

# Onset of High Reactivity in Palladium Catalyzed Low-temperature Methane Combustion

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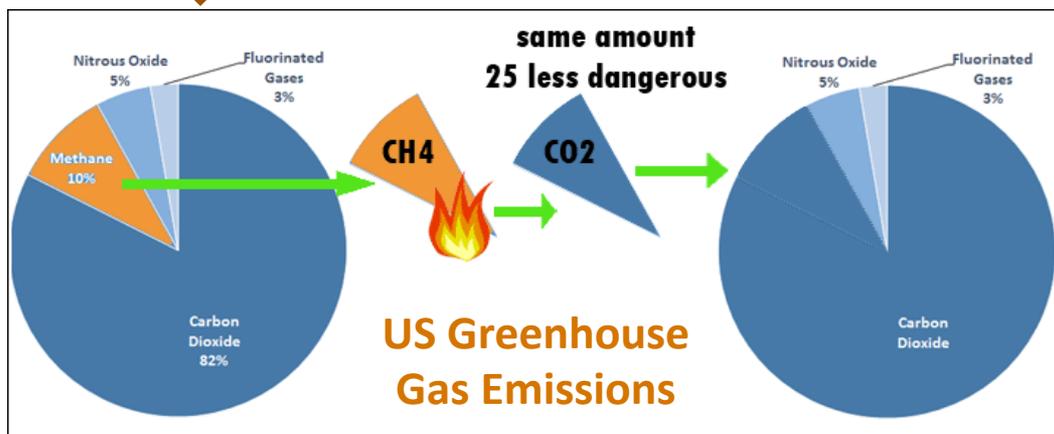
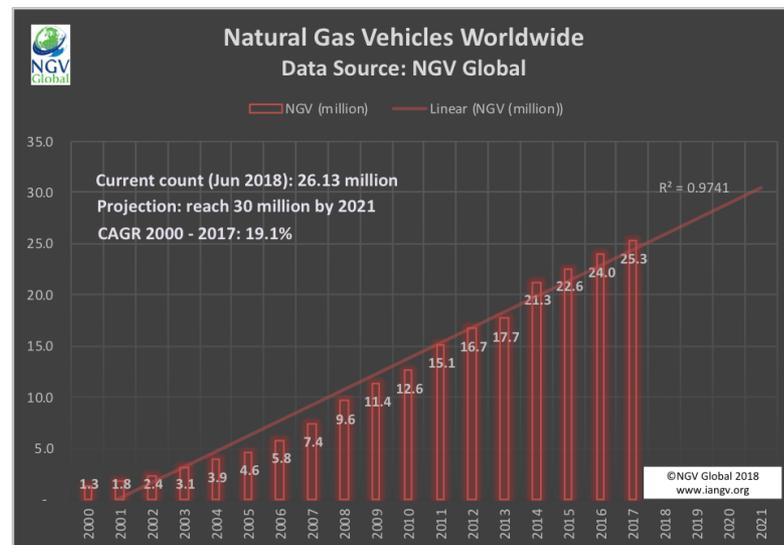
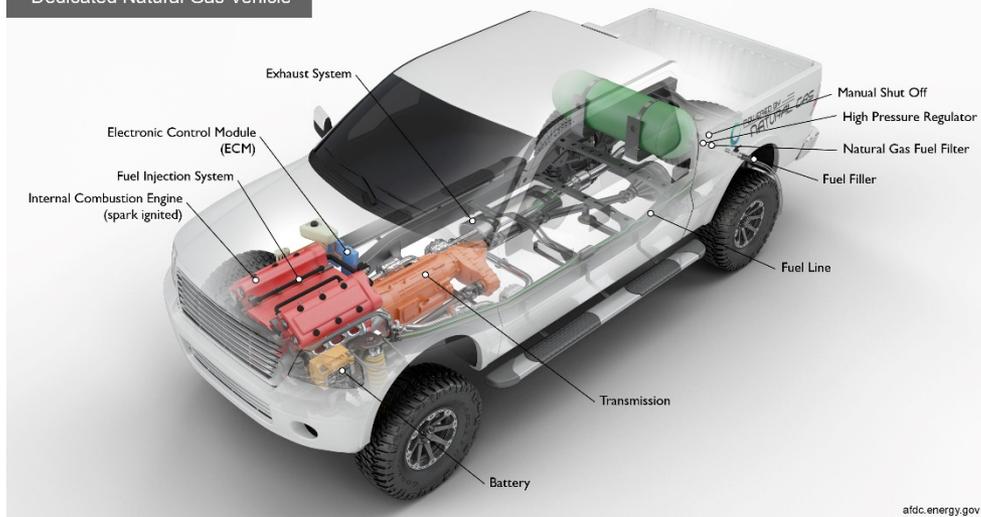
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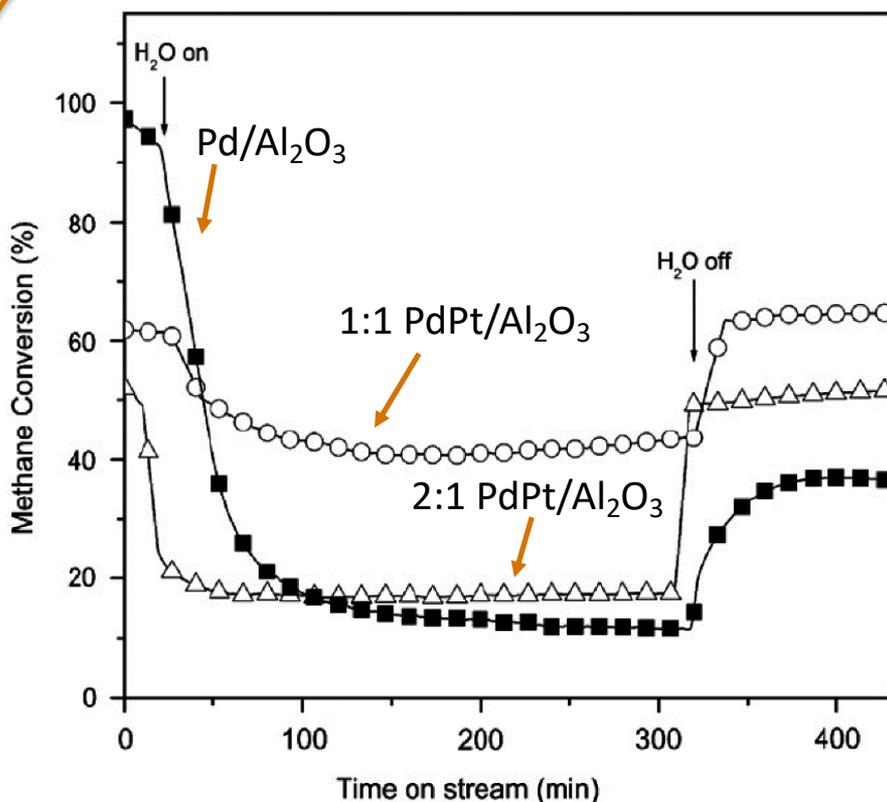
# Introduction

Dedicated Natural Gas Vehicle



- ▶ Advantages: 1. Abundance; 2. Higher fuel efficiency than gasoline/diesel; 3. Reduced CO<sub>2</sub>, NO<sub>x</sub>, SO<sub>x</sub>, PM emissions.
- ▶ Disadvantage: greenhouse effects of unburned methane (more harmful than CO<sub>2</sub>).

# Issues with Industrial Pd/Al<sub>2</sub>O<sub>3</sub> catalyst



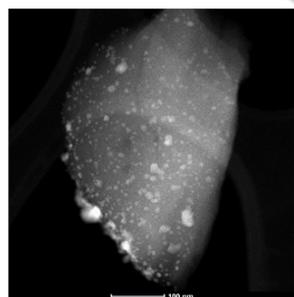
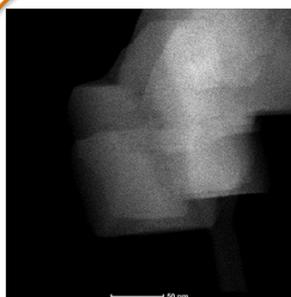
1.5% CH<sub>4</sub>/air feed gas, GHSV=100,000h<sup>-1</sup>, 5 vol.% of steam at 500 °C.

Gholami R. et al. *Catalysts*. 2015, 5, 561-594

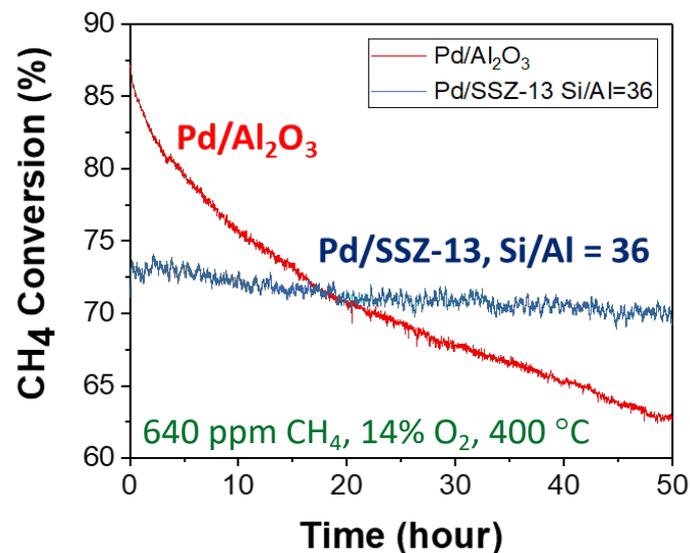
- ▶ Commercial Pd/Al<sub>2</sub>O<sub>3</sub> catalyst suffers from rapid deactivation in the presence of H<sub>2</sub>O vapor. Likely causes include (1) sintering; (2) the transformation from an active PdO phase to a inactive Pd(OH)<sub>2</sub> phase; or (3) accumulation of hydroxyl groups on the support.
- ▶ This deactivation can be mitigated via alloying, but typically at the expense of substantial rate loss.
- ▶ It is highly desirable to design new catalysts with low-temperature activity comparable to Pd/Al<sub>2</sub>O<sub>3</sub>, but with much better stability.

# A promising new catalyst: Pd/SSZ-13

- ▶ In the past 2 years, we studied low temperature methane combustion on 3% Pd supported on SSZ-13 with various Si/Al ratios (from 6 to 36), and compared them with a standard 3% Pd supported on  $\gamma$ - $\text{Al}_2\text{O}_3$ .
- ▶ Key discoveries are:
  - Support hydrophobicity greatly influences Pd location and dispersion.
  - At Si/Al = 6, Pd diffuses into the zeolite bulk. This catalyst displays low activity and low stability.
  - At Si/Al = 36, PdO stays on the external surface. This catalyst displays high activity and much improved stability in comparison to Pd/ $\text{Al}_2\text{O}_3$ .

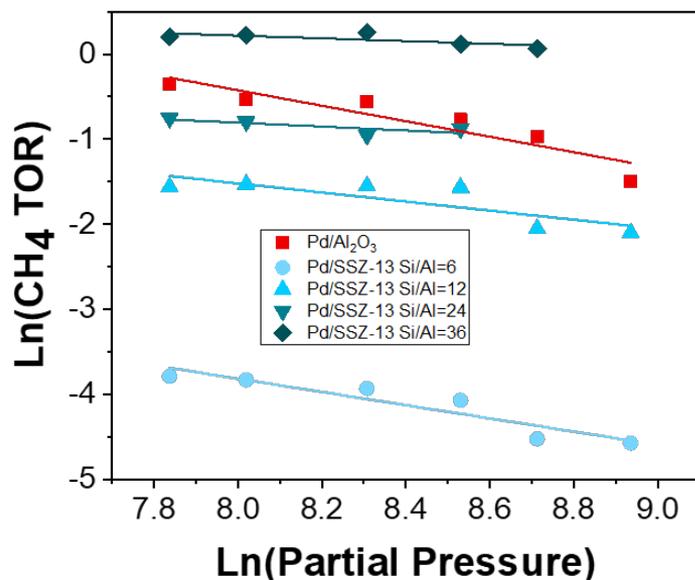


- ▶ Pd/SSZ-13, Si/Al=6 no PdO particles observed;
- ▶ Pd/SSZ-13, Si/Al=36 PdO particles  $6.7 \pm 3.3$  nm



# A promising new catalyst: Pd/SSZ-13

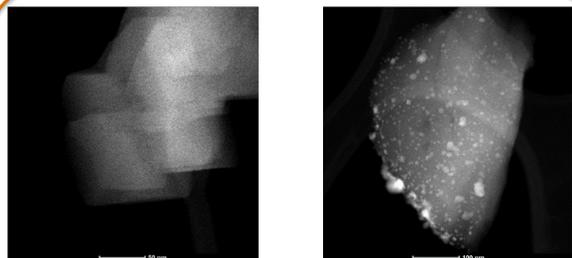
## Power-law dependence on H<sub>2</sub>O partial pressure



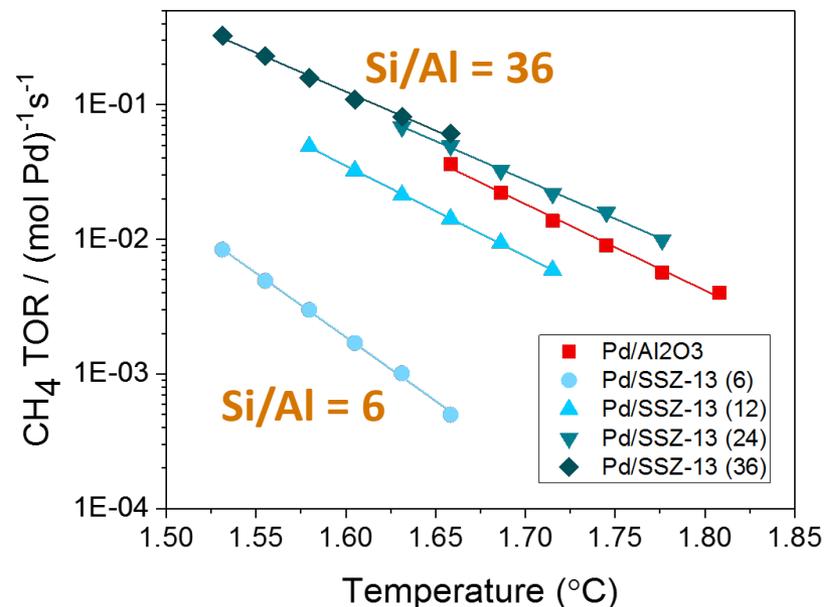
Catalyst	H <sub>2</sub> O order
3% Pd/Al <sub>2</sub> O <sub>3</sub>	-0.91
3% Pd/SSZ-13 Si/Al=6	-0.78
3% Pd/SSZ-13 Si/Al=12	-0.53
3% Pd/SSZ-13 Si/Al=24	-0.23
3% Pd/SSZ-13 Si/Al=36	-0.16

- ▶ High Si/Al ratio (24, 36) Pd/SSZ-13 catalysts display much weaker H<sub>2</sub>O inhibition than Pd/Al<sub>2</sub>O<sub>3</sub>.
- ▶ Support hydrophobicity is critical in influencing stability of supported Pd catalysts in low-temperature methane combustion.

# External surface PdO versus Pd diffused to the zeolite bulk



- ▶ Pd/SSZ-13, Si/Al=6 no PdO particles observed;
- ▶ Pd/SSZ-13, Si/Al=36 PdO particles  $6.7 \pm 3.3$  nm



Catalyst	Pd dispersion	Apparent activation Energy (kJ/mol)	Turnover rate at 350 °C (s <sup>-1</sup> )
Si/Al = 6	26	164	0.2
Si/Al = 36	3	110	12.2

- ▶ Pd dispersion determined via a standard H<sub>2</sub>-O<sub>2</sub> titration method (Benson, J. E., Hwang, H. S., and Boudart, M., *J. Catal.* **30**, 146 (1973).).
- ▶ Low-temperature turnover rates are very different. (1) external surface PdO much more active than Pd species within zeolite bulk, (2) or only a portion of the in-bulk Pd catalyzes the reaction?

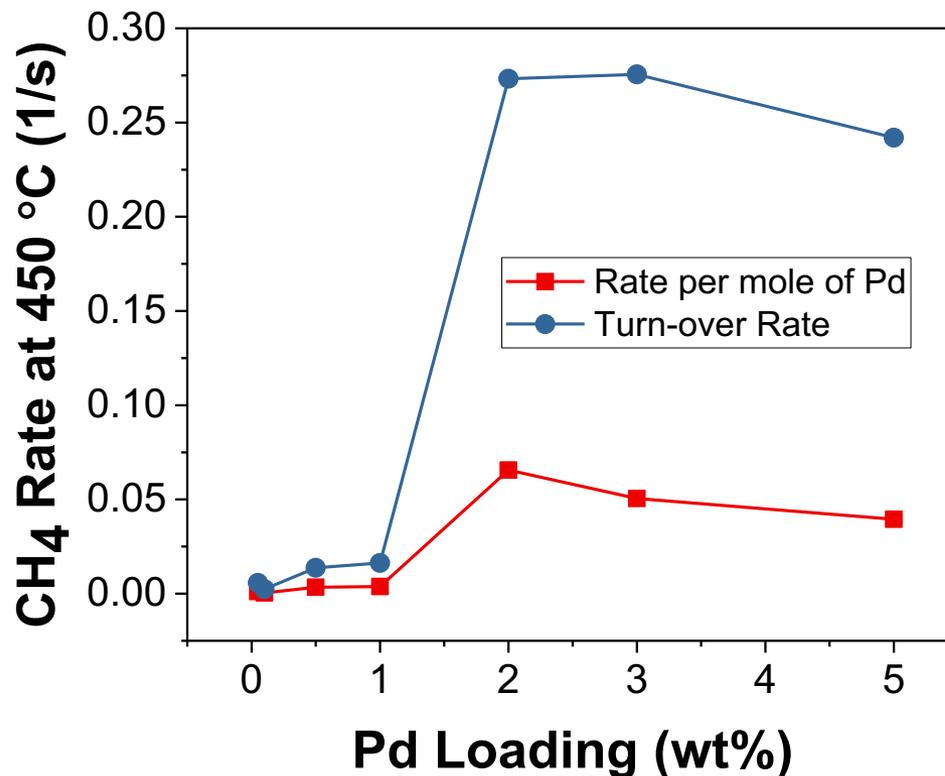
# For the “in zeolite bulk” Pd species, which one catalyzes CH<sub>4</sub> combustion?

- ▶ From our PNA studies using the same Pd/SSZ-13 (Si/Al = 6) materials, a Pd loading dependence in NO trapping efficiency was found: ~100% Pd atomic efficiency was achieved at Pd loadings  $\leq 1.9$  wt%. At higher Pd loadings, efficiency decreases with increasing Pd loading.
- ▶ At low Pd loadings, Pd atoms are anticipated to stay as isolated Pd(II) cations in ion-exchange positions; at high Pd loadings, clustering is expected.
- ▶ At Si/Al = 6, is there a Pd loading dependence in CH<sub>4</sub> combustion activity?
  - If so, we are able to pin-point which “in bulk” Pd species is more active in catalyzing methane combustion.
  - We can further probe how different Pd species catalyze the reaction differently.
- ▶ Prepared a series of Pd/SSZ-13 (Si/Al = 6) catalysts with Pd loadings from 0.1 to 5.0 wt%. Studies low-temperature methane combustion on these catalysts.

# Outline

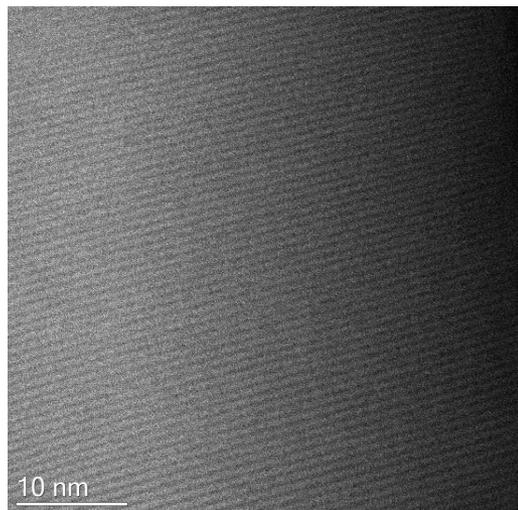
- ▶ CH<sub>4</sub> combustion testing.
- ▶ Scanning TEM imaging.
- ▶ Atom probe tomography (APT).
- ▶ XANES.
- ▶ PdO quantification and reaction rate normalization.
- ▶ Conclusions.

# CH<sub>4</sub> combustion testing

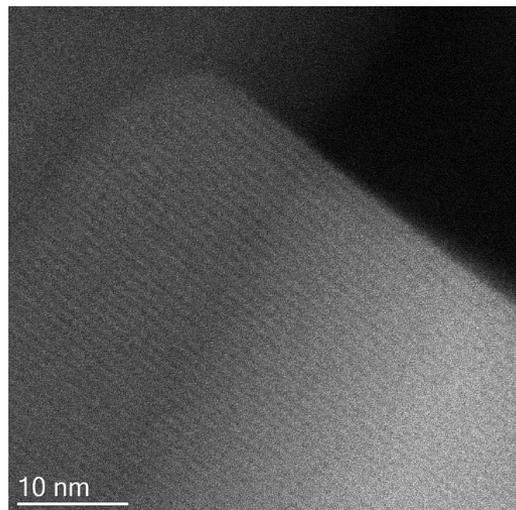


Reaction Condition: 60 mg catalyst. Total flow 300 ml/min. Concentrations: 640 ppm CH<sub>4</sub>, 14% O<sub>2</sub>, 5% CO<sub>2</sub> and 2.5% H<sub>2</sub>O, balanced with N<sub>2</sub>.

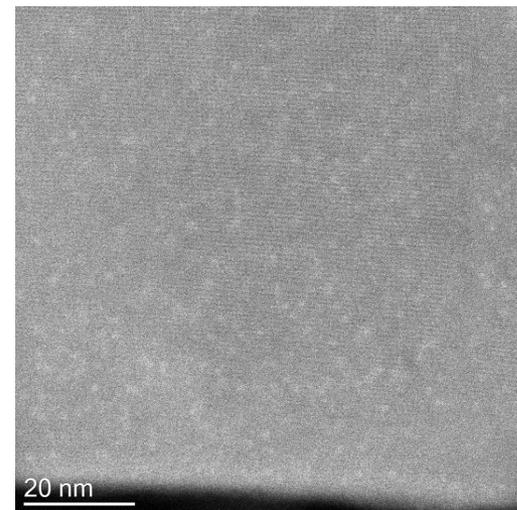
- ▶ There is indeed a strong Pd loading dependence in catalyst activity.
- ▶ This suggests that PdO particles are much more active than isolated Pd(II) cations.



0.1% Pd



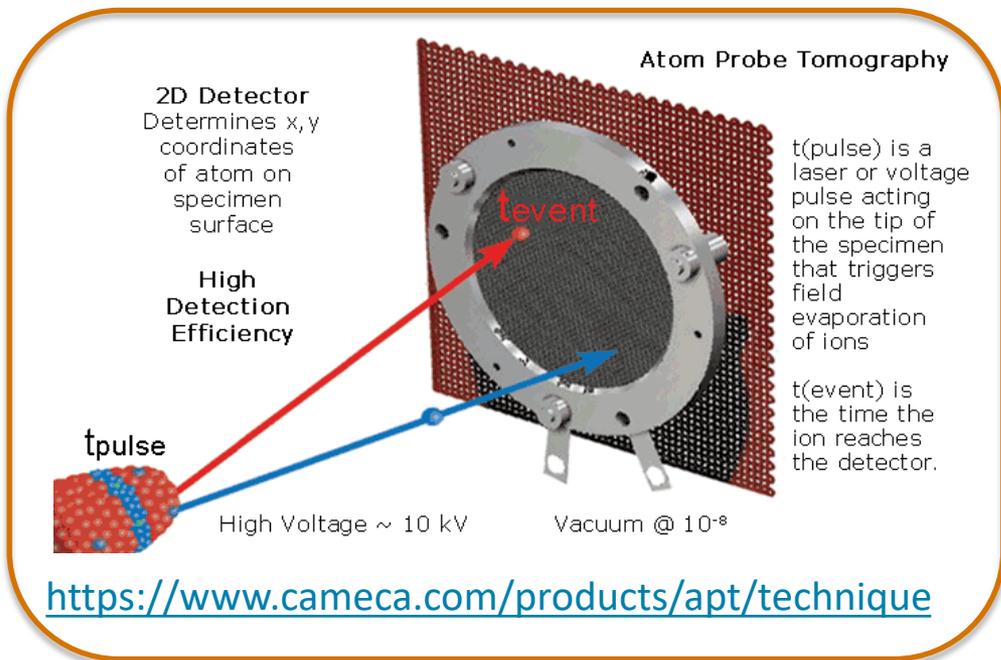
1.0% Pd



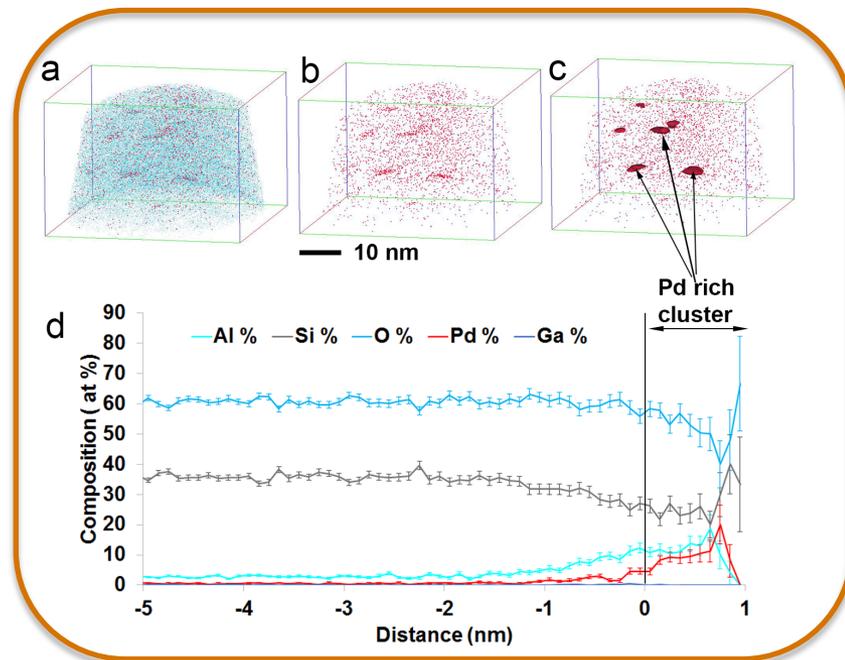
3.0% Pd

- ▶ STEM imaging confirmed our hypothesis (based on our PNA work and methane combustion kinetics) that Pd clustering only occurs above a certain threshold. This threshold is between 1-2% Pd loading at Si/Al = 6.
- ▶ The PdO clusters are rather uniformly distributed, with sizes around 1 nm.
- ▶ STEM conducted on “spent” catalysts.

# Atom Probe Tomography (ATP)

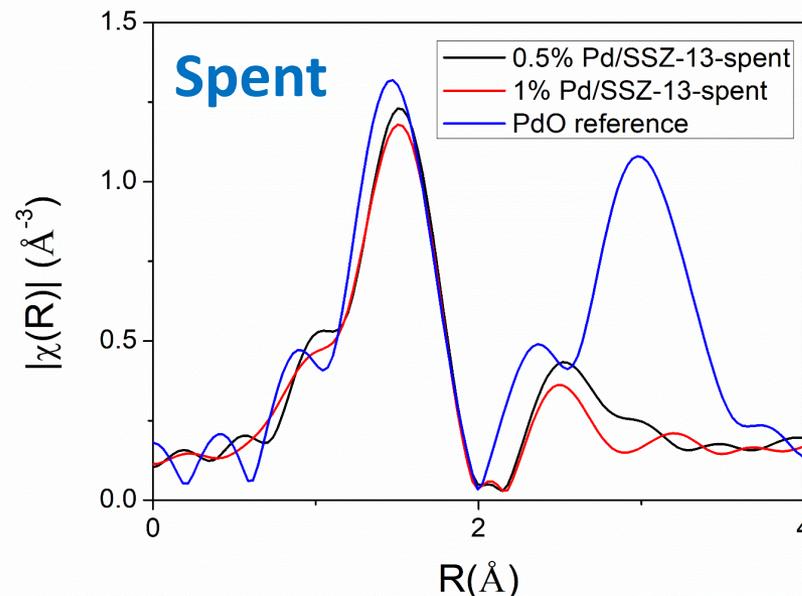
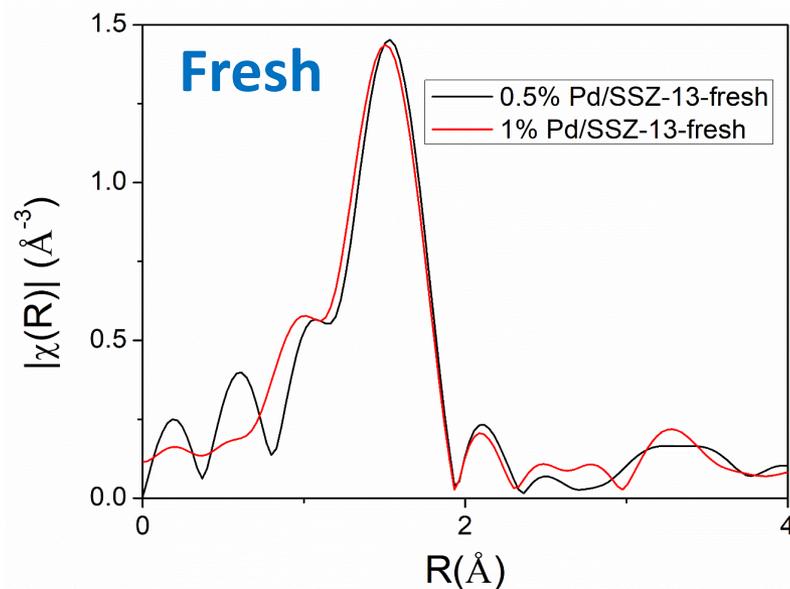


<https://www.cameca.com/products/apt/technique>



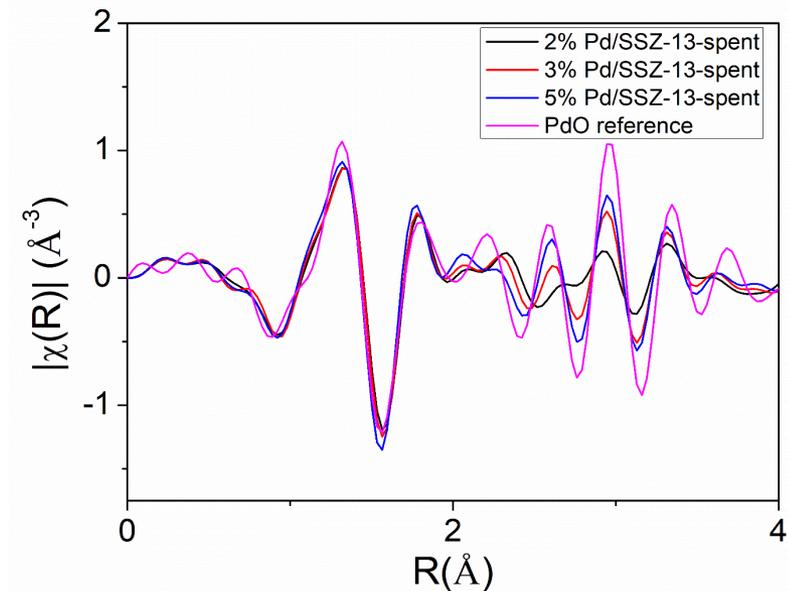
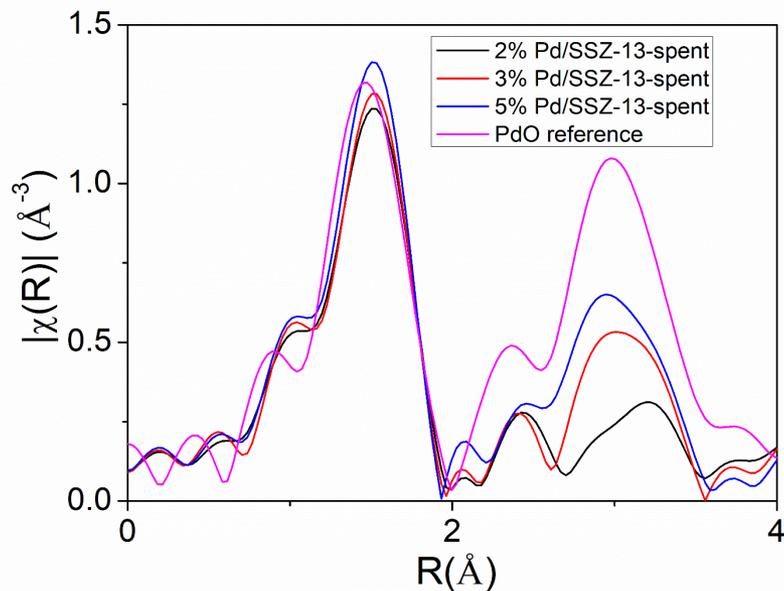
- ▶ PdO particles with radii of  $\sim 1$  nm are detected in 2% Pd/SSZ-13 (Si/Al = 6). No such particles are observed in 1% Pd/SSZ-13 (data not shown).
- ▶ The formation of such particles requires damage/deformation of a few neighboring CHA unit cells.
- ▶ Al enrichment near the PdO particles indicate redispersion of elements in such damaged unit cells: Al shows high affinity to PdO.

# XANES of fresh and spent catalysts



- ▶ 0.5-1% Pd/SSZ-3 fresh catalysts don't show second shell scattering consistent with Pd single atom catalysts.
- ▶ 0.5-1% Pd/SSZ-3 spent catalysts have a second shell inconsistent with a PdO reference.
- ▶ This second shell may be attributed to extremely small PdO<sub>x</sub> clusters, but this is not consistent with the STEM results.
- ▶ More likely this is due to formation of Pd-O-Al structure.

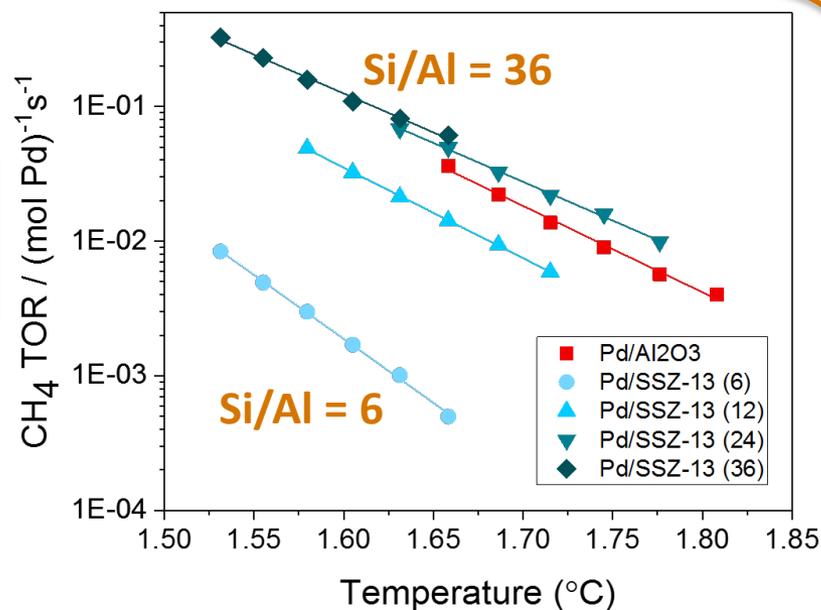
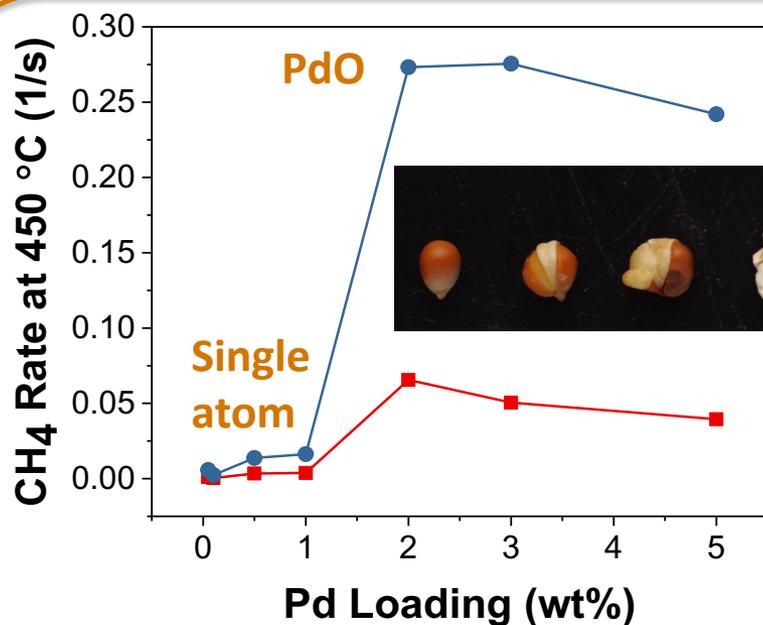
# XANES of fresh and spent catalysts



- ▶ 2-5%Pd/SSZ-3 spent catalysts are consistent with the PdO reference.
- ▶ Particle size increases with higher Pd loading.
- ▶ Consistency between  $\text{CH}_4$  combustion reaction testing (PdO more active than single atoms), STEM imaging, and XAS.

# Fair comparison in CH<sub>4</sub> combustion rates

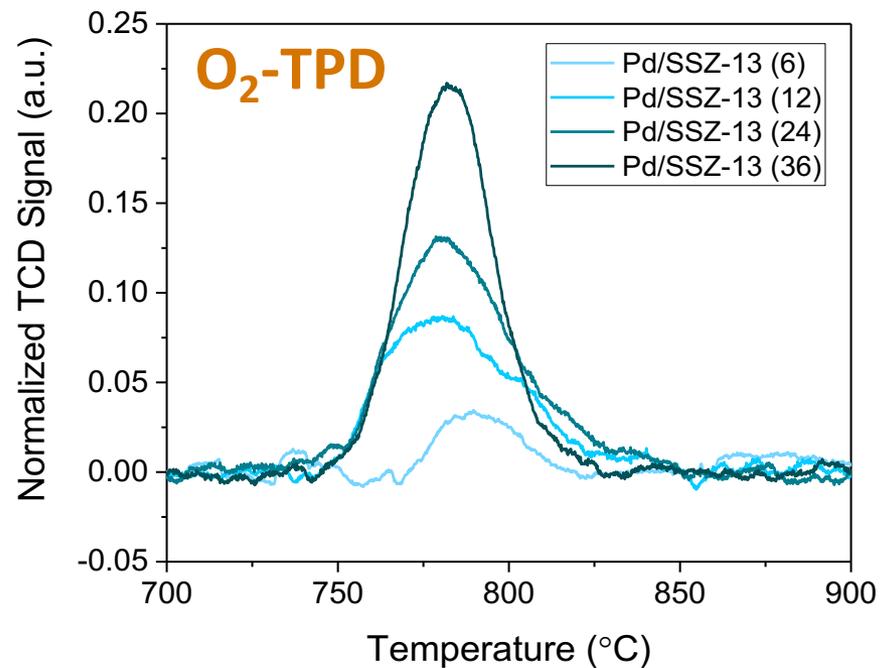
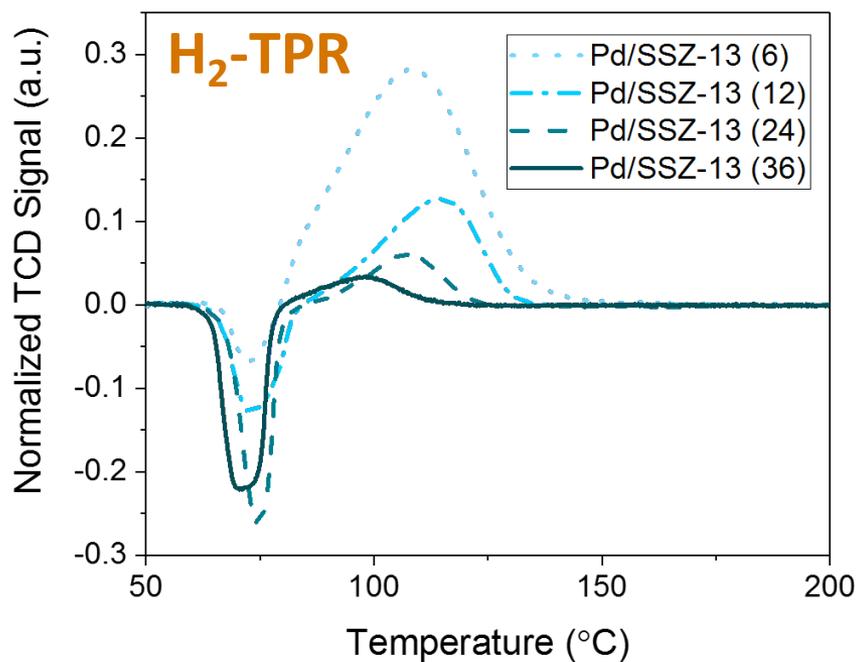
- ▶ When PdO is the active phase (low temperature, O<sub>2</sub> rich), turnover rates are in most cases poorly estimated.
- ▶ Standard titration methods, e.g., CO, H<sub>2</sub>, H<sub>2</sub>-O<sub>2</sub> titrations examine metallic Pd, or Pd covered with chemisorbed oxygen. The actual PdO surface composition and exposure are very different.



- ▶ Turnover rates on single atoms are much lower than on PdO.
- ▶ Quantify PdO amount in each catalyst, and normalize rate based on that.

# Quantification of “in bulk” PdO

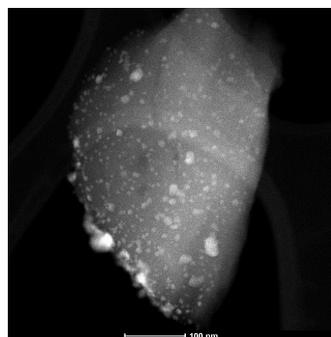
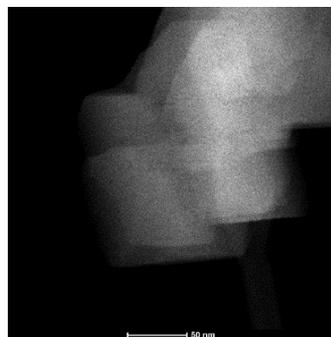
- ▶ We are able to qualitatively describe the embedded PdO species with STEM and APT. But how do we quantify them?



- ▶ H<sub>2</sub>-TPR: PdO + H<sub>2</sub> → Pd + H<sub>2</sub>O; Pd + H<sub>2</sub> → PdH<sub>x</sub>. Less quantitative.
- ▶ TPD: PdO → Pd + ½O<sub>2</sub>. More quantitative.

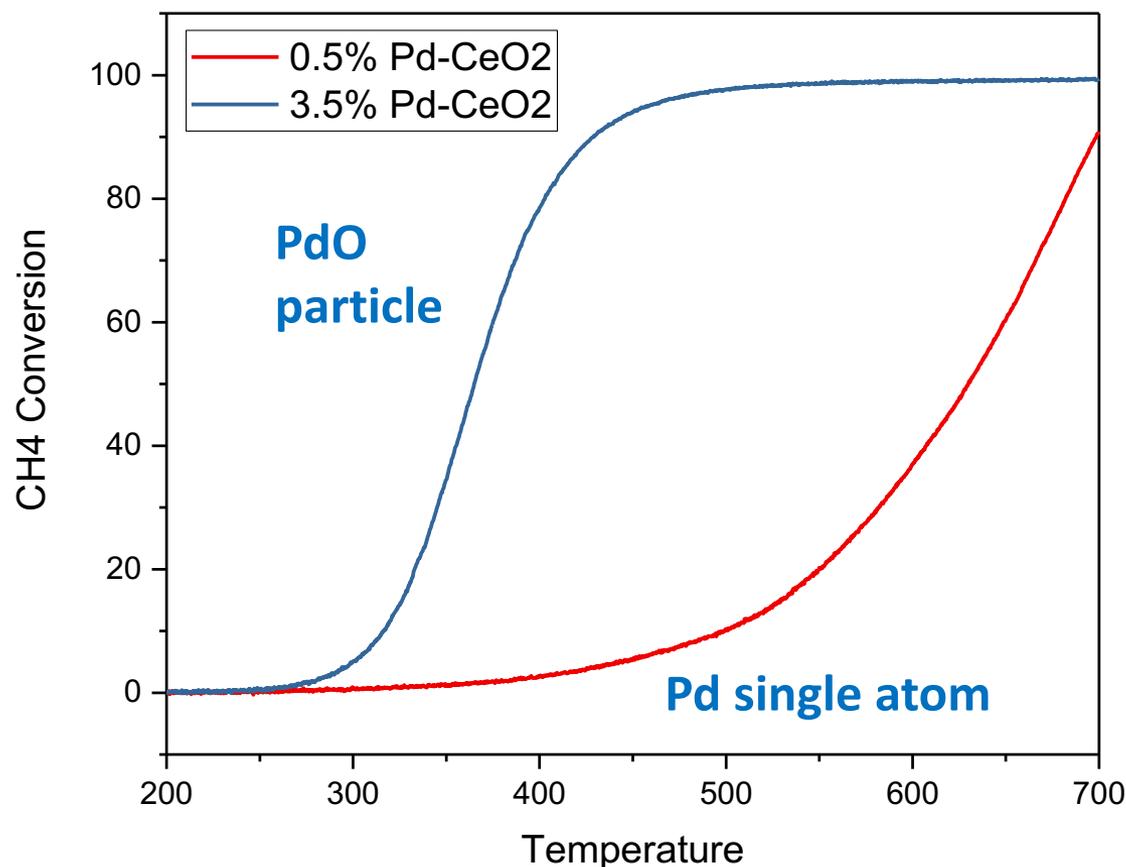
# Comparison between activities of “in bulk” and external surface PdO sites

Catalyst	Particle Size (nm)	ICP Pd loading (wt%)	Dispersion by H <sub>2</sub> -O <sub>2</sub> titration (%)	PdO fraction by TPO (%)	Rate per mole of Pd at 350 C (10 <sup>-2</sup> /s)	TOR at 350 C (10 <sup>-2</sup> /s)	Rate per mole of PdO at 350 C (10 <sup>-2</sup> /s)
Pd/Al <sub>2</sub> O <sub>3</sub>	4.9 ± 1.2	2.6	16	100	1.3	8.0	1.3
Pd/SSZ-13 (6)	--	2.7	26	12	0.05	0.2	0.4
Pd/SSZ-13 (36)	5.2 ± 3.3	2.8	3	81	0.4	12.2	0.5

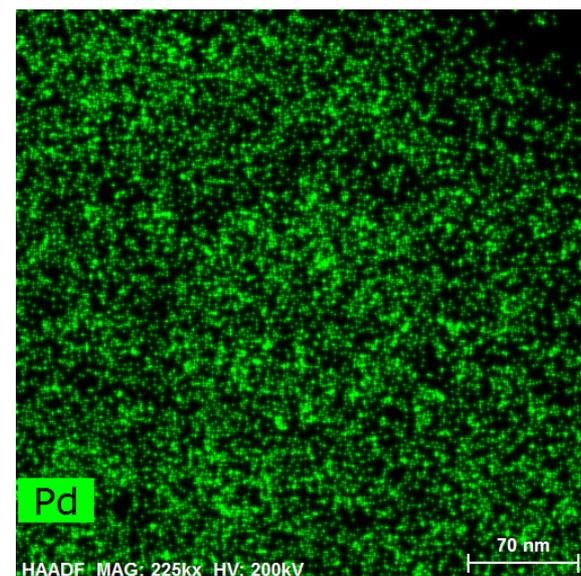


- ▶ On a per mole of PdO basis, CH<sub>4</sub> conversion rates between embedded and external surface PdO are rather similar.
- ▶ On a per PdO surface area basis (assuming spherical particles), CH<sub>4</sub> conversion rates on embedded PdO particles are ~30% those of external surface PdO particles. Likely explanation is that the SSZ-13 (Si/Al = 6) support cannot prevent water inhibition; therefore does not show any advantage than the SSZ-13 (Si/Al = 36) support.
- ▶ Beneficial confinement effects for embedded PdO, if any, are not significant enough to lead to appreciable rate enhancement.
- ▶ Hydrophobic SSZ-13 supported PdO particles do not have intrinsic activities higher than PdO on Al<sub>2</sub>O<sub>3</sub>; the only advantage is improved catalyst stability.

# CeO<sub>2</sub> supported Pd atom vs. PdO



3.5% Pd/CeO<sub>2</sub>



- ▶ The same Pd single atom vs. PdO particle catalytic difference is found on oxide supports: single atoms are much less active than PdO particles.
- ▶ CH<sub>4</sub> and O<sub>2</sub> activation requires surface ensembles larger than single atoms.

- ▶ On a hydrophilic SSZ-13 (Si/Al = 6) support, Pd tends to diffuse into the zeolite bulk rather than stay on the external surface.
- ▶ At Pd loadings  $\leq 1.0$  wt%, Pd stays exclusively as isolated Pd(II) cations as evidenced by STEM, APT, XANES and O<sub>2</sub>-TPD studies. At higher Pd loadings, embedded PdO particles develop.
- ▶ The formation of such PdO particles coincides with high methane combustion activity.
- ▶ Via quantification of PdO contents in various catalysts and normalization of methane combustion rates based on PdO contents, it is concluded that PdO particles both embedded in SSZ-13 bulk and deposited on SSZ-13 external surface do not have intrinsic activities higher than PdO on alumina.
- ▶ On both zeolite and CeO<sub>2</sub> supports, single atom Pd sites are much less active than PdO in catalyzing low temperature methane combustion.

# Acknowledgements

- ▶ DOE Office of Energy Efficiency and Renewable Energy/Vehicle Technologies Office for the sole financial support of this work (managers Ken Howden and Gurpreet Singh).
- ▶ Research conducted partially using DOE user facility, EMSL, located at PNNL.

