



**Pacific Northwest**  
NATIONAL LABORATORY

*Proudly Operated by **Battelle** Since 1965*

# Low-Temperature Oxidation

YANRAN CUI, FENG GAO, JAMIE HOLLADAY, KEN RAPPE, YONG WANG (P.I.)  
PACIFIC NORTHWEST NATIONAL LABORATORY

SHENG DAI  
OAK RIDGE NATIONAL LABORATORY

JUNE 12, 2019

ACE056

This presentation does not contain any proprietary, confidential, or otherwise restricted information

## Timeline

- ▶ 3-yr project funded by Lab Call
  - ▶ Start date – Dec. 2017
  - ▶ End date – Nov. 2020
- ▶ 50% complete

## Budget

- ▶ FY18-FY20: \$1.2M
  - PNNL - \$900K
  - ORNL - \$300
- ▶ Funding received: \$1.2M

## Barriers

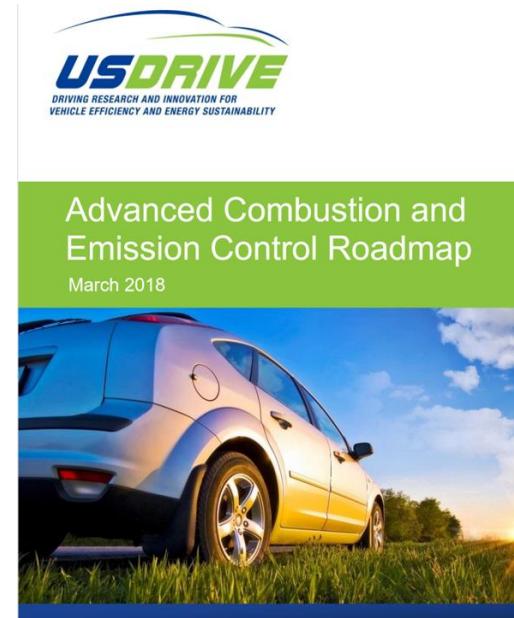
- ▶ Lack of cost-effective emission control
- ▶ Durability of emissions control devices
- ▶ Effective dissemination of information

## Partners

- ▶ Pacific Northwest National Laboratory
- ▶ Oak Ridge National Laboratory
- ▶ Cummins, Inc
- ▶ Johnson Matthey
- ▶ GM

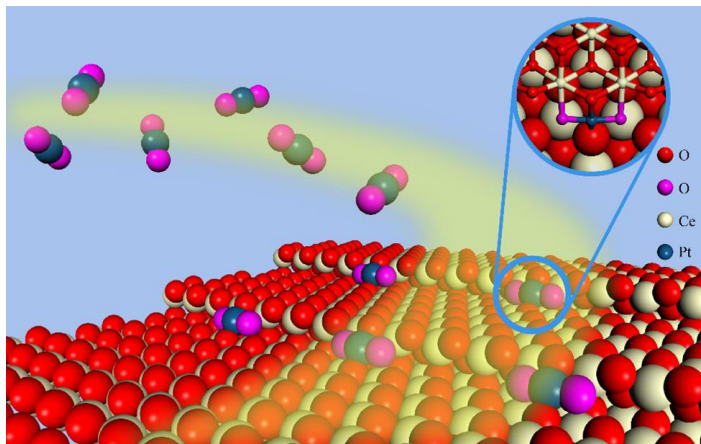
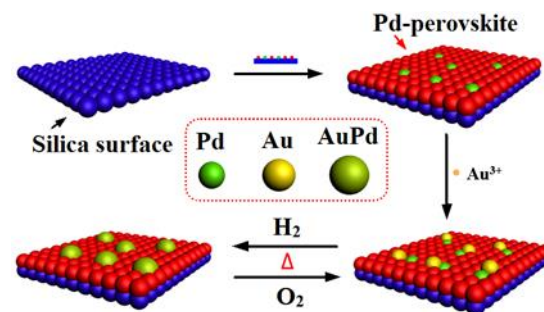


- ▶ Increasing internal combustion engine efficiency through advanced aftertreatment
  - Technologically-proven and cost-effective approach to:
    - Improving the fuel economy of the nation's fleet in near- to mid-term.
    - Reducing dependence on foreign oil and reducing carbon emissions.
- ▶ Driven by U.S. EPA Tier 3 Bin 30 emission standard.
- ▶ Requires aftertreatment technologies integrated with the combustion approaches.
- ▶ CH<sub>4</sub> regulated as greenhouse gas emission
  - 100-yr global warming potential (GWP): 
$$GWP_{100yr}^{CH_4} = 28 \times GWP_{100yr}^{CO_2}$$
  - Implemented on a cap basis, 30 mg/mile.
- ▶ NG engines require an aftertreatment system with improved methane (CH<sub>4</sub>) oxidation at lower temperatures.



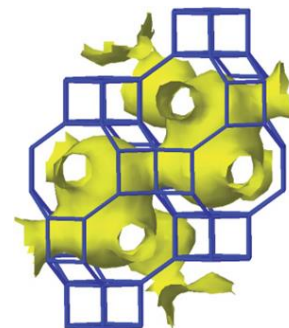
# Approach/Strategy

- ▶ Focus on Pd which shows the best performance at low temperature
- ▶ Fine tune Pd properties with atomic level controlled bimetallic and metal oxide approach



- ▶ Mitigate water inhibition using stable Chabazite supports

- ▶ Tailor the Pd and support interaction using single atom catalysts
  - Synthesized by atom trapping
  - Improved activity
  - Reduce the use of Pd
  - Maintain high durability



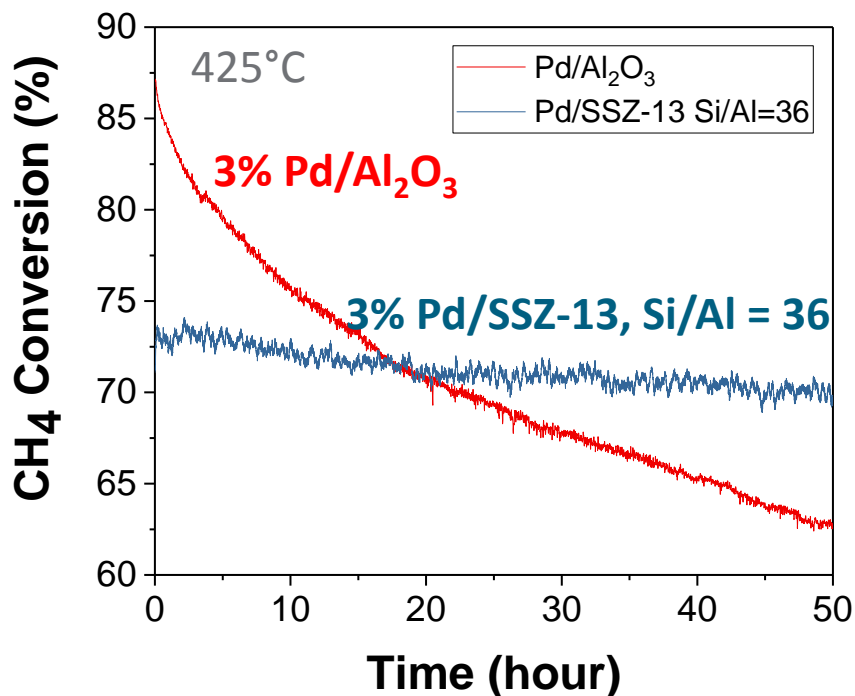
# Technical Milestones and Go/No-Go Decisions

## Milestones:

	Milestone Description	Date	Status
Milestone	Demonstrate enhanced activity by mitigating water inhibition	6/30/2018	<b>Complete</b>
Milestone	Stabilize Pd active sites through a double confinement strategy	3/31/2019	<b>Complete</b>
Go/No-Go	Demonstrate >70% methane conversion at <350°C	6/30/2019	<b>Complete</b>
Milestone	Developing a high entropy oxide support for methane combustion	11/30/2020	On track
Milestone	Demonstrate >95% methane conversion at <350°C without detrimental effect by sulfur and steam	11/30/2020	On track

# Pd/SSZ-13 (Si/Al = 36) Is ~10 Times More Stable Than Pd/Al<sub>2</sub>O<sub>3</sub>

120 mg catalyst; total flow 300 ml/min; GHSV ~ 100k h<sup>-1</sup>; ramping rate 3 °C/min;  
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>



Catalyst	Ea (kJ/mol)	TOR (10 <sup>-2</sup> mol CH <sub>4</sub> /surface Pd/s) at 350 °C
3% Pd/Al <sub>2</sub> O <sub>3</sub>	109	8.0
3% Pd/SSZ-13 Si/Al=6	164	0.2
3% Pd/SSZ-13 Si/Al=12	137	3.3
3% Pd/SSZ-13 Si/Al=24	110	9.7
<b>3% Pd/SSZ-13 Si/Al=36</b>	<b>110</b>	<b>12.2</b>

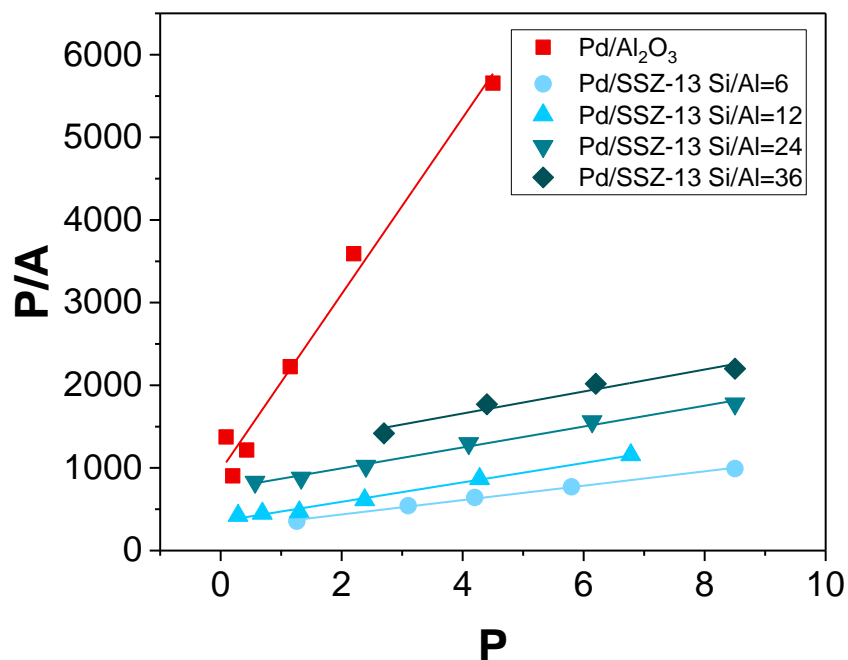
- ▶ Higher Si/Al ratio exhibits higher catalyst stability through higher hydrophobicity of the support
- ▶ Pd remains as external surface PdO particles
  - Similar nature of the active Pd sites in Pd/Al<sub>2</sub>O<sub>3</sub> and Pd/SSZ-13 (Si/Al = 36).
- ▶ PdO particles much more active for methane combustion versus isolated Pd ions and small PdO<sub>x</sub> clusters

# Increasing Support Hydrophobicity Mitigates Both PdO Transformation to Pd(OH)<sub>2</sub> and Surface –OH Accumulation, Leading to Increased Catalyst Stability



Pacific Northwest  
NATIONAL LABORATORY

Proudly Operated by Battelle Since 1965



Catalyst	K (Pa <sup>-1</sup> )
3% Pd/Al <sub>2</sub> O <sub>3</sub>	1.10
3% Pd/SSZ-13 Si/Al=6	0.33
3% Pd/SSZ-13 Si/Al=12	0.33
3% Pd/SSZ-13 Si/Al=24	0.17
3% Pd/SSZ-13 Si/Al=36	0.12



Support

Transformation of PdO to Pd(OH)<sub>2</sub>

Burch et al. *Appl. Catal., A* 1995, 123, 173–184.



Support

Accumulation of hydroxyl groups

Schwartz et al *J. Phys. Chem. C* 2012, 116, 8587–8593

- ▶ Al<sub>2</sub>O<sub>3</sub> has the strongest tendency to adsorb H<sub>2</sub>O while H<sub>2</sub>O affinity decreases with increasing Si/Al ratio on SSZ-13

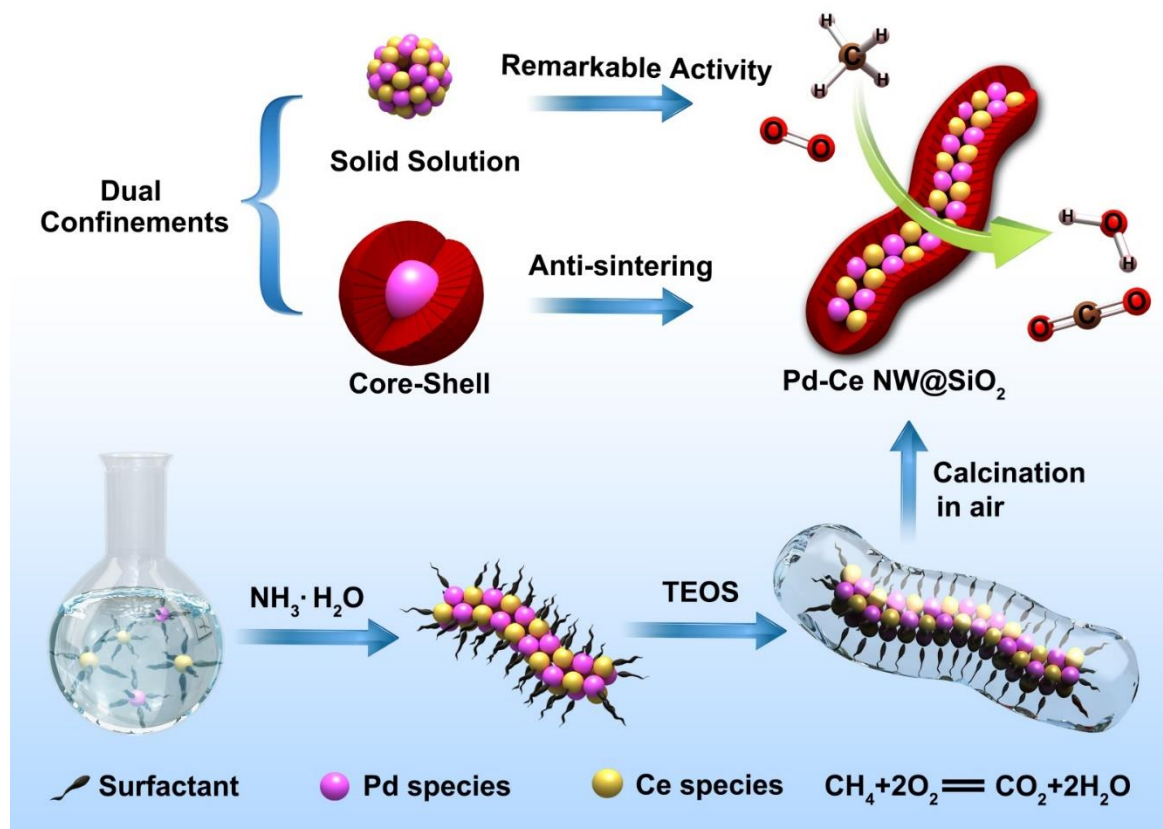
# Double Confinement Strategy Enables the Synthesis of Highly Stable Pd Catalysts



Pacific Northwest  
NATIONAL LABORATORY

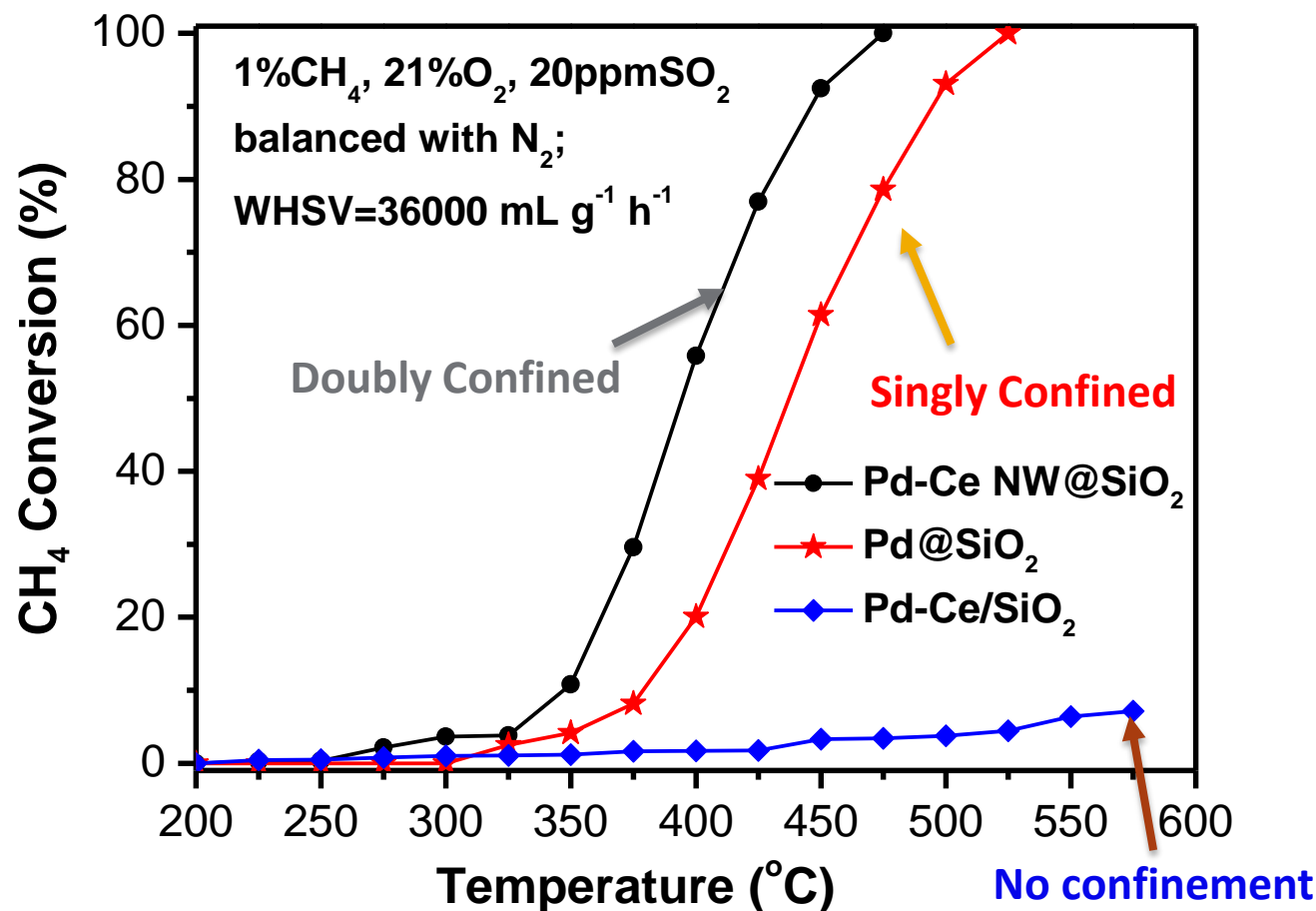
Proudly Operated by **Battelle** Since 1965

- ▶ Capitalizing the recent development of synthesizing doubly confined Pd-CeO<sub>x</sub> solid solution@SiO<sub>2</sub> core-shell hetero-structured catalysts with high performance in methane activation.
- ▶ Investigating the effect of various synthesis parameters on the stabilities and activities of doubly confined Pd-CeO<sub>x</sub>.

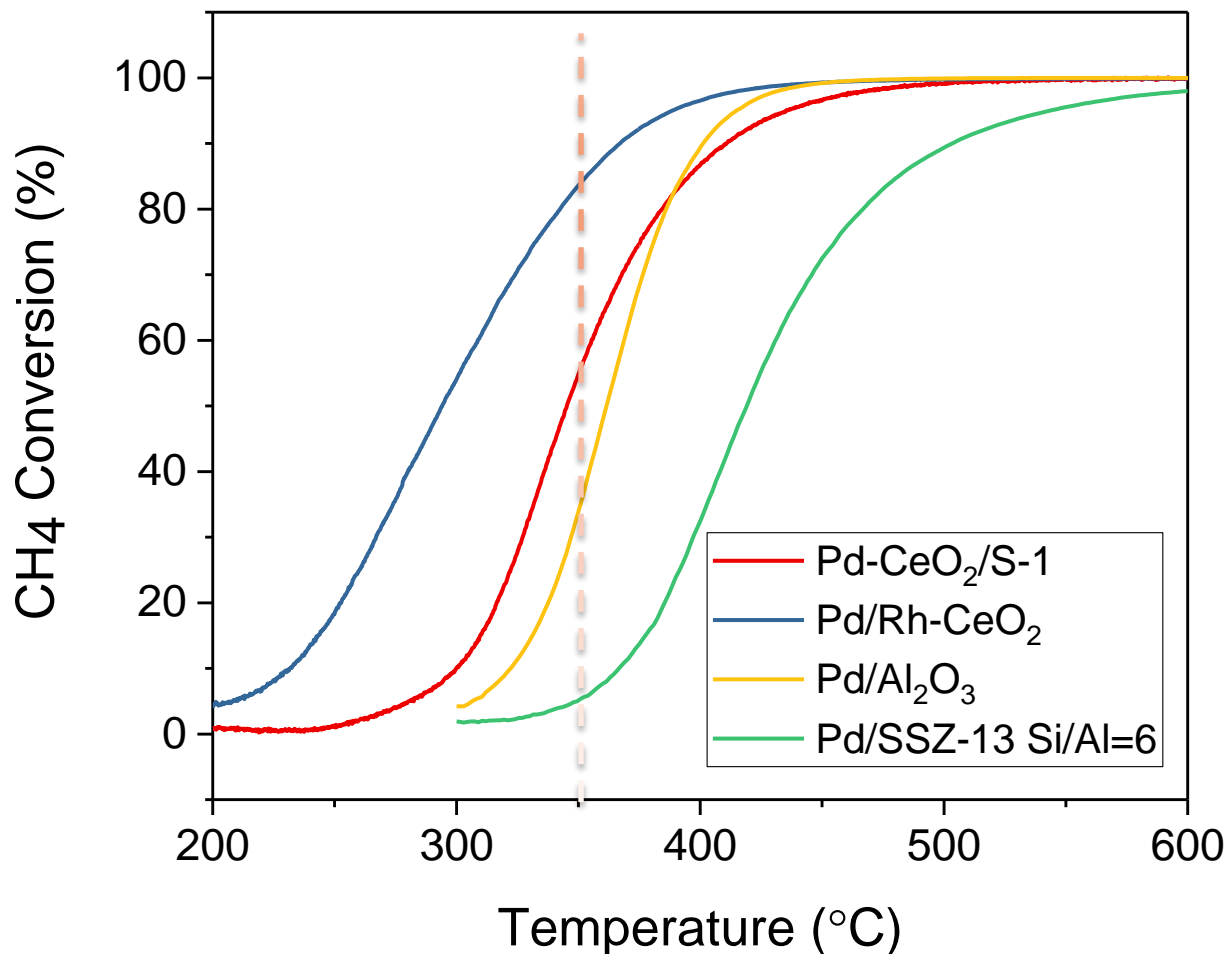


Peng, Zhang, Dai, et. al., *Angew. Chem.*, 2018, 57, 8953-8957

# Doubly Confined Pd-Ce NW@SiO<sub>2</sub> Exhibited High Methane Oxidation Activity



# Single Atom Pd/Rh-CeO<sub>2</sub> Exhibits Promising Low Temperature Activity Near 250°C and Achieves >80% CH<sub>4</sub> Conversion at 375°C



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>.  
SV = 300 L/g-h, 60 mg catalyst, ramp rate 3°C/min.

# T<sub>50</sub> Comparison with Open Literature Reports

Catalysts	T50 (C)	Reaction Condition
<b>Pd/Rh-CeO<sub>2</sub></b>	<b>300</b>	<b>640 ppm CH<sub>4</sub>, 14% O<sub>2</sub>, 5% CO<sub>2</sub>, 2.5% H<sub>2</sub>O, balance N<sub>2</sub>, SV=300 L/g-h (our work)</b>
Pd/Al <sub>2</sub> O <sub>3</sub>	550	1% CH <sub>4</sub> in air, total flow, SV=2820 L/g-h [1]
Pd/Al <sub>2</sub> O <sub>3</sub> -NiO	400	1% CH <sub>4</sub> in air, SV=48 L/g-h [2]
Pd/ZrO <sub>2</sub>	380	1% CH <sub>4</sub> , 4% O <sub>2</sub> , balance He, SV=72 L/g-h [3]
Pd-CeO <sub>2</sub> by Ball-Milling method	450	0.5% CH <sub>4</sub> , 2% O <sub>2</sub> in He, SV=90 L/g-h [4]
Pd@CeO <sub>2</sub> (core-shell)	300	0.5% CH <sub>4</sub> , 2% O <sub>2</sub> , balanced Ar, SV=200 L/g-h [5]
Pd/ZSM-5	410	1% CH <sub>4</sub> , 4% O <sub>2</sub> , 5% H <sub>2</sub> O, balanced N <sub>2</sub> , 50 mg catalyst, no flow information [6]
Pd/HMS	350	0.3% CH <sub>4</sub> , 2.4% O <sub>2</sub> balanced with He, SV=60 L/g-h [7]
PdAu/SiC	400	1% CH <sub>4</sub> , 20% O <sub>2</sub> and balanced N <sub>2</sub> , SV=12.9 L/g-h [8]

[1] P. O. Thevenin, E. Poceroba, L. J. Pettersson, H. Karhu, I. J. Vayrynen, and S. G. Jaras, *J. Catal.* 2002, 207, 139–149.

[2] H. Widjaja, K. Sekizawa, K. Eguchi, H. Arai, *Catalysis Today* 1999, 47, 95–101.

[3] C. A. Muller, M. Maciejewski, R. A. Koeppel, A. Baiker, *Catalysis Today* 1999, 47, 245–252.

[4] M. Danielis, S. Colussi, C. D. Leitenburg, L. Soler, J. Llorca, and A. Trovarelli, *Angew.Chem.Int. Ed.* 2018, 57,10212 –10216

[5] M. Cargnello, J. J. Delgado Jaén, J. C. Hernández Garrido, K. Bakhmutsky, T. Montini, J. J. Calvino Gámez, R. J. Gorte, P. Fornasiero, *Science*, 2012, 337, 713–716.

[6] A. W. Petrov, D. Ferri, O. Kröcher, and J. A. van Bokhoven, *ACS Catal.* 2019, 9, 2303–2312

[7] A.M. Venezia, R. Murania, G. Pantaleo, G. Deganello, *J. Catal.* 2007, 251, 94–102

[8] X. Guo, P. Brault, G. Zhi, A. Caillard, G. Jin, C. Coutanceau, S. Baranton, and X. Guo, *J. Phys. Chem. C* 2011, 115, 11240–11246.

# Accomplishments – Responses to Previous Years Reviewers' Comments

Not reviewed in 2018

# Collaboration and Coordination with Other Institutions

## Collaborators/Coordination

- ▶ Oak Ridge National Laboratory (Sheng Dai, Melanie Debusk, Jim Parks, Josh Pihl, Vitaly Prikhodko, Todd Toops) – new synthesis approaches, baseline performance/testing conditions, regular teleconfs
- ▶ Cummins (Krishna Kamasamudram, Yuhui Zha, Xiang Wang) – regular teleconfs
- ▶ Johnson Matthey (Haiying Chen) – baseline commercial samples
- ▶ GM (Wei Li) – guidance on surrogates and testing conditions

## Acknowledgements

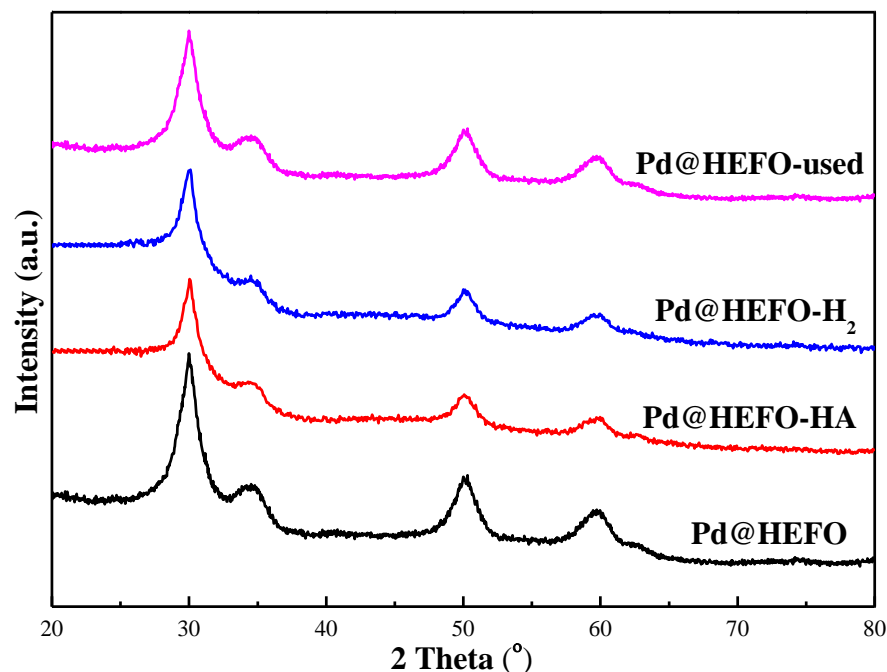
- ▶ DOE Vehicle Technologies Program: Gurpreet Singh and Ken Howden

# Remaining Challenges and Barriers

- ▶ Effect of  $\text{SO}_2$  poison on  $\text{CH}_4$  conversion and protection of active sites from  $\text{SO}_2$
- ▶ Maximizing the precious metal usage
- ▶ Cyclic stability

# Proposed Future Work

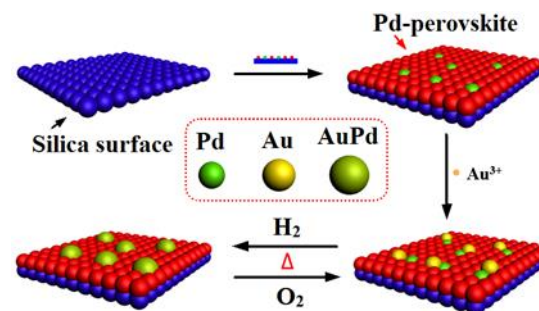
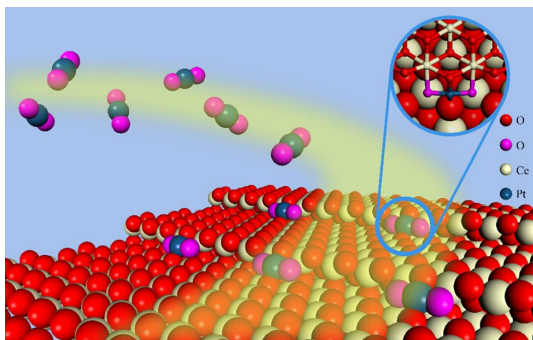
- ▶ Study the effects of S on the candidate materials.
- ▶ Identify the degradation mechanism of under cyclic operations.
- ▶ Integrate the concept of hydrophobicity control with doubly confined metal oxides.
- ▶ Investigate the control of pore sizes of SiO<sub>2</sub> coatings.
- ▶ Study the effect of the thickness of SiO<sub>2</sub> coatings on catalytic stabilities and activities.
- ▶ Investigate the use of high entropy fluoride oxide (HEFO) supports for stabilizing Pd active sites for CH<sub>4</sub> oxidation.



XRD patterns of Pd@HEFOs treated under different conditions, respectively. HA: Hydrothermal Aging

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

- ▶ Bimetallic single atom Pd/Rh-CeO<sub>2</sub> achieved >80 CH<sub>4</sub> conversion at 375°C.
- ▶ SSZ-13 support hydrophobicity was found to strongly influence Pd location, dispersion, and activity
- ▶ High Si/Al ratios (high hydrophobicity) favors catalyst activity and stability for CH<sub>4</sub> oxidation.
- ▶ PdO nanoparticles are much more active than isolated Pd ions or PdOx clusters for methane combustion.
- ▶ Doubly confined metal oxides were identified to increase Pd stability and activity.

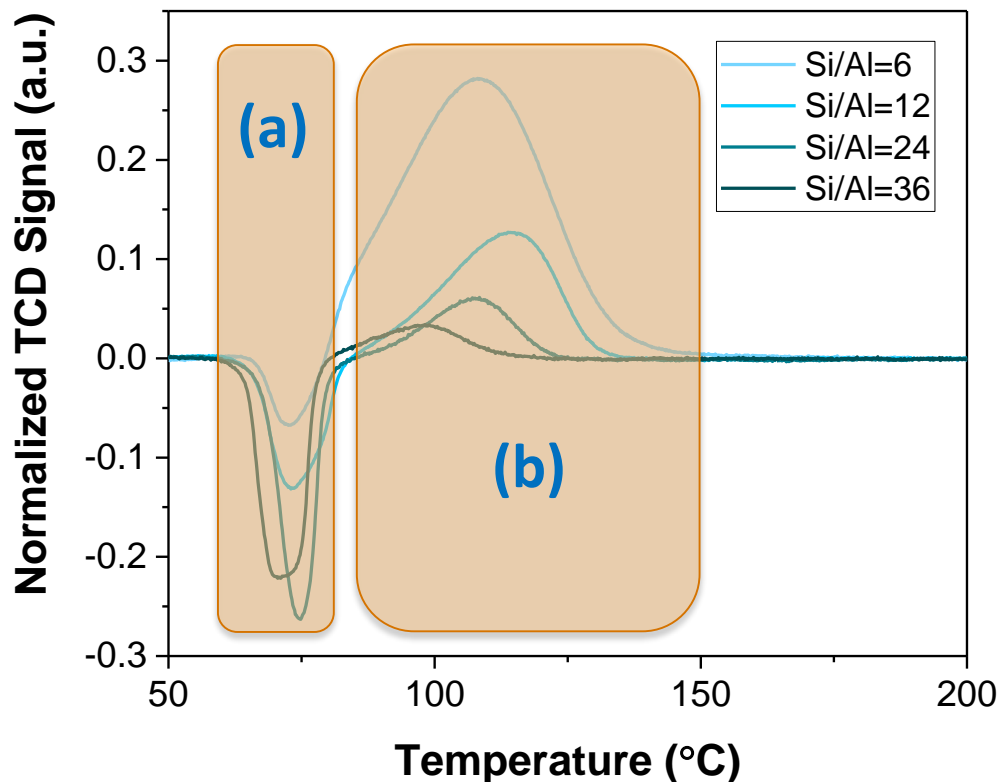




**Pacific Northwest**  
NATIONAL LABORATORY

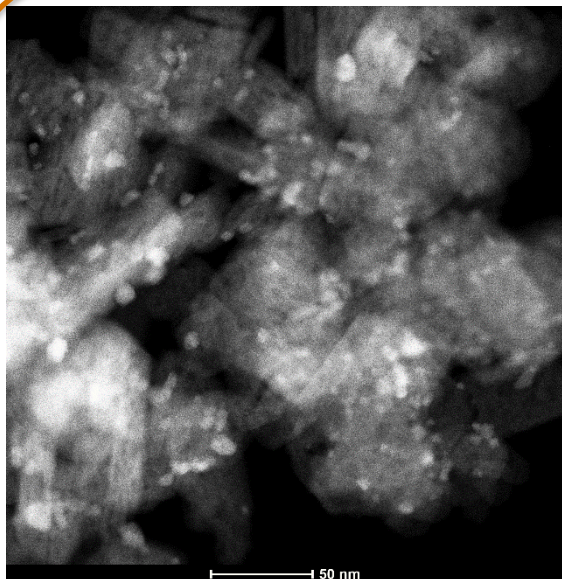
*Proudly Operated by **Battelle** Since 1965*

# Technical Backup Slides

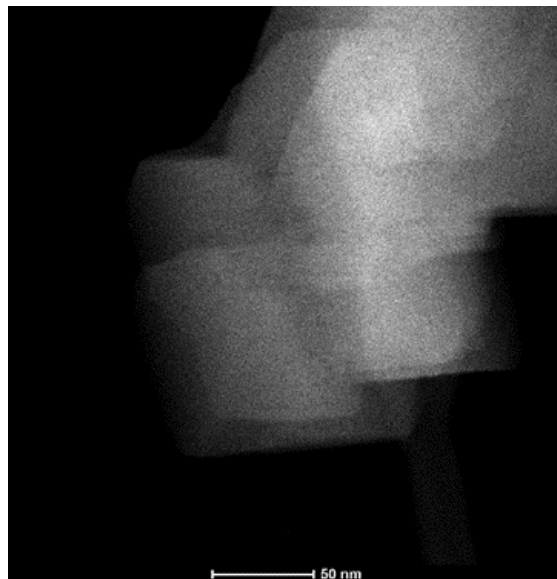


- ▶ Negative peaks (a): PdH decomposition. Metallic Pd originates from reduction of PdOx clusters during sample pretreatment (i.e., prior to ramping).
- ▶ Positive peaks (b): reduction of isolated Pd(II) ions, i.e.,  $\text{Pd}^{2+} + \frac{1}{2} \text{H}_2 = \text{Pd}^+$ .
- ▶ As Si/Al ratio increases, PdOx ↑ and isolated Pd<sup>2+</sup> ↓.

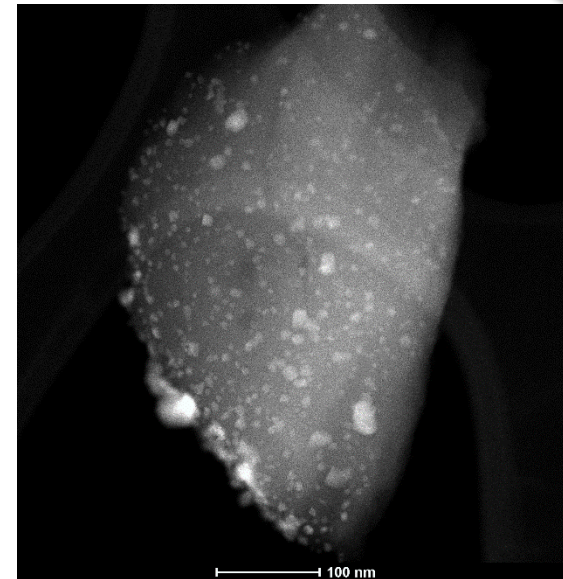
# TEM imaging



Pd/Al<sub>2</sub>O<sub>3</sub> 4.9 ± 1.2 nm



Pd/SSZ-13, Si/Al=6  
No particles observed

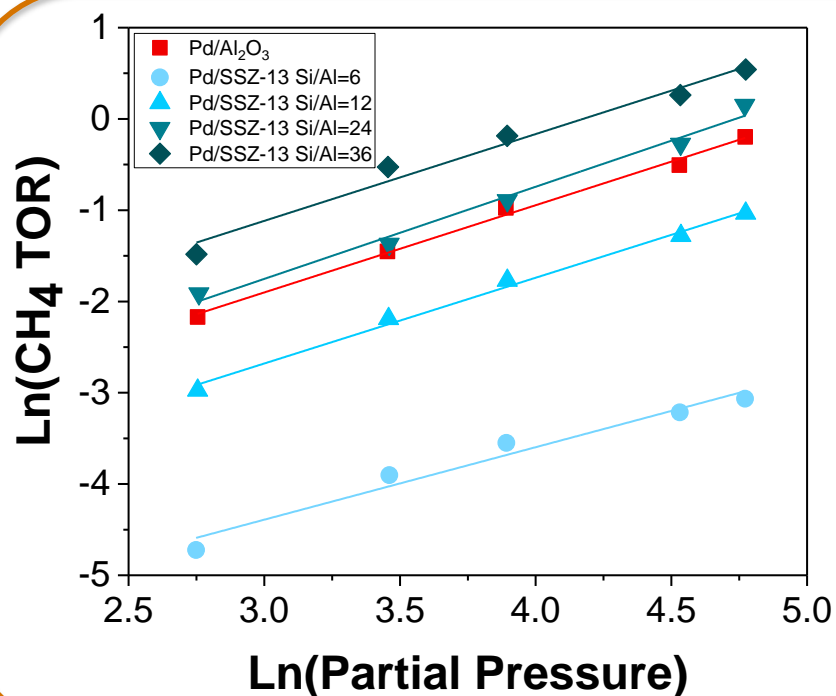


Pd/SSZ-13, Si/Al=36  
6.7 ± 3.3 nm

- ▶ At high Si/Al ratios, Pd predominately stays as external surface PdO particles on SSZ-13, the same as on Al<sub>2</sub>O<sub>3</sub>. This similarity is well reflected by reaction kinetics.
- ▶ At low Si/Al ratios, Pd penetrates inside the zeolite bulk. The majority stays as TEM invisible isolated Pd<sup>2+</sup> ions. Even the remaining PdOx clusters are too small to be detected by TEM.
- ▶ Isolated Pd ions and small PdOx clusters are much less active than PdO particles in methane combustion.

# Power-law Dependence on Kinetics

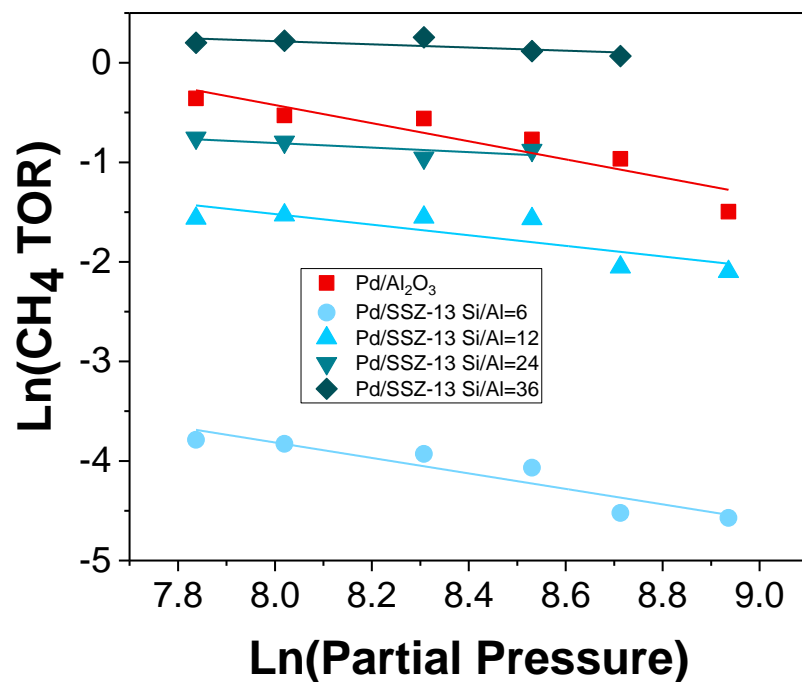
$$r = k \exp\left(-\frac{E_a}{RT}\right) P_{CH_4}^a P_{O_2}^b P_{H_2O}^c$$



Catalyst	CH <sub>4</sub> order
3% Pd/Al <sub>2</sub> O <sub>3</sub>	0.96
3% Pd/SSZ-13 Si/Al=6	0.79
3% Pd/SSZ-13 Si/Al=12	0.94
3% Pd/SSZ-13 Si/Al=24	1.01
3% Pd/SSZ-13 Si/Al=36	0.95

- ▶ 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.

# Power-law Dependence on Kinetics



Catalyst	H <sub>2</sub> O order
3% Pd/Al <sub>2</sub> O <sub>3</sub>	-0.91
3% Pd/SSZ-13 Si/Al=6	-0.78
3% Pd/SSZ-13 Si/Al=12	-0.53
3% Pd/SSZ-13 Si/Al=24	-0.23
3% Pd/SSZ-13 Si/Al=36	-0.16

- ▶ As Si/Al ratio increases, hydrophobicity of the support increases. Meanwhile, the apparent reaction order with respect to H<sub>2</sub>O decreases. This demonstrates a correlation between support hydrophobicity and catalyst resistance to water inhibition.
- ▶ Higher Si/Al ratio contributes to the higher stability of the catalysts.