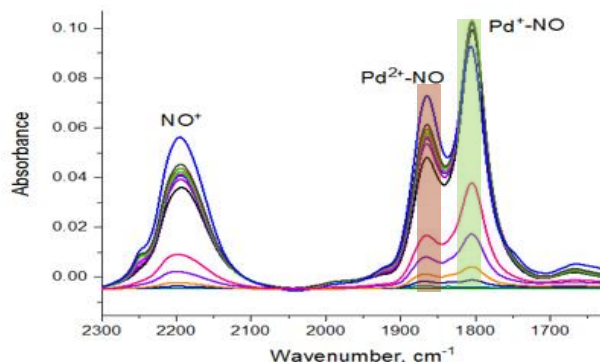
EXAFS and XANES characterization shows Pd is atomically dispersed, in 2+ oxidation state with Pd<sub>1</sub>O<sub>4</sub> sites



Cryo HAADF-STEM imaging



FTIR of NO and CO adsorption confirms high dispersion of Pd

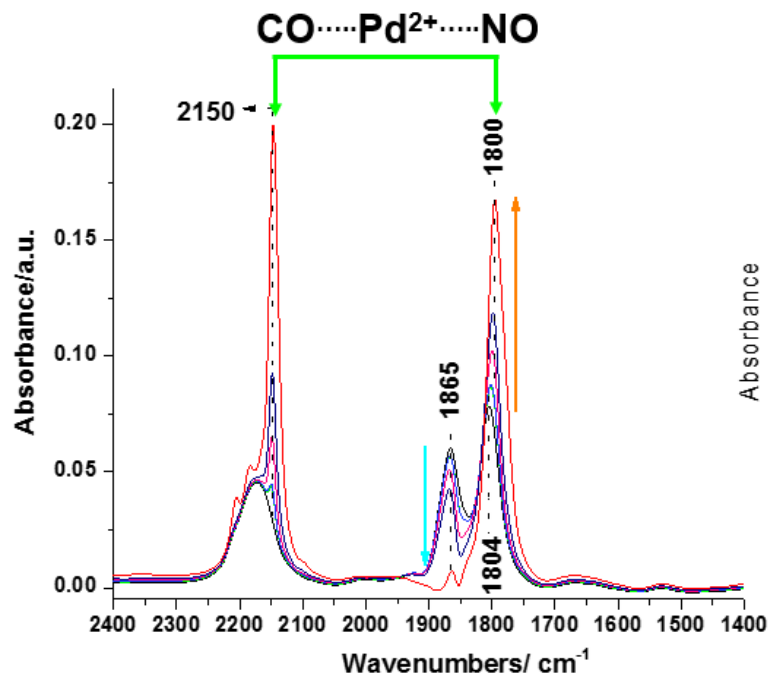


DFT for Pd (Pd-NO) /SSZ-13

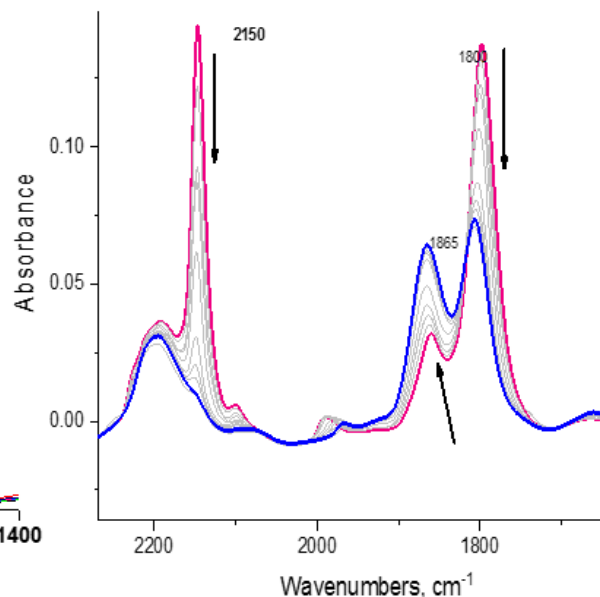
Str.	$\nu(L)^a$	$d(Pd-L)^a$	$d(Pd-O_{260})$
Pd <sup>+</sup>			221;222;225
Pd <sup>+</sup> H <sub>260</sub>			215;218;224;228
Pd <sup>+</sup> (NO)	1806	180	219;230
Pd <sup>2+</sup>			206.206.214.214
Pd <sup>2+</sup> (NO)	1845	194	218;219;232;233

# Accomplishments

## Under Industrially-relevant Conditions (CO and H<sub>2</sub>O in the PNA stream) Pd(II)(NO)(CO) Forms and Is Responsible for Increased PNA Adsorption



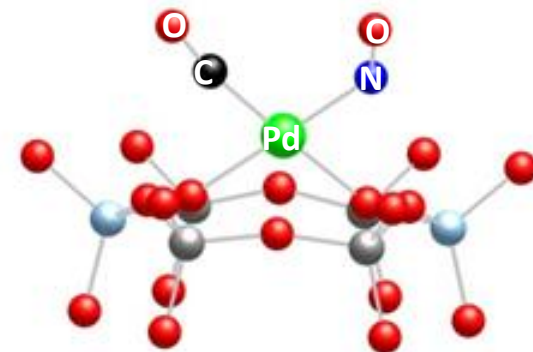
### CO.....Pd<sup>2+</sup>.....NO evacuation



- ▶ FTIR and DFT provides evidence for selective formation of only Pd(II)(NO)(CO) complex:  
 $\text{Pd(II)-NO} + \text{CO} \rightarrow \text{OC-Pd(II)-NO}$
- ▶ 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

### DFT calculations for various Pd(CO)<sub>x</sub>(NO)<sub>y</sub> complexes and structure of Pd(NO)(CO)/SSZ-13

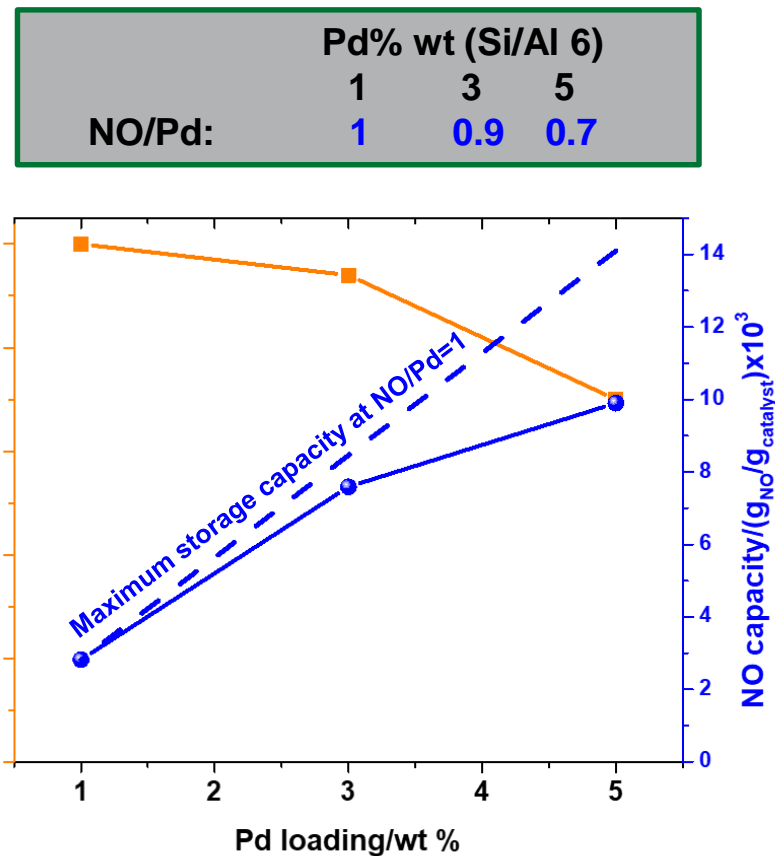
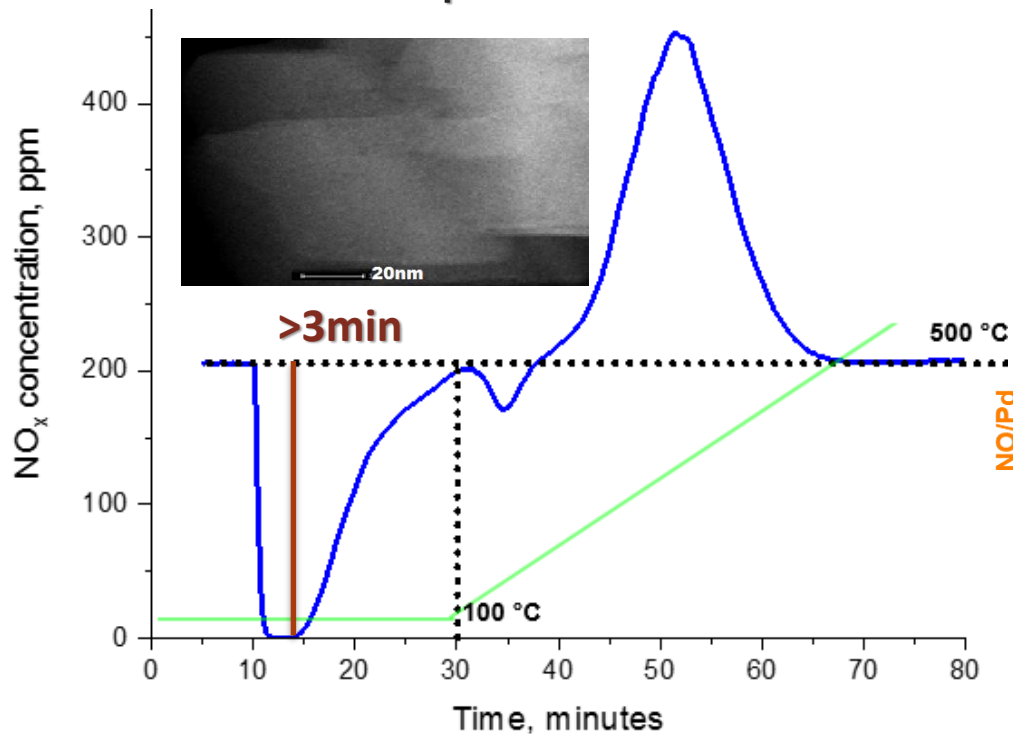
Str.	$\nu(\text{L})^a$	$d(\text{Pd-L})^a$	$d(\text{Pd-O}_{\text{NO}})$
Pd <sup>2+</sup> (CO)(NO)	2145/1822	193/199	213;218
Pd <sup>2+</sup> (CO) <sub>2</sub> (NO)	2129;2109/1825	198;198/231	219;220
Pd <sup>2+</sup> (CO)(NO) <sub>2</sub>	2145/1865;1811	199/214;214	240;240



# Accomplishments

## 3wt% Pd/SSZ-13 Achieves ~8 mg NO<sub>x</sub>/g-catalyst Storage with NO/Pd of 0.9

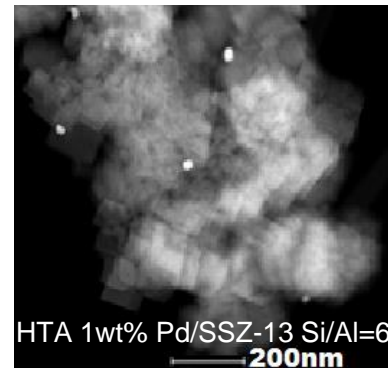
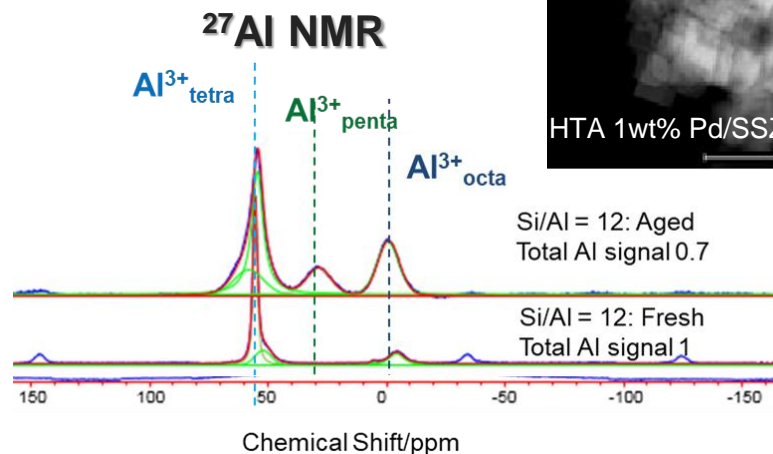
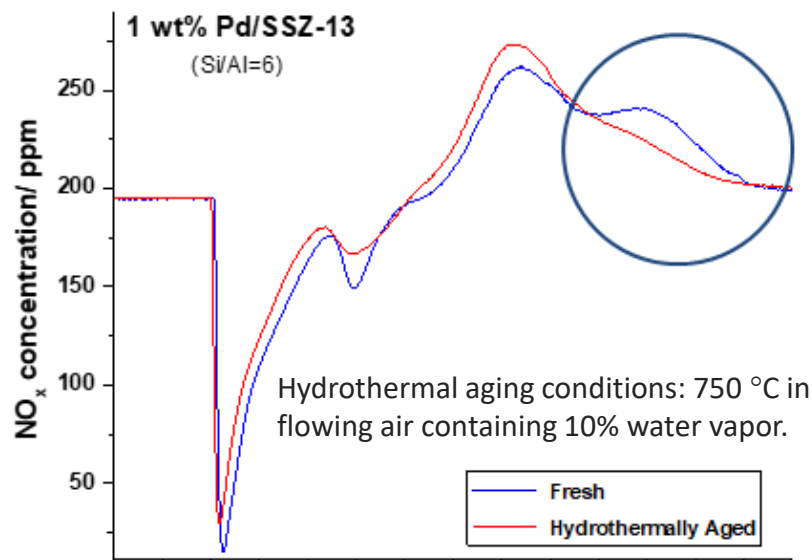
### HAADF-STEM and PNA performance of 3wt% Pd/SSZ-13



- ▶ Higher wt% Pd lowers NO/Pd ratio.
- ▶ Total abatement of NO<sub>x</sub> achieved during cold start for >3 minutes over 3wt% Pd/SSZ-13.
- ▶ These are the best PNA materials ever reported under practical conditions (GHSV=105,000hr<sup>-1</sup>).
- ▶ No further improvement of NO/Pd ratio =1 is possible due to stoichiometry of Pd(NO) and Pd(NO)(CO) complexes

# Accomplishments

## Hydrothermal Aging Causes Agglomeration of PdO, Leading to Reduced PNA Efficiency ( $\sim 10\%$ )



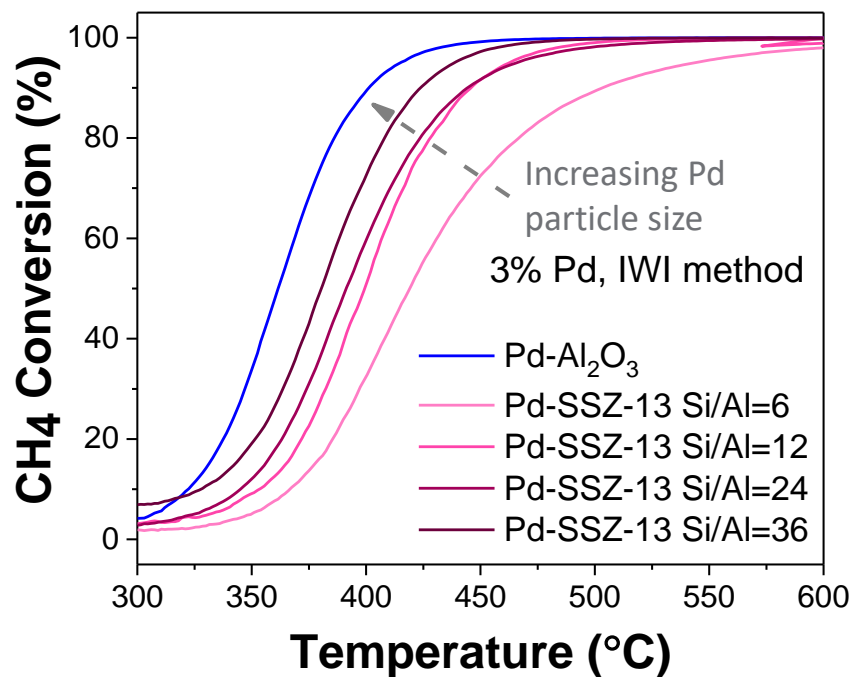
- ▶ Hydrothermal aging reduces total NO<sub>x</sub> storage efficiency of Pd/Zeolite materials and eliminates the high-temperature NO<sub>2</sub> desorption stage.
- ▶ <sup>27</sup>Al NMR confirms deterioration of framework Al, and explains the formation of PdO nanoparticles (confirmed by HAADF-STEM, synchrotron high-energy cryo XRD and pair distribution function)

# Accomplishments

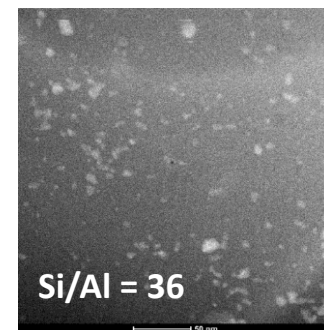
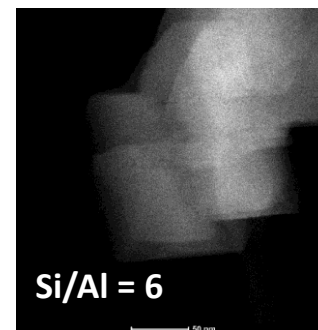
## Pd/SSZ-13 Catalysts Allow the Establishment of Structure-Activity Correlation from Atomically dispersed Pd to Pd Particles for Methane Oxidation

Catalyst	Pd-SSZ-13 Si/Al=6	Pd-SSZ-13 Si/Al=12	Pd-SSZ-13 Si/Al=24	Pd-SSZ-13 Si/Al=36
Pd Dispersion (%)	26.1	7.1	5.9	2.4

Note: H<sub>2</sub>-O<sub>2</sub> titration method, reduced samples.



120 mg catalyst. Total flow 300 ml/min. Concentrations: 640 ppm CH<sub>4</sub>, 14% O<sub>2</sub>, 5% CO<sub>2</sub> and 2.5% H<sub>2</sub>O, balanced with N<sub>2</sub>, 3°C/min



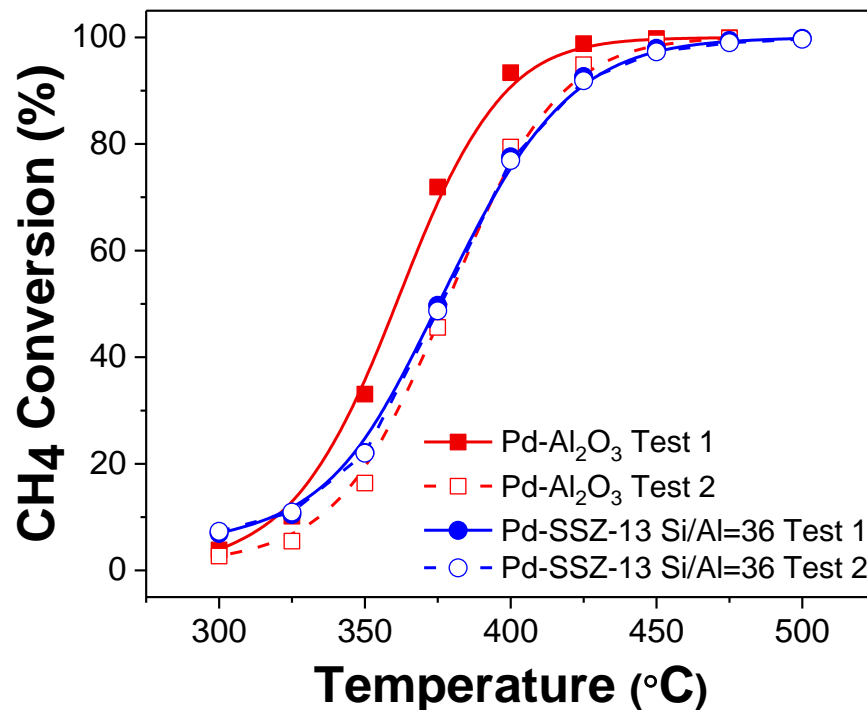
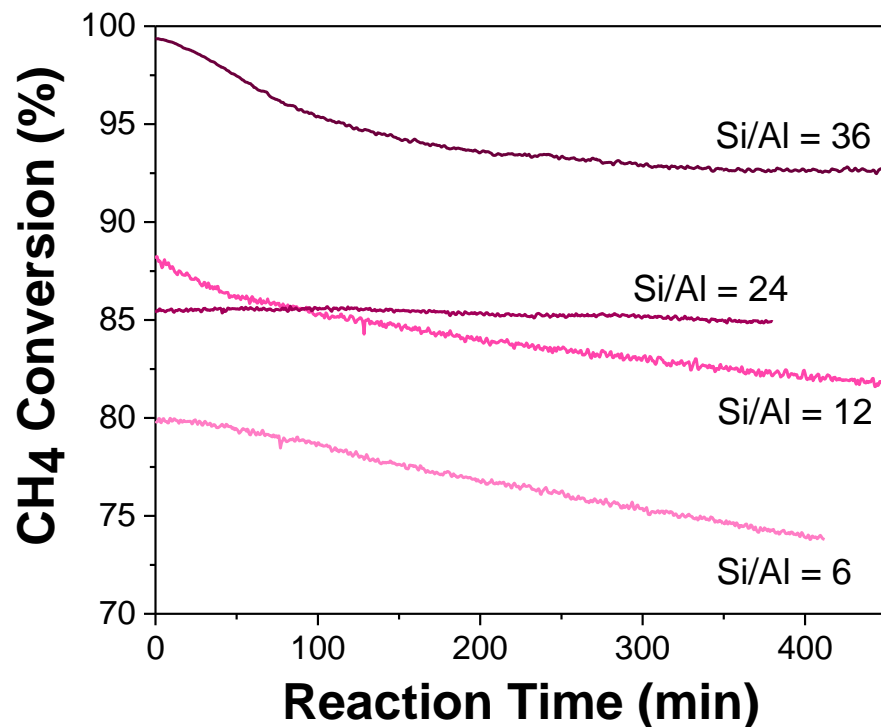
(5.3±1.9 nm)

Increasing Pd particle size

- ▶ Si/Al ratio (i.e., hydrophilicity) of the support plays decisive role in Pd dispersion.
- ▶ Pd particle size increases with increasing Si/Al ratio for Pd/SSZ-13.
- ▶ Methane oxidation activity increases with increasing Pd particle size

# Accomplishments

## Hydrophobicity of Pd-SSZ-13 with a High Si/Al Ratio Improves the Catalyst Stability



- ▶ At Si/Al = 24 and 36, Pd/SSZ-13 catalysts display excellent stability.
- ▶ The reference Pd-Al<sub>2</sub>O<sub>3</sub> catalyst shows better initial activity but deactivates with time on stream. Pd/SSZ-13 (Si/Al = 36) shows little deactivation with repeated use.
- ▶ Enhanced stability for Pd/SSZ-13 (Si/Al = 36) may be due to high hydrophobicity of the support, therefore the H<sub>2</sub>O inhibition effect is suppressed.



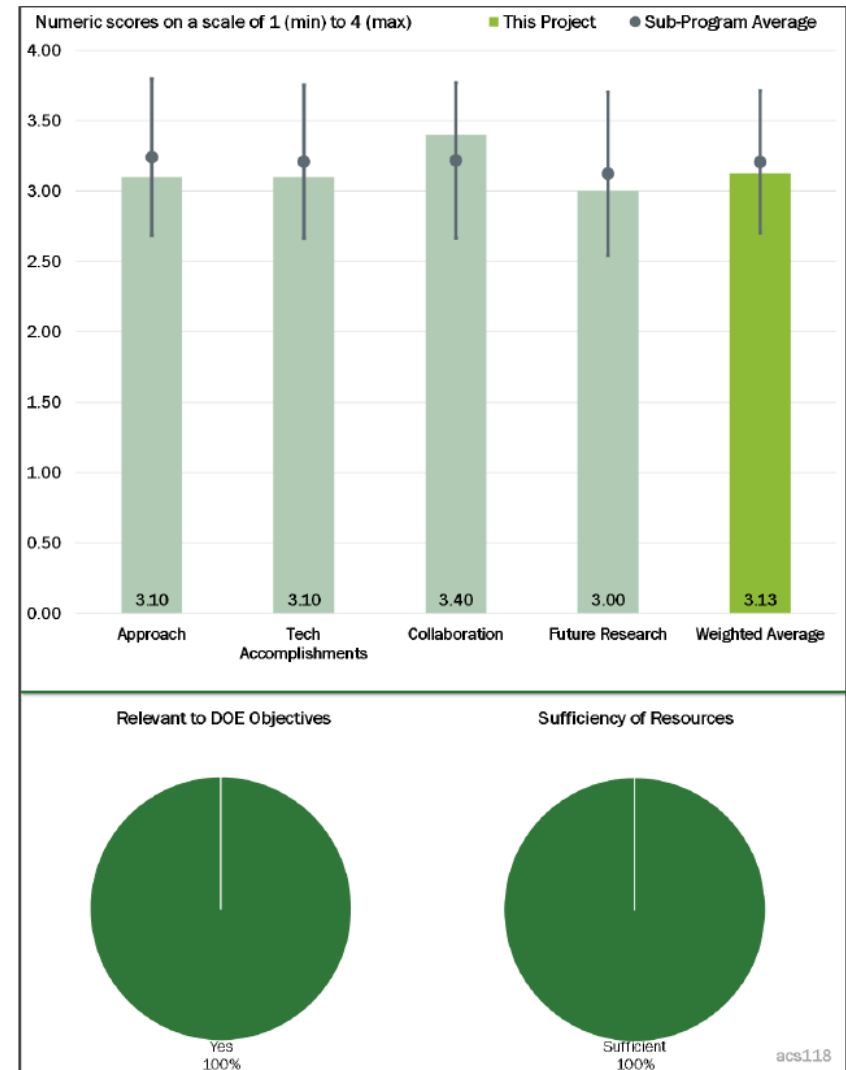
# Accomplishments – Responses to Previous Years Reviewers' Comments

- ▶ Nearly all the comments from the reviewers last year were very supportive and complimentary.
- ▶ Some comments/recommendations included:

1. ....difficult/unlikely to expect synergy among the three areas under investigation here. ...This may likely create a situation where resources are spread thin, potentially slowing down progress significantly..
2. ..the PNA future plans ..knowing the aging effects and poisoning effects is the next step
3. .... does not believe the particulate work is of high value...

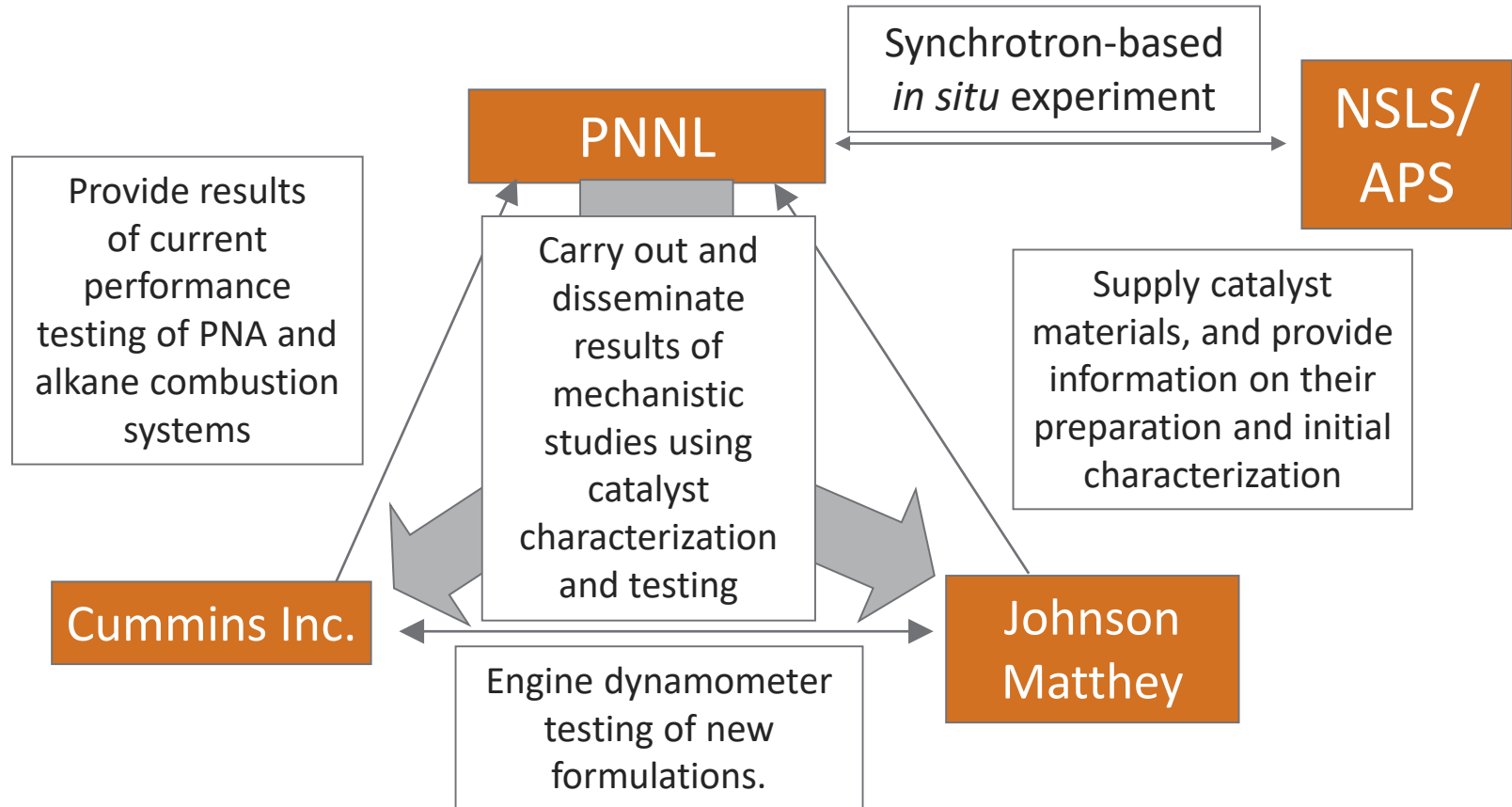
- ▶ **PNNL response:**

1. We shifted the focus on PNA.
2. We have conducted the hydrothermal aging studies (slide 11).
3. We discontinued the particulate work so that the resources can be spent on the important PNA area.





# Collaboration and Coordination



- ▶ Conference calls to discuss the results.
- ▶ Annual face-to-face CRADA Review was held in Columbus, IN. (Dec. 2017)





# Remaining Challenges and Barriers

- ▶ Understand the effects of sulphur and other exhaust emission gas components (e.g. hydrocarbons) on the NO<sub>x</sub> storage and release properties of zeolite-based PNAs.
- ▶ Elucidate the effect the PNA material on the SCR catalyst performance at temperatures of optimum SCR operation.
- ▶ Further clarify the changes in the storage phase during the entire NO<sub>x</sub> uptake and release cycle.



# Proposed Future Work

- ▶ Focus on the development of thermally stable PNA materials.
- ▶ Conduct sulphur poisoning experiments under relevant engine operating conditions.
- ▶ Understand the effect of sulphur poisoning on the NO<sub>x</sub> uptake/release properties of zeolite-based PNA materials.
- ▶ Conduct structure – function relationship studies operando to further clarify the changes in the structure/composition of the PNA active phase during the entire catalytic cycle.
- ▶ Study the effect of other gaseous exhaust emission component gases on the performance of PNAs.

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

- ▶ We systematically studied and identified factors governing performance of Pd/Zeolite PNA materials: preparation route, Pd loading, Si/Al ratio.
- ▶ We were able to load between 1 and 3 wt% of atomically dispersed Pd into small-pore SSZ-13 micropores.
- ▶ Total abatement of NO<sub>x</sub> was achieved during cold start for >3 minutes over 3wt% Pd/SSZ-13 with nearly full utilization of Pd (NO/Pd ratio = 0.9).
- ▶ Dealumination upon hydrothermal aging (HTA) causes Pd from the micropore to aggregate into PdO particles and slightly decreases total PNA storage capacity.
- ▶ Atomically dispersed Pd species are less active for methane oxidation, and the hydrophobicity of SSZ-13 improves the catalyst stability by suppressing water inhibition.

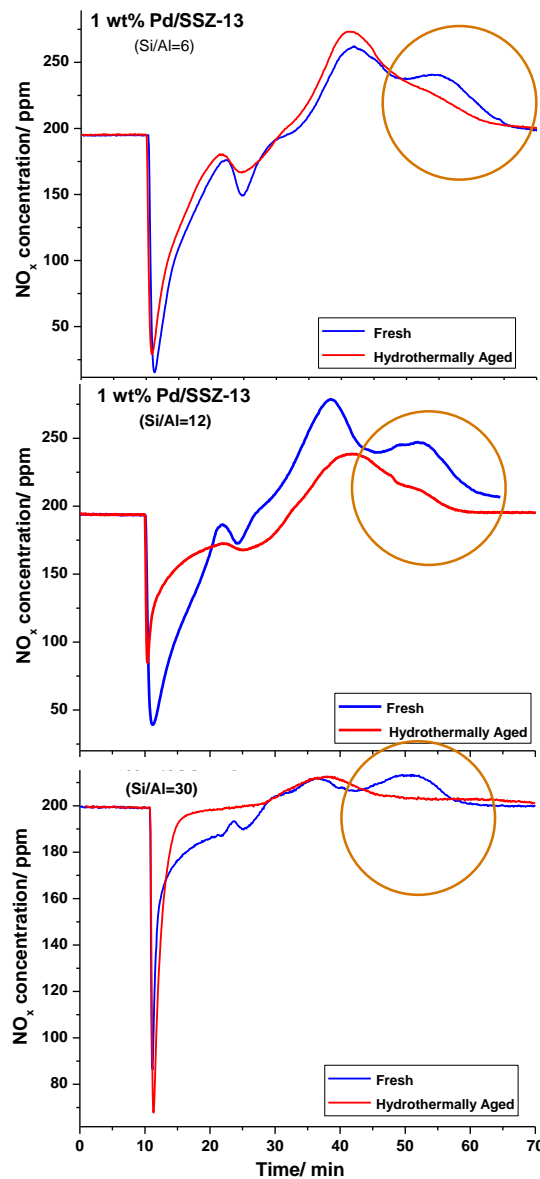


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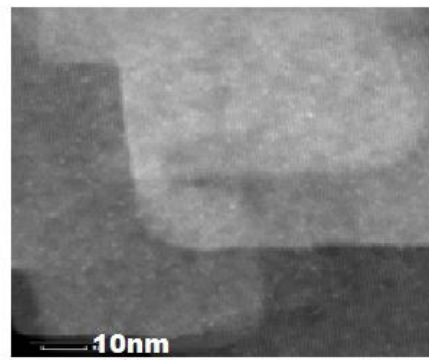
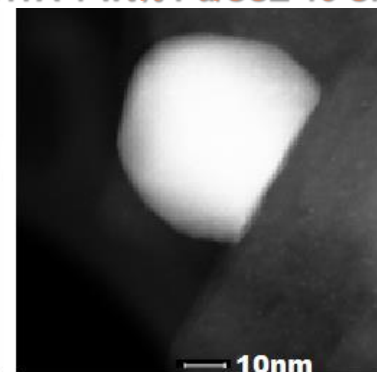
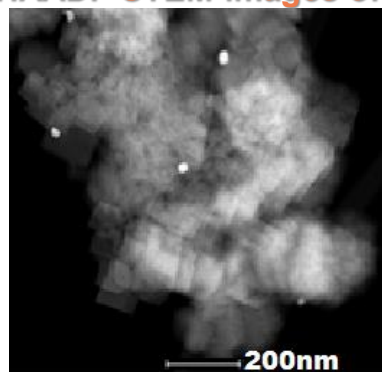
# Technical Backup Slides

# Hydrothermal Aging Effect on PNA Performance



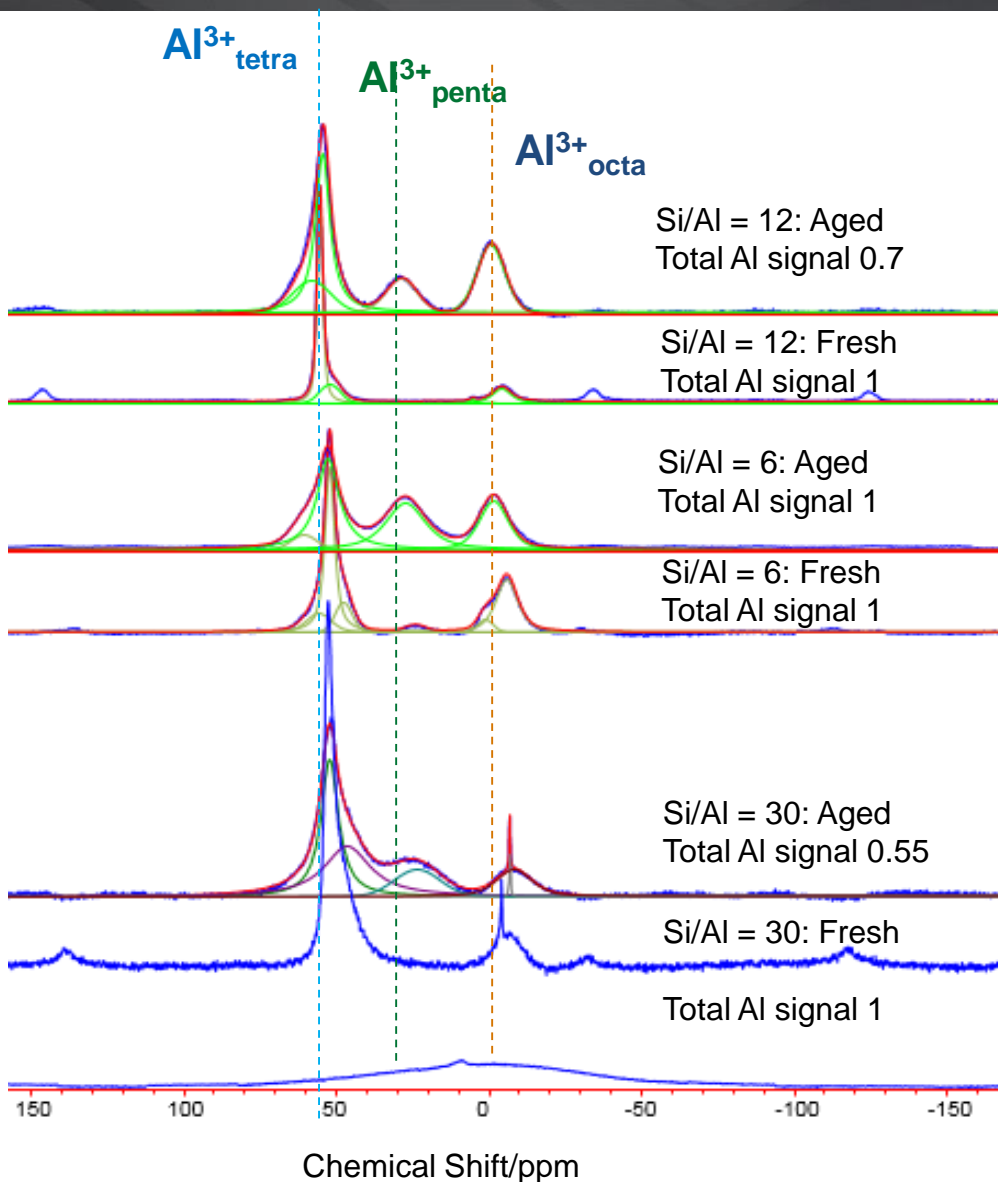
- Hydrothermal aging conditions: 750 °C in flowing air containing 10% water vapor.
- Two effects: (1) always reduces total NO<sub>x</sub> storage efficiency of Pd/Zelite materials. (2) release temperature change. Reduction or removal of the high-temperature NO<sub>2</sub> desorption stage.

## HAADF-STEM images of HTA 1 wt% Pd/SSZ-13 Si/Al=6



- HTA causes Pd to migrate and agglomerate into PdO nanoparticles

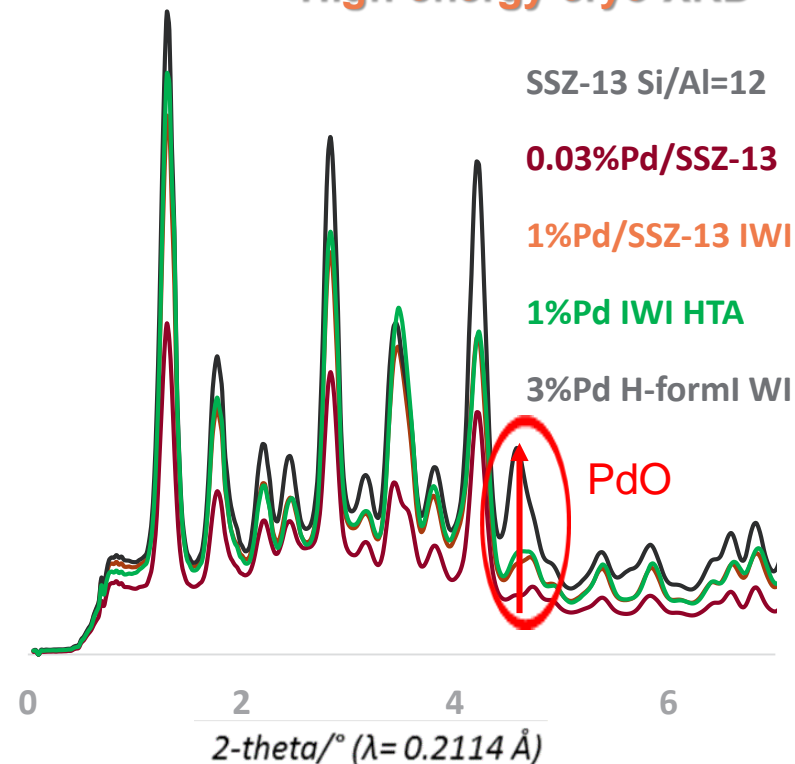
# $^{27}\text{Al}$ NMR of 1wt% HTA Pd/SSZ-13 Samples



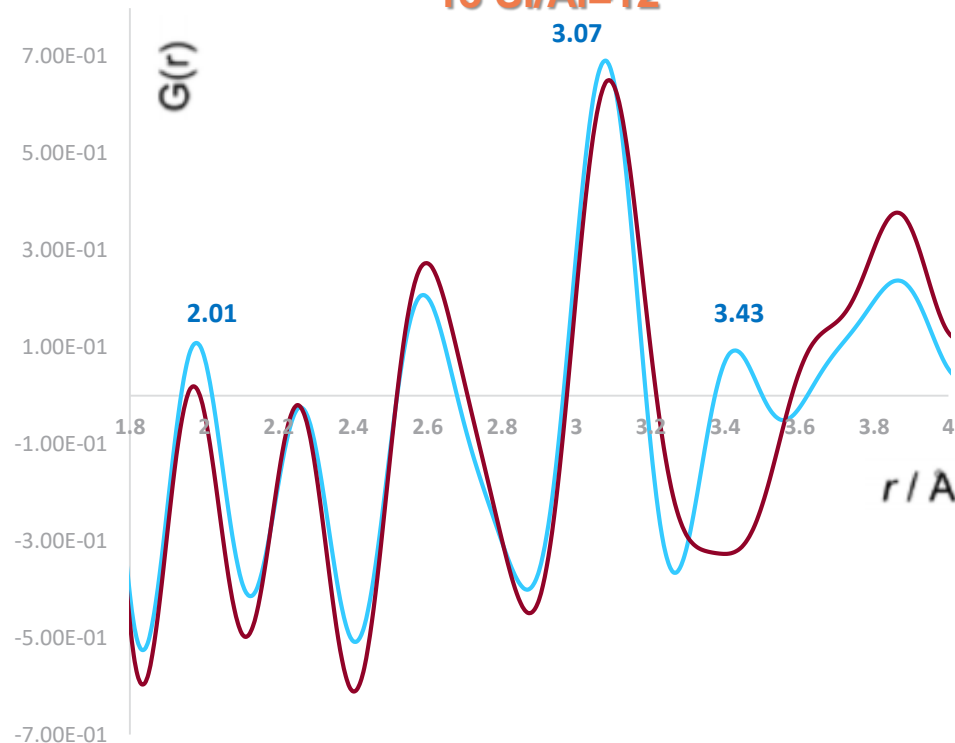
- Upon hydrothermal aging a large number of  $\text{Al}^{3+}_{\text{penta}}$  ions form on both materials (Si/Al=6 and 12).
- HTA also results in the broadening of the  $\text{Al}^{3+}_{\text{tetra}}$   $^{27}\text{Al}$  NMR signal, due to the significant changes in the environment around these ions.
- HTA leads to deterioration of Bronsted acidity and framework Al which are key in stabilizing isolated Pd ions
- This explains the formation of PdO nanoparticles upon HTA and decrease of PNA performance

# Synchrotron High-energy Cryo XRD and Pair Distribution Function (PDF) Studies on HTA Samples

## High-energy cryo XRD

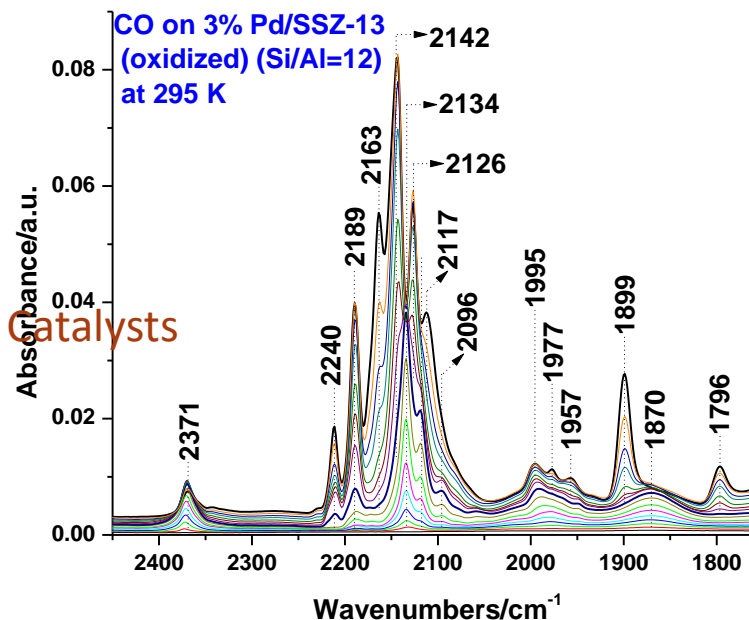
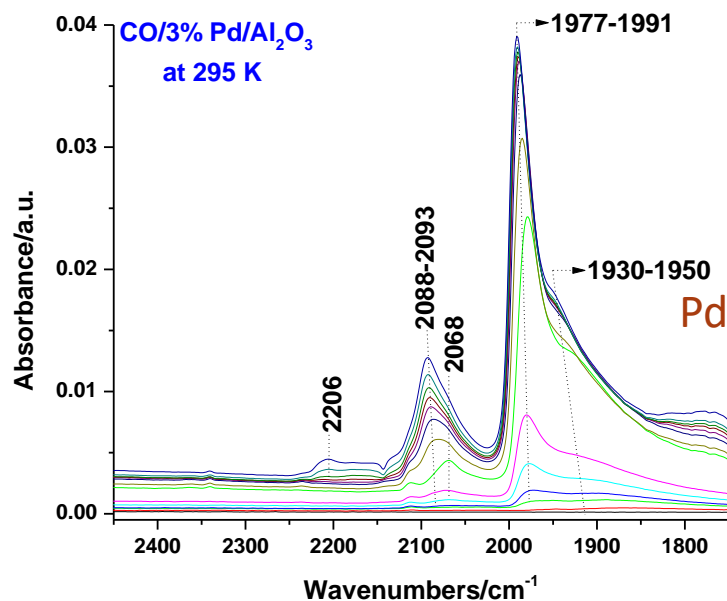


## PDF of 1 wt% fresh and HTA Pd/SSZ-13 Si/Al=12



- Synchrotron XRD and PDF have much higher sensitivity than regular XRD and can reveal the formation of minor phases
- PDF indicates **the formation of bulk-like PdO** with typical Pd-O, Pd-Pd and Pd-Pd bond distances 203, 307 and 347 picometers, respectively
- **All data on HTA samples thus indicate that changes in PNA are related to dealumination with the following PdO agglomeration on the external area of SSZ-13**

# Why There Is A Strong Particle Size Dependence for Pd/SSZ13? Why High Pd Dispersion Leads to Low Activity?

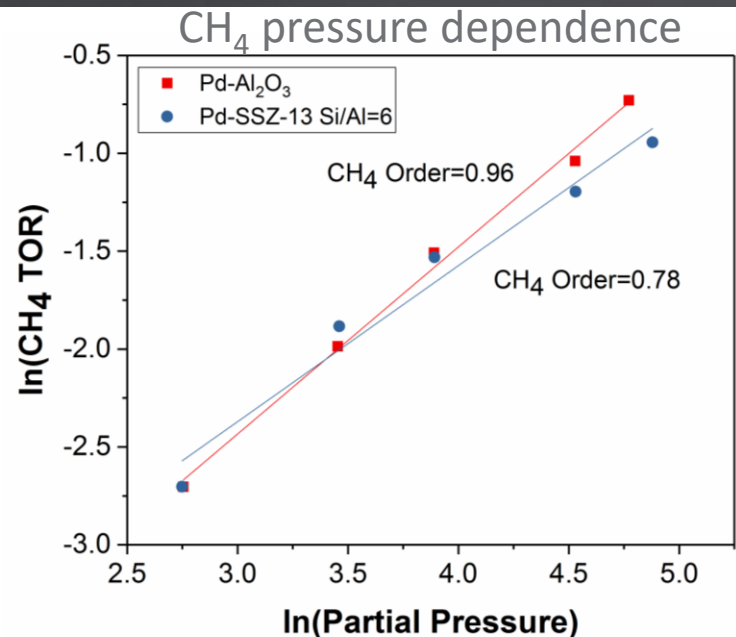
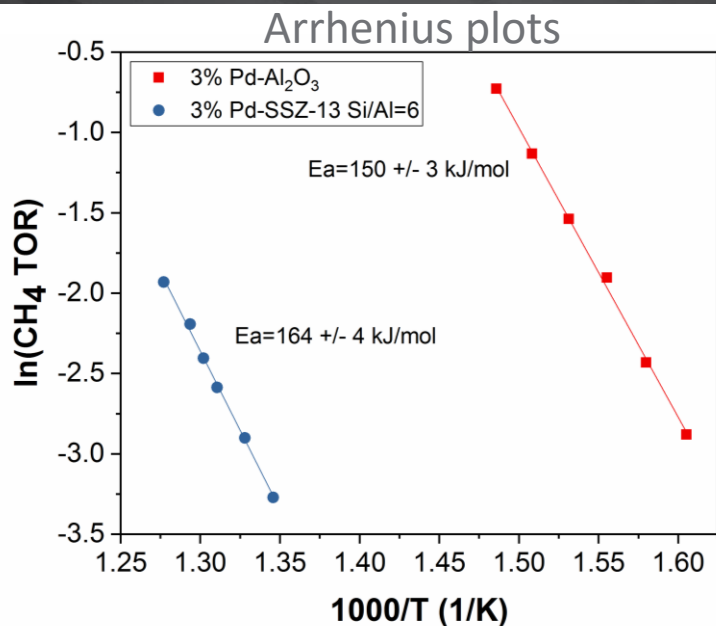


Pd/SSZ-13 Catalysts

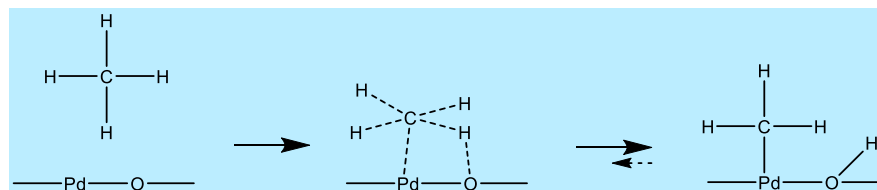
- ▶ Besides TEM imaging, CO titration FTIR also indicates that Pd/SSZ-13 contains high amounts of isolated Pd sites at low Si/Al ratios.
- ▶ Isolated Pd sites and very small PdO clusters have low activity in catalyzing methane combustion?



# Kinetic Studies of Methane Oxidation on Pd-SSZ-13



Catalyst	TOR (mol CH <sub>4</sub> /surface Pd/s) at 400 °C
3% Pd-Al <sub>2</sub> O <sub>3</sub>	0.48
3% Pd-SSZ-13 Si/Al=6	0.002



CH<sub>4</sub> pressure dependence indicates that on isolated Pd or small clusters, either the CH<sub>4</sub> transition state, or the CH<sub>3</sub>(a) intermediate has considerable stability. First C-H bond cleavage is no longer the sole kinetically relevant step. Weaker C-H cleavage capacity leads to lower activity.