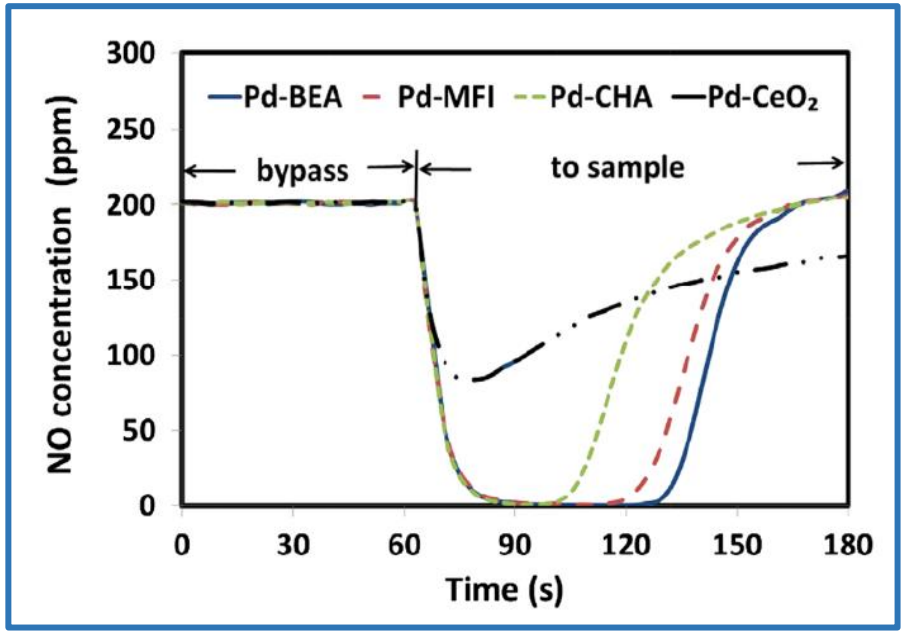
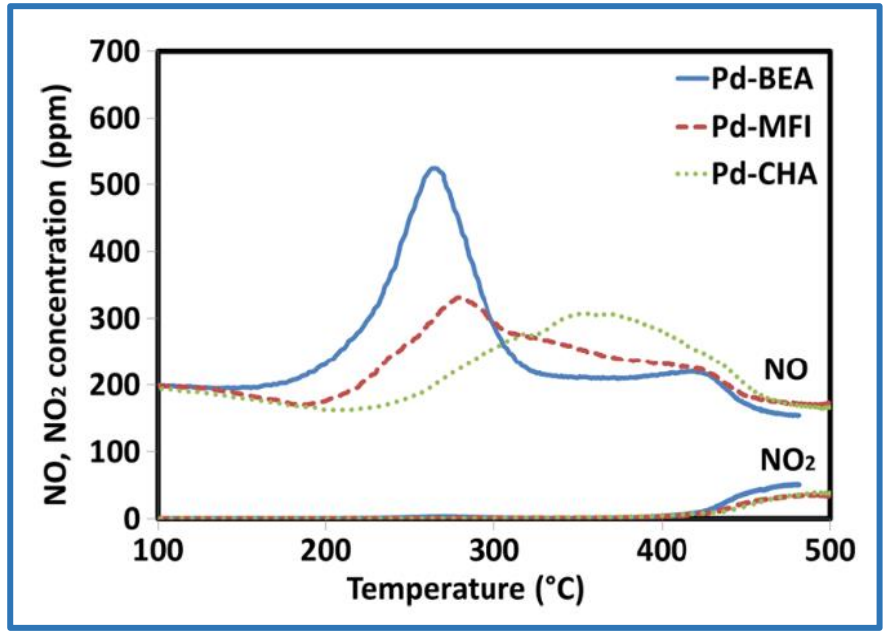
Degradation Mechanism of Pd/Zeolite Passive NOx Adsorbers: The Interchange Between Particles & Cations

Yuntao (Kevin) Gu, CLEERS Workshop, Sep 18th, 2020

What do we know about PNAs?





Pd/Zeolites exhibit great low temperature NOx storage capacity and reasonable NOx release temperature

- **Ion-exchanged Pd is responsible for the low temperature NOx storage**

Chen, H.-Y. et.al. *Catalysis Letters*, *146*(9), 1706–1711

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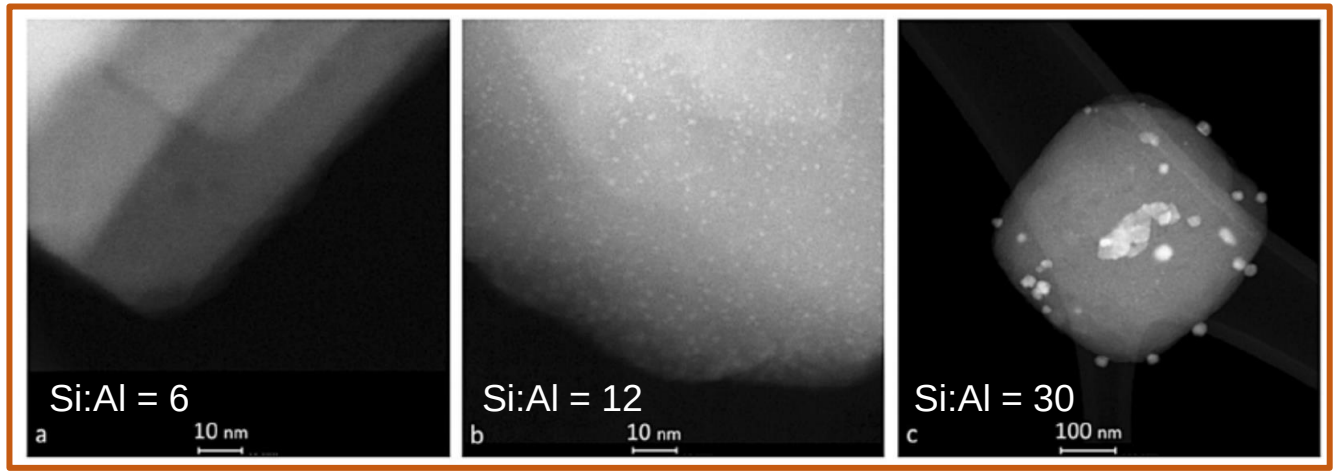

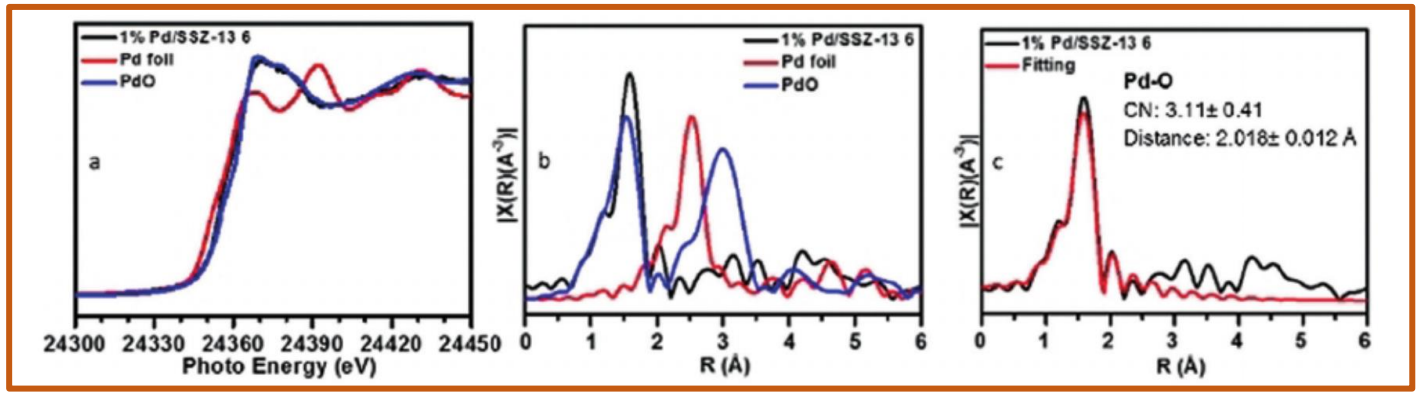

NOx storage capacity can be maximized by atomically dispersing Pd

- **100% Pd ion-exchange leads to NO:Pd=1:1**

K. Khivantsev et. al., *Angew. Chemie Int. Ed.* 57 (2018) 16672–16677.

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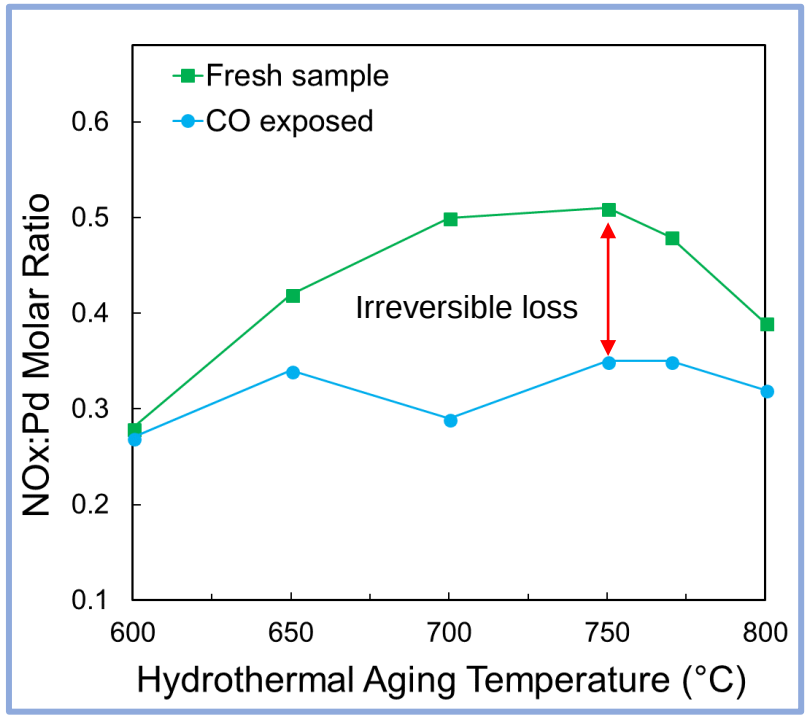

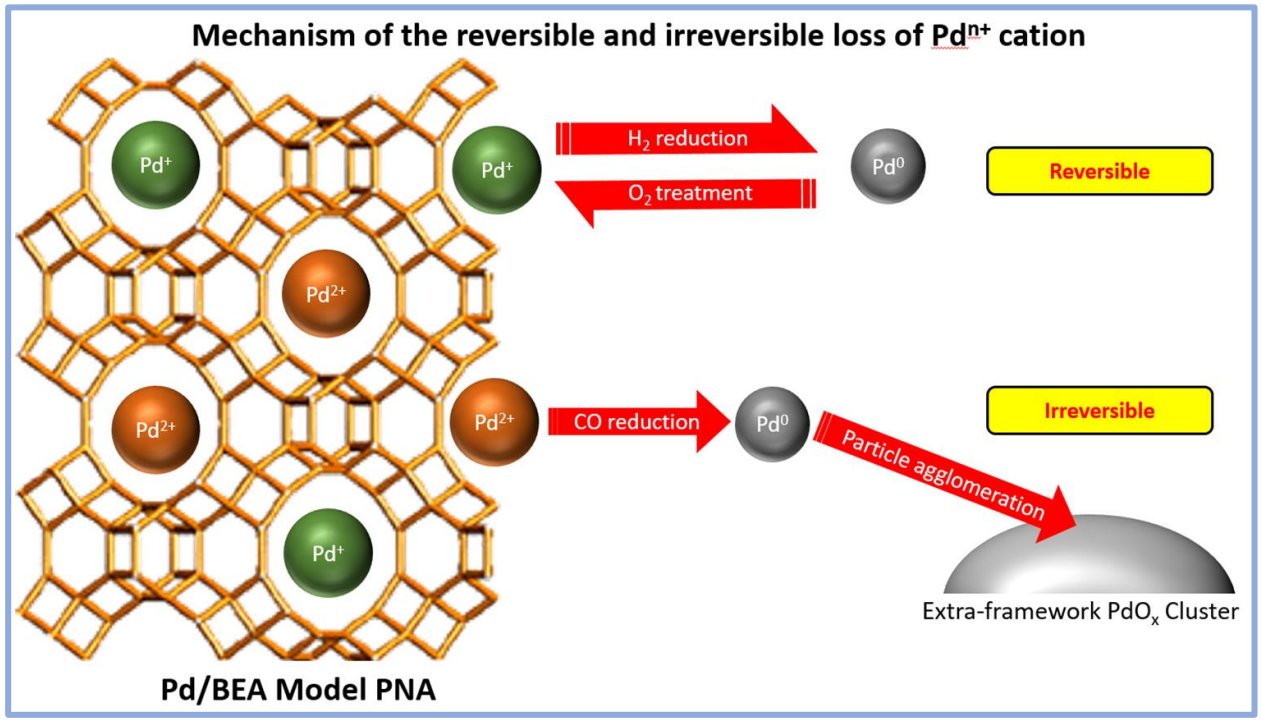

Pd/BEA irreversibly losses part of the NOx storage capacity when exposed to low temperature CO

- **CO exposure leads to the detrimental formation of PdO particles**

Y. Gu, et. al., *Appl. Catal. B Environ.* 258 (2019) 118032.

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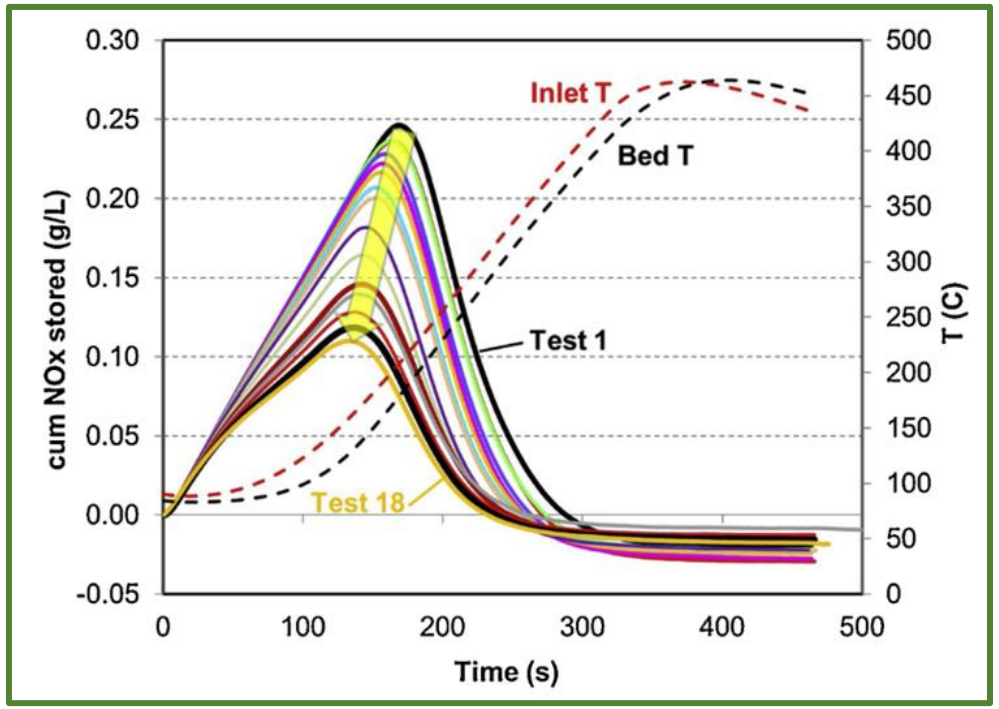
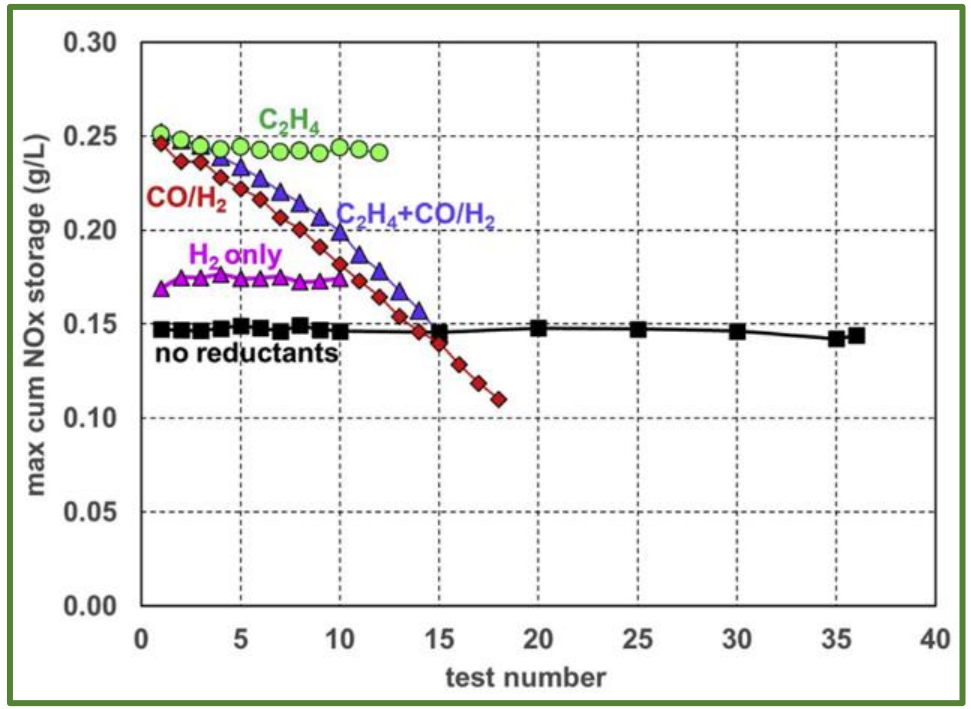


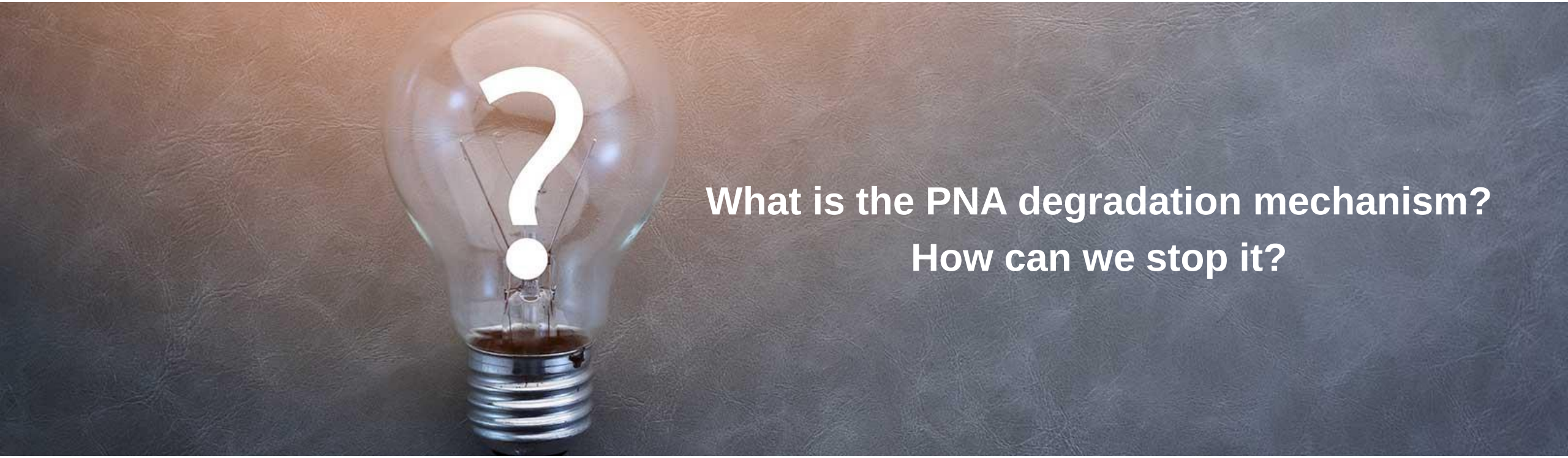


Pd/SSZ-13 degrades similarly as Pd/BEA when exposed to CO during NO-TPD cycles

- **CO induced degradation appears to be a universal behavior of Pd/zeolites**

J.R. Theis, et. al., *Catal. Today.* (2020).

Today's objective



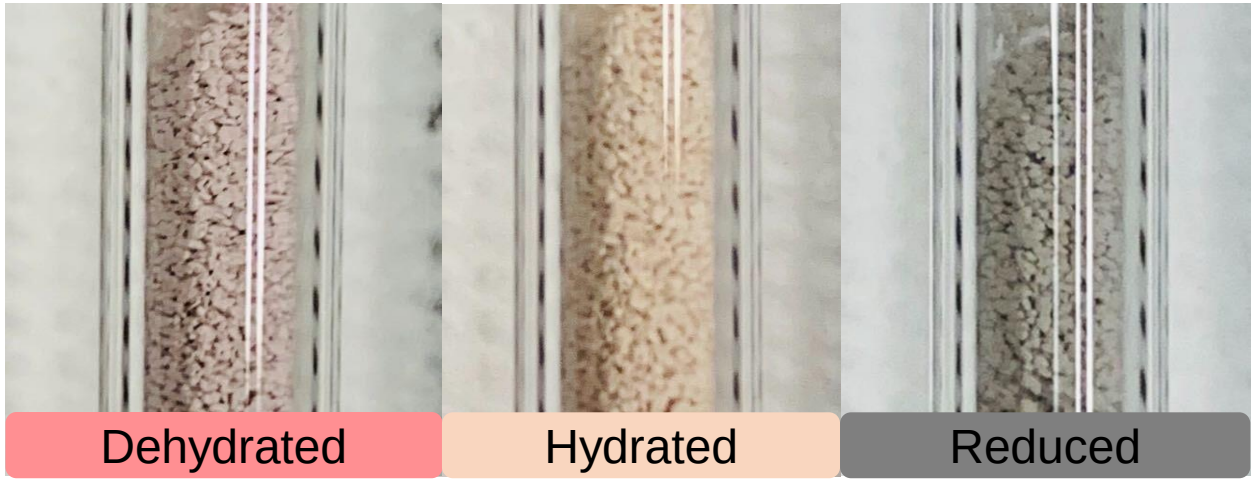
What is the PNA degradation mechanism?

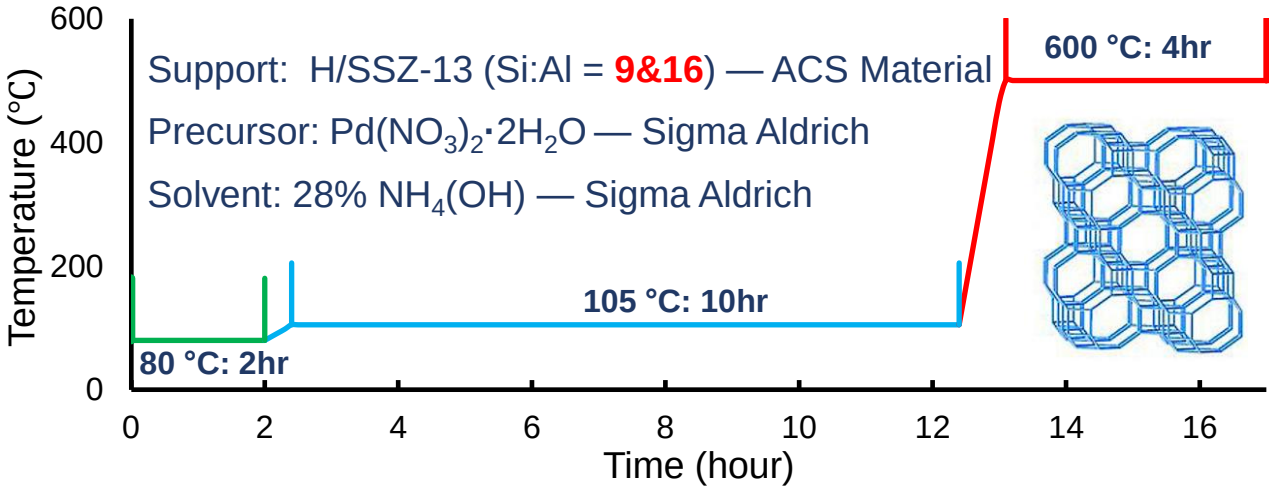
How can we stop it?

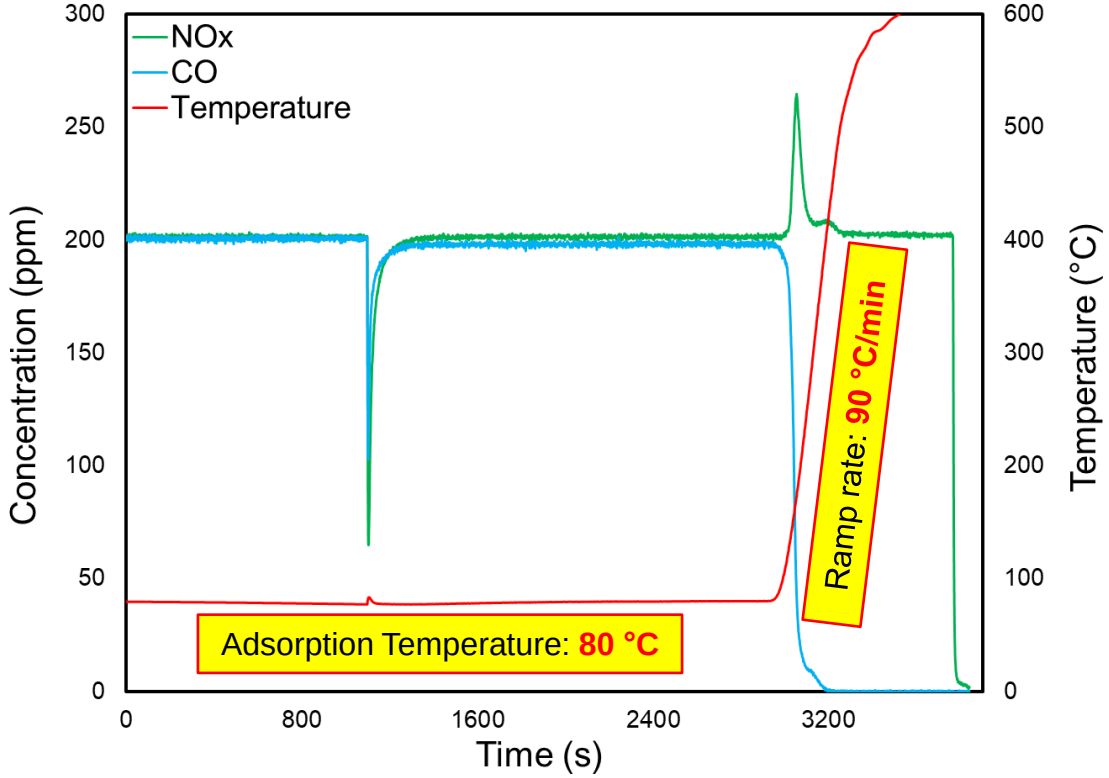
https://en.oxforddictionaries.com/punctuation/question-mark

Experimental Methods & Materials

Synthesis → Pretreatment → Simulate exhaust from bypass → Switch from bypass to reactor → Start temperature program





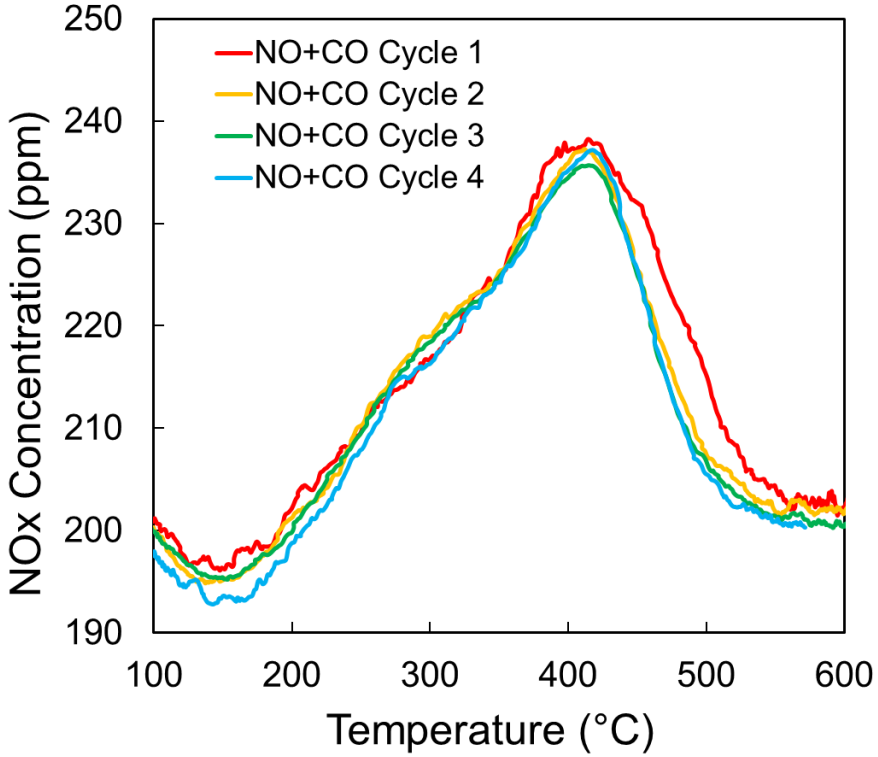


O_2 pretreatment (45 min.): 10% O_2 balanced by N_2, 600 °C
PNA experiment: 200 ppm NO, 200 ppm CO, 10% O_2, 5% H_2O balanced by N_2. (GHSV: 60,000 hr^{-1})

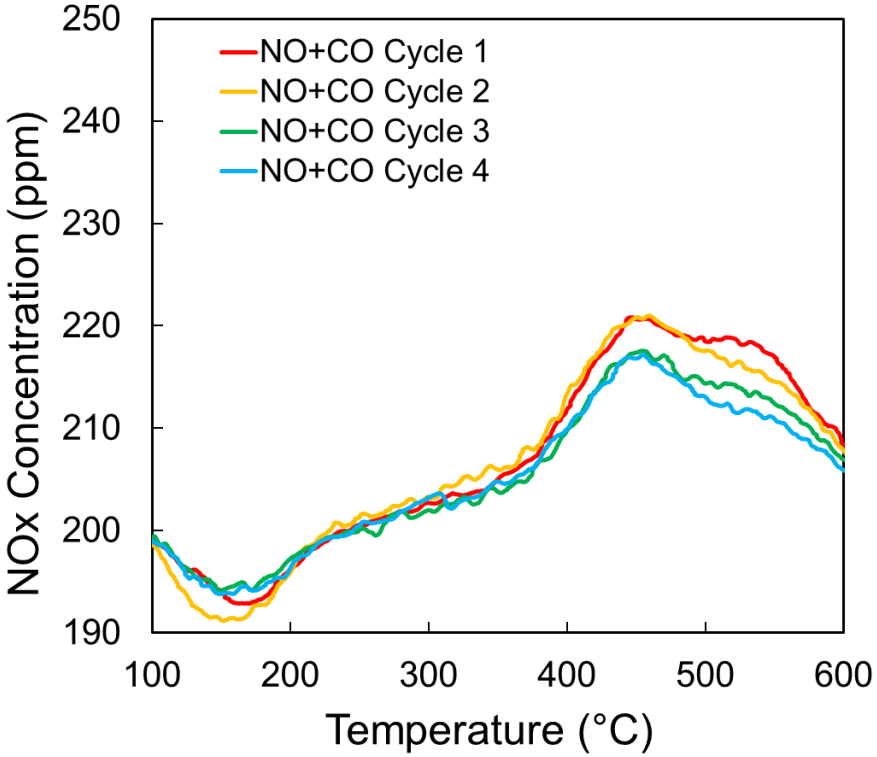
Difference Between IE100& IE50

Distinct results of repetitive NOx-TPD profiles

IE100: Pd/SSZ-13 – **Si:Al=9**



IE50: Pd/SSZ-13 – **Si:Al=16**



Sample	Support	1st NOx:Pd	4th NOx:Pd	Si/Al		Pd Loading	
				Nominal	ICP	Target	ICP
IE100*	H-SSZ-13	1.05 ± 0.1	0.91 ± 0.1	10	**9**	1 wt.%	**0.84 wt.%**
IE50*	H-SSZ-13	0.55 ± 0.1	0.38 ± 0.1	15	**16**	1 wt.%	**0.79 wt.%**

* EXAFS, H2-TPR and STEM Imaging were employed to characterize the samples studied

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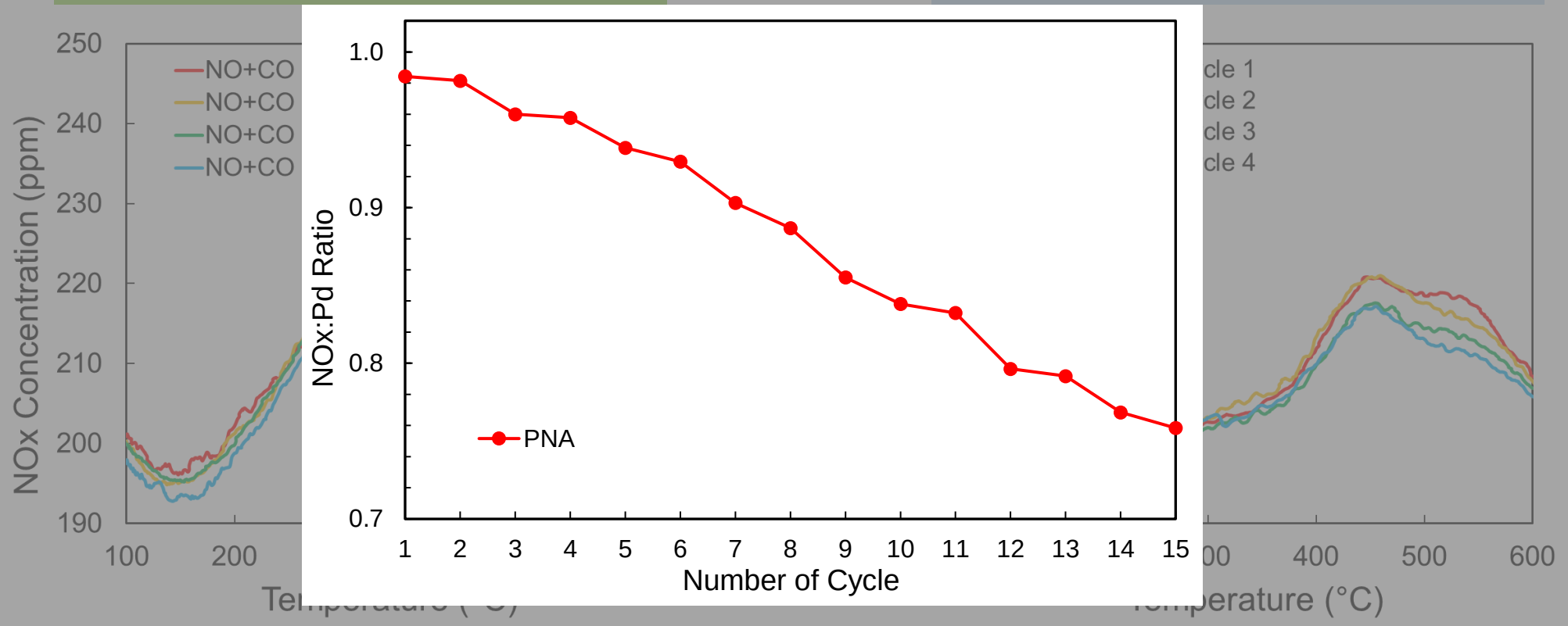

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Distinct results of consecutive CO light-off behavior

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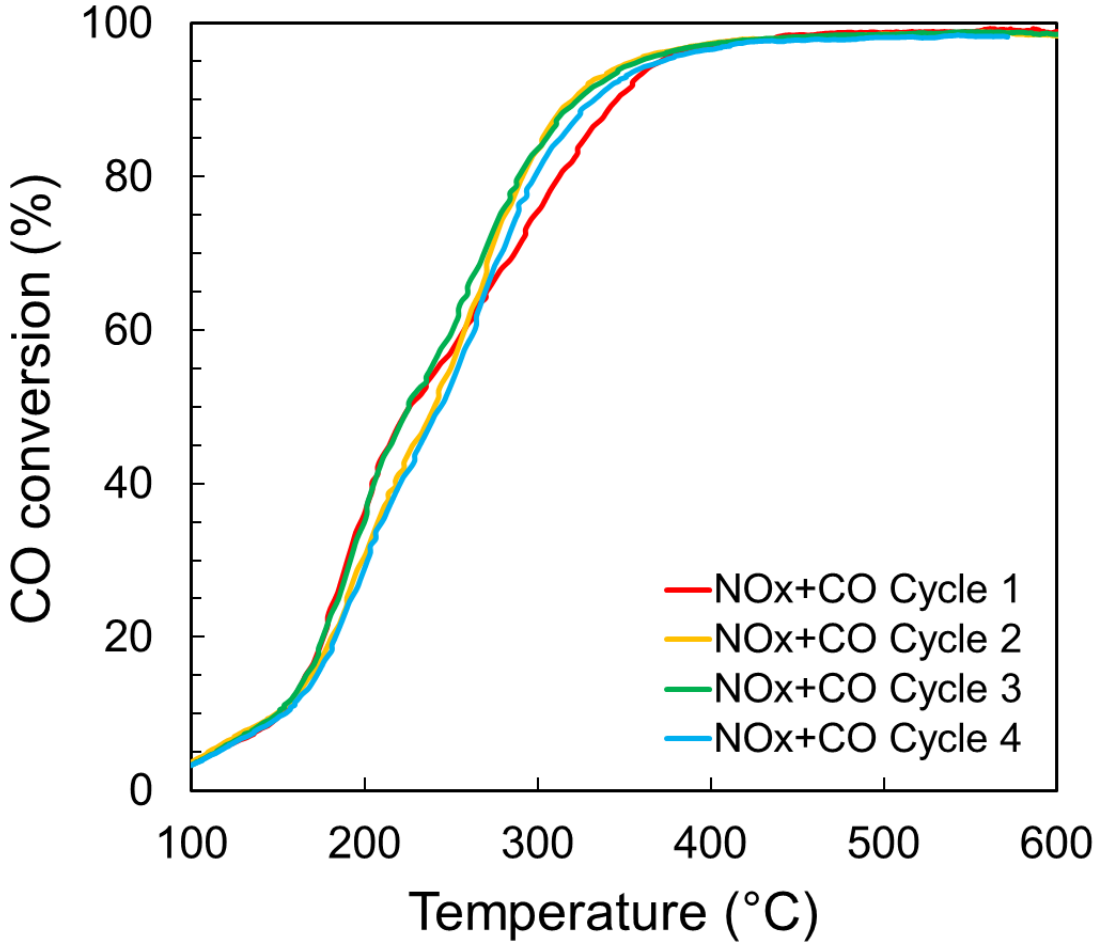

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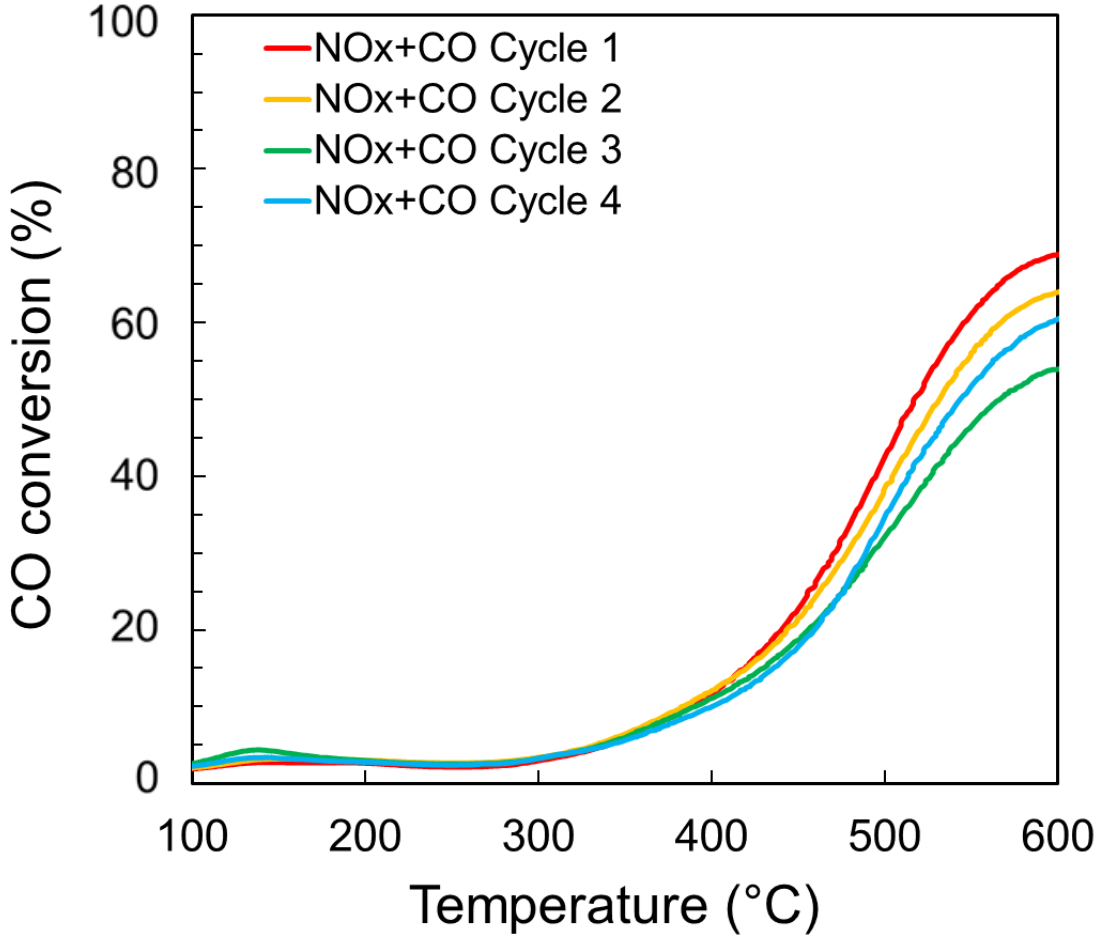

CO Oxidation Kinetics

Effect of hydration, NO adsorption and Pd distribution

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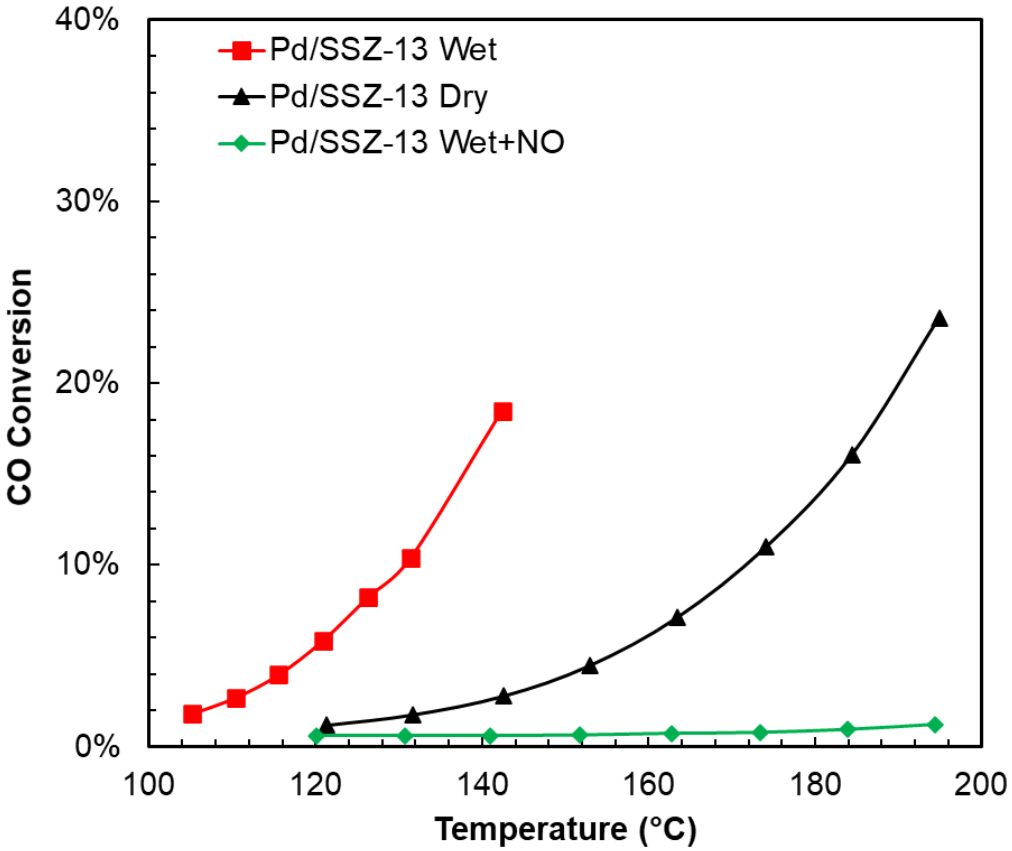

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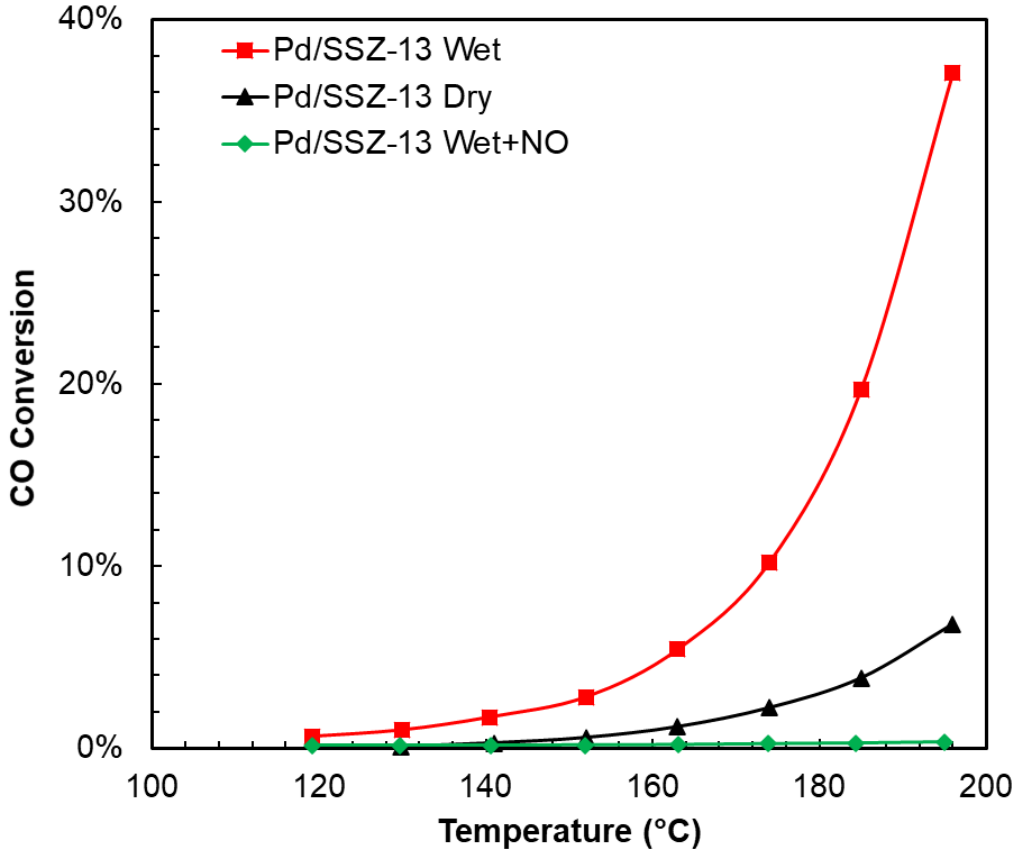


CO oxidation activity: **Hydrated** Pd cations > **Dry** Pd Cations> Pd **Particles**> **NO adsorbed** hydrated Pd cations

What Happened During NOx-TPD?

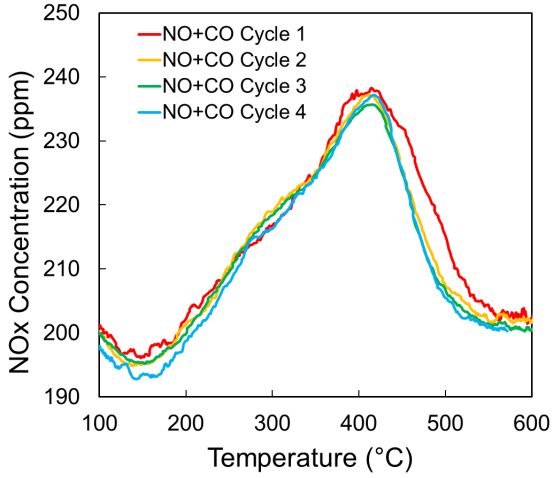
Key reactions:

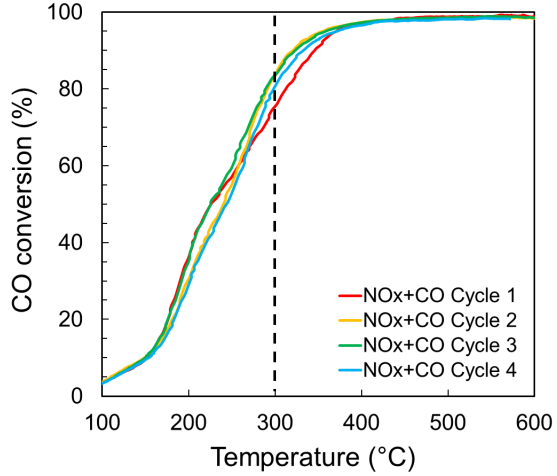
			Influence on CO oxidation
1	$ZPd^{II}(NO)(H_2O)_3 \longrightarrow Z_2Pd^{II}(H_2O)_4 + NO$	NO desorption	↑
2	$Z_2Pd^{II}(H_2O)_4 \longrightarrow Z_2Pd^{II} + 4H_2O$	H_2O desorption	↓

Reduction of Pd^{II} by CO

How do NOx trapping and CO oxidation affect each other?

IE100 - Si:Al=9





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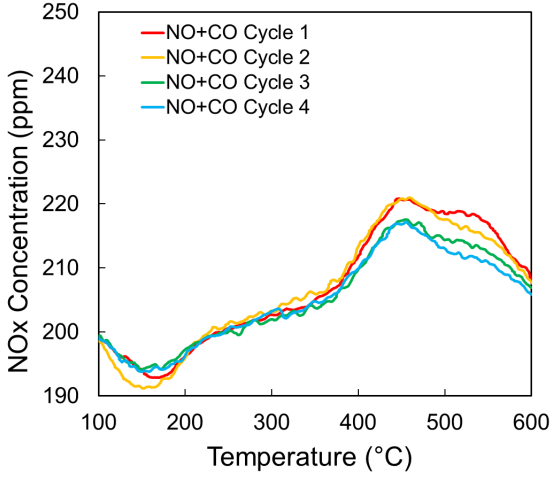
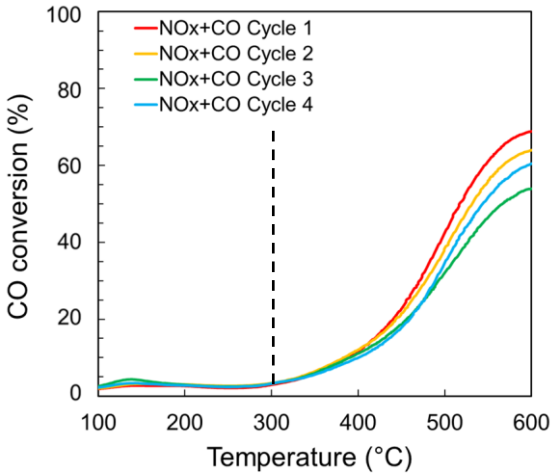
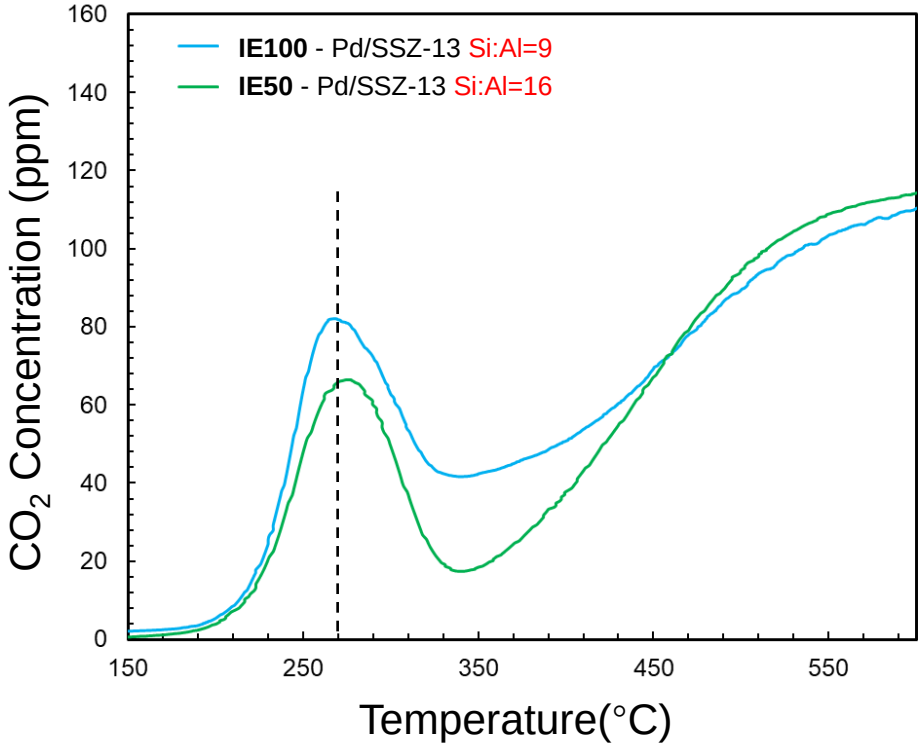




CO – Temperature programmed reduction



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3	$Z_2Pd^{II}(H_2O)_4 + CO$	$\longrightarrow$ $Pd^0 + CO_2 + 2ZH + 3H_2O$	Pd^{II} reduction by CO	↓

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3	$Z_2Pd^{II}(H_2O)_4 + CO$	$\longrightarrow$ $Pd^0 + CO_2 + 2ZH + 3H_2O$	Pd^{II} reduction by CO	↓
4	$Pd^0 + ½\ O_2$	$\longrightarrow$ PdO	Pd Re-oxidation	→
5	$PdO + 2ZH$	$\longrightarrow$ $Z_2Pd^{II} + H_2O$	Pd^{II} regeneration (Protonolysis)	↑

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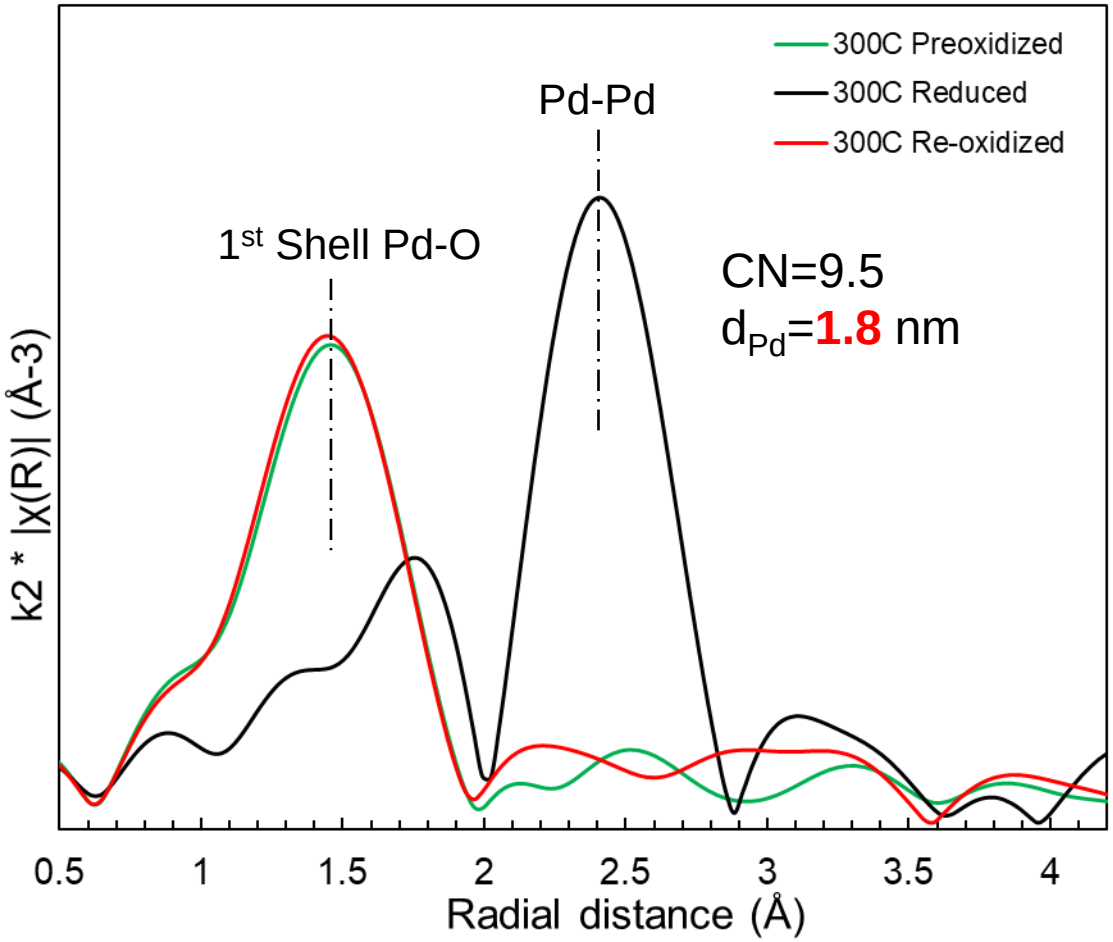
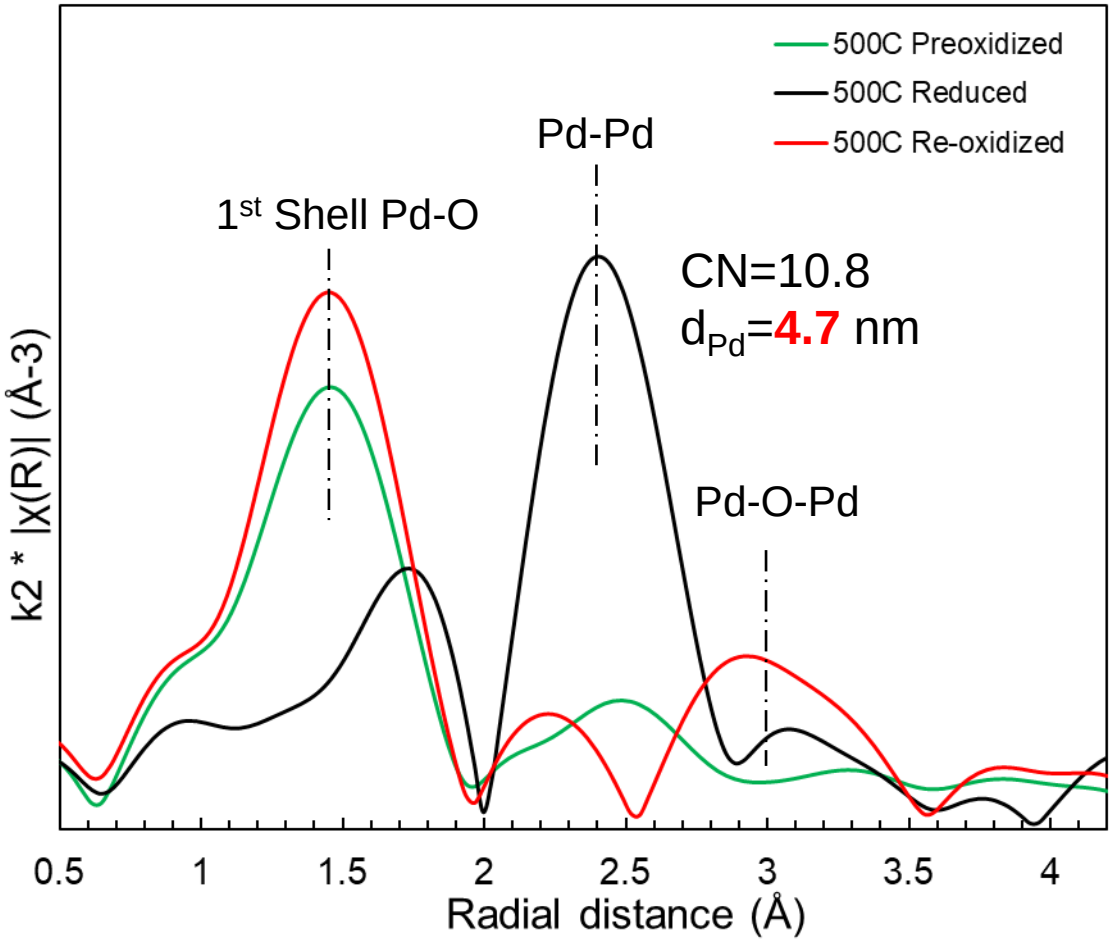
Reduction and Reoxidation Dynamics

In-situ EXAFS Characterization of Pd/SSZ-13

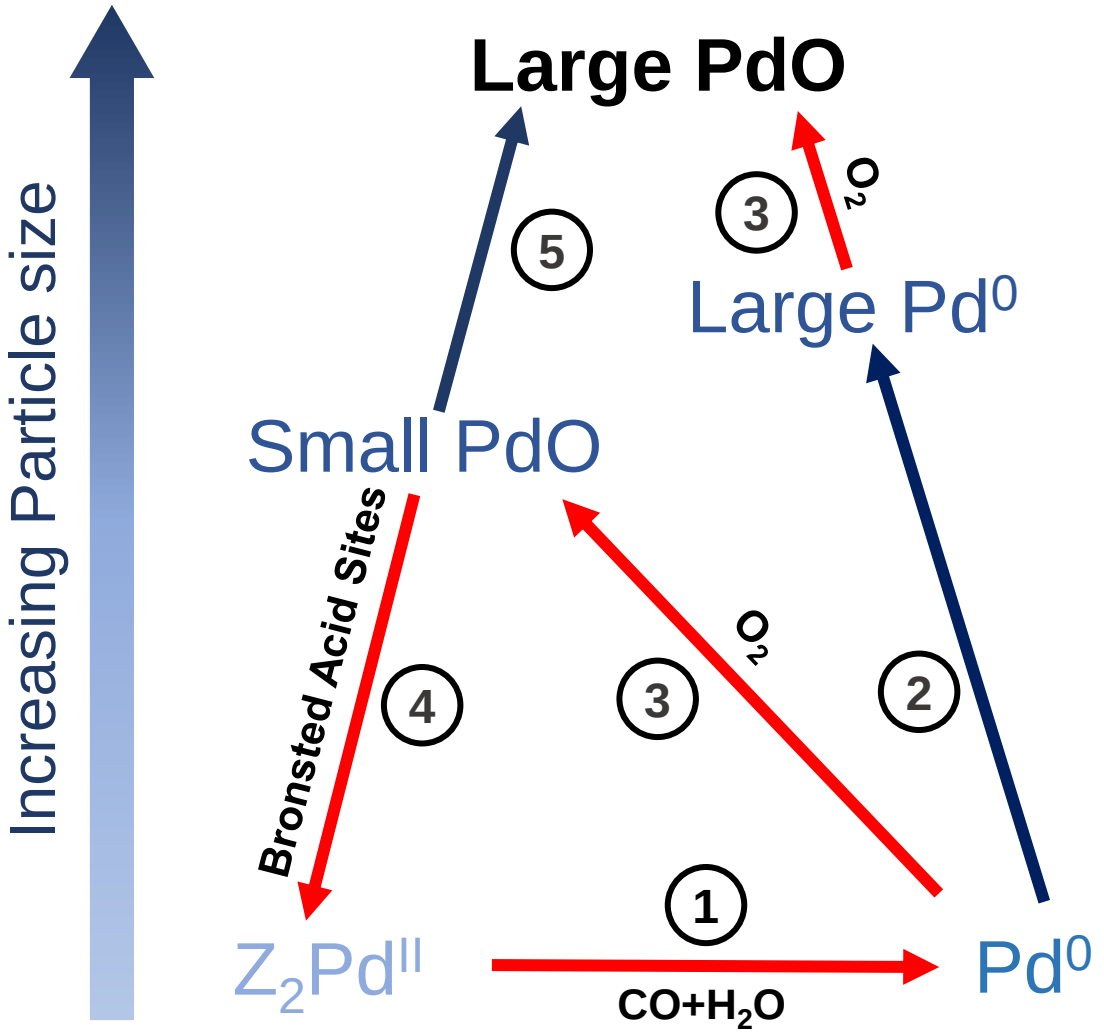
O_2 @600 °C | $O_2 + H_2O$ @300 or 500 °C | $CO + H_2O$ @300 or 500 °C | O_2 @300 or 500 °C

Preoxidized **Reduced** **Reoxidized**





Deactivation Mechanism:
Particle Agglomeration vs. Protonolysis

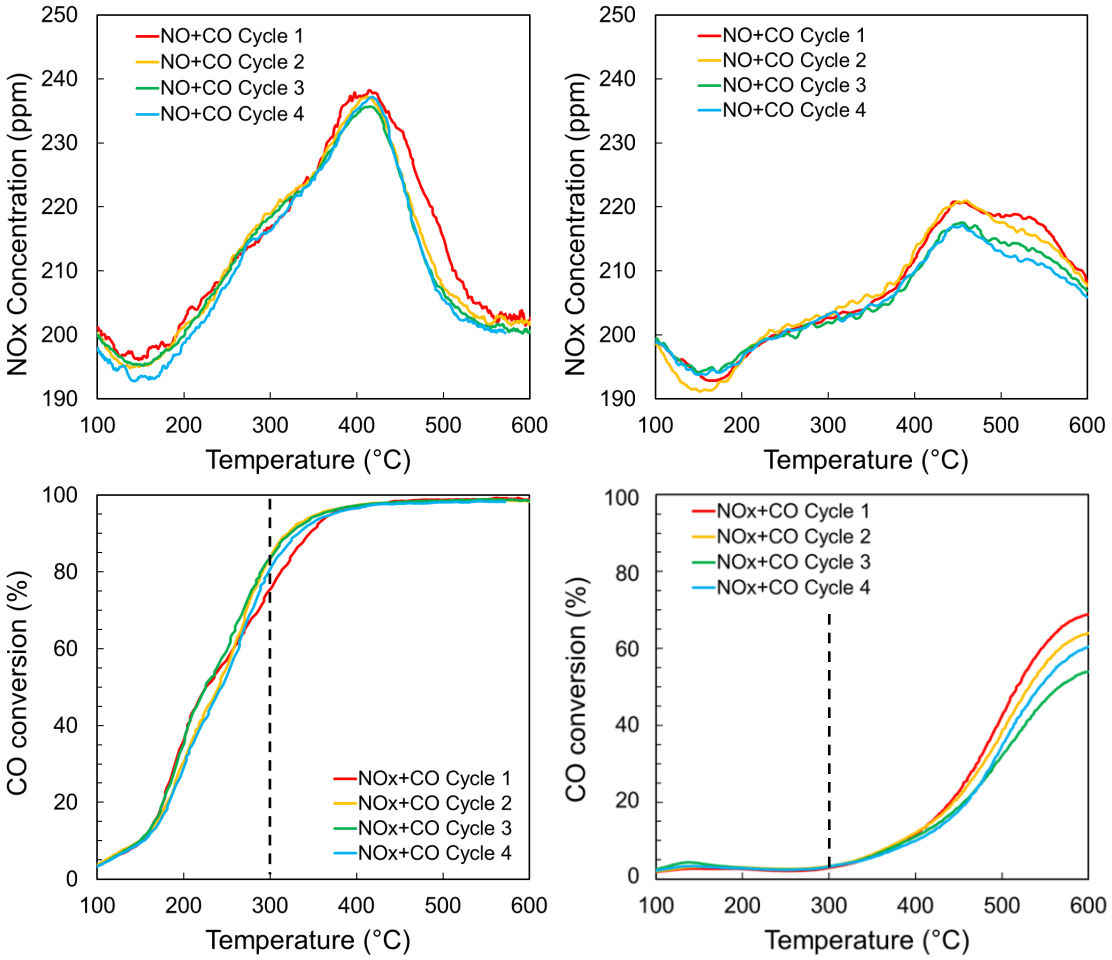


1. $Z_2Pd^{II} + CO + H_2O \longrightarrow Pd^0 + CO_2 + 2ZH$
2. Pd agglomeration
3. $Pd^0 + ½\ O_2 \longrightarrow PdO$
4. $PdO + 2ZH \longrightarrow Z_2Pd^{II} + H_2O$
5. PdO agglomeration

Summary & Conclusions

IE100 - Si:Al=9

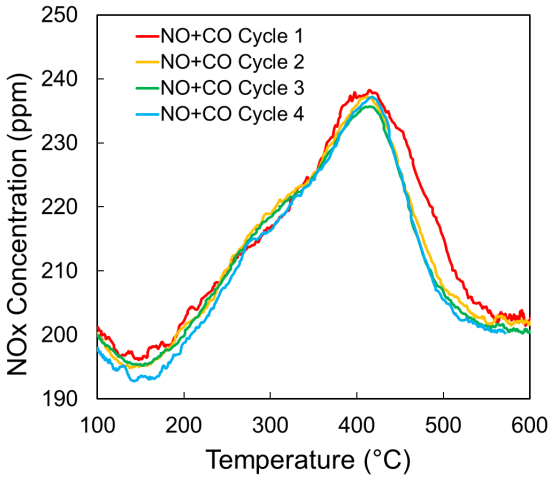
IE50 - Si:Al=16

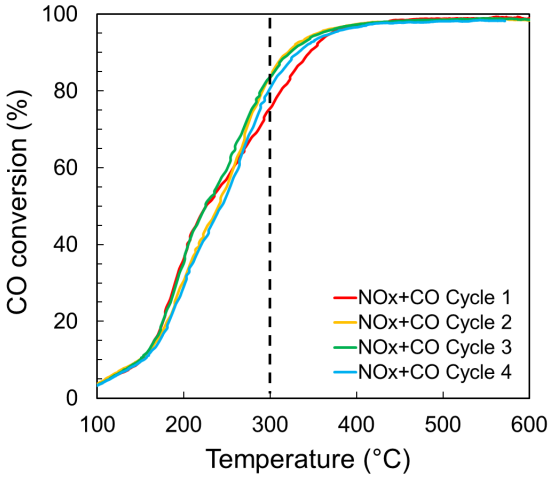


- CO + H_2O lead to the reduction of Pd^{II} and formation of Pd particles
- O_2 can re-oxidize Pd into PdO and regenerate Pd^{II} via protonalysis
- Particle agglomeration and protonalysis are competing reactions during reoxidation
- Only **high temperature CO exposure** leads to the formation of big PdO particles and irreversible PNA degradation

Proposed Solution
Integration of PNA with DOC

IE100 - Si:Al=9





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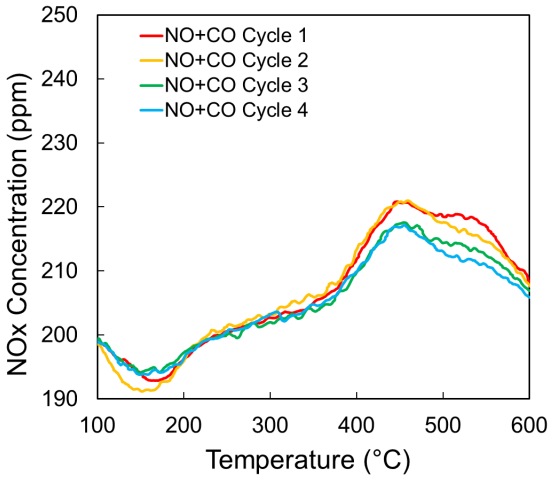
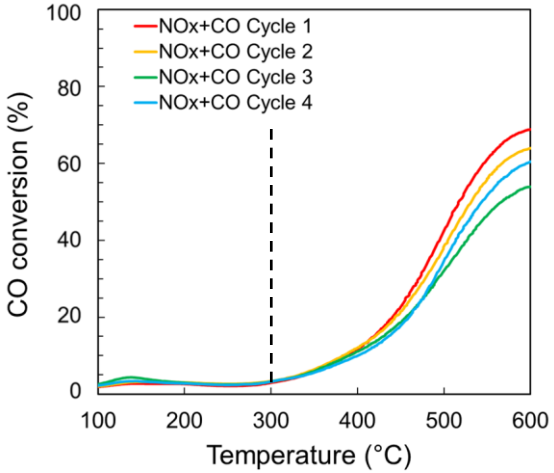
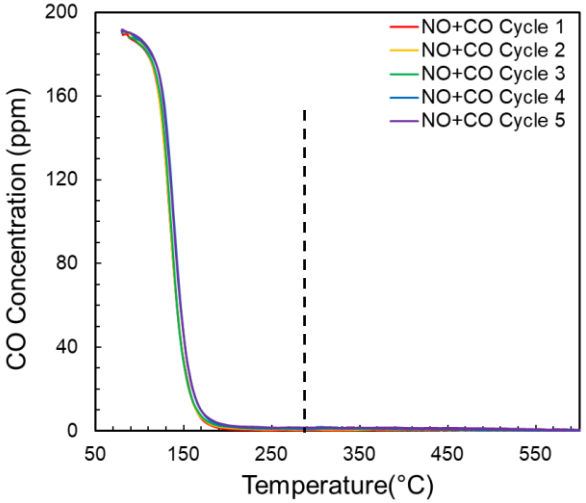
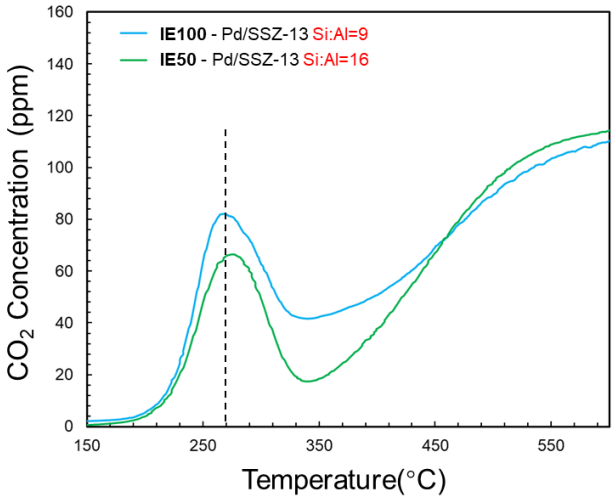
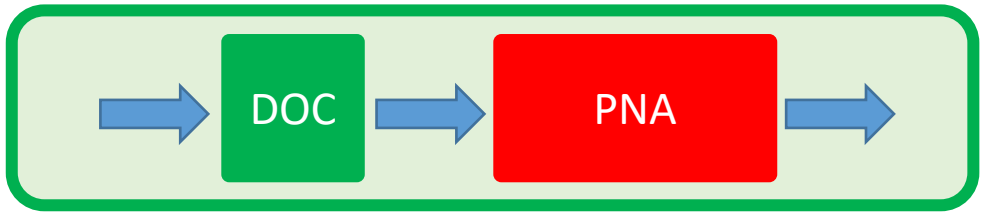




DOC – Pt/Al_2O_3







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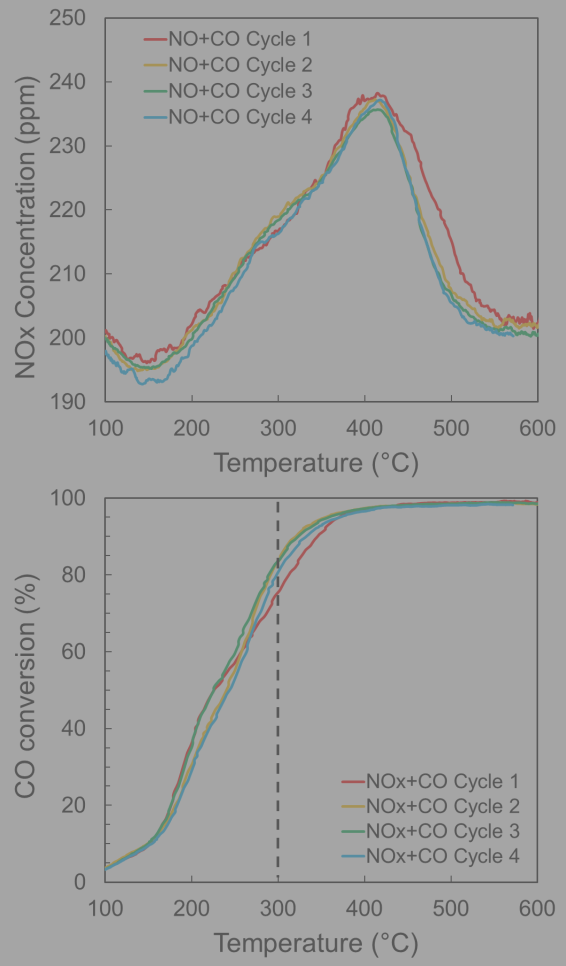

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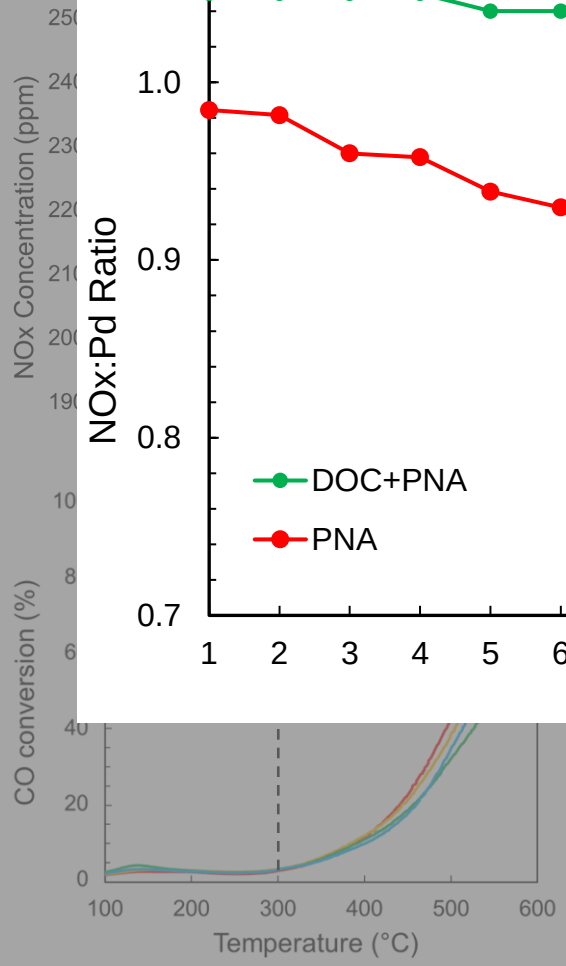

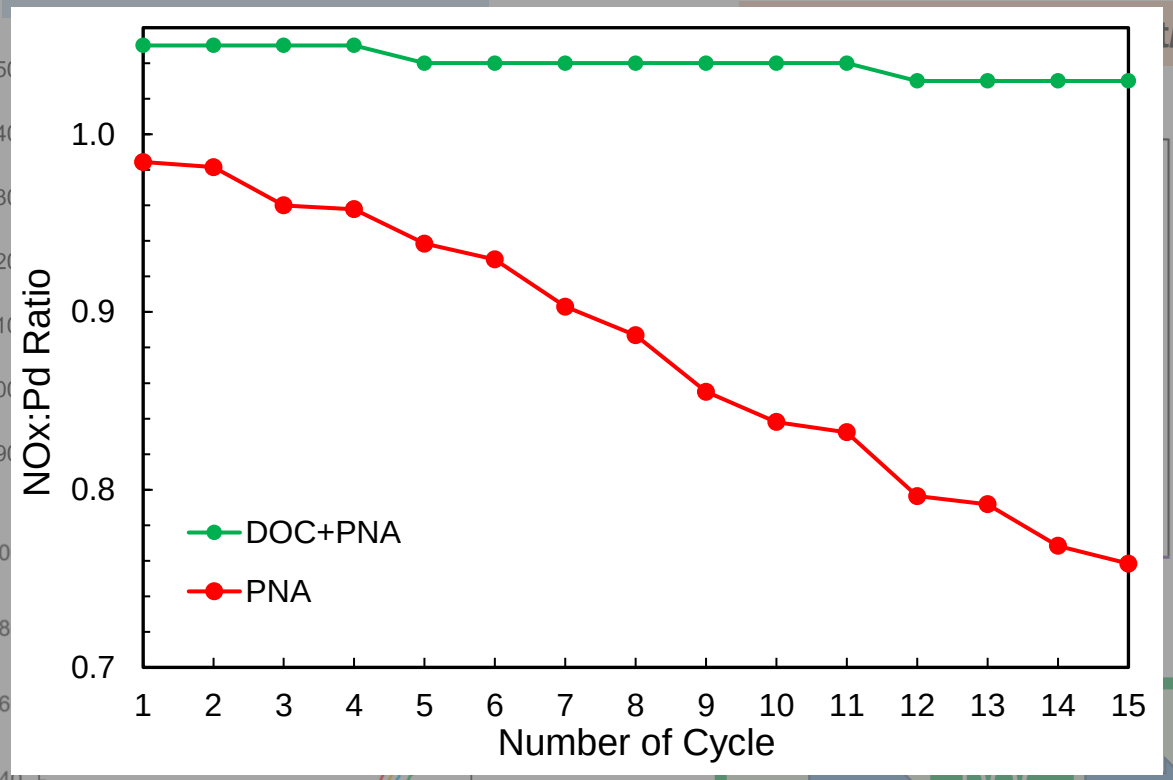

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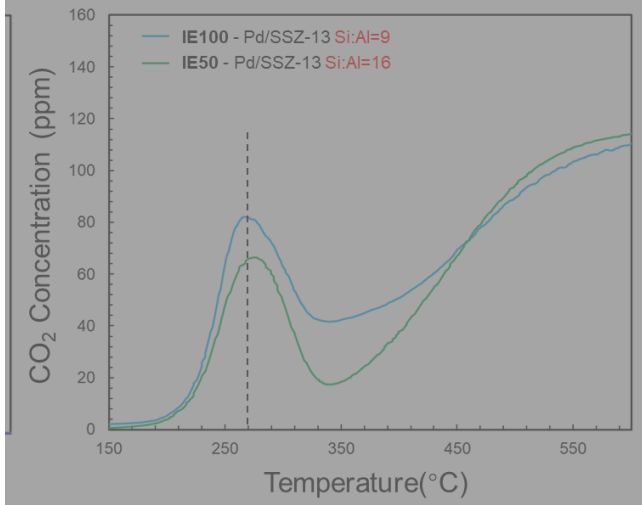

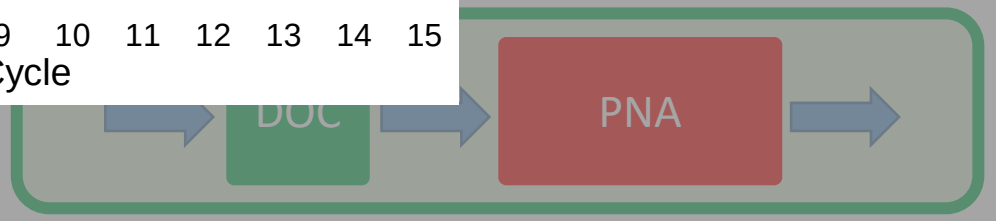

Acknowledgement

Advisor: **Bill Epling**

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Prof. Robert Davis

Prof. Christopher Paolucci

Keka Mandal

Yu-Ren Chen, Silvia Marino, Ryan Zelinsky, Yuntao(Kevin) Gu, Lai Wei, Natalia Diaz

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4	Pd agglomeration		↓
5	$Pd^0 + ½\ O_2 \rightarrow PdO$	Pd Re-oxidation	→
6	PdO agglomeration		↓
7	$PdO + 2ZH \rightarrow Z_2Pd^{II} + H_2O$	Pd^{II} regeneration (Protonolysis)	↑