Design and Optimization of Structured Multi-Functional Trapping Catalysts for Conversion of Hydrocarbons and NOx from Diesel and Advanced Combustion Engines

Mike Harold (PI), Lars Grabow (University of Houston)
Bill Epling (CoI; University of Virginia)
Cary Henry, Robert Henderson, Minnie Lahoti (SwRI)
Todd Toops (Oak Ridge National Laboratory)
Sharan Sethuraman (Johnson Matthey Inc.)
Kiran Premchand (FCA Inc.)

June 12, 2019

ACE129

Overview

Timeline

- Start: October 1, 2017
- End: September 30, 2020
- ~40% complete

Budget

- Total project funding
  - DOE: $2,103,549
  - UH & partners: $245,311
- Funding received
  - FY19: $1,285,527

Barriers/Targets

- Develop robust emission control for advanced low temperature combustion (LTC) engines
- Achieve light-off for CO + HC oxidation below 150 ºC while maintaining NOx emissions at 0.2 g/bhp-h
- "Cold start" increasingly important source of emissions: Cannot achieve 2025 regulations without new strategy for NOx & HCs
- Passive NOx adsorbers (PNAs): new concept requiring development and optimization
- Hydrocarbon traps (HCTs) not fully realized, especially in combination with PNA

Partners

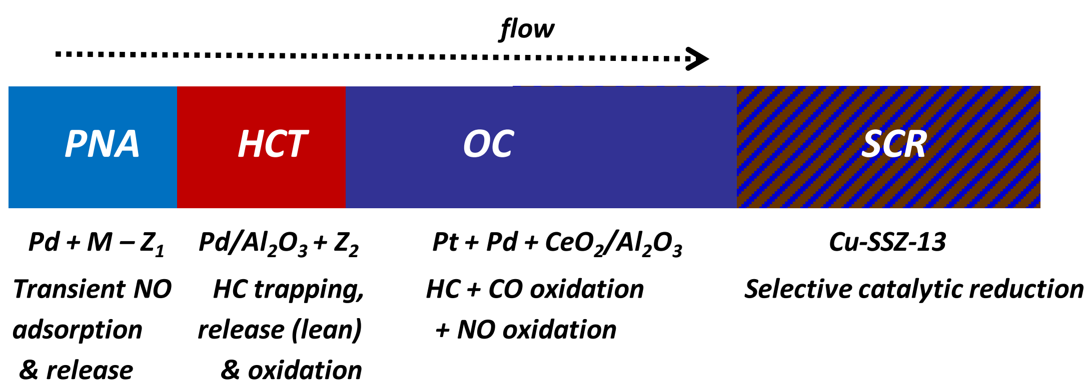
- U. Houston (lead)
- University of Virginia
- Johnson Matthey Inc.
- Southwest Research Institute
- Oak Ridge National Lab
- FCA Inc.

Project Objective

Research, develop, and demonstrate a multi-functional, catalyzed trap that will enable vehicles with advanced combustion strategies to meet Tier 3 emissions standards while achieving the 150 °C challenge for sustained co-oxidation of HCs and CO and ≥90% NO trapping and release during warmup. Develop the

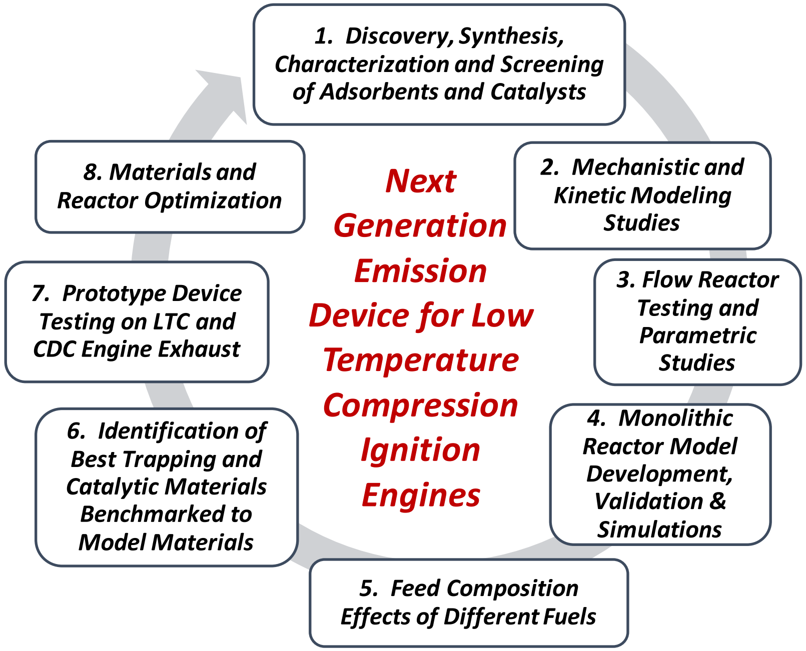
LHCNT = Lean HydroCarbon NOx Trap

to reduce emissions of HCs and NOx from advanced combustion engines.



Approach and Collaborations

- **University of Houston**
  - *Mike Harold (PI), Lars Grabow*
  - Flow reactor catalyst evaluations; Computational catalysis (DFT); Kinetic & reactor modeling
- **University of Virginia**
  - *Bill Epling (CoI)*
  - Hydrocarbon trap and catalyst deactivation
- **Oak Ridge National Laboratory**
  - *Todd Toops, Jim Parks*
  - New catalyst formulation and evaluations
- **Johnson Matthey Inc.**
  - *Sharan Sethuraman*
  - Baseline catalyst synthesis & characterization
- **Southwest Research Institute**
  - *Cary Henry, Bob Henderson, Minnie Lahoti*
  - Combustion and emission product speciation
- **Fiat Chrysler Automobiles Inc. (FCA)**
  - *Kiran Premchand*
  - Scale-up and vehicle testing of LHCNT prototype



BP1 Milestones

BP1-M#	Milestone	Type	Description	Status
BP1-M1	Material discovery	Technical	Identify at least one material each for HC trapping, HC oxidation, and NO adsorption from descriptor-based DFT.	Completed for HC oxidation, NO adsorption
BP1-M2	Baseline material performance testing complete	Technical	Complete flow reactor performance testing of the baseline LHCNT material in terms of quantifying sustained low temperature oxidation activity, NO trapping and release coupled with HC trapping and oxidation.	Completed for PNA; HCT and oxidation
BP1-M3	Exhaust speciation completed	Technical	Complete exhaust speciation for gasoline, diesel, and ethanol+gasoline blends.	Completed for diesel; to be completed in 4Q
BP1-M4	Kinetic model validated	Technical	Develop, tune and validate monolith reactor model containing the global kinetics of the baseline LHCNT material.	Kinetic/reactor model complete for NO trapping on Pd/ZSM-5; Pd/BEA, coupled NO + HC trapping
BP1-Go/NoGo	Identification of candidate material completed	Go/No Go	Identify at least one LHCNT material that, by 150°C, achieves light-off of the USDRIVE feed mixture and 90% NO trapping and release.	Baseline PNA (Pd/SSZ-13) + OC (Alloy/SiO_2) meet NO trapping and low temp. light-off targets.

Project Activities

Simulated Exhaust → **PNA** | **HCT** | **OC** → *Treated Exhaust*

Baseline: ***Pd /SSZ-13*** ***Pd/Al_2O_3 + BEA*** ***Pt + Pd + CeO_2/Al_2O_3***

PNA

- Baseline: Pd/H-SSZ-13
  - DFT calculations
  - Simple, complex feeds
- Pd/H-ZSM-5
  - Simple feeds
  - Microkinetic model
  - Reactor model
- Pd/H-BEA
  - Coupled NO + C_3H_6 trapping, release & conversion
  - Reactor modeling
- (Pd + Fe)/ZSM-5, (Pd+Cu)/SSZ-13
  - Scouting studies

HCT

- Baseline: Pd/H-BEA
  - Simple, complex feeds
- Pt/H-ZSM-5
  - Simple feeds

OC

- Baseline: Pt+Pd/CeO_2
  - Simple, complex feeds
- Pd alloy
  - Sequential with PtPd
  - Powder, monolith
- CCCM, w & w/o & PGM
  - Powder, monolith

Project Activities

Baseline: ***Pd /SSZ-13*** ***Pd/Al_2O_3 + BEA*** ***Pt + Pd + CeO_2/Al_2O_3***

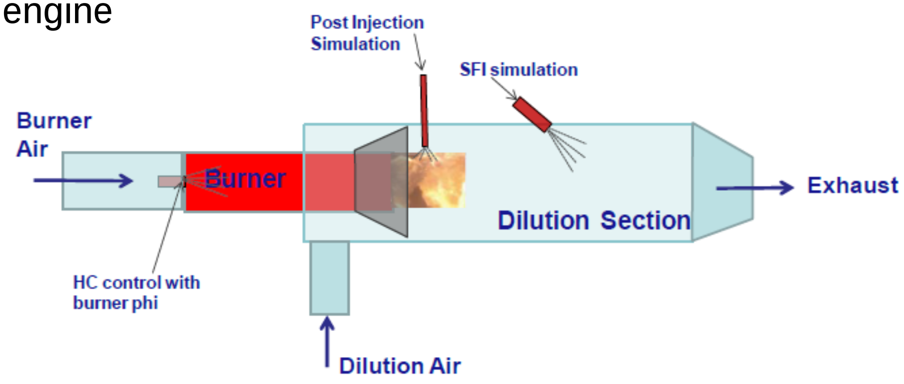
- Baseline: Pd/H-SSZ-13
  - DFT calculations
  - Simple, complex feeds
- Pd/H-ZSM-5
  - Simple feeds
  - Microkinetic model
  - Reactor model
- Pd/H-BEA
  - Coupled NO + C_3H_6 trapping, release & conversion
  - Reactor modeling
- (Pd + Fe)/ZSM-5, (Pd+Cu)/SSZ-13
  - Scouting studies

- Baseline: Pd/H-BEA
  - Simple, complex feeds
- Pt/H-ZSM-5
  - Simple feeds

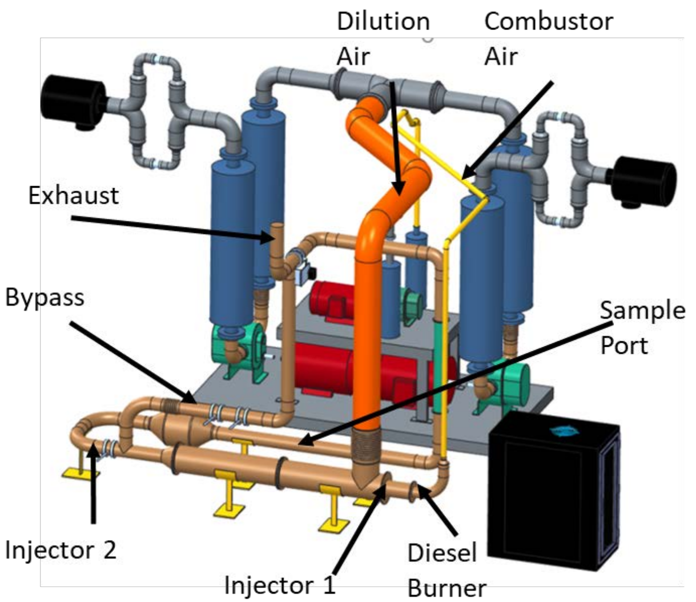
- Baseline: Pt+Pd/CeO_2
  - Simple, complex feeds
- Pd alloy
  - Sequential with PtPd
  - Powder, monolith
- CCCM, w & w/o & PGM
  - Powder, monolith

Exhaust speciation benchmarking

- Hydrocarbon speciation data for ~2013 era diesel engine
- Varied RPM (1375 – 2125), loads (25-50%)
- To be compared with
  - USDRIVE clean diesel protocol
  - Advanced low temperature diesel
  - Low temperature gasoline with EGR
- Equipment & methods
  - ECTO-Lab (SwRI) combustion test stand
  - Emission sample bags
  - Analytical: ~200 species measured using GC, GC-MS

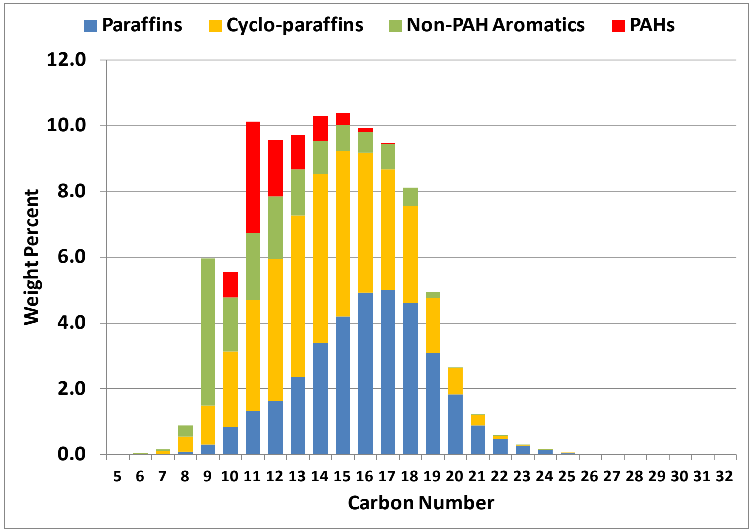


ECTO-Lab = Exhaust Composition Transient Laboratory



Exhaust speciation benchmarking

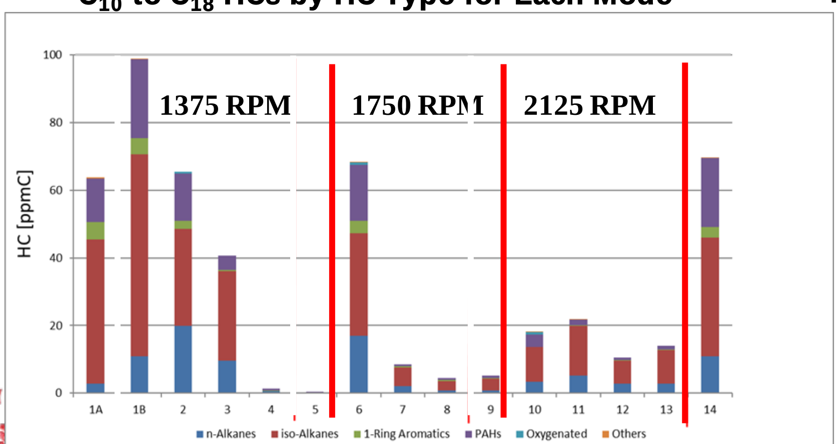
Diesel Speciation by Carbon Number and Molecule Type



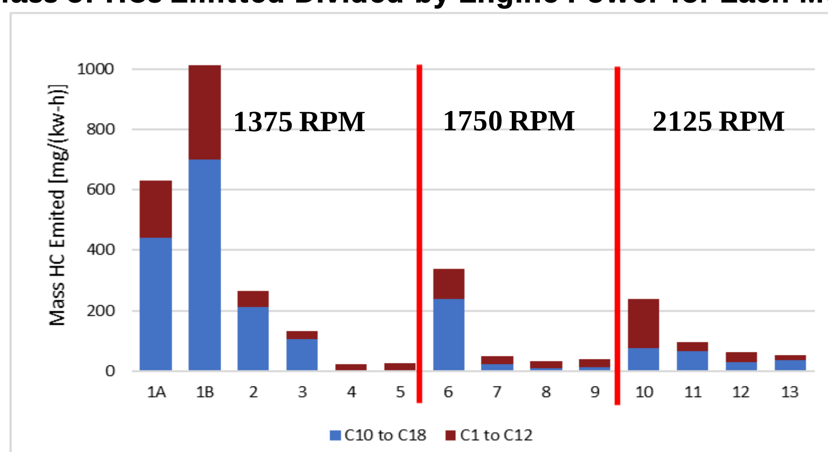
Engine Test Conditions

Speed [RPM]	Load Fraction [-]	Mode	Load [N-m]	Duration [s]
1375	10%	1A	120.74	1500.2
	10%	1B	120.34	1500.1
	25%	2	300.8	1500.2
	50%	3	601.96	1500.1
	75%	4	901.43	1500.2
	Full	5	1198.66	1500
1750	25%	6	293.25	1500.2
	50%	7	588.31	1500.1
	75%	8	879.99	1500
	Full	9	1168.13	1500
2125	25%	10	249.36	1500.1
	50%	11	497.67	1500.1
	75%	12	745.41	1500
	Full	13	994.72	1500
800	Idle	14	0.73	1500.1

C_{10} to C_{18} HCs by HC Type for Each Mode

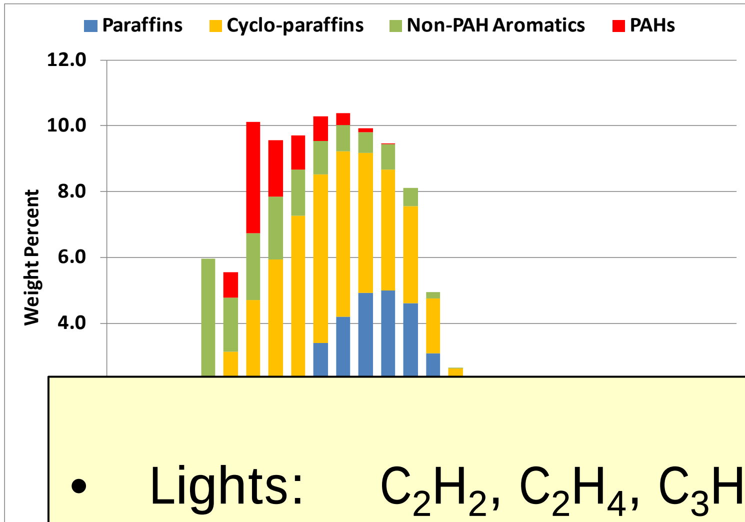


Mass of HCs Emitted Divided by Engine Power for Each Mode



Exhaust speciation benchmarking

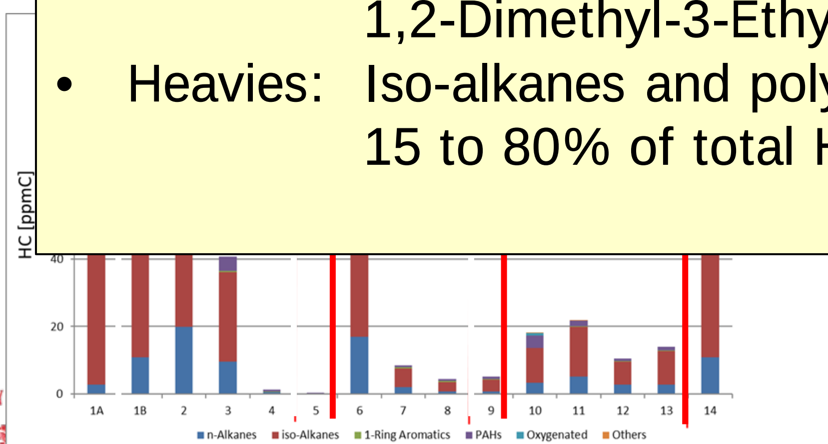
Diesel Speciation by Carbon Number and Molecule Type

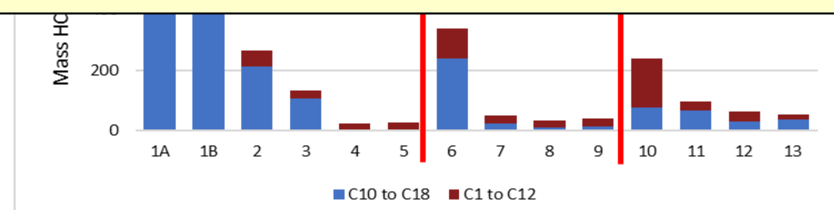


Engine Test Conditions

Speed [RPM]	Load Fraction [-]	Mode	Load [N-m]	Duration [s]
1375	10%	1A	120.74	1500.2
	10%	1B	120.34	1500.1
	25%	2	300.8	1500.2
	50%	3	601.96	1500.1
	75%	4	901.43	1500.2
	Full	5	1198.66	1500
1750	25%	6	293.25	1500.2
	50%	7	588.31	1500.1
	75%	8	879.99	1500
	Full	9	1168.13	1500
	25%	10	249.36	1500.1

- Lights: C_2H_2, C_2H_4, C_3H_6 are main olefins
  H_2CO important component
  1,2-Dimethyl-3-Ethylbenzene most prominent aromatic
- Heavies: Iso-alkanes and polyaromatic hydrocarbons
  15 to 80% of total HCs; decreasing with speed & load





Materials and Conditions

Catalytic Materials

PNA: 1 wt.% **Pd** / **SSZ-13** (90%), Al_2O_3 (10%), 1.5 g wc/in^3 **(Baseline)**
1 wt.% **Pd** + 1 wt.% **Cu** / **SSZ-13** (90%), Al_2O_3 (10%), 1.5 g wc/in^3 **(New)**
1 wt.% **Pd** / **ZSM-5** (90%), Al_2O_3 (10%), 1.5 g wc/in^3
1 wt.% **Pd** + 1 wt.% **Fe** / **ZSM-5** (90%), Al_2O_3 (10%), 1.5 g wc/in^3 **(New)**
2 wt.% **Pd** / **BEA** (90%), Al_2O_3 (10%), 1.5 g wc/in^3

HCT: 1 wt.% **Pd** / **BEA** (90%), Al_2O_3 (10%), 1.5 g wc/in^3 **(Baseline)**

OC: **Pt**(0.5 wt.%)/**Pd**(0.5 wt.%)/ **CeO_2**(15%), Al_2O_3 (85%), 1.5 g wc/in^3 **(Baseline)**
'**CCC**' = **CuO** + **Co_2O_3** + **CeO_2** ternary oxide (varied compositions) **(NEW)**
Pd Alloy/SiO_2 (patent disclosure in preparation) **(NEW)**

Simulated Emission Feeds

	O_2	H_2O	CO_2	NO	CO	H_2	C_2H_4	C_7H_{12}	$C_{12}H_{26}$
Complex (USDRIVE)	12%	6%	6%	200 ppm	500 ppm	100 ppm	200 ppm	43 ppm	58 ppm
Hybrid	12%	6%	6%	200 ppm	*Varied combinations & concentrations*				
Simple	12%	6%	6%	200 ppm	X	X	X	X	X

Project Activities

Simulated Exhaust → **PNA** | **HCT** | **OC** → *Treated Exhaust*

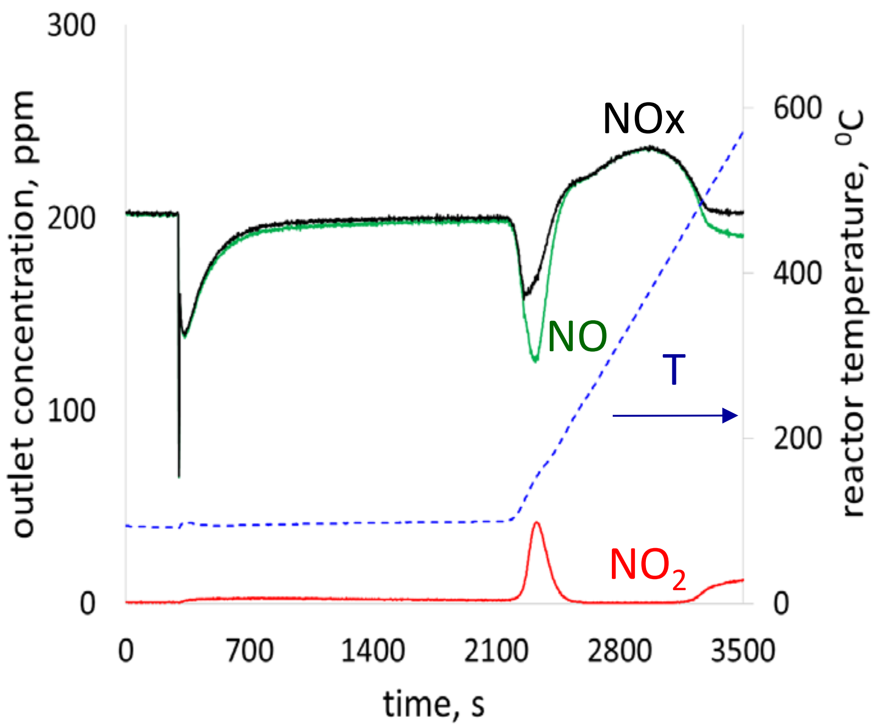
Baseline: *Pd /SSZ-13* | *Pd/Al_2O_3 + BEA* | *Pt + Pd + CeO_2/Al_2O_3*

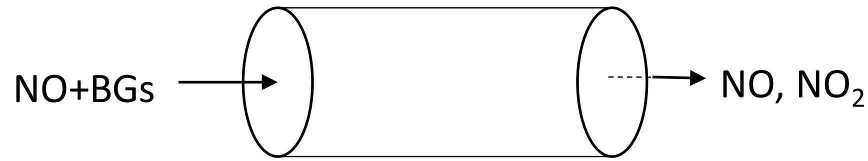
- Baseline: Pd/H-SSZ-13
  - DFT calculations
  - Simple, complex feeds
- Pd/H-ZSM-5
  - Simple feeds
  - Microkinetic model
  - Reactor model
- Pd/H-BEA
  - Coupled NO + C_3H_6 trapping, release & conversion
  - Reactor modeling
- (Pd + Fe)/ZSM-5, (Pd+Cu)/SSZ-13
  - Scouting studies

- Baseline: Pd/H-BEA
  - Simple, complex feeds
- Pt/H-ZSM-5
  - Simple feeds

- Baseline: Pt+Pd/CeO_2
  - Simple, complex feeds
- Pd alloy
  - Sequential with PtPd
  - Powder, monolith
- CCCM, w & w/o & PGM
  - Powder, monolith

NO uptake and release

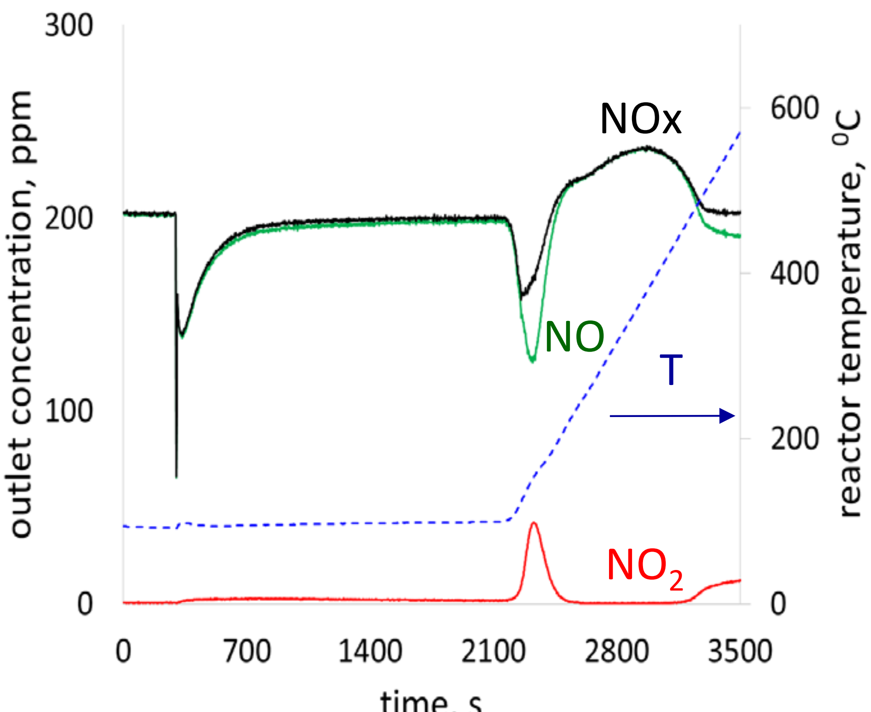


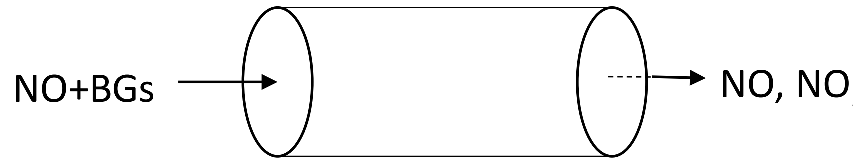


- H_2O competes for adsorption on Brønsted acid sites
- Two NO adsorption areas
  - *Low temp*: adsorption on Pd^{2+} and/or $[Pd^{II}OH]^+$
  - *High temp*: adsorption on Pd^{2+}, $[Pd^{II}OH]^+$, Pd^+, & Brønsted acid sites (freed by the water desorption)?
- NO_2 release immediately after the temperature ramp
- NOx released at temperatures higher than 200°C

NOx (ads)/NOx(des)	NOx/Pd
~ 1	~ 1

NO uptake and release





- H_2O competes for adsorption on Brønsted acid sites
- Two NO adsorption areas
  - *Low temp*: adsorption on Pd^{2+} and/or $[Pd^{II}OH]^+$
  - *High temp*: adsorption on Pd^{2+}, $[Pd^{II}OH]^+$, Pd^+, & Brønsted acid sites (freed by the water desorption)?

- Baseline PNA effective in trapping NO for simple & complex feeds

- NO_2 release immediately after the temperature ramp
- NOx released at temperatures higher than 200°C

NOx (ads)/NOx(des)	NOx/Pd
~ 1	~ 1

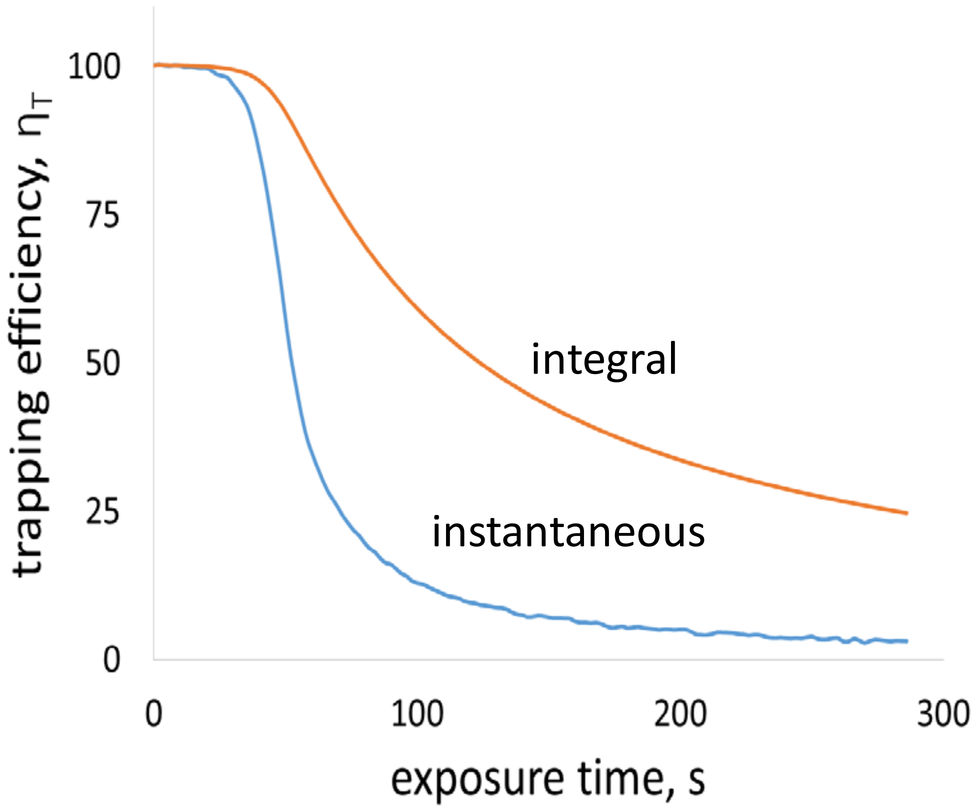
NOx trapping efficiency

Instantaneous trapping efficiency:

$$\eta = \left(1 - \frac{F_{NOx}}{F_{NO_{in}}}\right)$$

Integral trapping efficiency:

$$\eta_T = \frac{1}{\tau}\int_0^{\tau}\left(1 - \frac{F_{NOx}}{F_{NO_{in}}}\right)dt$$



NOx trapping efficiency vs. exposure time
@ 100 C and GHSV = 30,000 hr^{-1}

Breakthrough time ~ 60s

NO/Pd ~1 in wet feed conditions

→ Efficient material for NOx trap and release

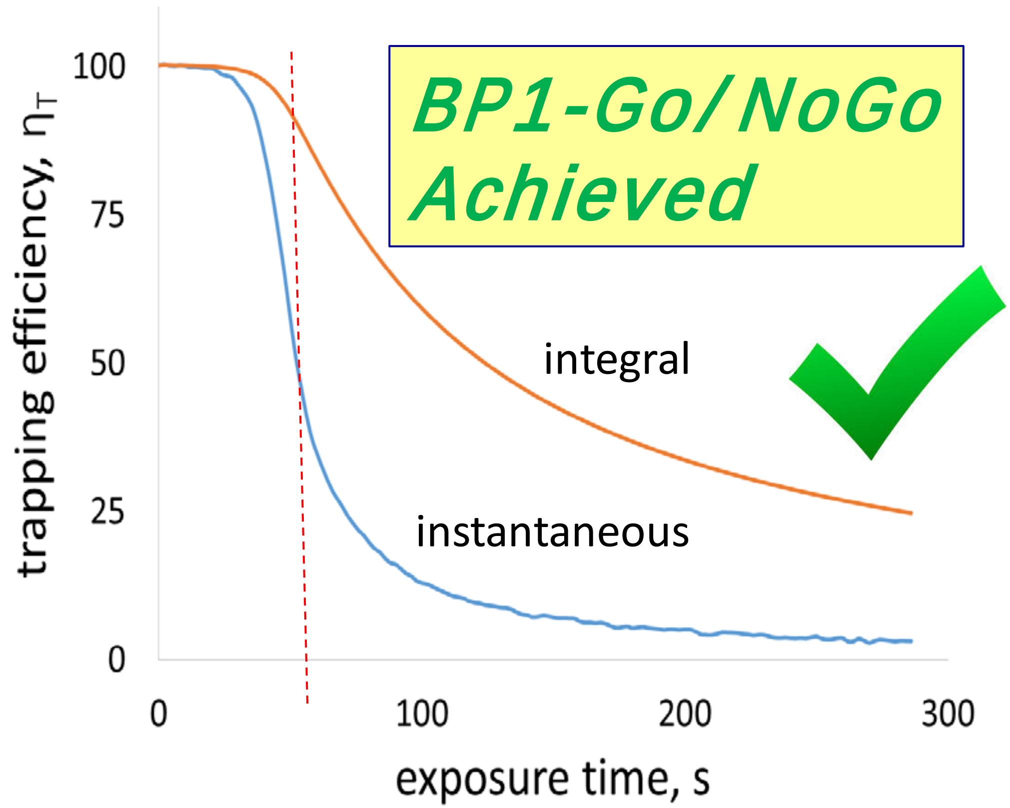
NOx trapping efficiency

Instantaneous trapping efficiency:

$$\eta = \left(1 - \frac{F_{NOx}}{F_{NO_{in}}}\right)$$

Integral trapping efficiency:

$$\eta_T = \frac{1}{\tau}\int_0^{\tau}\left(1 - \frac{F_{NOx}}{F_{NO_{in}}}\right)dt$$



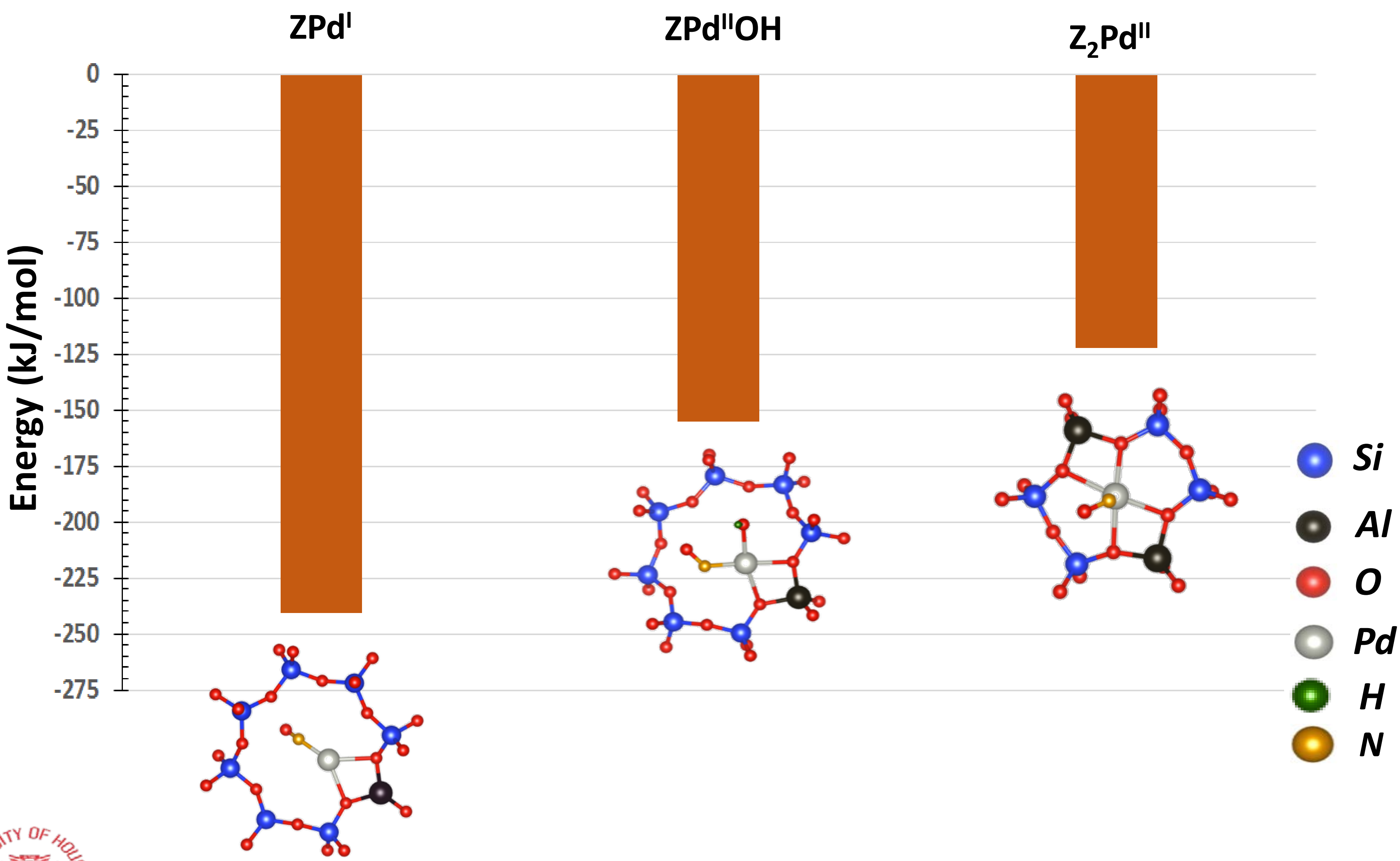
Breakthrough time ~ 60s ... **re time**

NO/Pd ~

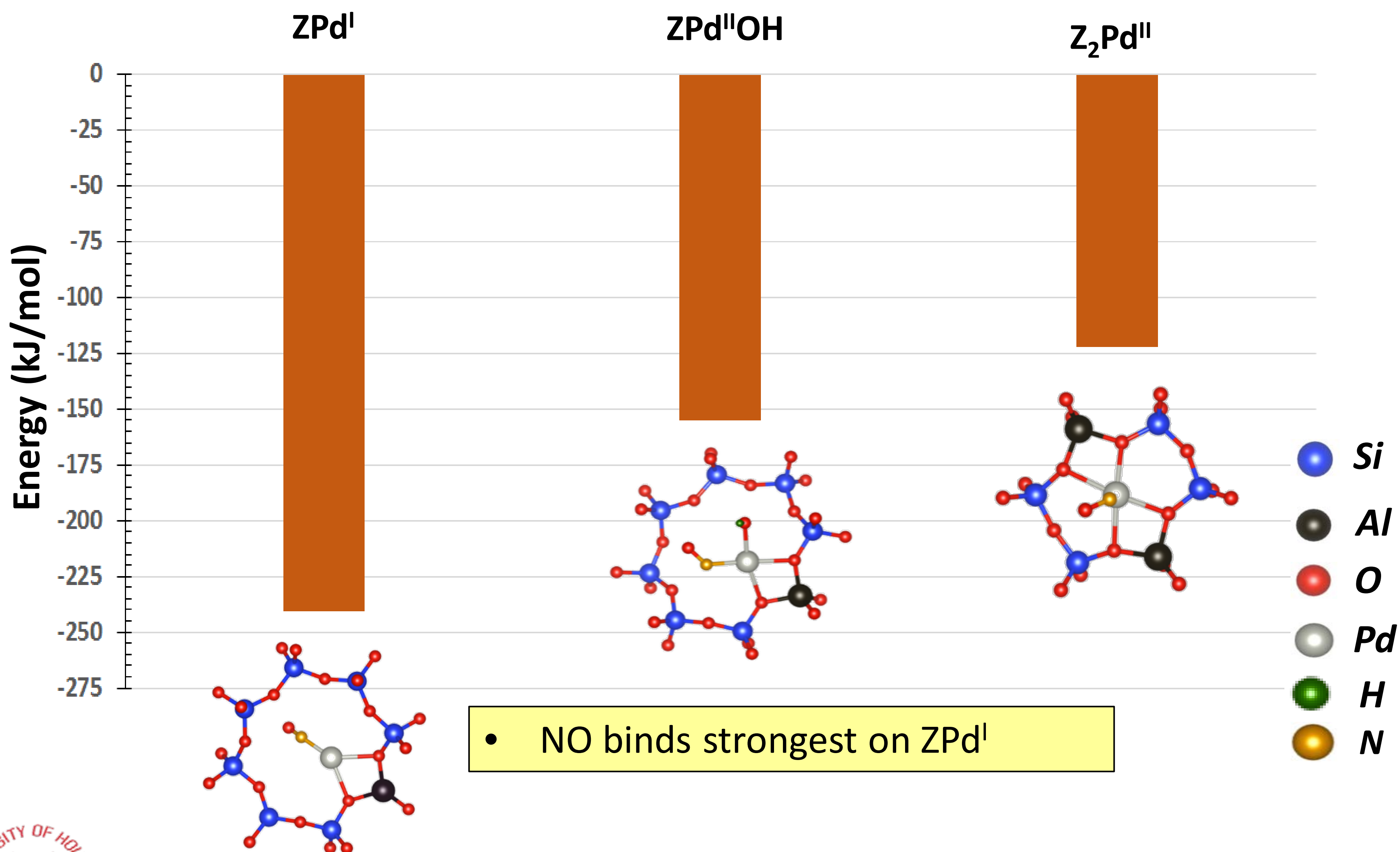
- Baseline PNA captures all of the NOx for ~1 minute for full USDRIVE feed mixture

→ **Efficient material for NOx trap and release**

NO adsorption energy on Pd cation sites

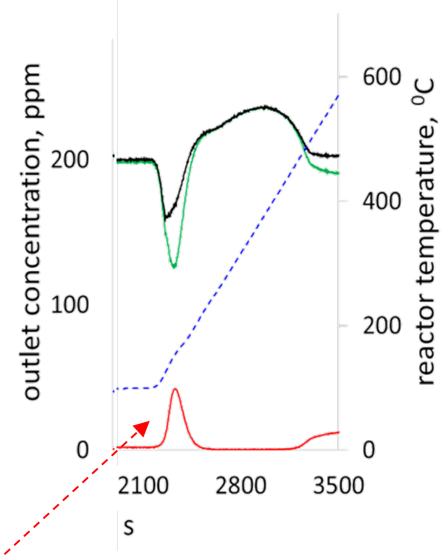


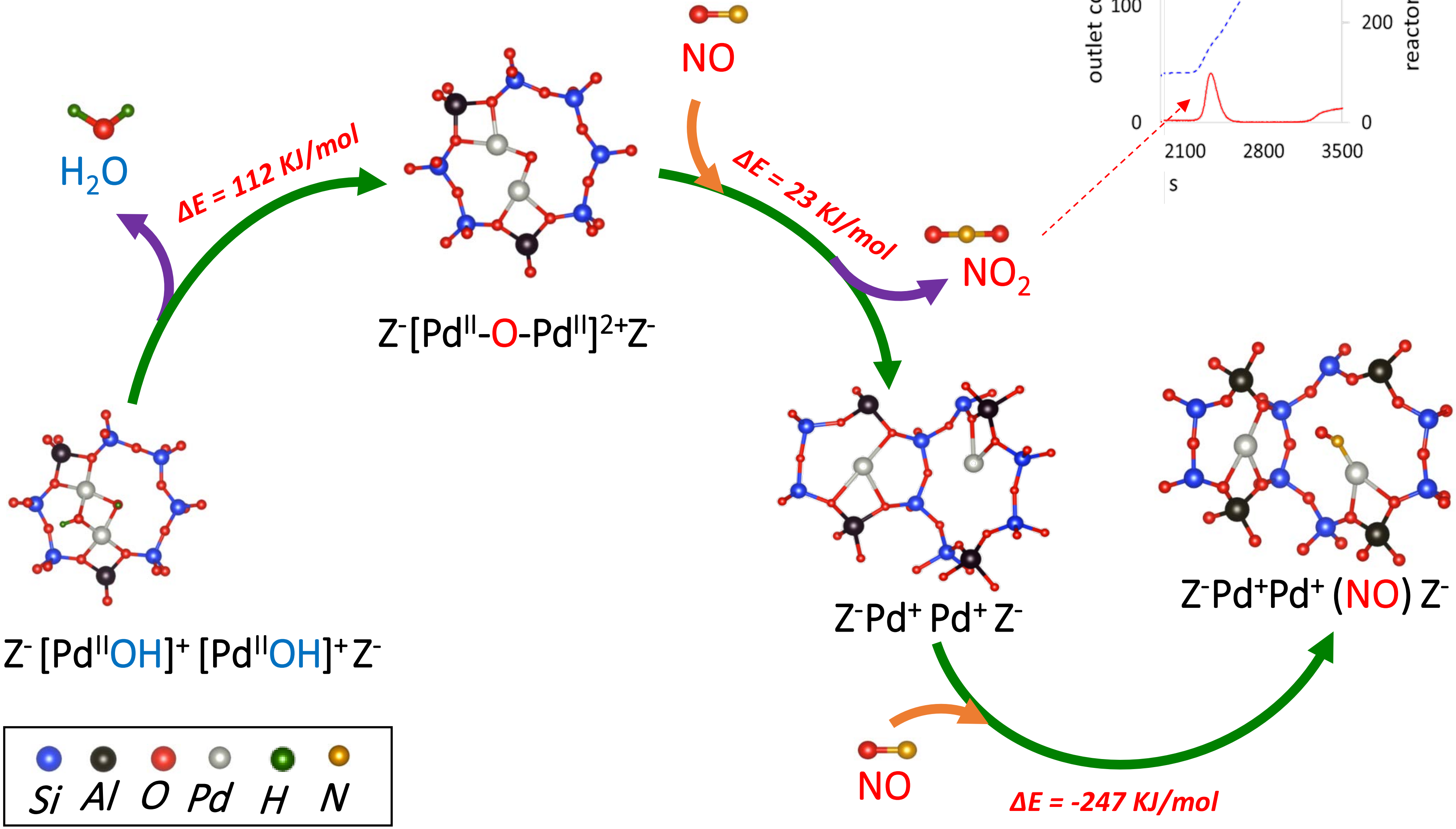
NO adsorption energy on Pd cation sites



- NO binds strongest on ZPd^{I}

Formation of ZPd^{I} sites





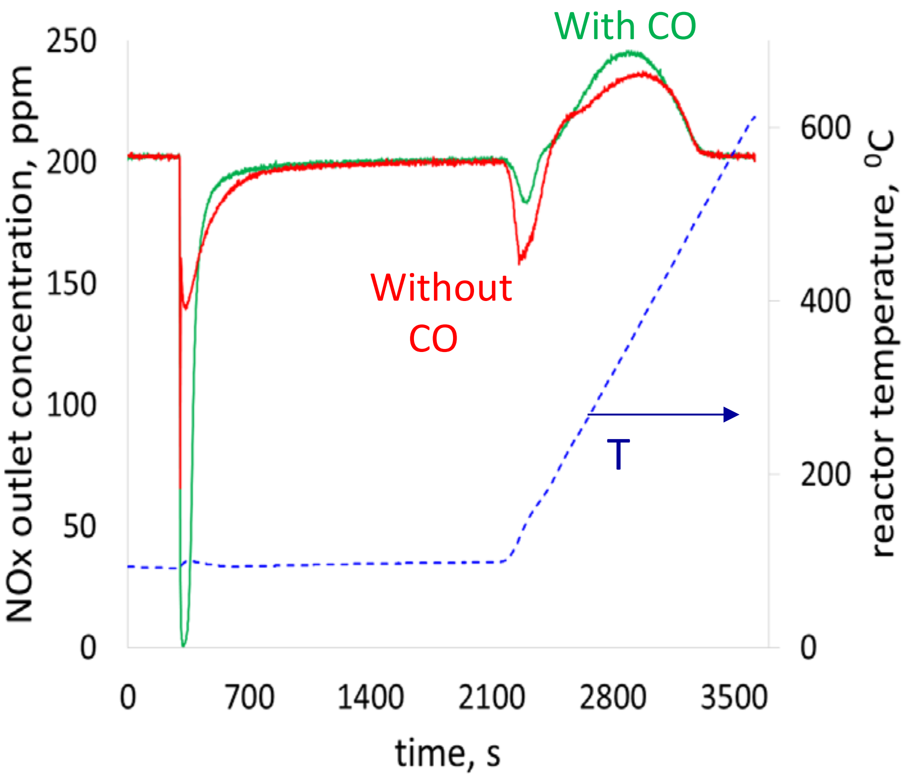
NO uptake and release in presence and absence of CO

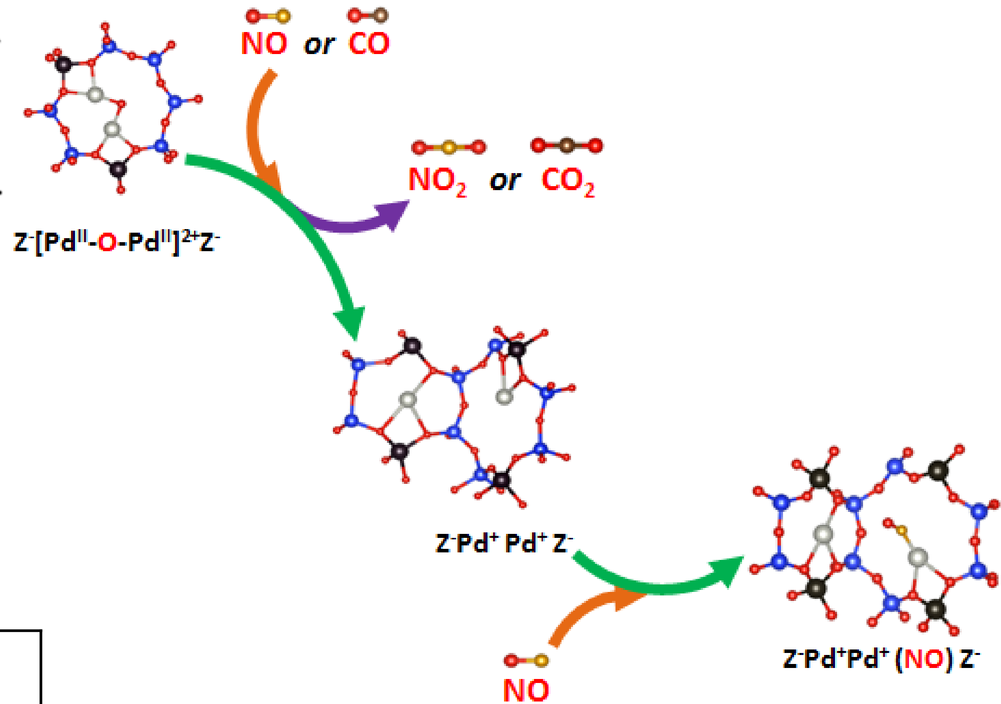
$Z^{-}[Pd^{II}\text{-}O\text{-}Pd^{II}]^{2+}Z^{-} + NO \rightarrow 2\ Z^{-}Pd^{+} + NO_2$

ΔE = 23 KJ/mol

$Z^{-}[Pd^{II}\text{-}O\text{-}Pd^{II}]^{2+}Z^{-} + CO \rightarrow 2\ Z^{-}Pd^{+} + CO_2$

ΔE = -179 KJ/mol





NOx (ads)/NOx(des)	NOx/Pd
~ 1	~ 1.2

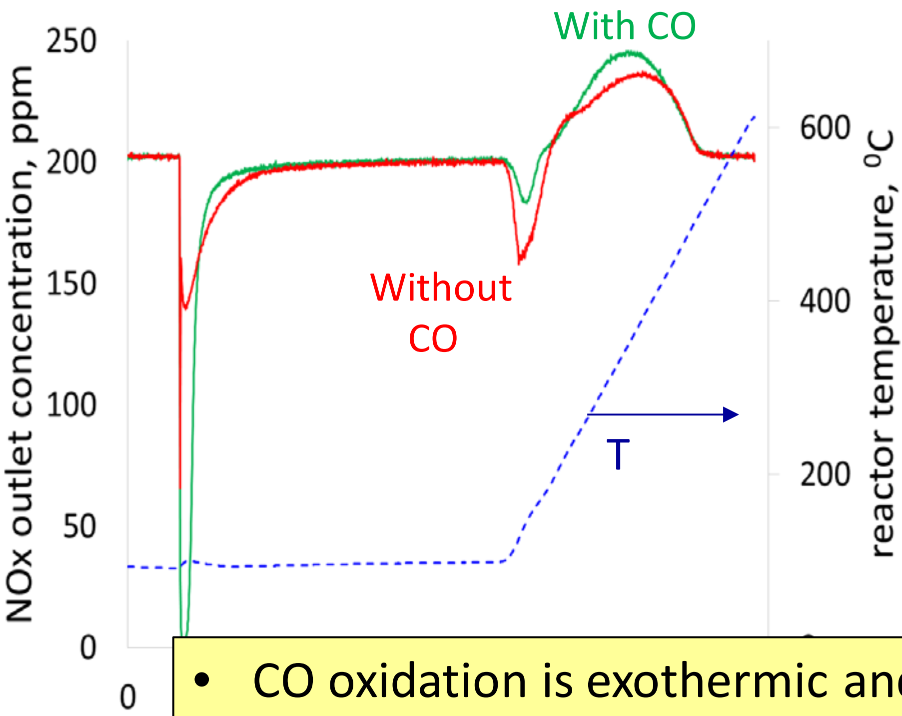
NO uptake and release in presence and absence of CO

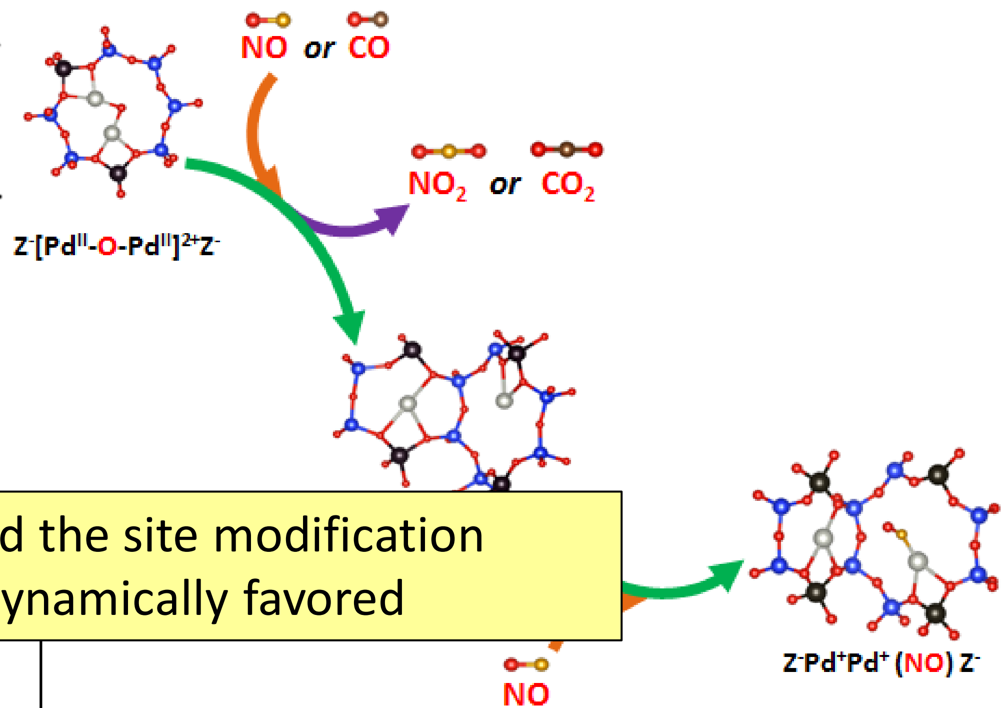
$Z^-[Pd^{II}\text{-}O\text{-}Pd^{II}]^{2+}Z^- + NO \rightarrow 2\ Z^-Pd^+ + NO_2$

ΔE = 23 KJ/mol

$Z^-[Pd^{II}\text{-}O\text{-}Pd^{II}]^{2+}Z^- + CO \rightarrow 2\ Z^-Pd^+ + CO_2$

ΔE = -179 KJ/mol

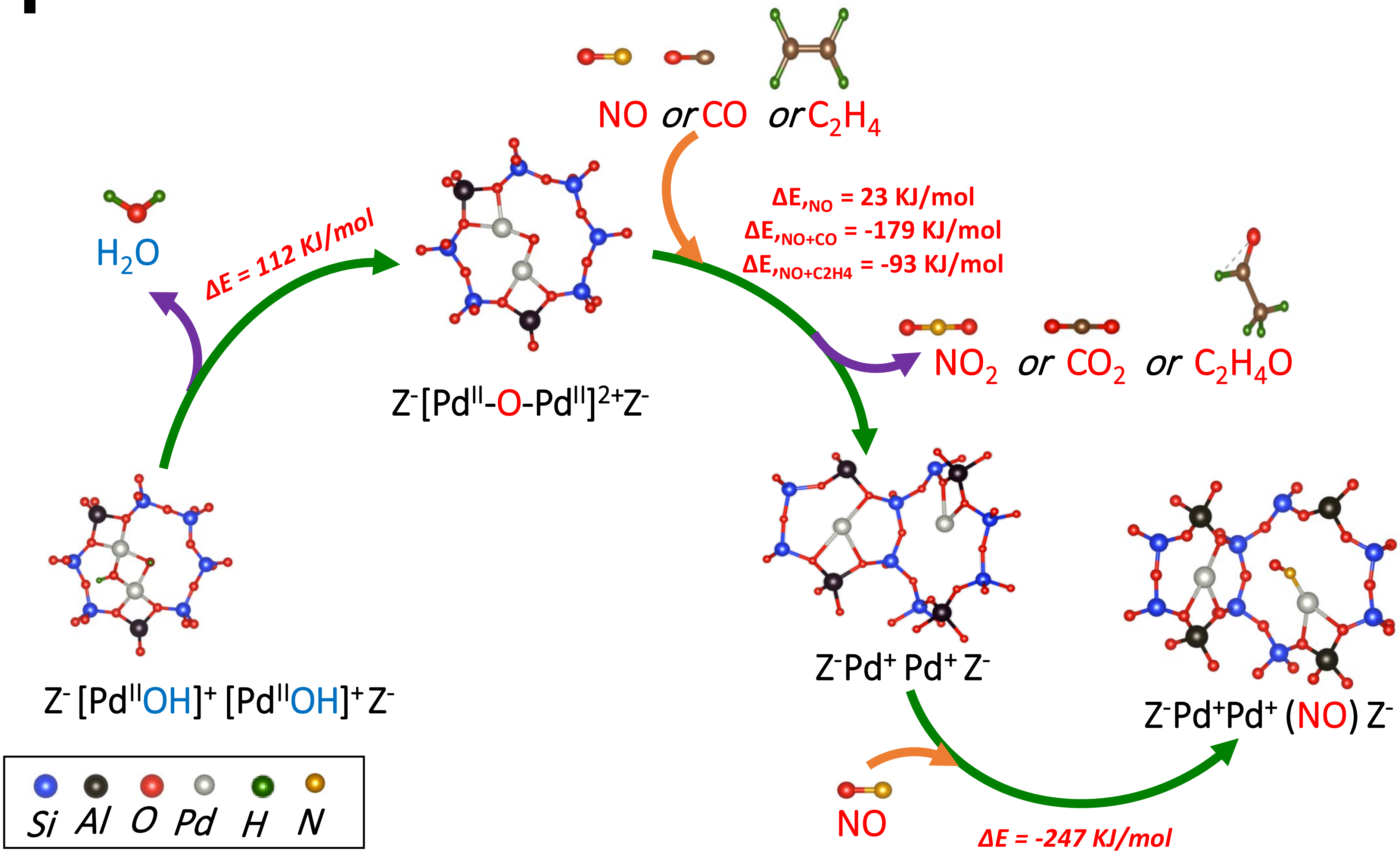




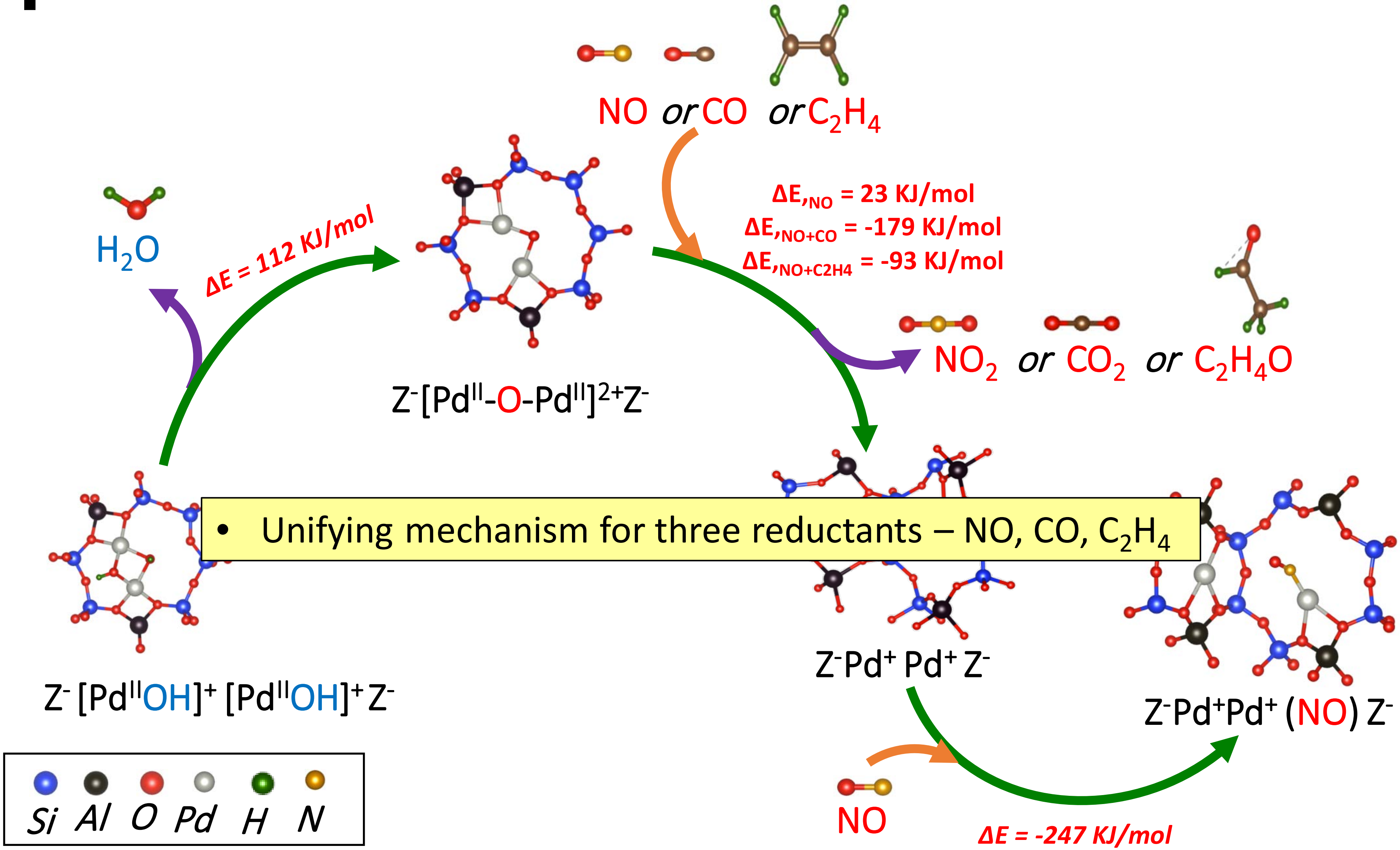
- CO oxidation is exothermic and the site modification from $Pd^{II}OH$ to Pd^+ is thermodynamically favored

NOx (ads)/NOx(des)	NOx/Pd
~ 1	~ 1.2

NO trapping mechanism in the presence of reductant

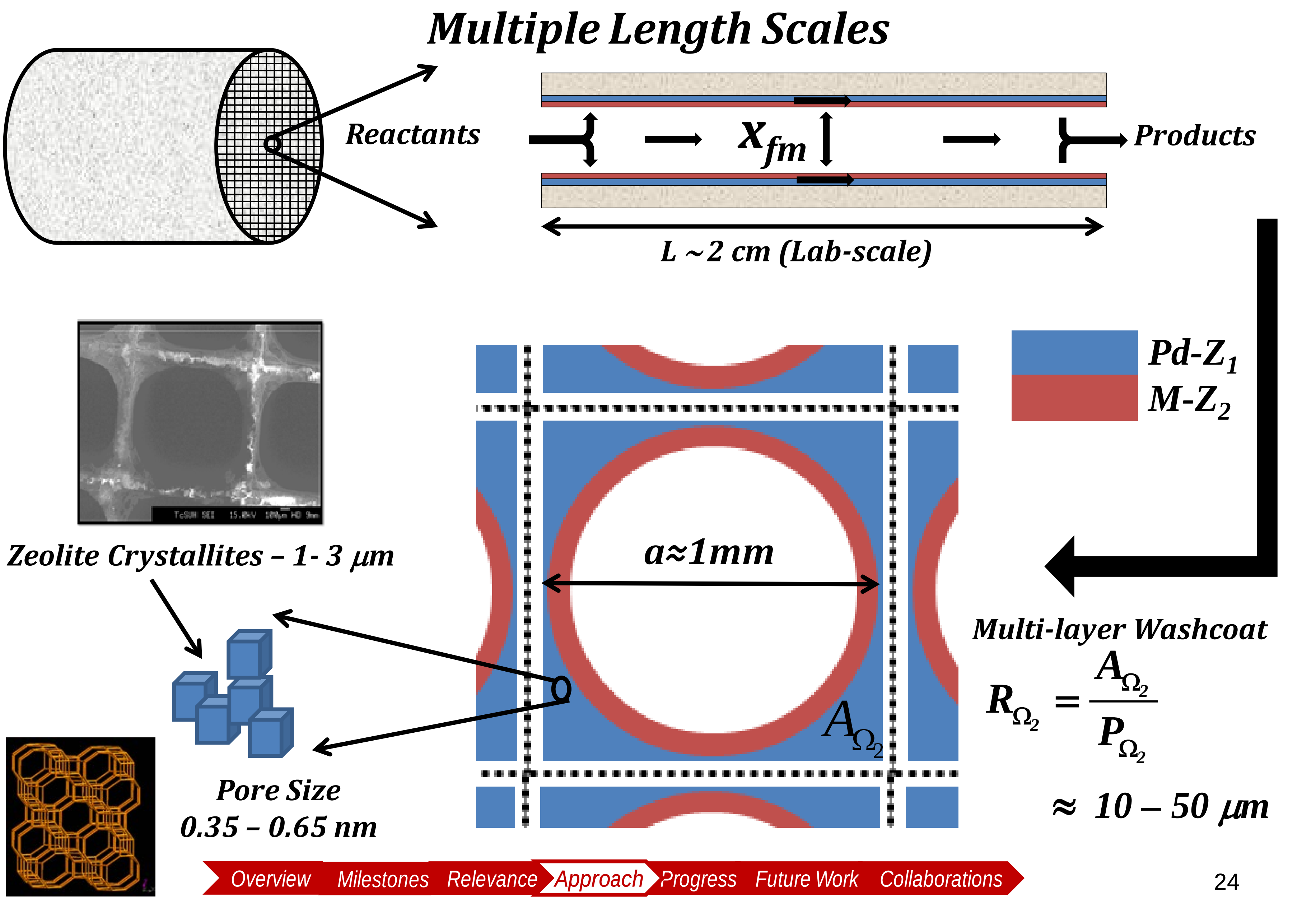


NO trapping mechanism in the presence of reductant



- Unifying mechanism for three reductants – NO, CO, C_2H_4

Monolith reactor model

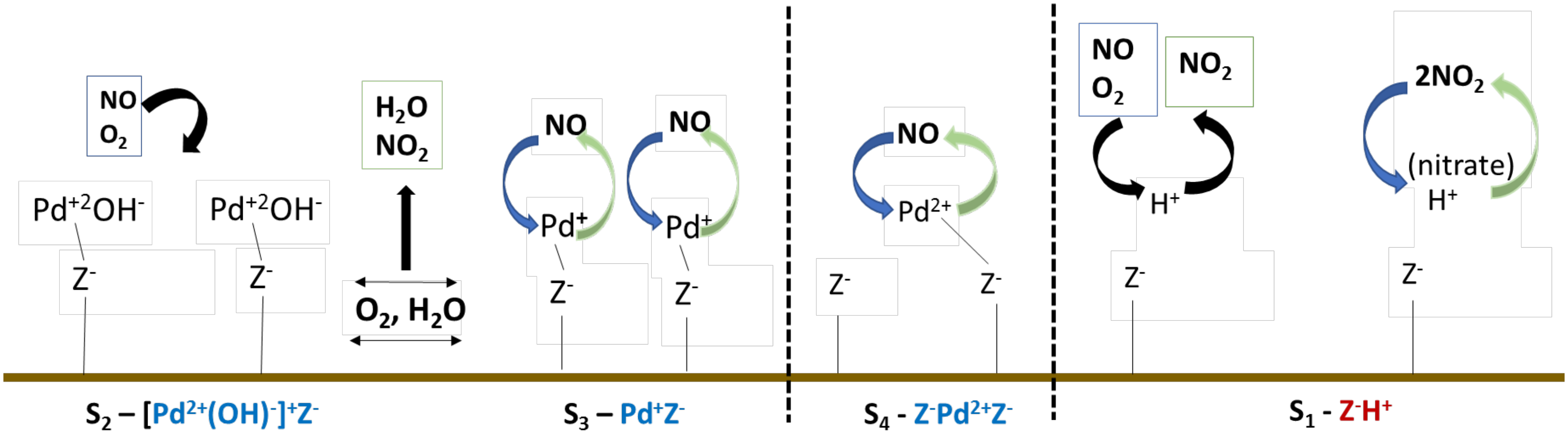


PNA microkinetic model (Pd/H-ZSM-5)

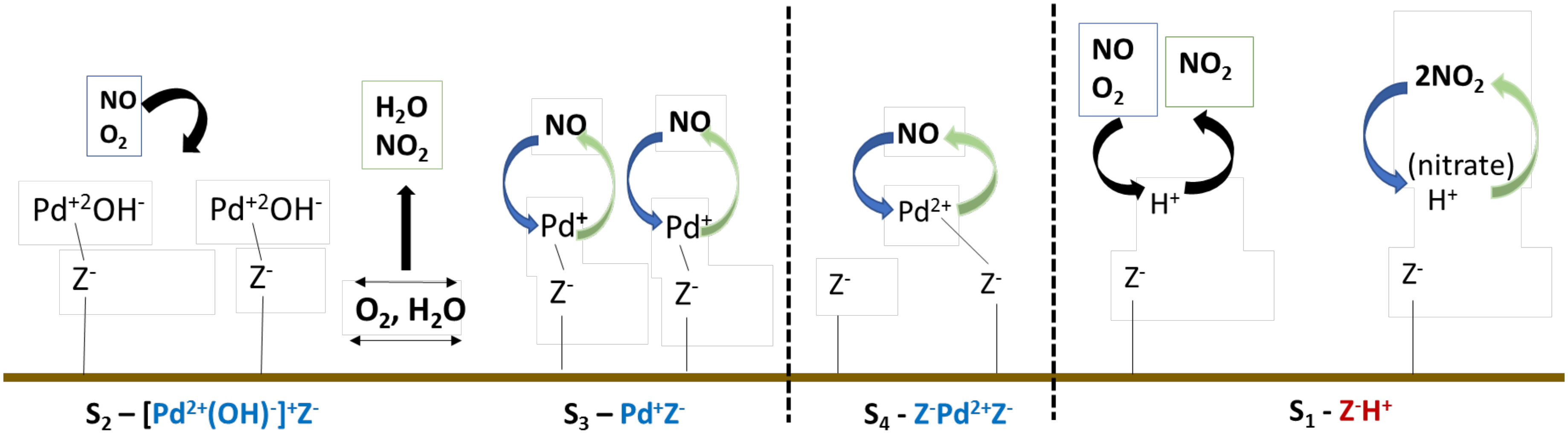
Scheme

- Build mechanism using combination of literature, molecular modeling (DFT), & experiments [kinetics, flow reactor, DRIFTS, etc.]
- Use calculated energy barriers from DFT, when literature estimates not available
- Estimate remaining parameters from "fitting" uptake + release, in sequence:
    - NO + O_2 on H-ZSM-5
        - NO + O_2 + H_2O on H-ZSM-5
            - NO + O_2 on Pd-H-ZSM-5
                - NO + O_2 + H_2O on Pd-H-ZSM-5
                    - NO + O_2 + H_2O + reductant (CO, C_2H_4, etc.) on Pd-H-ZSM-5
- Validate at other conditions, catalyst compositions, etc.
- Use model to define new experiments
- <u>When satisfied, use model to optimize PNA material</u>

PNA microkinetic model (Pd/H-ZSM-5)



PNA microkinetic model (Pd/H-ZSM-5)

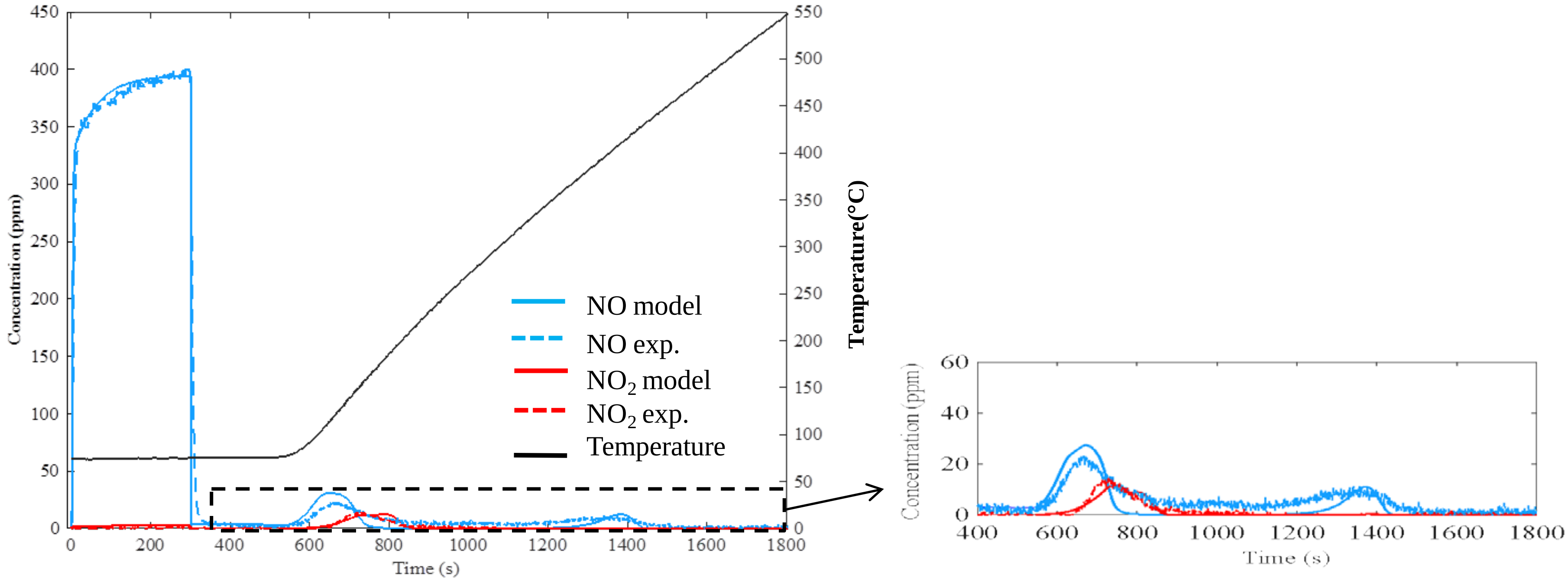


- Model accounts for key active sites confirmed from DFT calculations and DRIFTS measurements

PNA microkinetic model (Pd / H-ZSM-5)

$NO + O_2 + H_2O$ on 2wt.% Pd-H-ZSM-5 (VALIDATION)

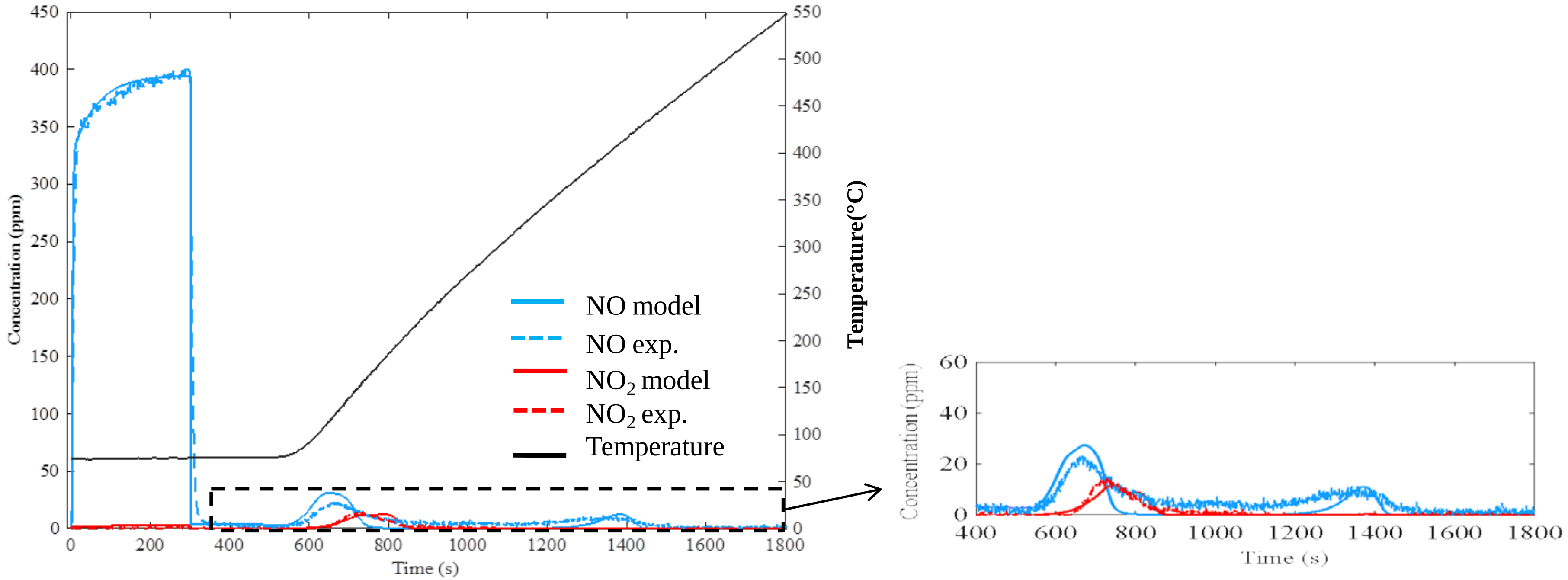
NO_x uptake at 80°C uptake & 1500 sccm



PNA microkinetic model (Pd / H-ZSM-5)

NO + O_2 + H_2O on 2wt.% Pd-H-ZSM-5 (VALIDATION)

NO_x uptake at 80°C uptake & 1500 sccm



- Model validated at higher Pd loading

Project Activities

Simulated Exhaust → **PNA** | **HCT** | **OC** → *Treated Exhaust*

Baseline: ***Pd /SSZ-13*** ***Pd/Al_2O_3 + BEA*** ***Pt + Pd + CeO_2/Al_2O_3***

- Baseline: Pd/H-SSZ-13
  - DFT calculations
  - Simple, complex feeds
- Pd/H-ZSM-5
  - Simple feeds
  - Microkinetic model
  - Reactor model
- Pd/H-BEA
  - Coupled NO + C_3H_6 trapping, release & conversion
  - Reactor modeling
- (Pd + Fe)/ZSM-5, (Pd+Cu)/SSZ-13
  - Scouting studies

- Baseline: Pd/H-BEA
  - Simple, complex feeds
- Pt/H-ZSM-5
  - Simple feeds

- Baseline: Pt+Pd/CeO_2
  - Simple, complex feeds
- Pd alloy
  - Sequential with PtPd
  - Powder, monolith
- CCCM, w & w/o & PGM
  - Powder, monolith

Hydrocarbon trap evaluations

- **Objective:** Evaluate uptake, release, and conversion of Clean Diesel (CD) feed on Baseline HCT (Pd/H-BEA) to quantify:
  - Uptake amount as function of time, temperature, etc.
  - Interaction effects between different feed components
  - Release and light-off temperature for different feeds
- **Status:**
  - Have evaluated for most binary mixtures and full feed; e.g.

Dodecane + Ethylene:	58 ppm dodecane, 200 ppm ethylene
Dodecane + CO:	58 ppm dodecane, 500 ppm CO
Dodecane + NO:	58 ppm dodecane, 200 ppm NO
Ethylene:	200 ppm ethylene
Ethylene + NO:	200 ppm C2H4, 200 ppm NO
Ethylene + CO:	200 ppm C2H4, 500 ppm CO
etc.	

CD Feed:

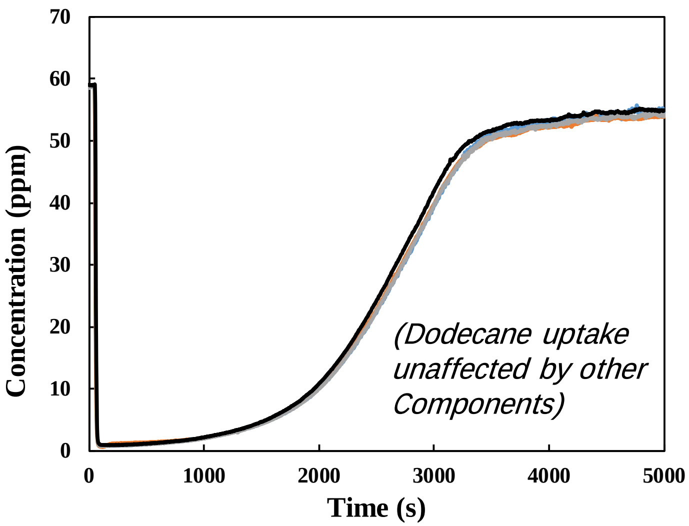
Species	Conc. (ppm)
NO	200
CO	500
H_2	100
C_2H_4	200
C_7H_8	43
$C_{12}H_{26}$	58

12% O_2,
6% CO_2,
6% H_2O,
Balance N_2

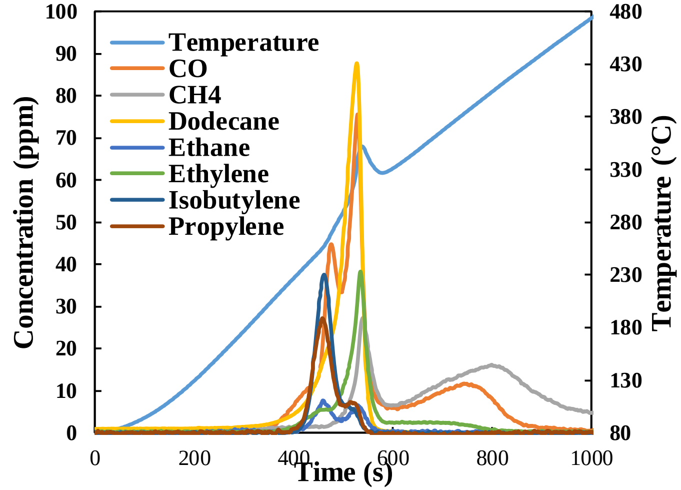
Hydrocarbon trap evaluations

Feeds: Dodecane & Dodecane + CO

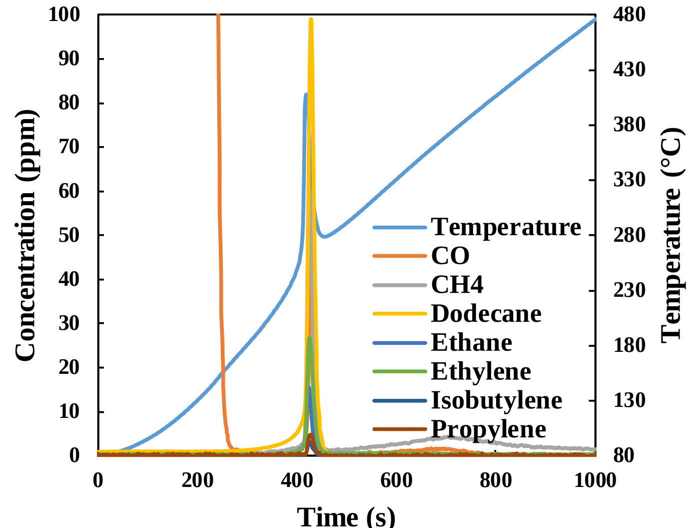
Dodecane Uptake



TPD – Dodecane



TPD – Dodecane + CO



Feeds:

Species	Conc. (ppm)
CO	500
$C_{12}H_{26}$	58

12% O_2, 6% CO_2, 6% H_2O, Balance N_2

Project Activities

Baseline: ***Pd /SSZ-13*** ***Pd/Al_2O_3 + BEA*** ***Pt + Pd + CeO_2/Al_2O_3***

PNA

- Baseline: Pd/H-SSZ-13
  - DFT calculations
  - Simple, complex feeds
- Pd/H-ZSM-5
  - Simple feeds
  - Microkinetic model
  - Reactor model
- Pd/H-BEA
  - Coupled NO + C_3H_6 trapping, release & conversion
  - Reactor modeling
- (Pd + Fe)/ZSM-5, (Pd+Cu)/SSZ-13
  - Scouting studies

HCT

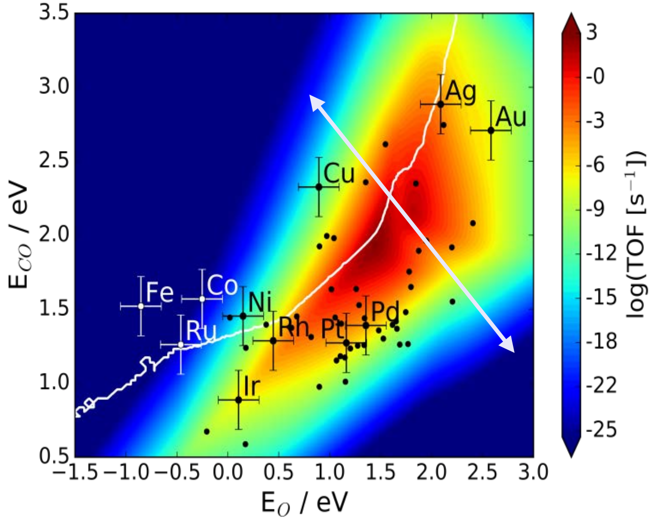
- Baseline: Pd/H-BEA
  - Simple, complex feeds
- Pt/H-ZSM-5
  - Simple feeds

OC

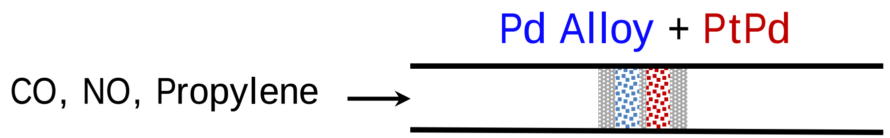
- Baseline: Pt+Pd/CeO_2
  - Simple, complex feeds
- Pd alloy
  - Sequential with PtPd
  - Powder, monolith
- CCCM, w & w/o & PGM
  - Powder, monolith

Low temperature oxidation catalyst for low co-oxidation of NO, CO & C_3H_6

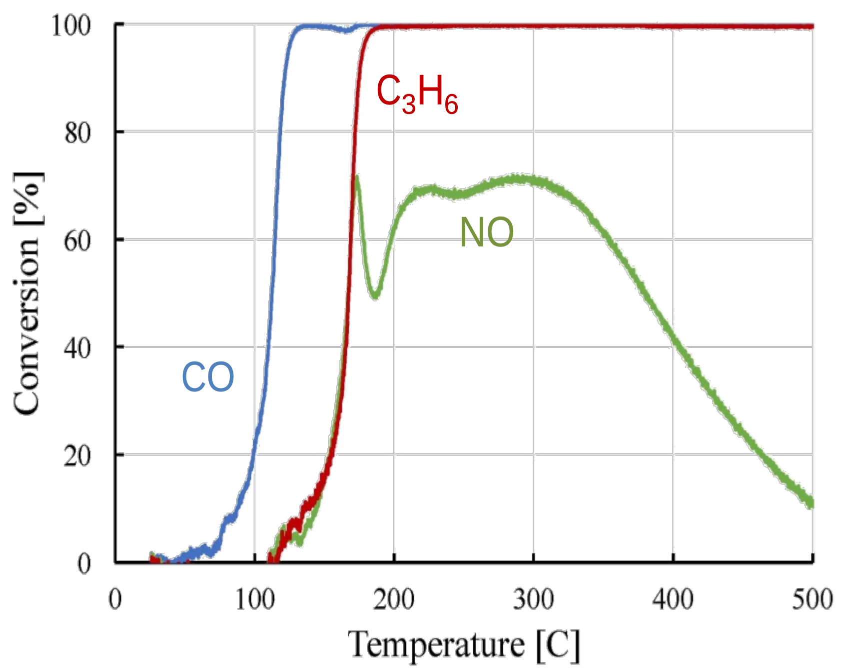
Descriptor DFT



Promising Pd alloy: High CO + NO co-oxidation activity with resistance to mutual inhibition

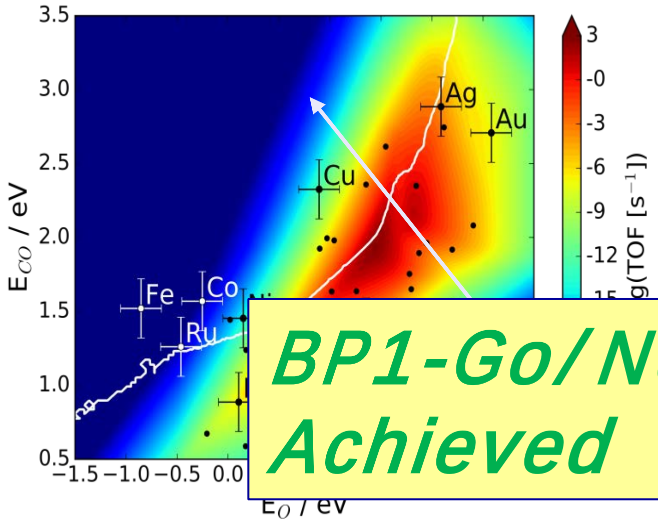


Conditions: 500 ppm CO, 200 ppm NO, 1000 ppm C_3H_6, 10% O_2, balance N_2, SV ~410 L/g h



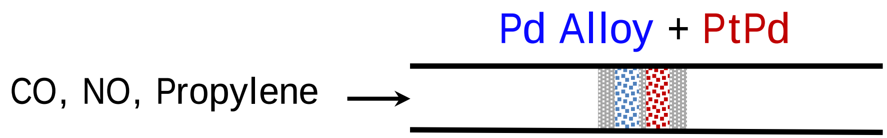
Low temperature oxidation catalyst for low co-oxidation of NO, CO & C_3H_6

Descriptor DFT

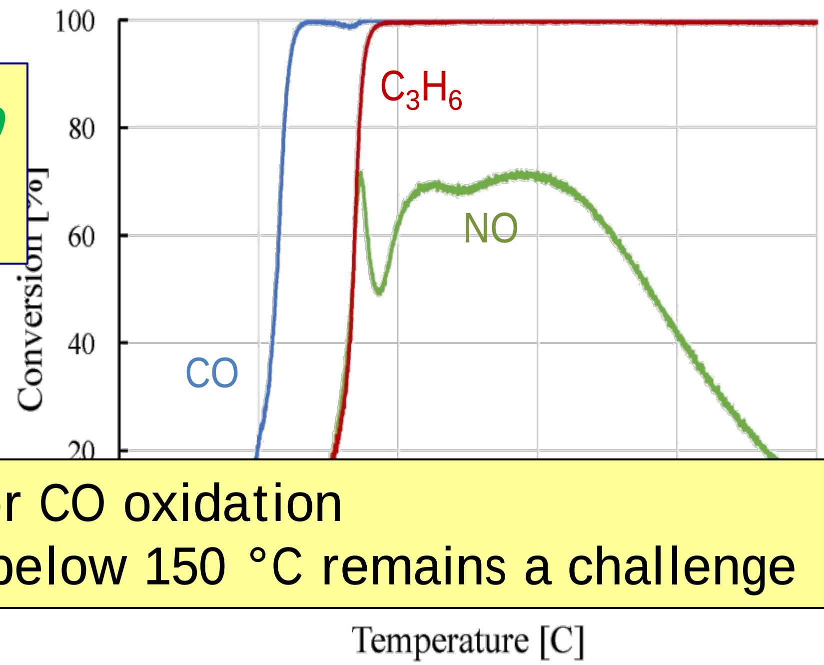


BP1-Go/NoGo Achieved

Promising Pd alloy: High CO + NO
co-oxid
resistar

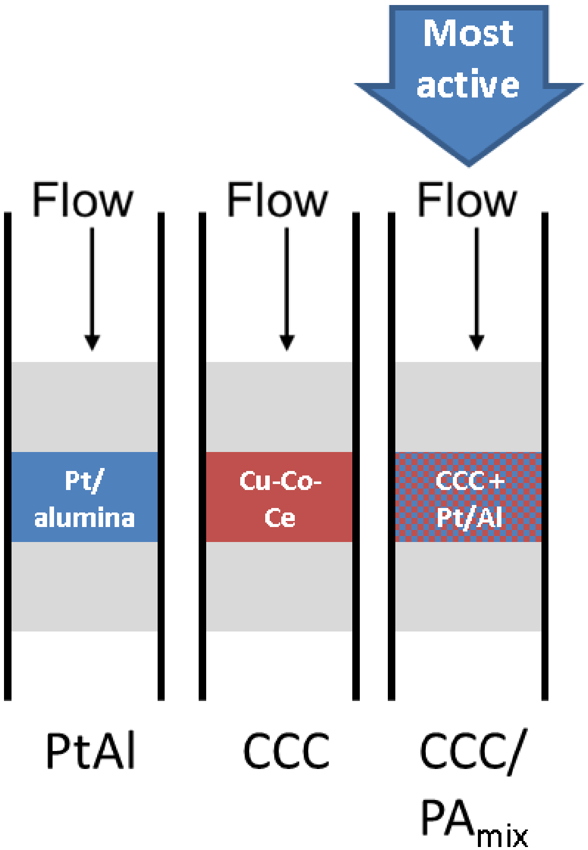


Conditions: 500 ppm CO, 200 ppm NO, 1000 ppm C_3H_6, 10% O_2, balance N_2, SV ~410 L/g h

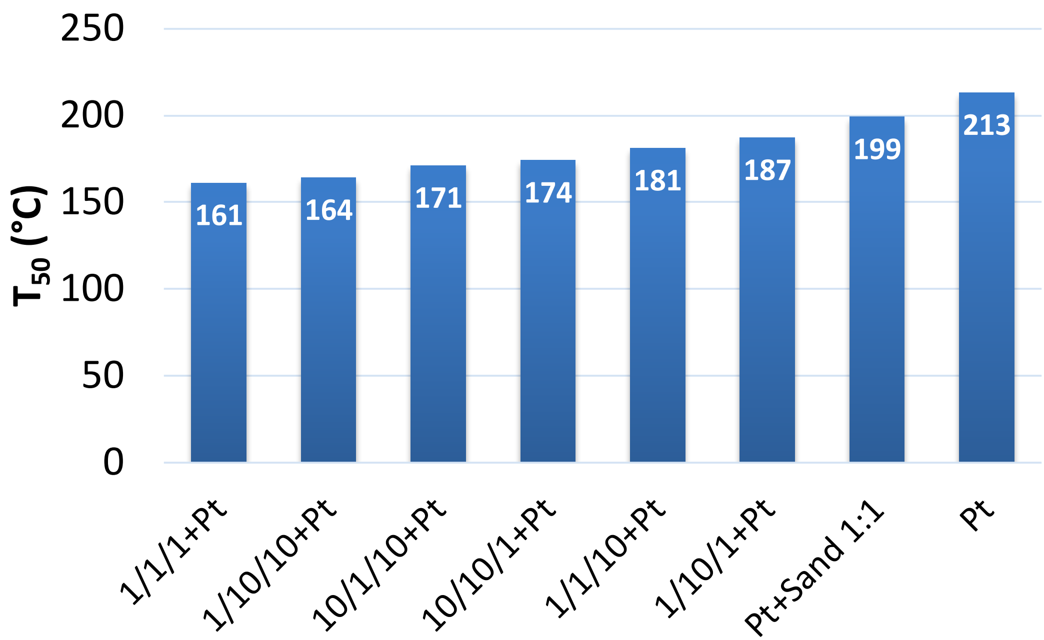


- Encouraging results for CO oxidation
- NO and HC oxidation below 150 °C remains a challenge

Low temperature oxidation catalyst: Co-oxidation of NO, CO & HCs



T_{50} of THC Conversion
CCC + 1% Pt/Al_2O_3 (1:1 wt.)
[CO]: 10,000ppm
[C_3H_6]: 500ppm
[C_3H_8]: 500 ppm   SV: 200 L/g h



CCC : Cu/Co/Ce mixed oxides with corresponding mass ratios #/#/#

Remaining Challenges & Barriers

- Good progress on BP1 & BP2 tasks and milestones
- Further development of new PNA, HCT, and OC materials
- Overcome mutual inhibition of NO and HC trapping
- Demonstrate consolidation of trapping & catalytic functions

Proposed Future Work

- Focus: BP2 milestones
- Continue descriptor DFT to identify new PNA, HCT, OC
- Target: Pd + M/H-SSZ-13 (PNA), CCC + Pt (OC)
- Use TAP + DRIFTS for mechanistic-based understanding and microkinetic model development
- Extend microkinetic + reactor model to Pd/H-SSZ-13
- Combine PNA + HCT + OC functions in sequence & parallel, including Pd/BEA + Pd/SSZ-13
- Expand reactor model for combined system

BP2 Milestones

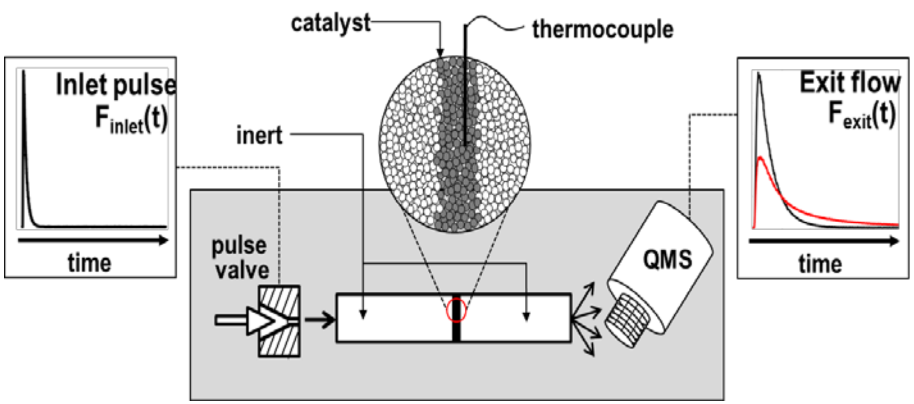
BP2-M#	Milestone	Type	Description	Status
BP2-M1	Additional materials discovery completed	Technical	Identify at least three additional materials from descriptor-based DFT.	Identified new PNA materials; Pd+Cu/SSZ-13, Pd+Fe/SSZ-13
BP2-M2	Microkinetic model development validated	Technical	Develop, tune and validate microkinetic models for new LHCNT materials for HC trapping, HC oxidation, and NO adsorption.	Completed for PNA: Pd/ZSM-5 & underway for Pd/SSZ-13; Underway for HCT: Pd/BEA and HC oxidation
BP2-M3	New material performance testing completed	Technical	Complete flow reactor performance testing of LHCNT material containing one or more new functions for HC trapping, HC oxidation, and NO adsorption, and compare performance to baseline LHCNT material.	Underway for sequential PNA + OC, dual-layer PNA+HCT+OC, and sequential CCC + PGM
BP2-M4	Monolith reactor model comparison of baseline and new materials	Technical	Develop, tune and validate monolith reactor model of new LHCNT material and compare to baseline LHCNT material.	Kinetic/reactor model complete for NO trapping on Pd/ZSM-5; underway for Pd/SSZ-13 and Pd/BEA
BP2-Go/NoGo	Identification of candidate material	Go/No Go	Develop and demonstrate predictive model that predicts performance of baseline LHCNT and which can be used for optimization.	Model for PNA with NO + CO + HC feed to be used to optimize material;.

Summary

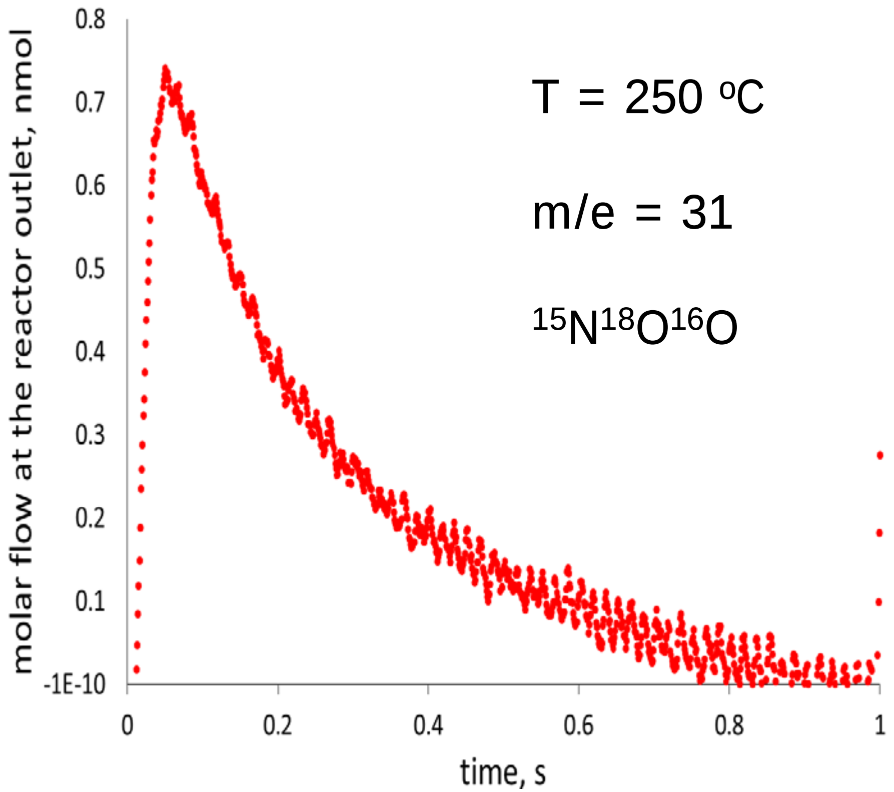
- **Relevance**
  - Enabling emergence of advanced, low temperature combustion engines
- **Approach**
  - Development of integrated NO + HC catalytic trap
  - From molecular-level discovery & mechanism to development & demonstration
- **Technical Accomplishments & Progress**
  - Good progress on all fronts; BP1 milestones achieved
  - PNA results encouraging; leads on new OC materials
  - PNA + HCT + OC baseline materials demonstrated
- **Collaborations & Coordination**
  - Cooperation: universities (UH+UVA), labs (ORNL+SwRI), industry (JM+FCA)
- **Proposed Future Research**
  - Convergence of materials, refinement, integration, modeling, & optimization

Technical Backup Slides

Isotopic labeling studies in TAP reactor



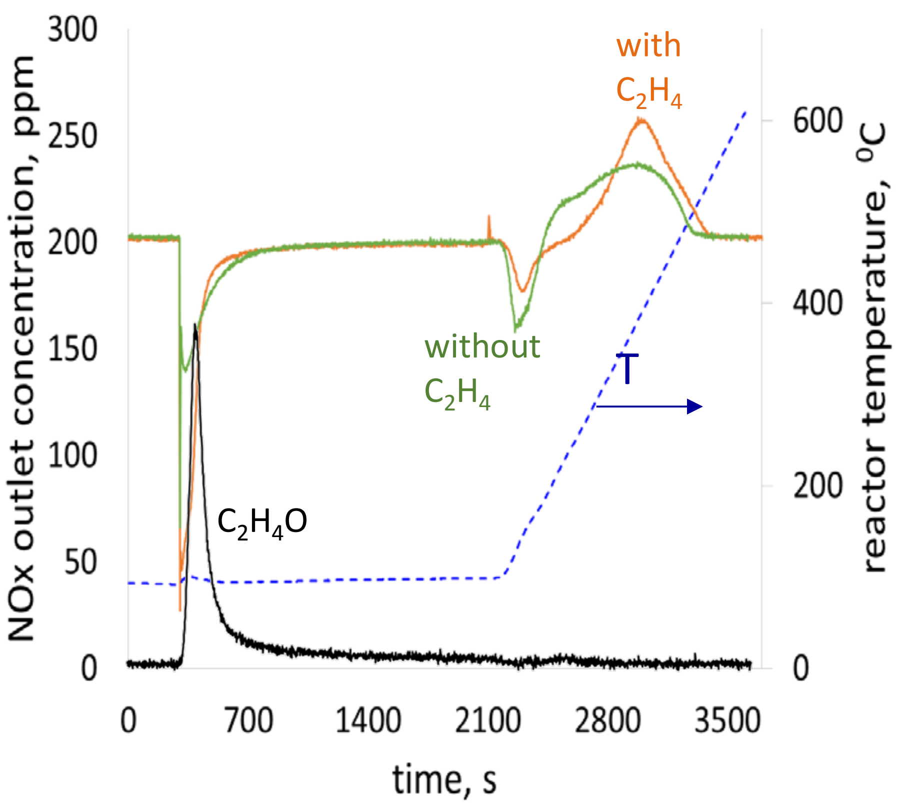
Catalyst pretreated with $^{16}O_2$
and pulsed with $^{15}N^{18}O$



$$^{15}N^{18}O + 2[Pd^{II}\,{}^{16}OH]^{+}Z^{-} \leftrightarrow {}^{15}N^{16}O^{18}O + 2Z^{-}Pd^{+} + H_2{}^{16}O$$

- Isotopic exchange of oxygen is consistent with DFT postulated reduction step

NO uptake and release in the presence of ethylene



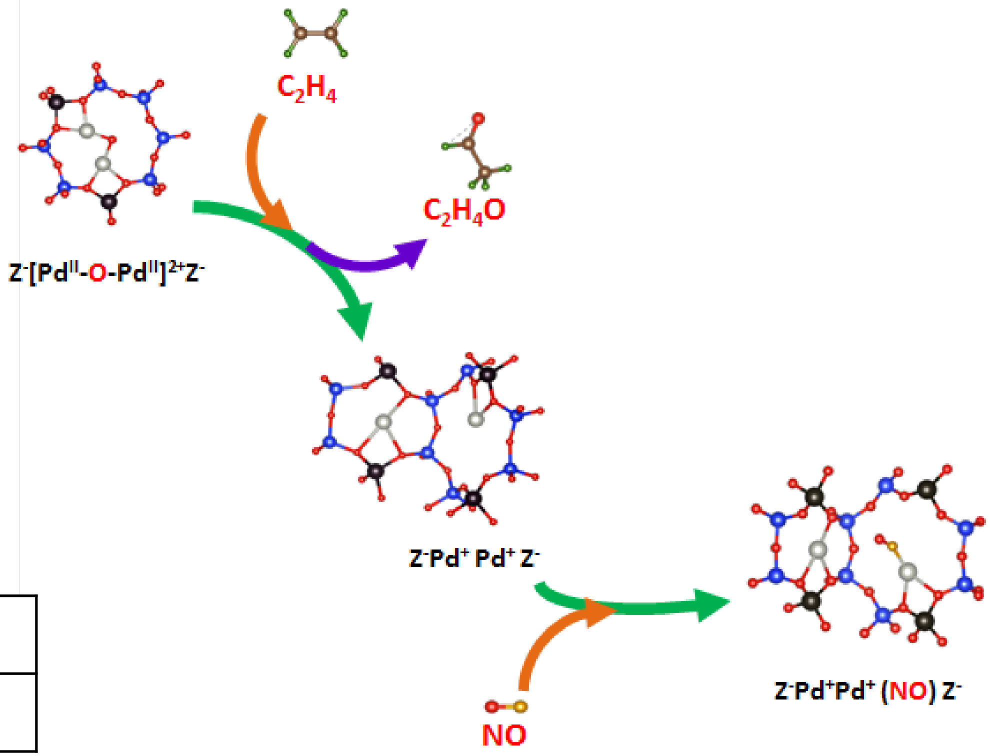
NOx (ads)/NOx(des)	NOx/Pd
~ 1	~ 1.2

$Z^-[Pd^{II}\text{-}O\text{-}Pd^{II}]^{2+}Z^- + NO \rightarrow 2\ Z^-Pd^+ + NO_2$

ΔE = 23 KJ/mol

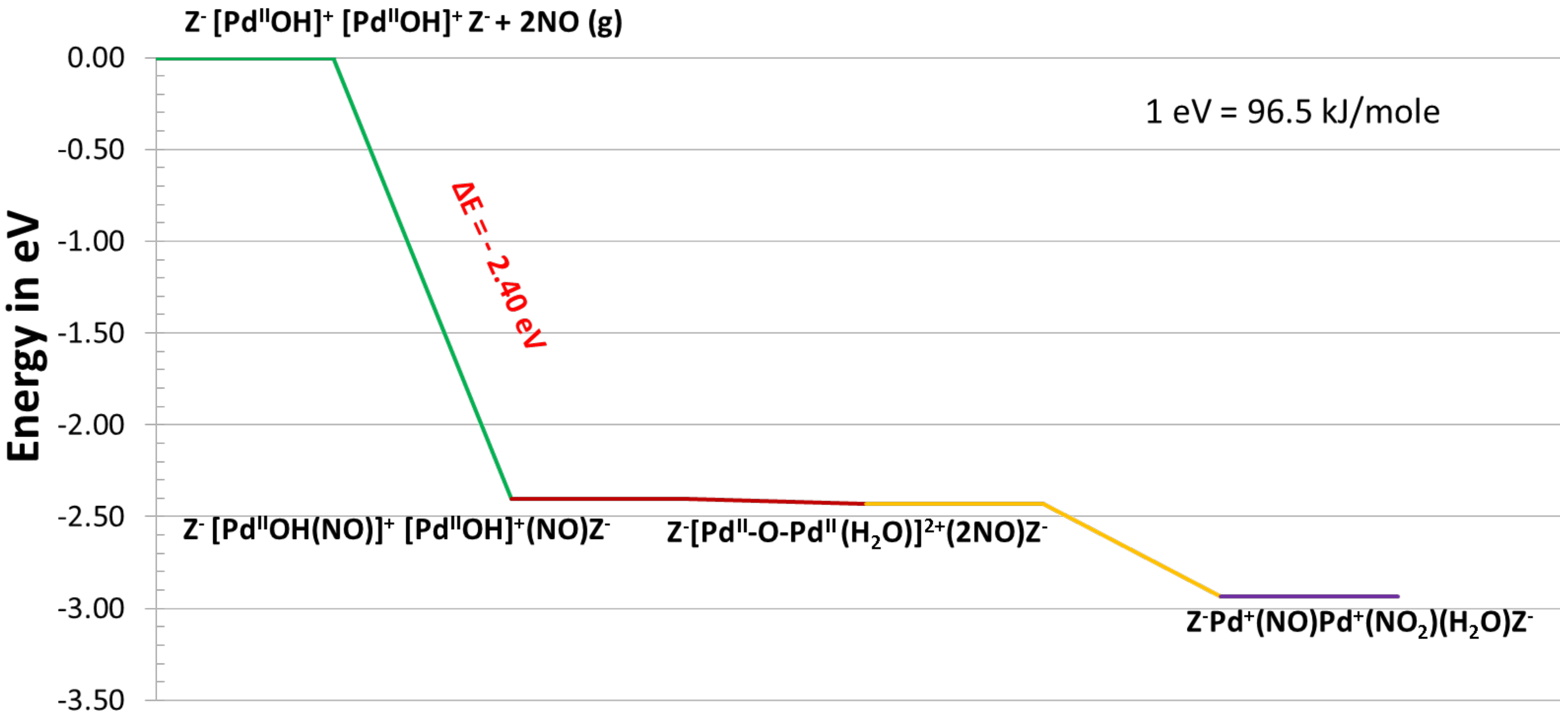
$Z^-[Pd^{II}\text{-}O\text{-}Pd^{II}]^{2+}Z^- + C_2H_4 \rightarrow 2\ Z^-Pd^+ + C_2H_4O$

ΔE = -93 KJ/mol

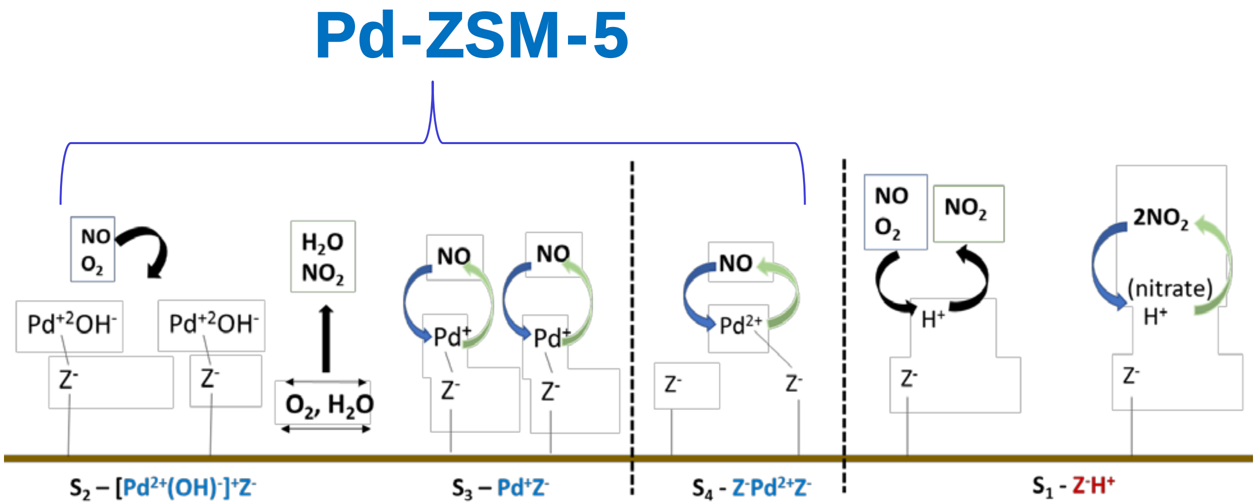


C_2H_4 oxidation is more exothermic and the site modification from $Pd^{II}OH$ to Pd^+ is thermodynamically favored with C_2H_4

Alternative NO uptake pathway forming NO-Pd(I)



PNA microkinetic model (Pd / H-ZSM-5)

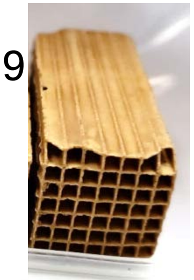


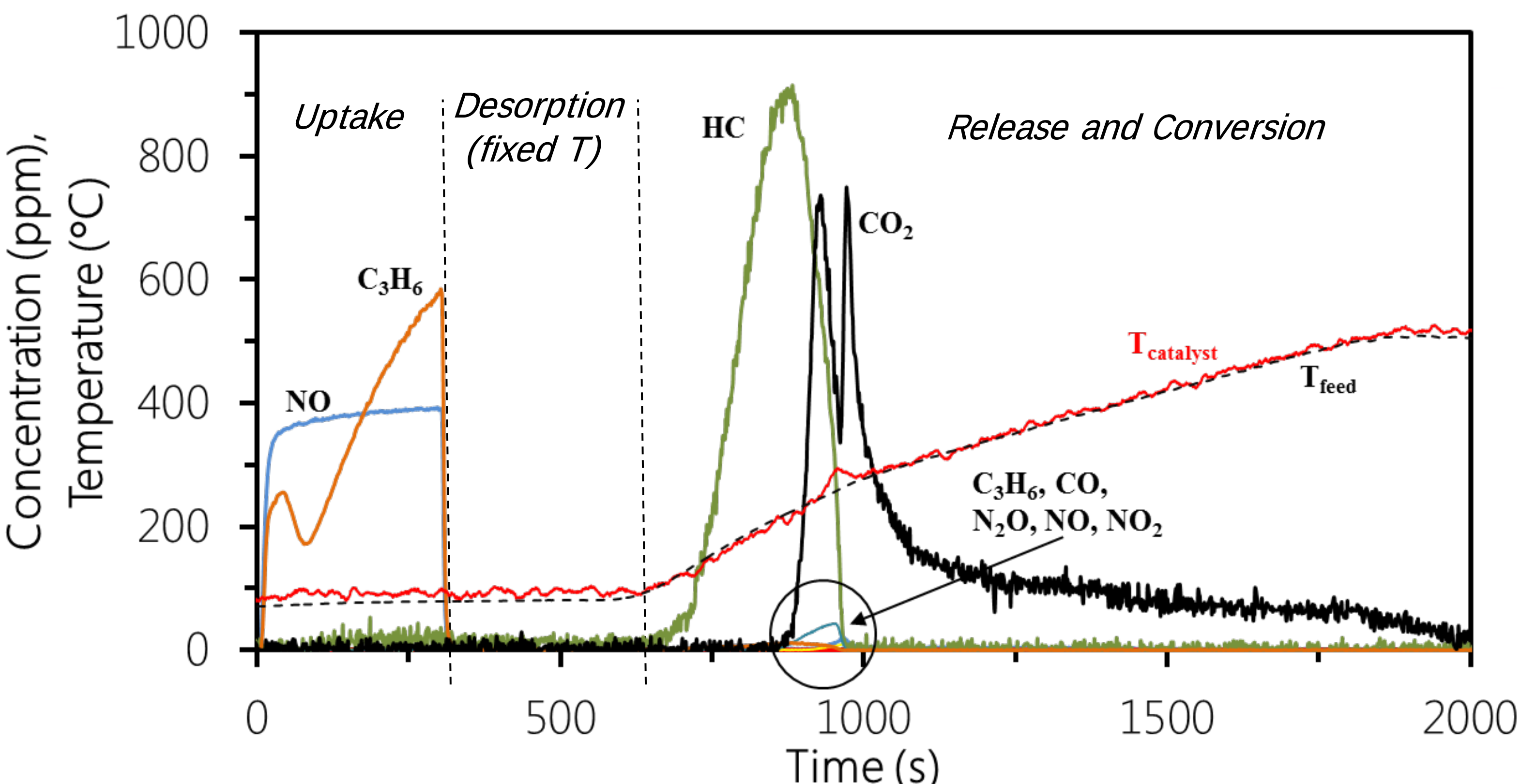
Reaction #	Reaction step	Rate expression (R_f)
R12	$NO + Z^{-}Pd^{2+}Z^{-} \leftrightarrow Z^{-}Pd^{2+}Z^{-} - NO$	$k_{12f}X_{NO}\theta_{vs2}C_{s2}$-$k_{12b}\theta_{NO-s2}C_{s2}$
R13	$NO + Z^{-}Pd^{2+}Z^{-} - NO \leftrightarrow Z^{-}Pd^{2+}Z^{-} - (NO)_2$	$k_{13f}X_{NO}\theta_{NO-s2}C_{s2}$-$k_{13b}\theta_{(NO)_2-s2}C_{s2}$
R14	$NO + Z^{-}Pd^{2+}Z^{-} - (NO)_2 \leftrightarrow Z^{-}Pd^{2+}Z^{-} - (NO)_3$	$k_{14f}X_{NO}\theta_{(NO)_2-s2}C_{s2}$-$k_{14b}\theta_{(NO)_3-s2}C_{s2}$
R15	$NO_2 + Z^{-}Pd^{2+}Z^{-} \leftrightarrow Z^{-}Pd^{2+}Z^{-} - NO_2$	$k_{15f}X_{NO_2}\theta_{vs2}C_{s2}$-$k_{15b}\theta_{NO_2-s2}C_{s2}$
R16	$NO + Z^{-}$[Pd( )	

Coupled NO + HC Trapping, Release & Conversion: Pd/H-BEA

Uptake Temperature: 80°C
Feed: 400 ppm NO, 800 ppm C_3H_6, 2% O_2

2wt% Pd-BEA, Si/Al = 19
1.5g wc/in^3; Al/Pd= 3.4





- Trap NO + HC at low temperature, then releases and oxidizes during temperature ramp