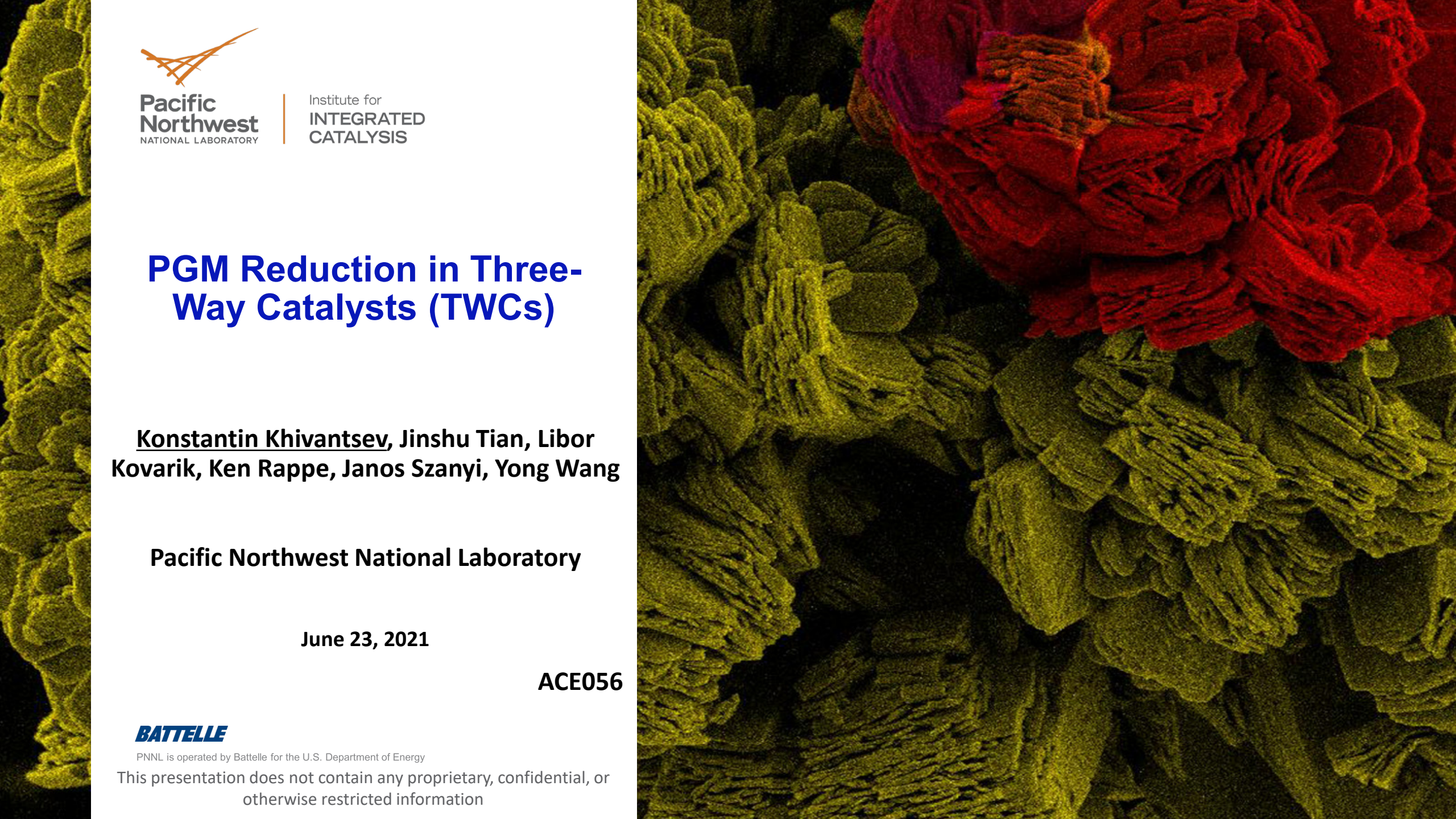

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Institute for INTEGRATED CATALYSIS

PGM Reduction in Three-Way Catalysts (TWCs)

Konstantin Khivantsev, Jinshu Tian, Libor Kovarik, Ken Rappe, Janos Szanyi, Yong Wang

Pacific Northwest National Laboratory

June 23, 2021

ACE056

BATTELLE

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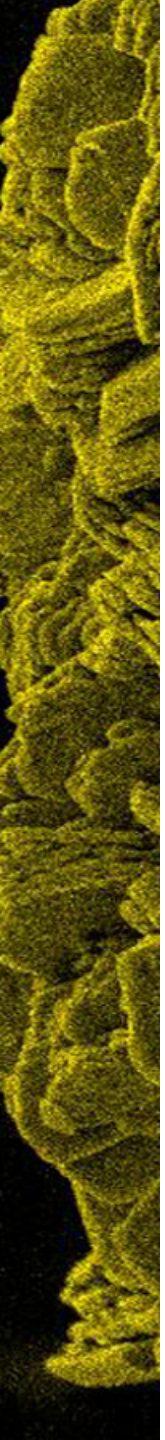

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PNNL Fundamental and CRADA Projects:
1) Address the "150°C Challenge", PGM Reduction, Durability, and Cost;
2) Aligns with Industrial Priorities - Exemplified by 8 AMR Presentations

ACE118 (Janos Szanyi)

ACE169 FOA (Yong Wang)

ACE027 (Feng Gao)

ACE159 FOA (Ken Rappe)

ACE158 FOA (GM) Khivantsev

ACE056 (Konstantin Wang)

ACE023 (Yong Wang)

ACE119 (Ken Rappe)

THE 150° CHALLENGE

PGM REDUCTION

Greatly reduced vehicle PGM content (FOA)

Washington State University | Stellantis | BASF We create chemistry | The University of New Mexico

Slashing PGM in catalytic converters (FOA)

GM | BASF We create chemistry | University of Central Florida | University of Virginia | Washington State University

Stellantis

BASF We create chemistry

SOFIA University

Advanced Storages

TWC

Low T CO Oxidation

The University of New Mexico

CARUS CORPORATION

SCR

LTAT Protocol

Cummins — Durability of SCR catalysts (Cummins)

Multi-functional Devices

KYMANETICS

Reduced Cost & Complexity for Off-highway Aftertreatment (FOA)

John Deere | Michigan Technological University | CARUS CORPORATION | KYMANETICS

John Deere — Advanced multi-Functional DPFs: DOC-on-filter (John Deere)

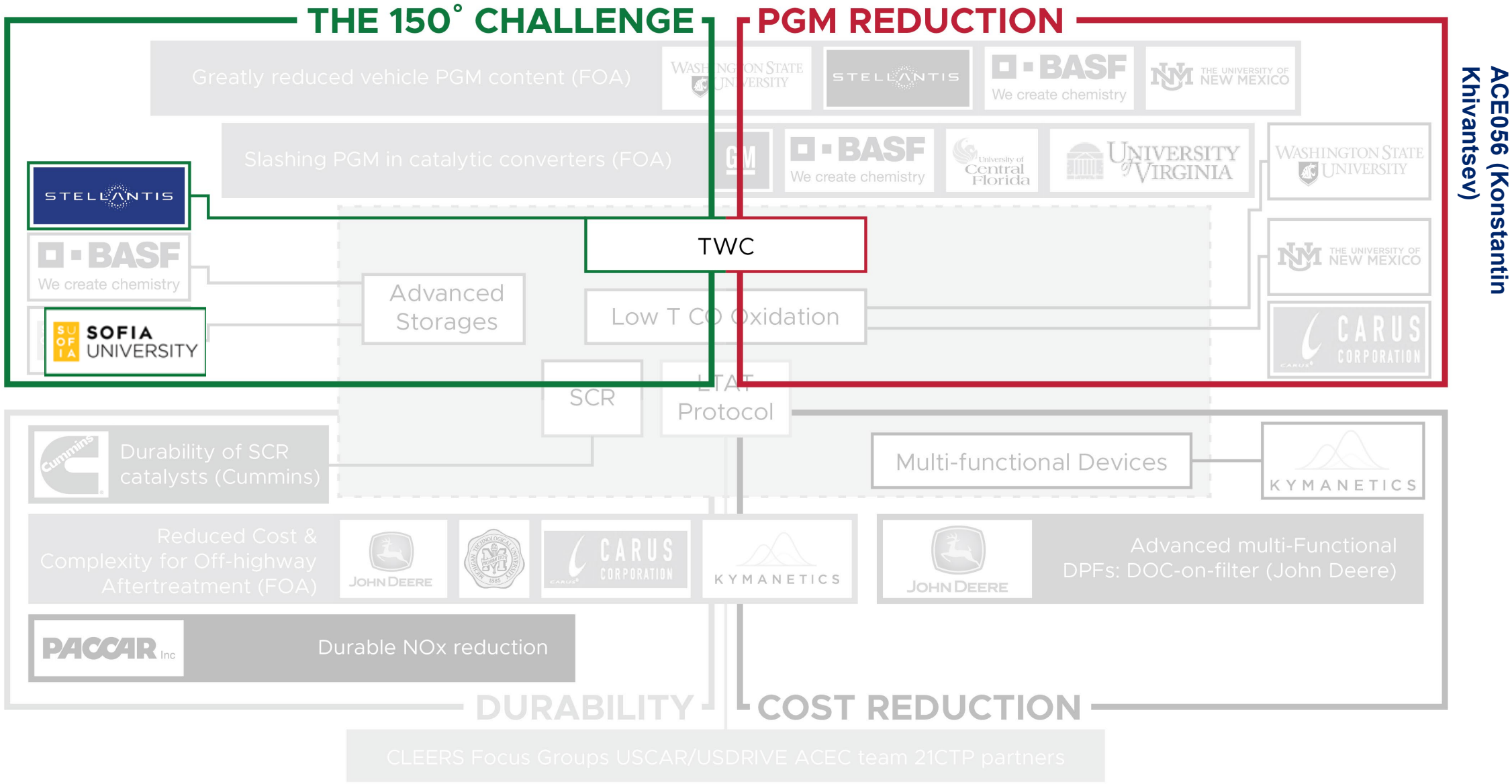
PACCAR Inc — Durable NOx reduction

DURABILITY

COST REDUCTION

CLEERS Focus Groups USCAR/USDRIVE ACEC team 21CTP partners

This TWC Project Specifically Addresses the "150°C Challenge" PGM Reduction Through Control of Metal-Support Interactions



Relevance

- Increasing the efficiency of internal combustion engines
  - dramatically **improves the fuel economy** of the nation's fleet of vehicles
  - **reduces** our **dependence on foreign oil and reducing carbon emissions**.

- The overarching **emissions goal** is the U.S. EPA Tier 3 Bin 30 emission standard.
- Aftertreatment technologies are required to be **integrated with the engine combustion** approaches.

- **Achieve greater than 90% conversion of criteria pollutants** (NO_x, CO, HCs) **at 150°C** for the full useful life of the vehicle (defined as the longer of 150,000 miles or 15 years).

- Require the research and **development of new and novel material combinations** that will enable **lower temperature catalytic performance, increased selectivity to inert species**, and optimal storage of pollutant and reductant species.

USDRIVE
DRIVING RESEARCH AND INNOVATION FOR VEHICLE EFFICIENCY AND ENERGY SUSTAINABILITY

Overview

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Timeline

- Status: On-going core R&D

Budget

- FY2021 funding – $ 331 K

Barriers and Technical Targets

- Emission controls contribute to durability, cost and fuel penalties
  - Decreasing PGM content
  - Increasing durability/stability
  - Low-temperature performance
- Improvement limited by:
  - Fundamental understanding of structure-activity relationships
  - Understanding of degradation mode
  - Development of model tools
- Effective dissemination of information

Partners

- **Stellantis** (USA), **University of Sofia** (Bulgaria): guidelines in catalyst evaluations; synergies in model materials

Milestones

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Milestones:

▶ Complete initial studies of TWCs for stoichiometric combustion engines	3/30/2021	complete
▶ Evaluate the impact of single-atom density on TWC performance	6/30/2021	on track

Approach

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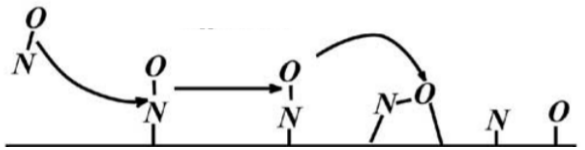
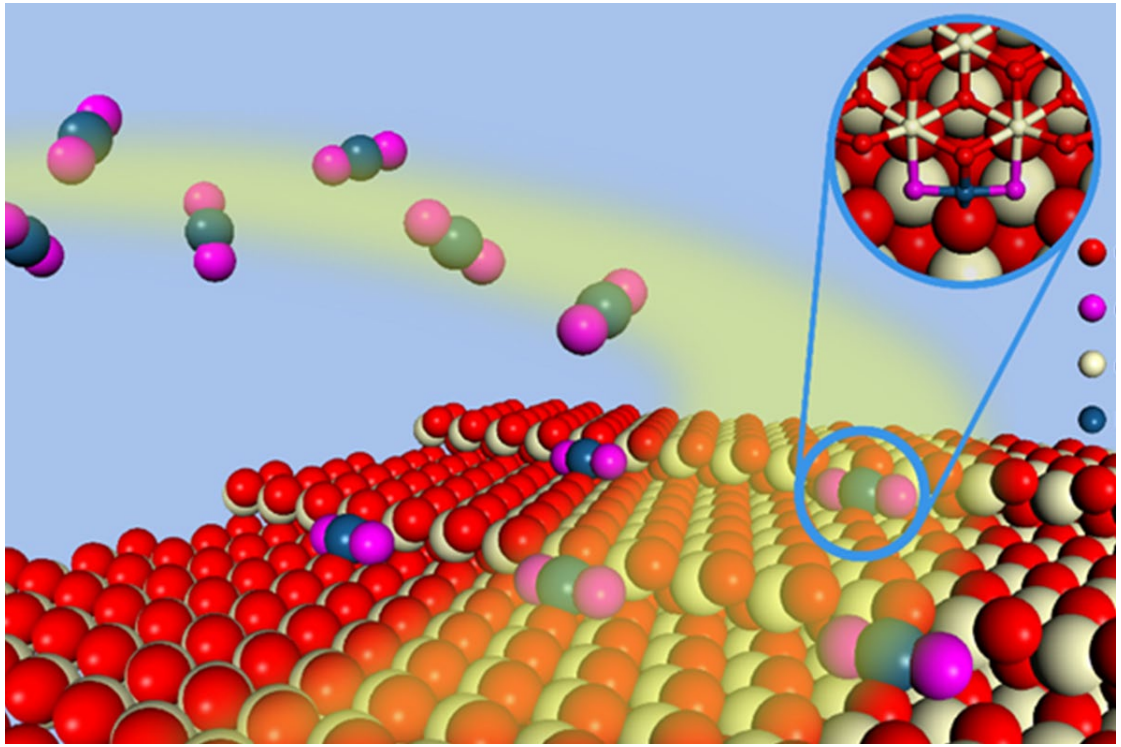
Paradigm shift in TWC NO reduction chemistry



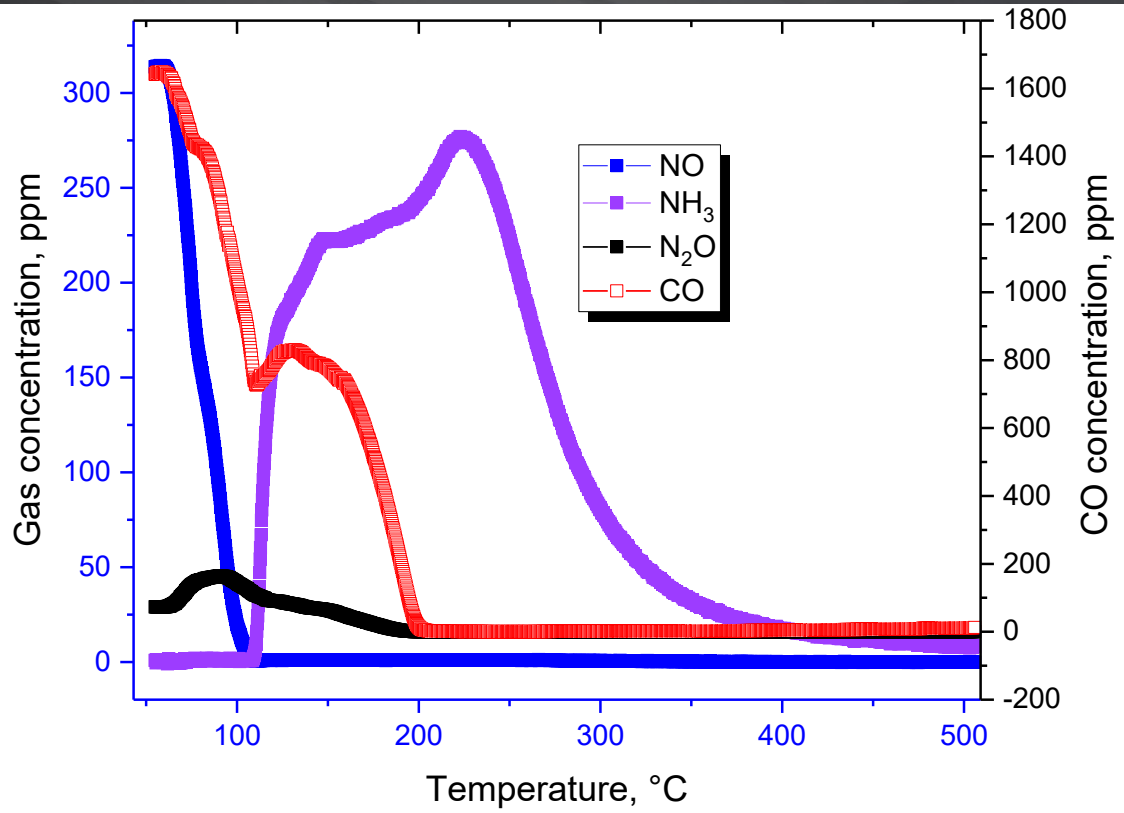
-N + -CO → NCO
-NCO + H_2O → NH_3 + CO_2
-N + NO → N_2O
-O + CO → CO_2
-N + -N → N_2

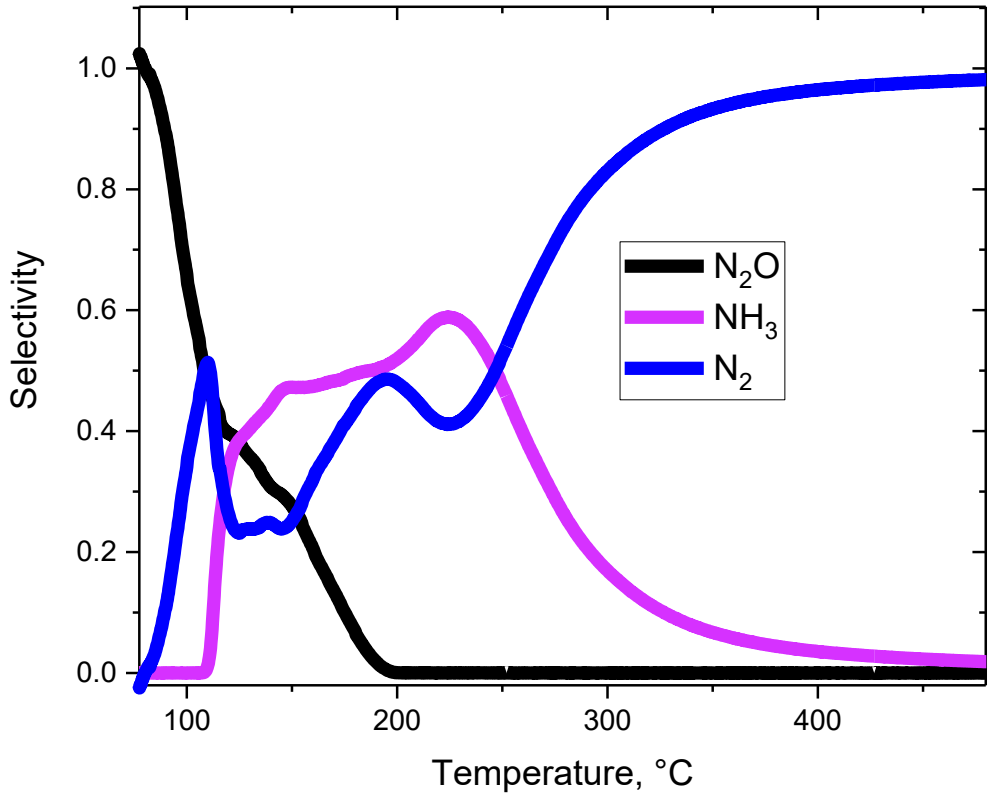
- Previous TWCs studies considered metallic surfaces but not the interface between single metal atoms and the support
- High-temperature atom trapping strategy to synthesize thermally stable single noble metal atoms on supports for NO reduction
- This requires special characterization tools
  - Institute for Integrated Catalysis (IIC)
  - Environmental Molecular Sciences Laboratory (EMSL)
- Work closely with our partners and sponsors
  - Stellantis (USA) (e.g., guidelines for TWC evaluation)
  - U. Sofia (Bulgaria) (collaboration with DFT modeling)



Kunwar *et al.*, ***ACS Catalysis***, 2019, 9, 3978-3990

Technical Accomplishments: thermally stable Rh atoms highly active for NO reduction

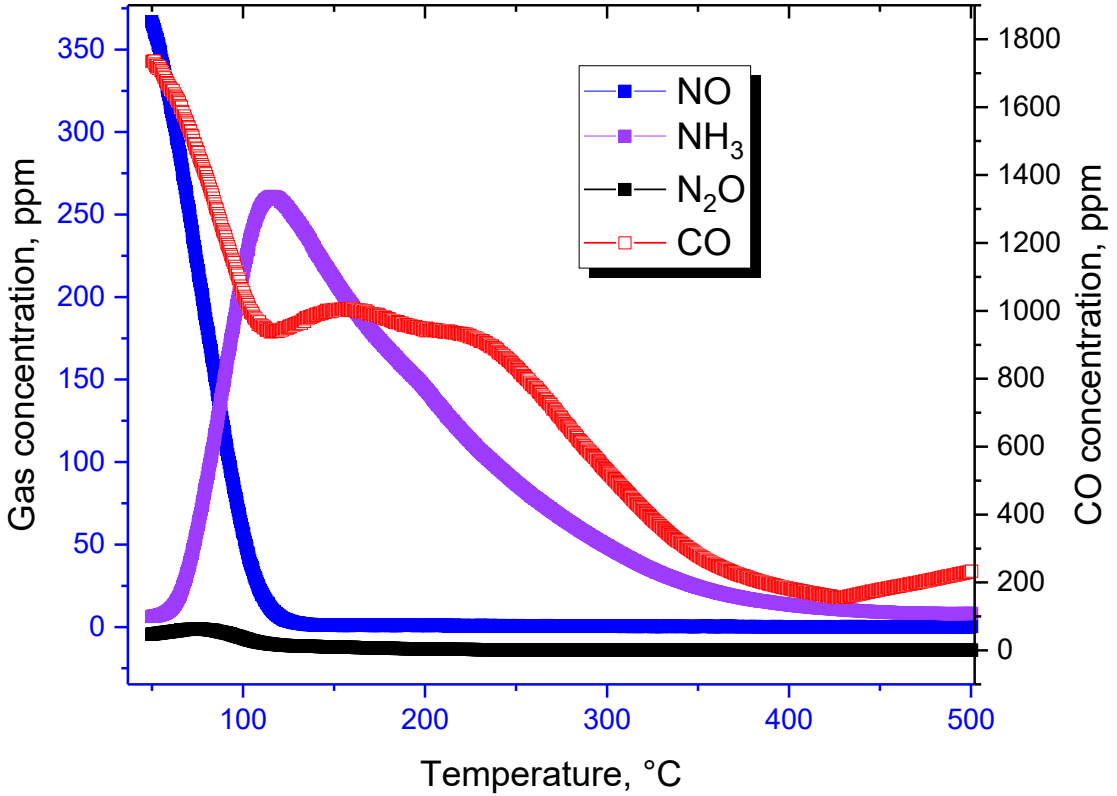


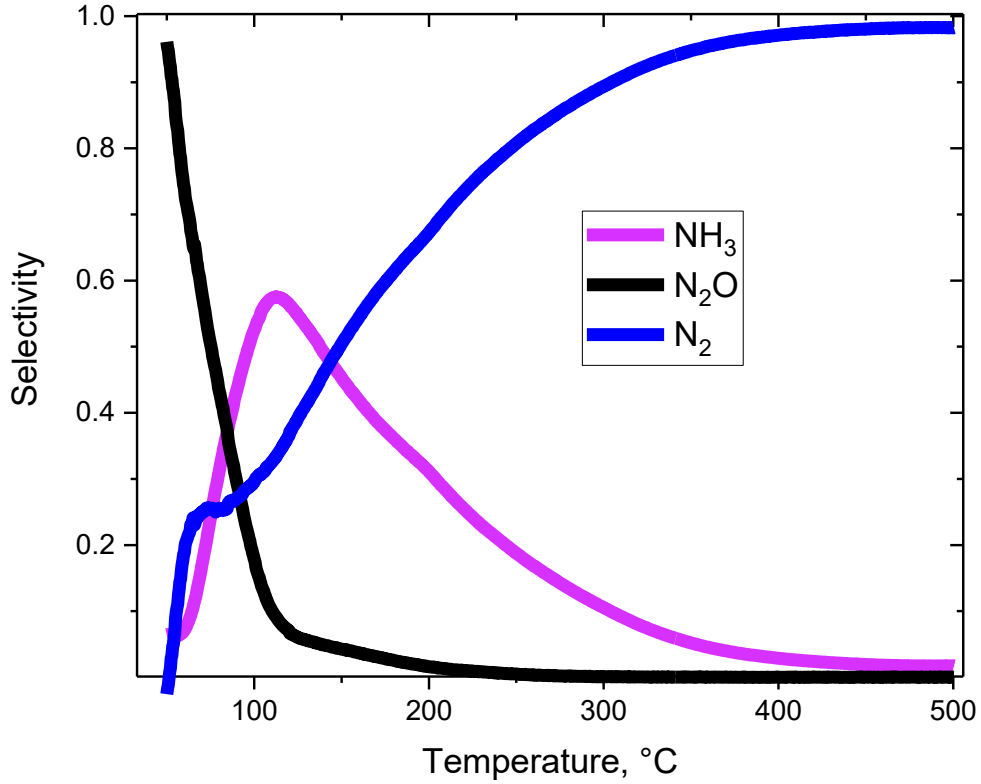


120 mg catalyst 0.5 wt% Rh/CeO_2. Total flow 300 ml/min. Concentrations: 460 ppm NO, 1750 ppm CO, ~2.6 % H_2O balanced with N_2. GHSV ~ 150 L/g*hr, ramp rate 2K/min

- 0.5 wt% Rh_1/Ceria is highly active for NO reduction by CO
- Full NO consumption achieved at ~115 °C

Technical Accomplishments: 0.1 wt% Rh_1/CeO_2: Full NO conversion at 125 °C





120 mg catalyst 0.1 wt% Rh/CeO_2. Total flow 300 ml/min. Concentrations: 460 ppm NO, 1750 ppm CO, ~2.6 % H2O balanced with N_2. GHSV ~ 150 L/g*hr, ramp rate 2K/min

- 0.1 wt% Rh_1/Ceria is highly active for NO reduction by CO
- Less N_2O is produced
- Full NO consumption achieved at ~125 °C: performance comparable to 0.5 wt% Rh sample

Technical Accomplishments: Rh_1/CeO_2:

Superior activity is due to Rh-O-Ce which is mechanistically similar to homogeneous organometallic Rh(I) catalysts

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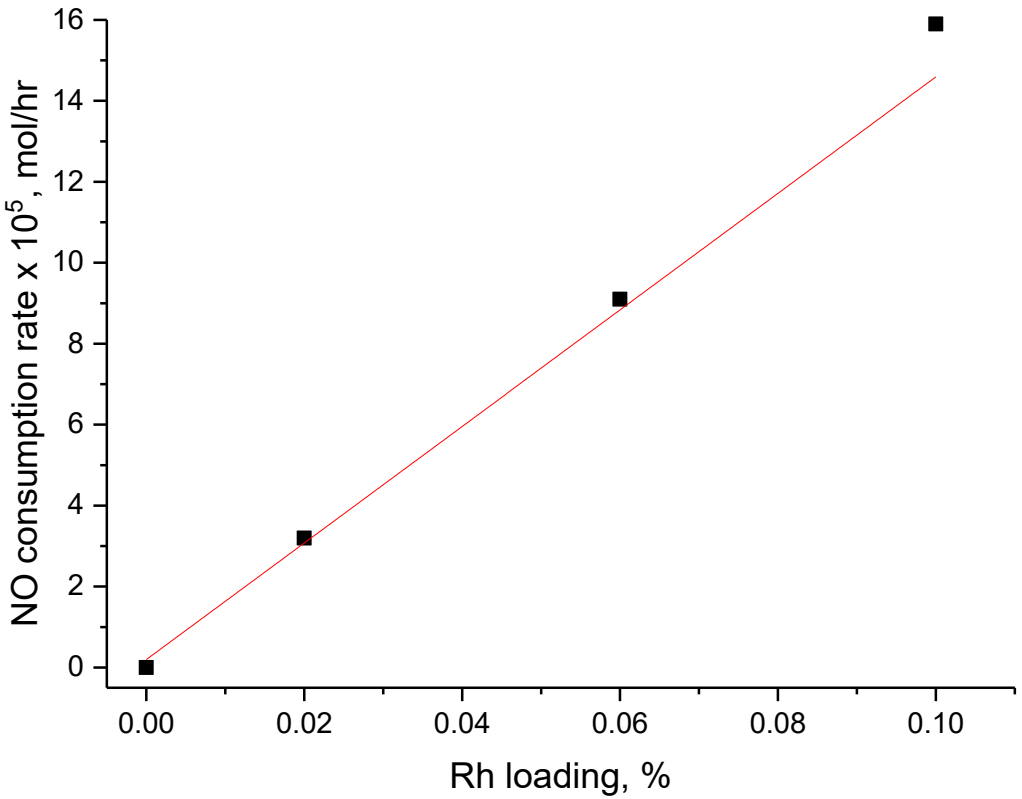
NO+ CO under dry conditions



T=175 ºC, GHSV=450 L/g*hr. 460 ppm NO, 1,800 ppm CO balanced in nitrogen. The rate at 0 wt% loading was fixed at 0.

- Homogeneous Rh(I) and Ru(II) complexes catalyze NO reduction by CO with a mechanism distinct from metallic surfaces (and at lower temperatures)
- Reaction rates scale linearly with [Rh(I)] concentration; CO and NO orders in the kinetic regime are ~0

CO and NO orders observed for dry (CO+NO) reaction on 0.1 wt% Rh/CeO_2 at 120 ºC and GHSV ~ 450 L/g*hr. At constant NO level (460 ppm) CO levels were varied: ~1,800, 2,700, 3,600 and 6,000 ppm). At constant CO level ~6,000 ppm NO levels were varied: ~ 220, 460 and 1,000 ppm.

Sample	NO order	CO order
0.1 wt% Rh/CeO_2	0	0

- Similar kinetics for heterogeneous single-atom systems suggest mechanisms analogous to homogeneous complexes

Technical Accomplishments: 0.1 wt% Rh *vs*. 0.5 wt% Rh/CeO_2 similar catalytic activity assessed with infra-red spectroscopy

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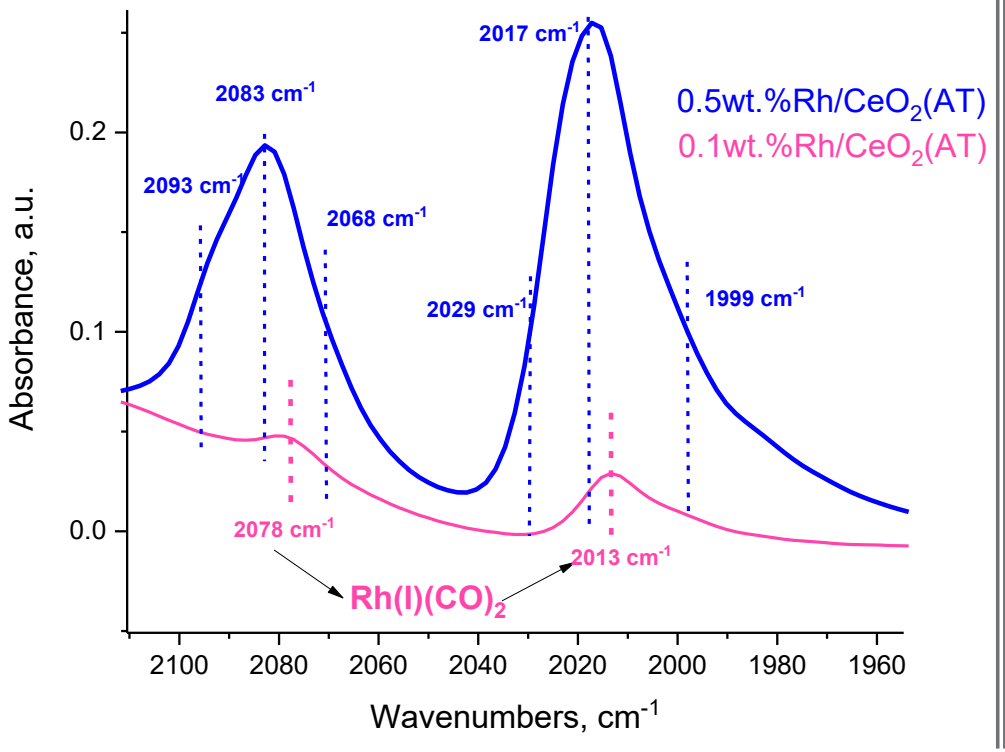
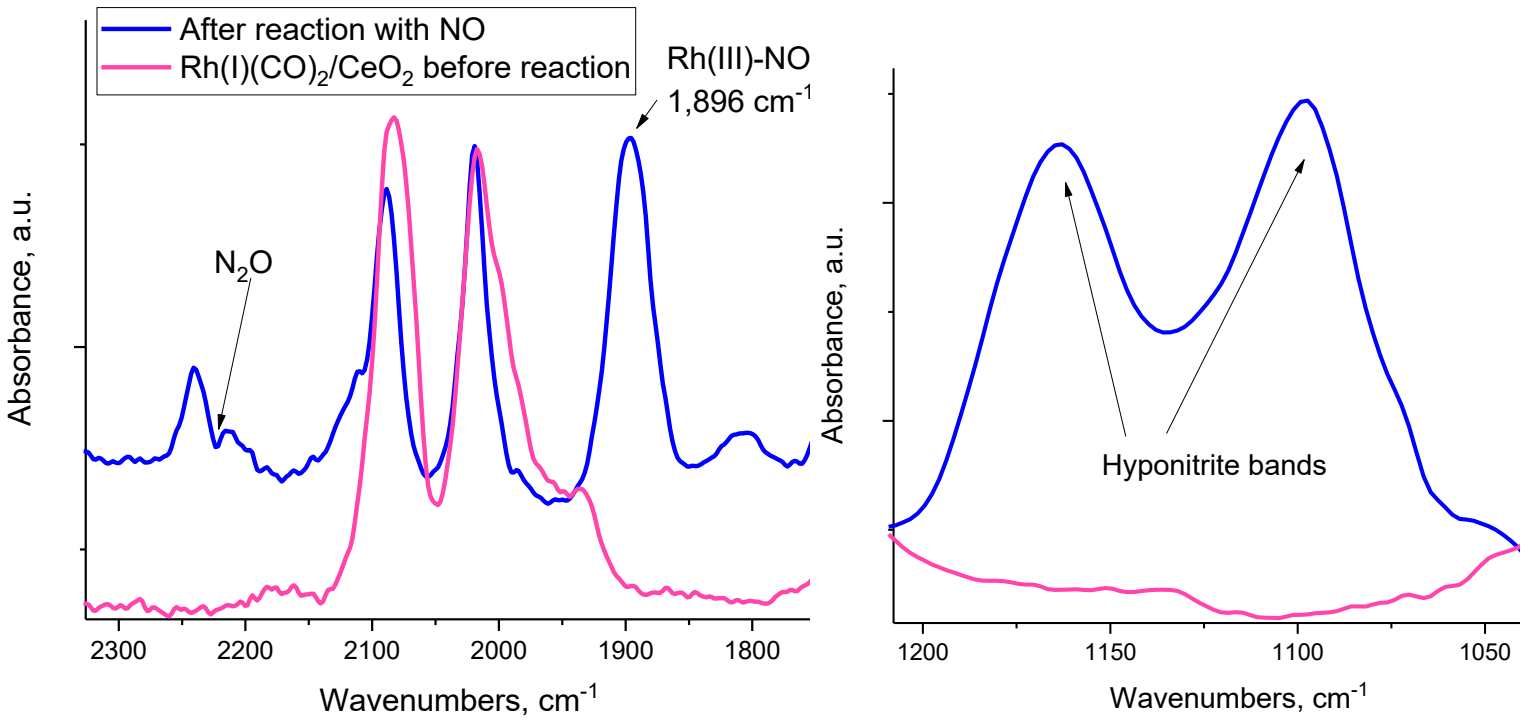
In-situ DRIFTS CO flow at 125 ºC



FTIR 0.5 wt% $Rh(I)(CO)_2/CeO_2$ with ~0.3 Torr NO at 60 ºC.



- 0.1 wt% Rh_1/Ceria is more uniform then 0.5 wt%: Rh(I) cations are less electropositive
- More electropositive Rh(I) cations are suggested to be less active
- NO oxidizes Rh(I) to Rh(III), with intermediacy of hyponitrite species, similarly to homogeneous Rh(I) complexes

Technical Accomplishments: NH_3 formation is governed by p(CO)/p(NO) parameter

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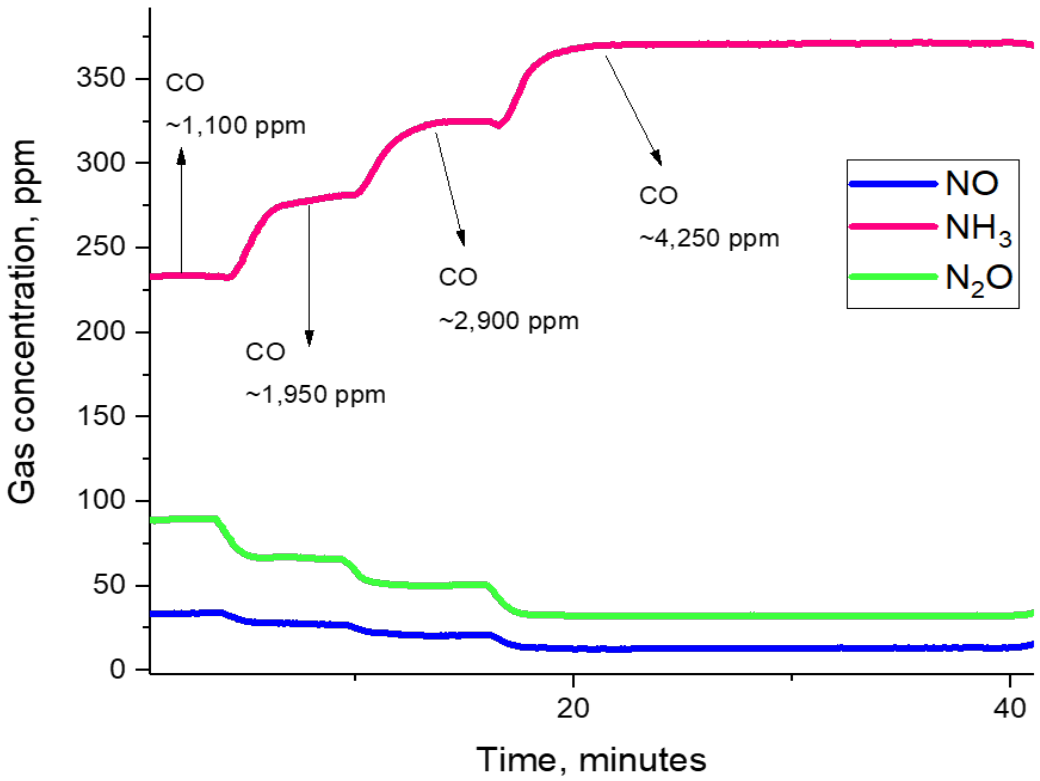
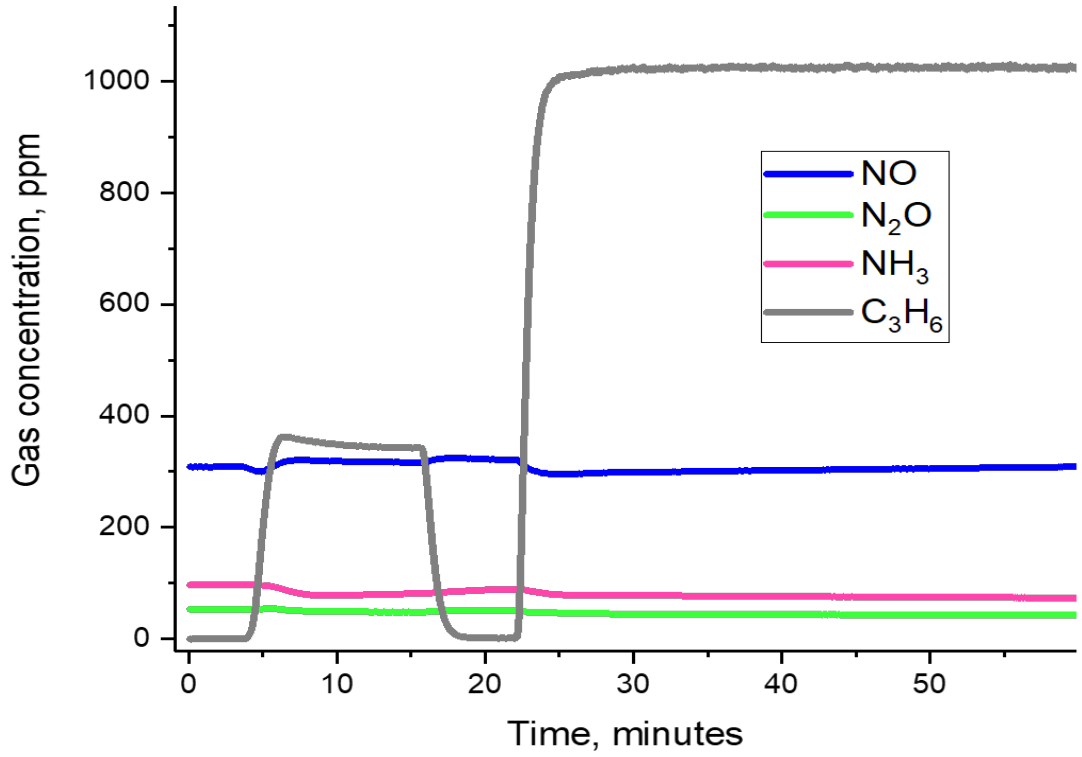
Effect of CO on ammonia production at 120 ° C



120 mg 0.1Rh/CeO_2. Total flow 300 ml/min. Concentrations: 460 ppm NO, 1750 ppm CO, ~2.6 % H2O balanced with N_2. GHSV ~ 150 L/g*hr, T=120 ° C

Minimal effect of propylene addition

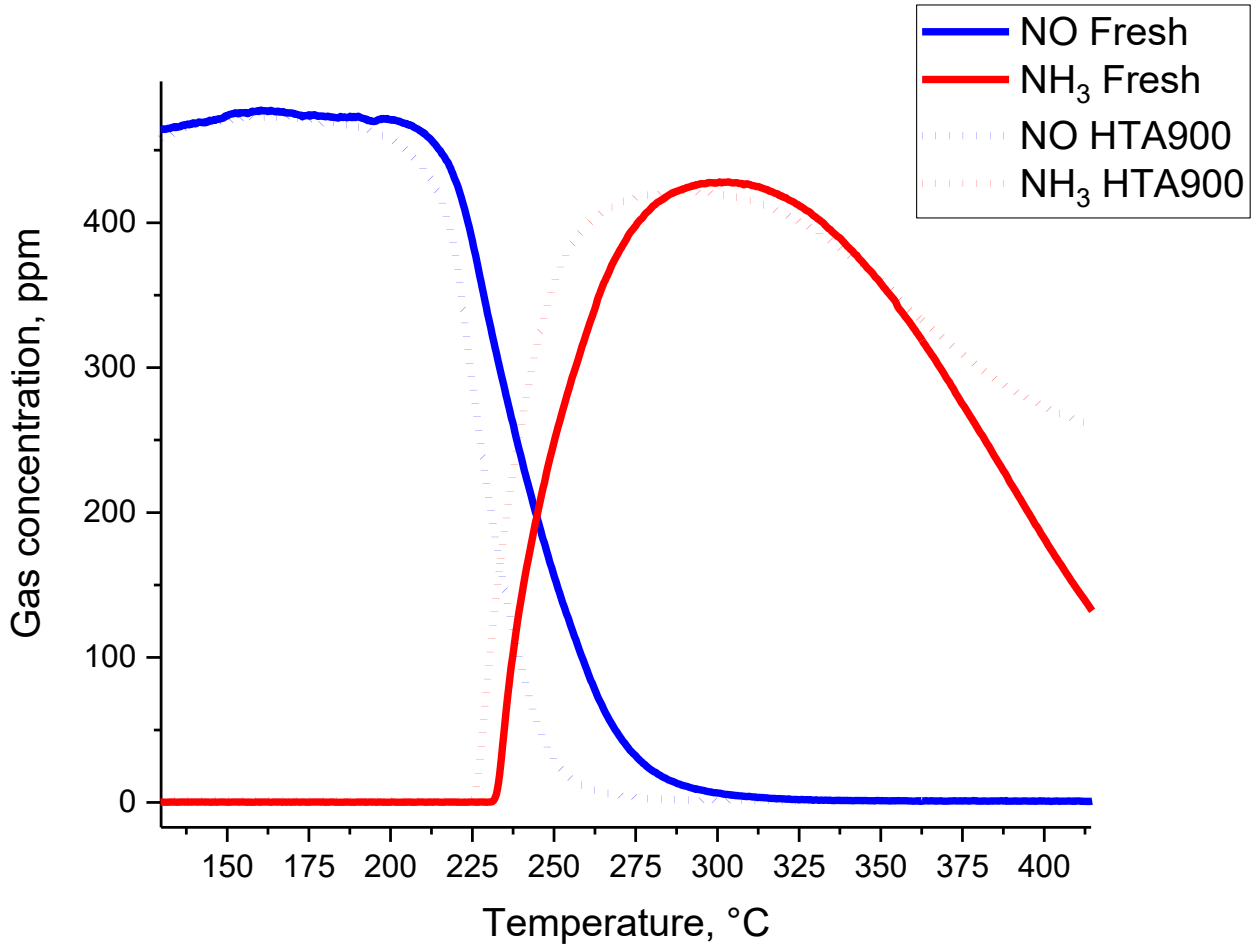


120 mg 0.1Rh/CeO_2. T=120 ºC and GHSV 450 L/g*hr (NO ~ 460 ppm, CO ~ 1,800 ppm, H_2O ~ 2.6 %, C_3H_6 levels of ~ 0, 360 and 1,100 ppm respectively).

- P(CO)/P(NO) parameter controls ammonia production
- Propylene minimally affects NO conversion

Technical Accomplishments: $Rh_1/(Ce/Zr)O_2$:

900 °C hydrothermally aged 0.1 wt% $Rh_1/(Ce/Zr)O_2$ presents highly active and stable catalyst under stoichiometric conditions



120 mg 0.1 wt% $Rh/(Ce/Zr)O_2$. Total flow 300 ml/min. 460 ppm NO, 7,000 ppm CO, ~3,500 ppm O_2, ~2.6% H_2O, balanced with N_2. GHSV ~ 150 L/g*hr, ramp rate 2K/min. HTA900 was hydrothermally aged in the presence of reactants/steam at 900 °C for 4 hours.

- Mixed Ceria-Zirconia oxides have higher stability than ceria
- Supporting 0.1 wt% Rh produces active NO reduction catalyst even under stoichiometric conditions
- The catalyst does not degrade after hydrothermal aging at 900 °C

Technical Accomplishments: M_1/CeO_2:
Pd_1 and Ru_1/CeO_2 catalysts with promising performance identified

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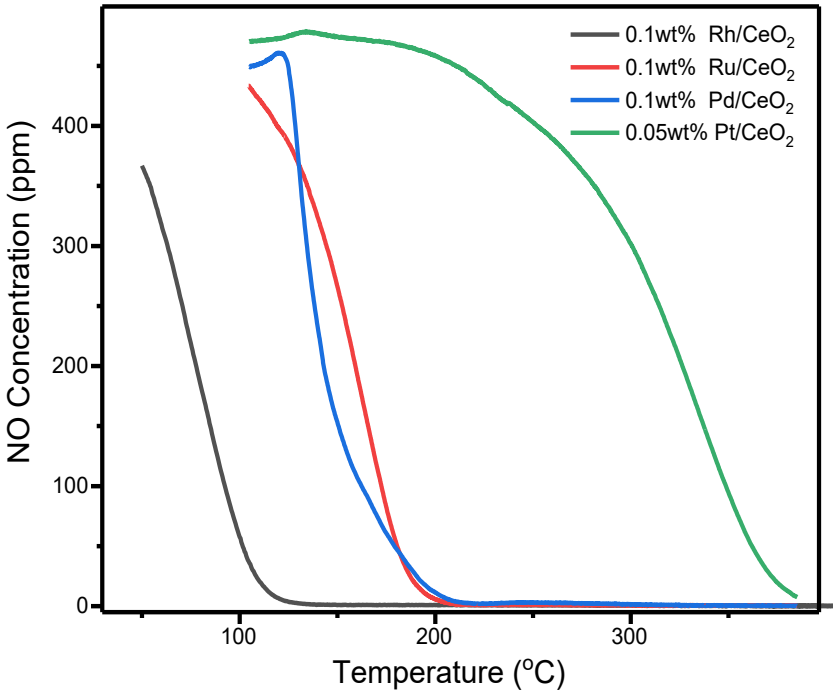

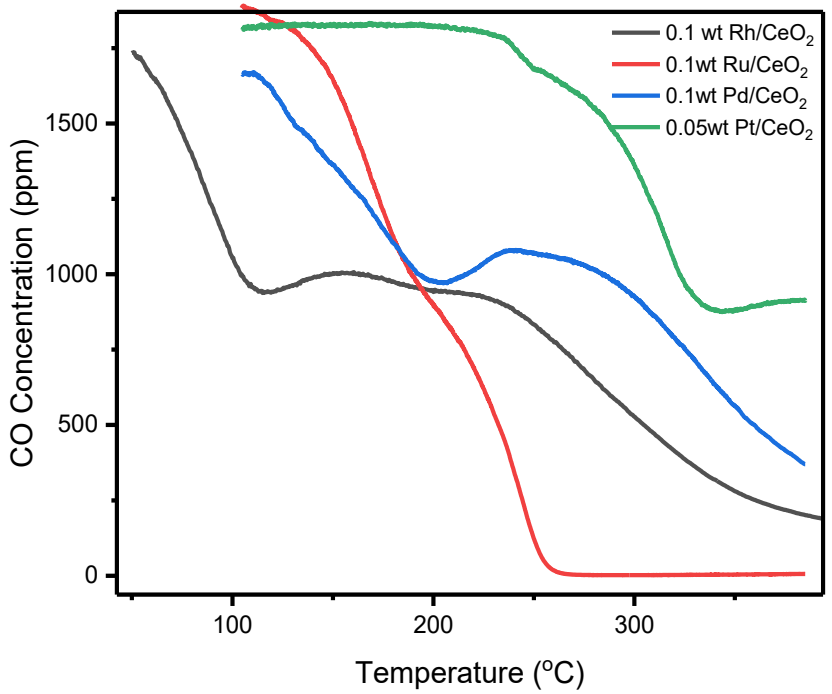

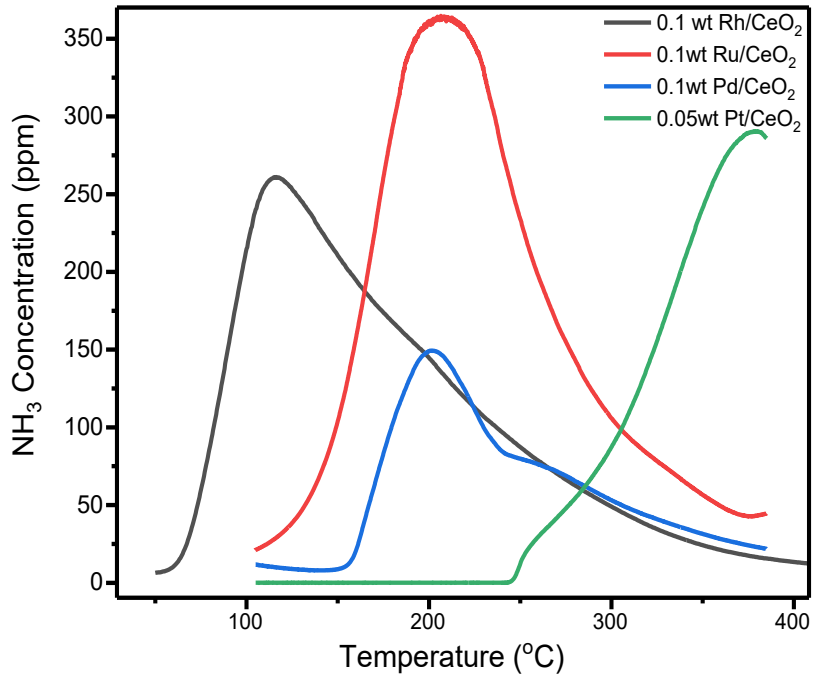

120 mg catalyst. Total flow 300 ml/min. Concentrations: 460 ppm NO, 1750 ppm CO, ~2.6 % H2O balanced with N_2. GHSV ~ 150 L/g*hr, ramp rate 2K/min

- 0.1 wt% Pd and Ru highly active for NO reduction by CO
- Pd produces the lowest amounts of ammonia; Ru - the highest amounts of ammonia
- 0.1 wt% Ru/ceria most active for CO abatement and water-gas-shift

Noble metal price ($ per ounce)

Platinum	~$1,200
Palladium	~$2,935
Rhodium	~$28,000
Ruthenium	~$351
Iridium	~$1498

Technical Accomplishments: overcoming Ru volatility by trapping Ru as single atoms in 0.1 and 0.5 wt% Ru

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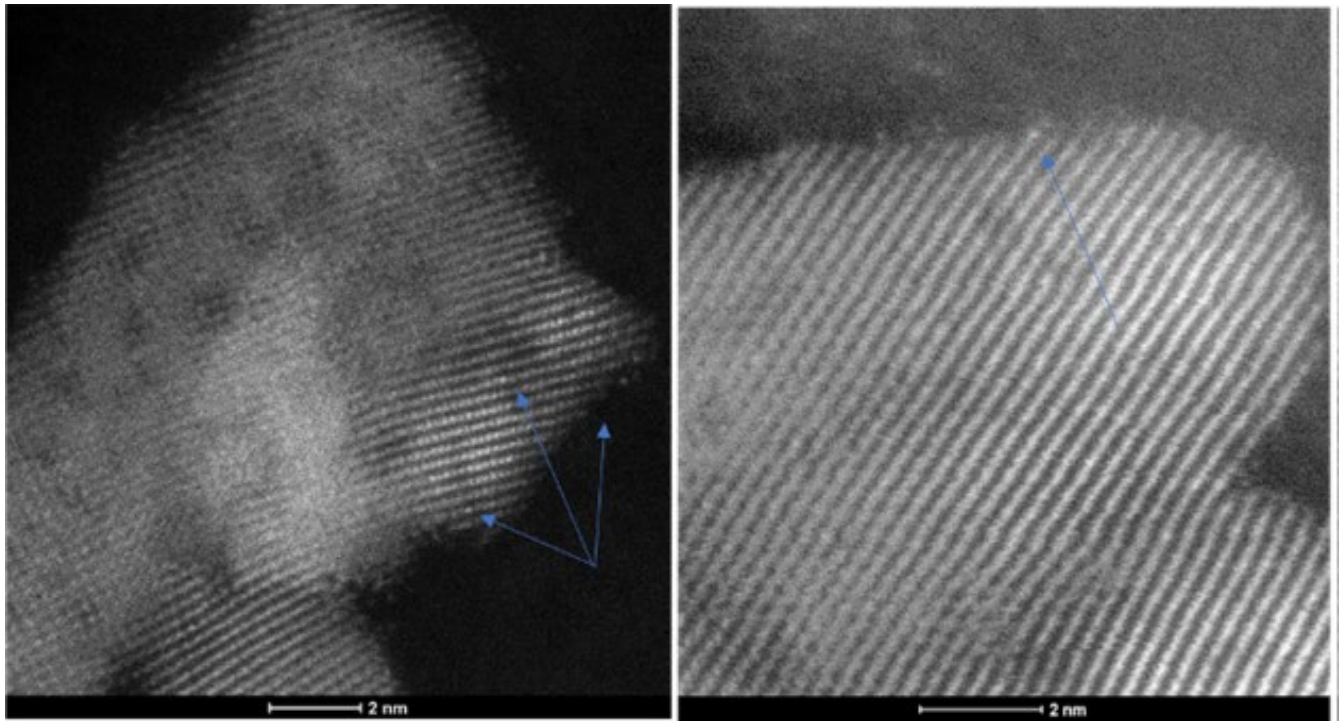
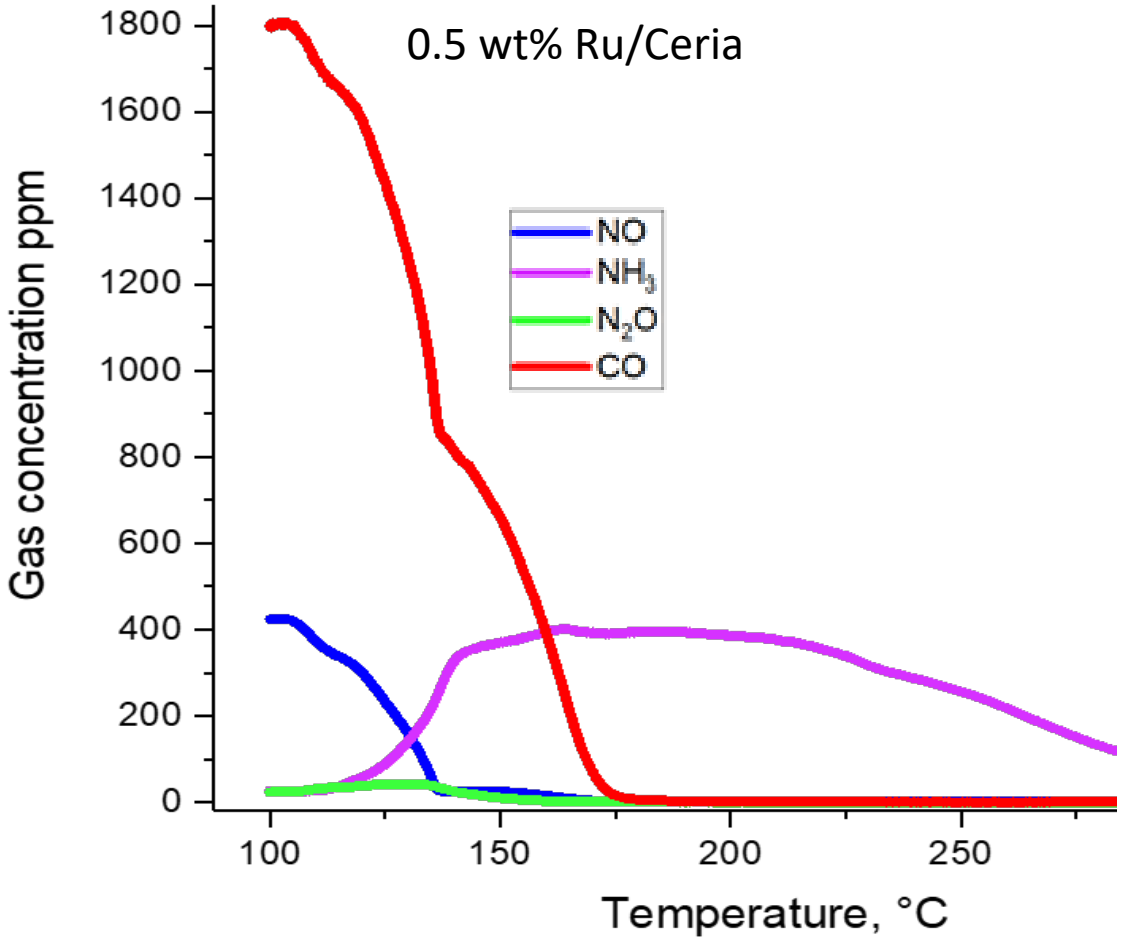
HAADF-STEM images of atom-trapped 0.5 wt% Ru/Ceria (Ru atoms observed)





- 0.5 wt% Ru_1/Ceria is successfully prepared with full Ru atomic dispersion: HAADF-STEM useful in observing Ru atoms
- Full NO conversion ~135 °C; full CO conversion at 175 °C
- Ruthenium is >80 times cheaper than Rh
- Single Ru atoms are trapped by ceria

120 mg catalyst Total flow 300 ml/min. Concentrations: 460 ppm NO, 1750 ppm CO, ~2.6 % H2O balanced with N_2. GHSV ~ 150 L/g*hr, ramp rate 2K/min

Ru_1/CeO_2: DFT calculations clarify the precise location and oxidation state of Ru and Ru-NO complexes on ceria

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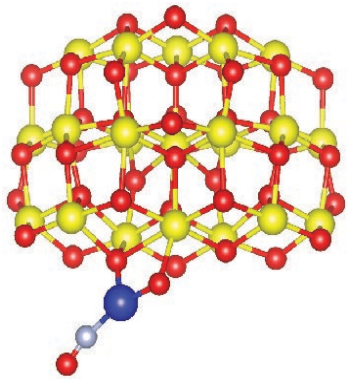
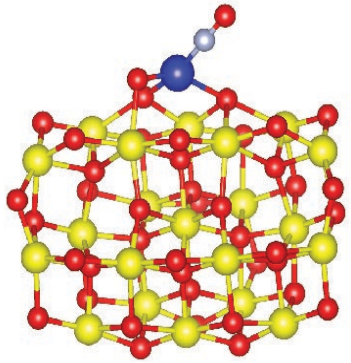
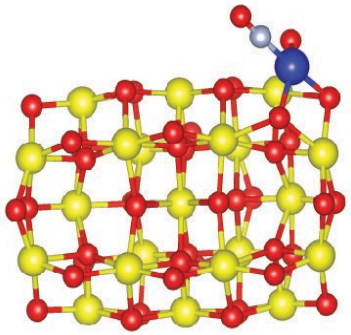


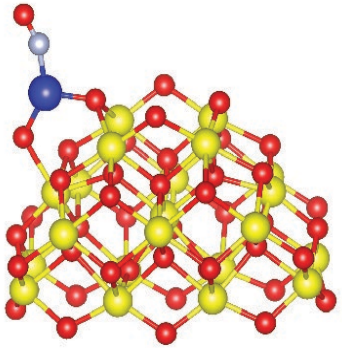
a-1O_NO



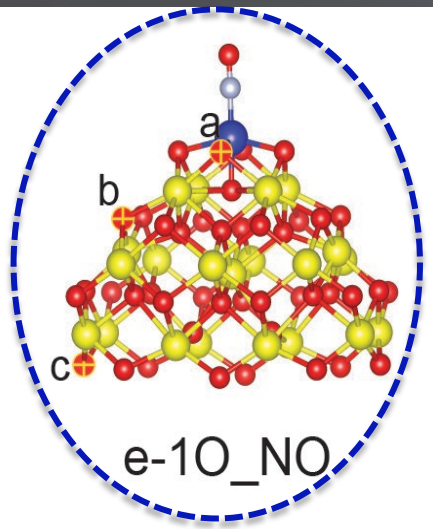
b-1O_NO



c-1O_NO



d-1O_NO



e-1O_NO

$RuO(NO)/Ce_{21}O_{42}$	E_{rel}[a]	BE[b]	E_{vac}	N_s[c]	$N_s(Ru)$[d]	#(Ce^{3+})[e]	q(Ru)[h]	Ru-O	Ru-N	Δ(N-O)[f]	ν(N-O)[g]
a-1O_NO	1.72	-3.11		1	0.8	0	1	184;190	179	2.3	1763
c-1O_NO	1.42	-2.26		1	0.7	0	1	195;200;204	177	1.4	1824
b-1O_NO	2.91	-1.03		1	0.7	0	1	185;209;224	177	1.7	1799
d-1O_NO	1.91	-1.65		1	0.7	0	1	182;190	178	2.7	1733
e-1O_NO	0.00	-3.00		1	0	1	2	191;212;213; 213; 213	179	1.1	1840
e-1O_NO_vac_b	2.08		3.32	1	0	3	2	192;212;212; 214; 215	178	1.2	1832
e-1O_NO_vac_a	0.00		1.24	3	0.25	4	2	198;199;202; 204	173	2.4	1788
e-1O_NO_vac_c	0.63		1.86	1	0	3	2	191;212;212; 212; 213	178	1.1	1837

- Ru(II) ions are located at (100) facets of ceria. Upon NO adsorption, NO donates an electron to Ce^{4+}, thus NO^+ ligand and a Ce^{3+} center are formed, while the formal charge of the Ru remains +2.
- Modeling of realistic ~ 1nm ceria nanoparticles with different facets

Responses to 2020 Reviewers' Comments

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Reviewers' Comments	PNNL Responses
It might be good to break up this project into several smaller projects where each is focused on one catalyst technology	TWC is presented separately in ACE056 (current presentation)
1) Activities related to TWCs show interesting results of almost over 90% NO reduction for temperatures as low as 100°C. One question related to TWC research is how representative are these results for TWC used in natural gas vehicles? 2) The reviewer commented that there is no mention of natural gas related TWC work and a decrease in NOx reduction with age. 3) It would be interesting to involve Cummins for TWC related work since Cummins is a leading NGV engine manufacturer, input on issues related to TWC for NG applications is important as well	Since NGVs are not widely used in the North American markets and they are not the current focus of OEMs, we have not studied these factors. If in the future the scope permits these studies, we intend to investigate them.
The Rh/Ce catalyst should be tested at stoichiometry and not the very rich conditions that were used (1,750 parts per million [ppm] CO, 460 ppm NO); this would probably reduce the NH3 formation on the test with H2O.	We initiated these studies for the promising Rh1/Ceria formulations (Slide 13).
…needs to look at the effects of sulfur poisoning and thermal aging on the single atom Rh/Ce catalyst. Since this is being developed as a TWC, aging temperatures of 900° to 950°C need to be assessed while using the ACEC aging protocol (neutral/rich/lean aging). The OSC of the Rh/Ce catalyst needs to be assessed, because OSC is so important for TWCs. The light off tests need to be assessed with air to fuel ratio (A/F) dithering to simulate actual vehicle operation.	We intend to test sulfur tolerance of promising formulations. Single-atom materials may offer beneficial properties compared to nanoparticles supported on ceria (that are widely used in industrial formulations). Promising Rh1 samples supported on modified ceria show promising stability even after 900 °C aging. Dithering studies will be performed in collaboration with our OEM collaborators such as Stellantis on most stable/active catalysts.

Collaboration and Coordination with other Institutions

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Collaborators/Coordination

- **U. of Sofia (Bulgaria)**: theoretical modeling by Hristiyan A. Aleksandrov and Georgi N. Vayssilov
- **Stellantis (USA)**: provide guidance toward practicality of TWC work
- **Ford (USA)**: discussions to understand OSC (oxygen storage capacity) of the materials

Remaining Challenges and Barriers

- Improvement of hydrothermal stability of TWC materials
- Clarification of deactivation modes; regeneration strategies for deactivated catalysts
- Sulfur tolerance of TWC formulations

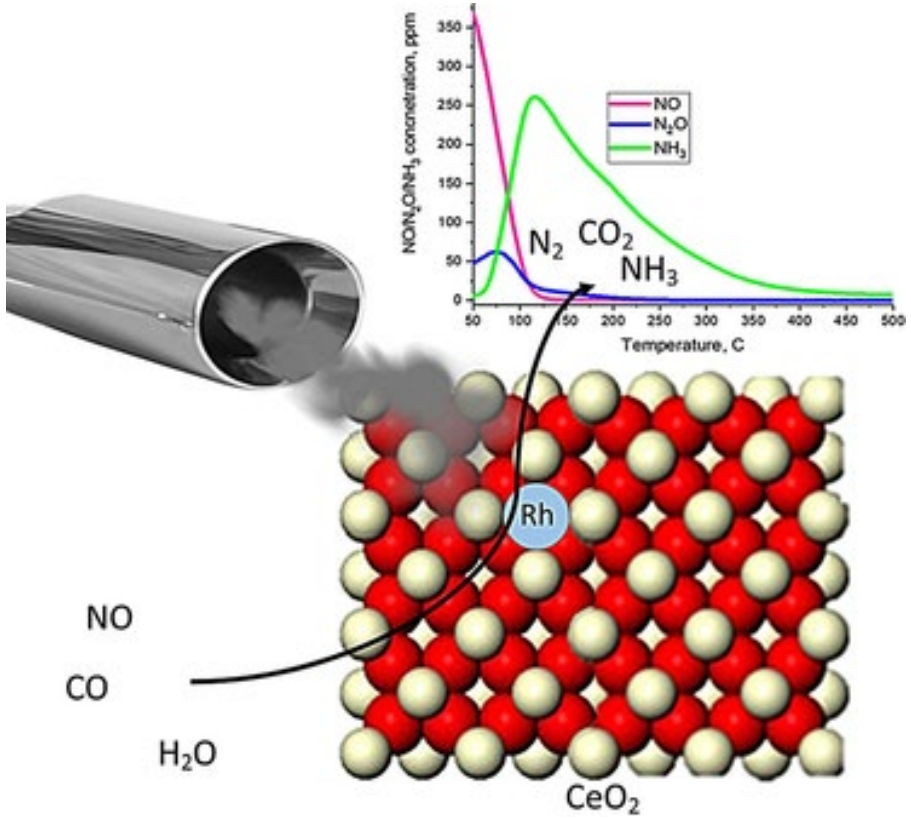
Proposed Future Work

- Investigate hydrothermal stability of promising TWC formulation
- Investigate sulfur tolerance and ways to re-activate sulfur-poisoned materials
- Understand the reasons behind TWC catalyst deactivation and ways to re-generate catalysts
- Develop theoretical models for Rh_1/ceria and evaluate the pathways for NO conversion with the aid of ab-initio quantum-mechanical calculations: this is of paramount importance for establishing predictive reactivity descriptors for a library of materials

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

Summary

- Prepared highly active catalysts with maximized interface between metal atoms (ions) and the support using atom trapping
- Identified ability of single-atom doped materials to perform NO reduction
- Showed lower Rh loadings (0.1 wt%) have ~ similar activity as 5 times higher (0.5 wt%) Rh-loaded catalysts
- Used spectroscopy tools to understand the mechanism and intermediates of NO reduction by CO



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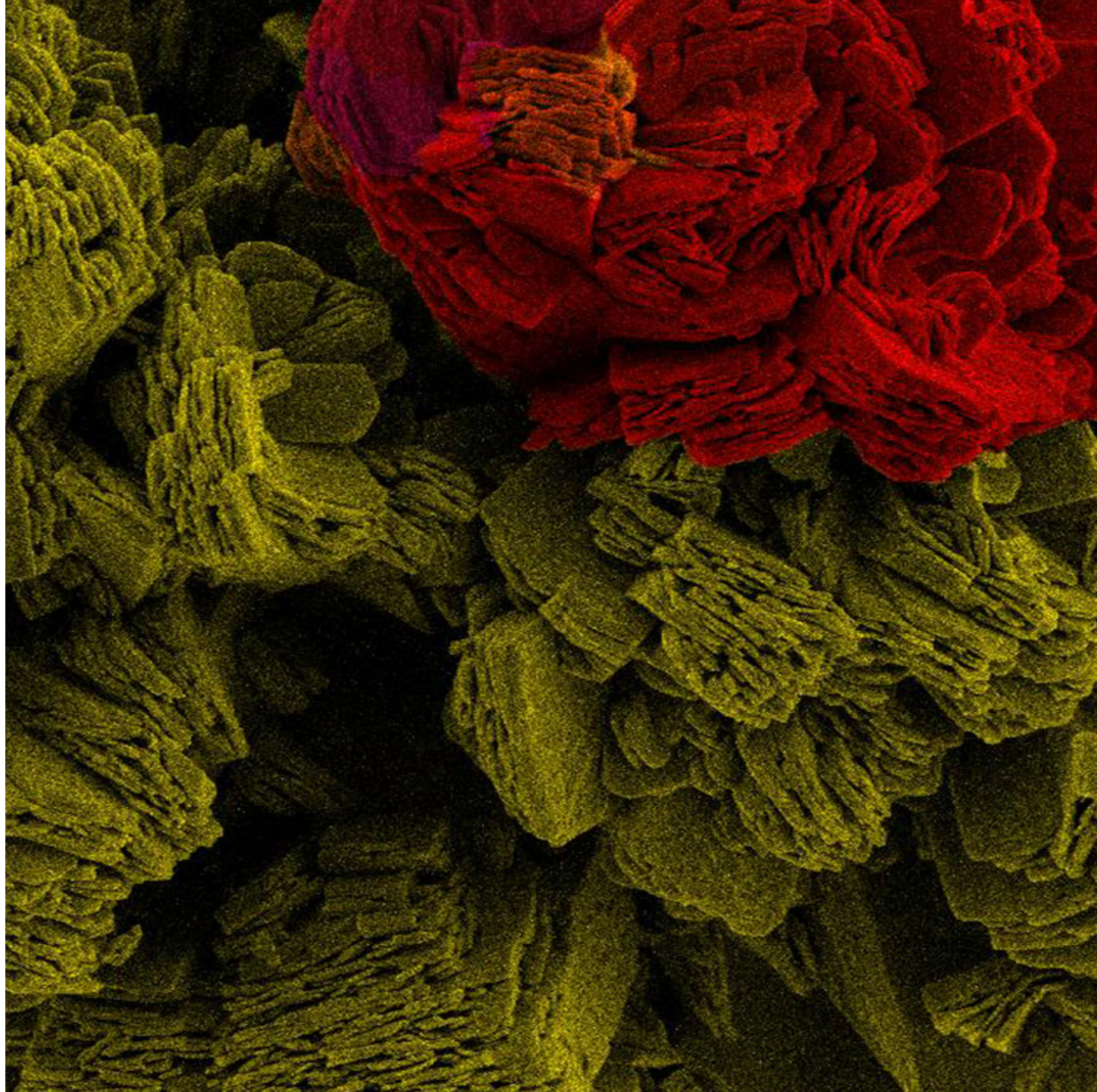
Acknowledgements

DOE EERE Vehicle Technologies Program:

Gurpreet Singh
Siddiq Khan
Ken Howden

Thank you



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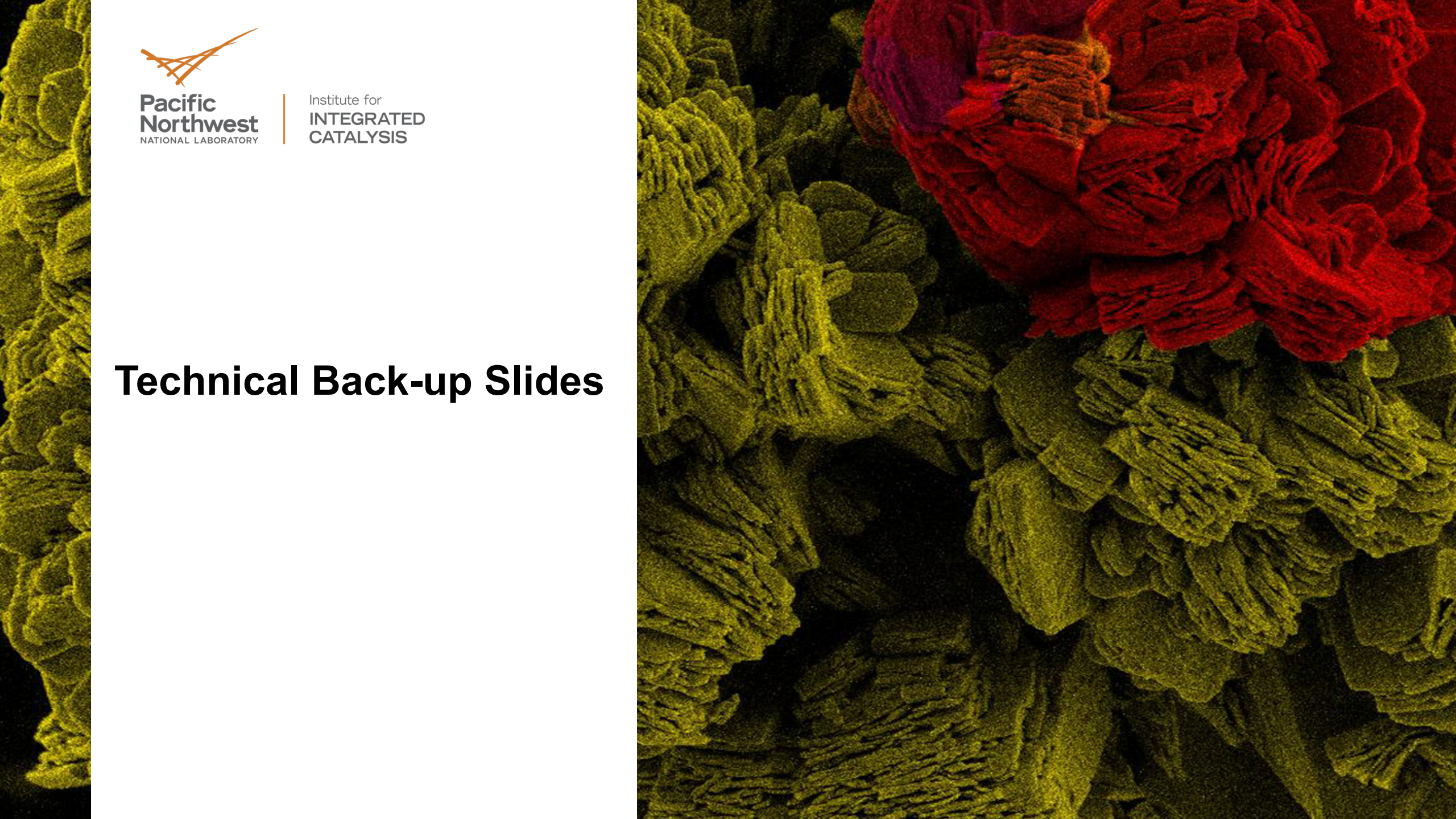
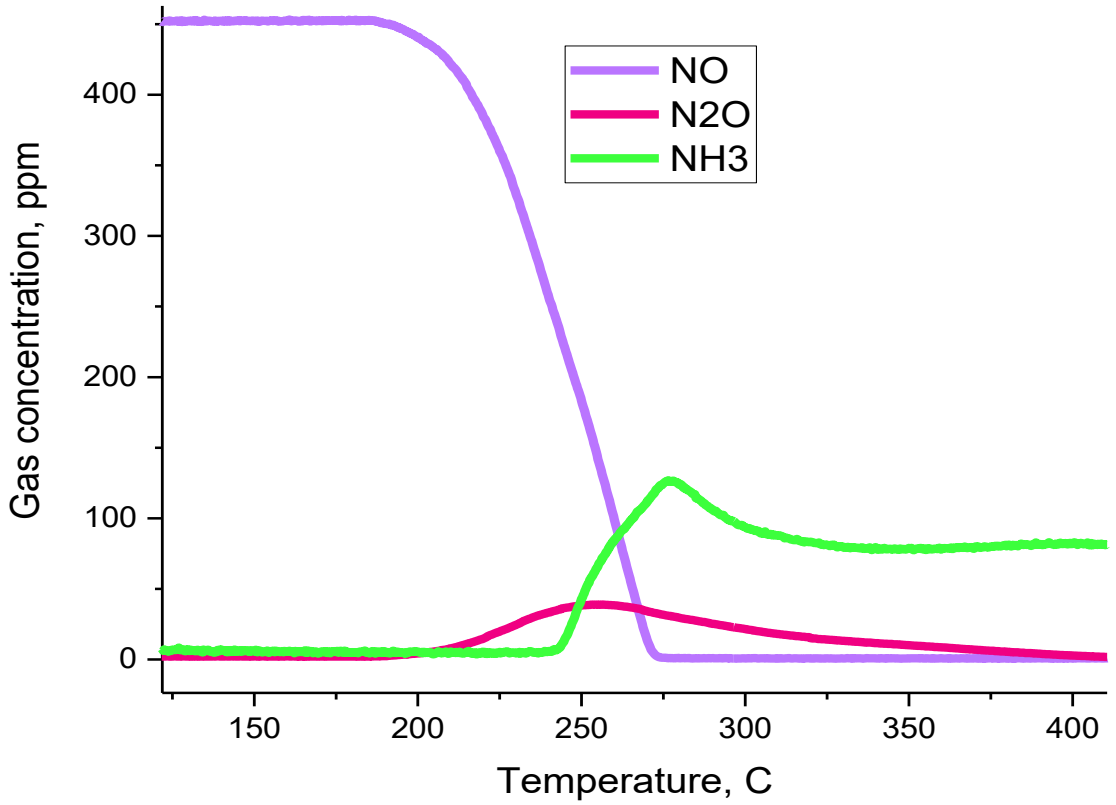
CATALYSIS

Technical Back-up Slides

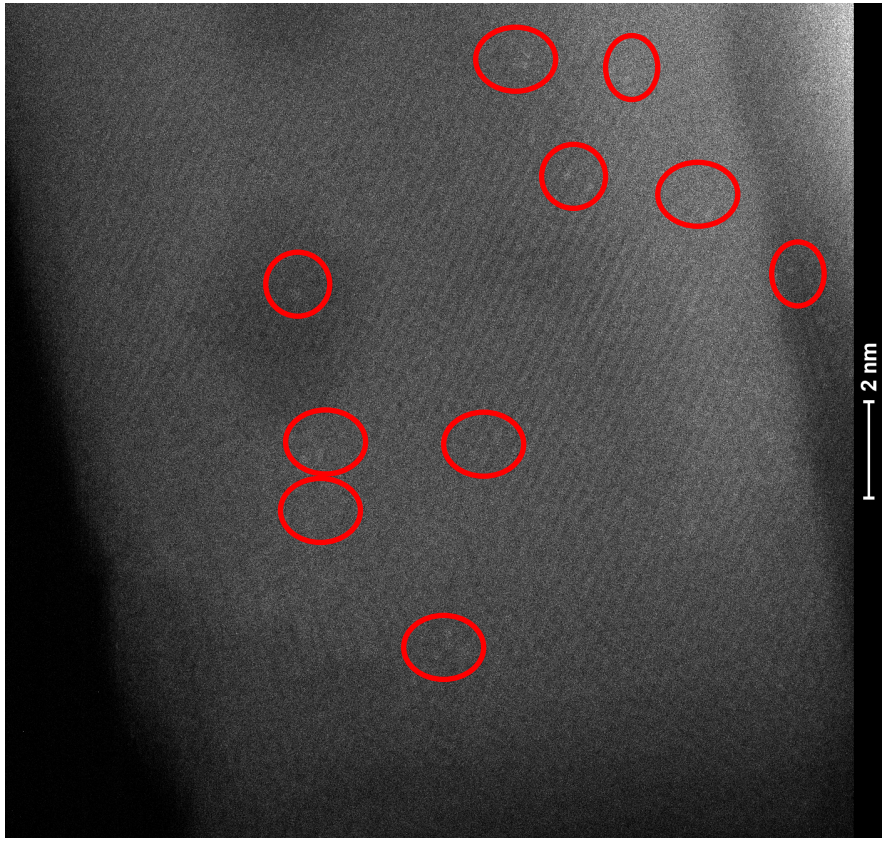


Isolated Rh atoms on redox-inactive alumina shown active for NO reduction by CO



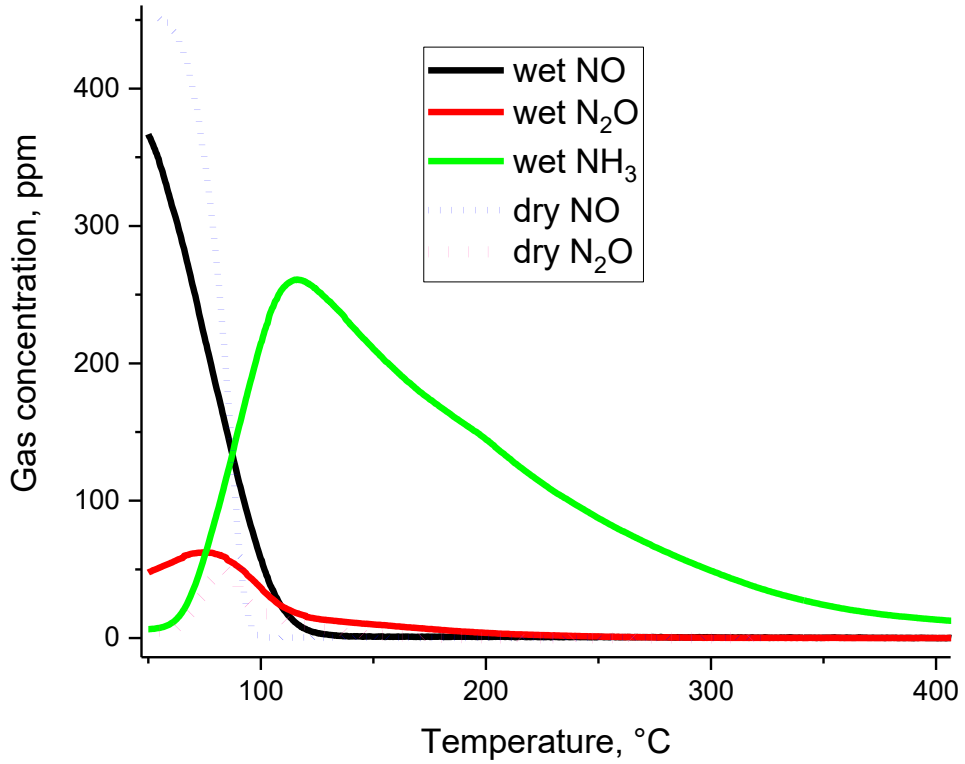
120 mg catalyst. Total flow 300 ml/min. Concentrations: 460 ppm NO, 1750 ppm CO, ~2.2% H2O, balanced with N_2. GHSV ~ 150 L/g*hr, ramp rate 2K/min

- ~0.1 wt% Rh_1/Alumina is active for NO reduction by CO
- Less active than ceria-supported samples
- Single Rh atoms are active sites on different supports



~0.1 wt% Rh/Alumina, HAADF-STEM images after 500 ° C reaction

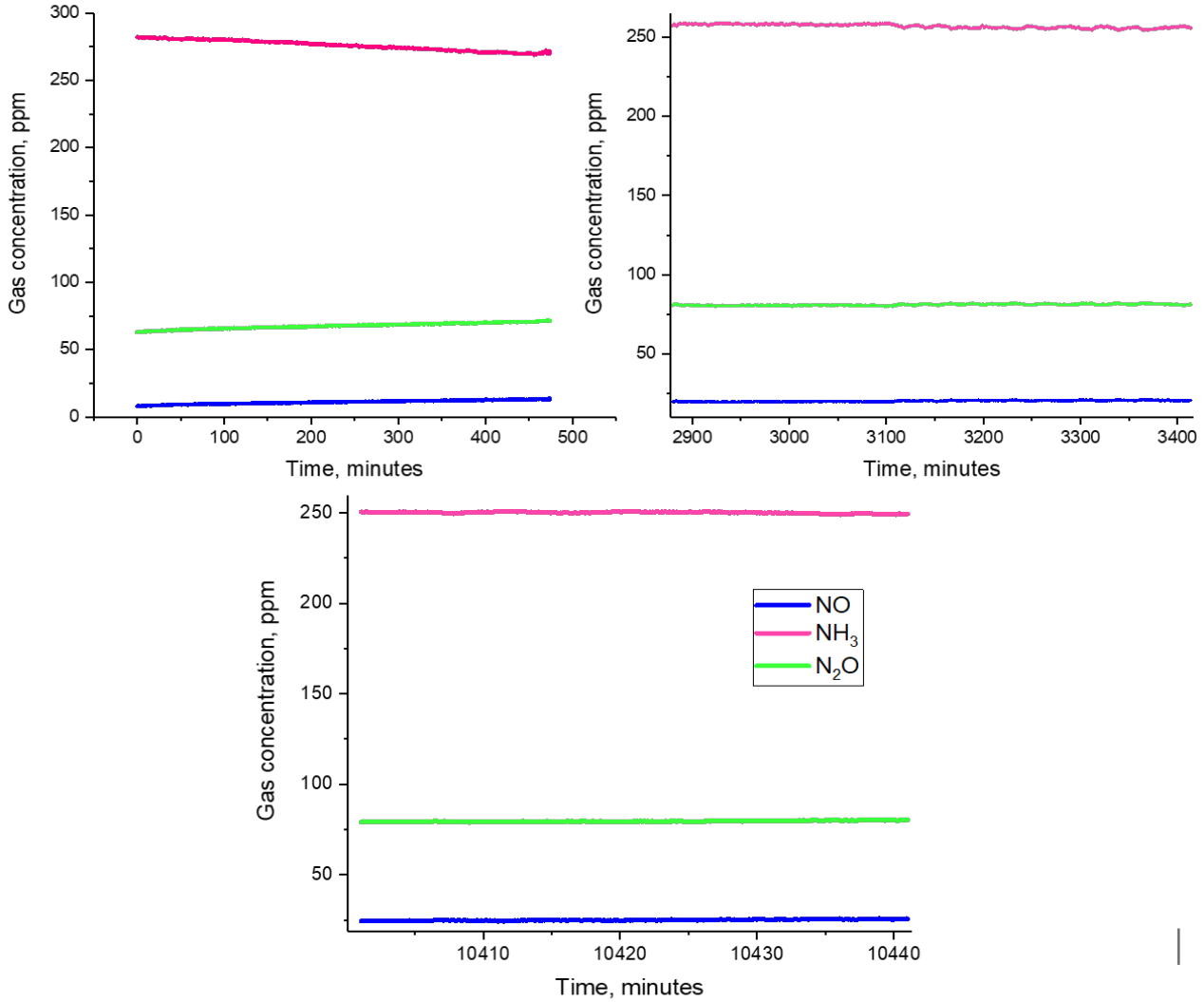
Compare NO+ CO under wet and dry conditions; Evaluate long-term stability for 0.1 wt% Rh/CeO_2



120 mg catalyst $0.1Rh/CeO_2$. Total flow 300 ml/min. Concentrations: 460 ppm NO, 1750 ppm CO, (~2.6 % H2O), balanced with N_2. GHSV ~ 150 L/g*hr, ramp rate 2K/min

- Water promotes reactivity
- Ammonia is formed in the presence of water
- Catalyst shows promising stability

0.1 wt% Rh/Ceria stable at 120 °C under wet conditions for ~ 7.3 days (NO level increases from ~10 ppm to 27 ppm; NH_3 level deceases from 275 to 250 ppm)



CO consumption is simultaneous with H_2O consumption during NH_3 formation: water-gas-shift reaction occurs!

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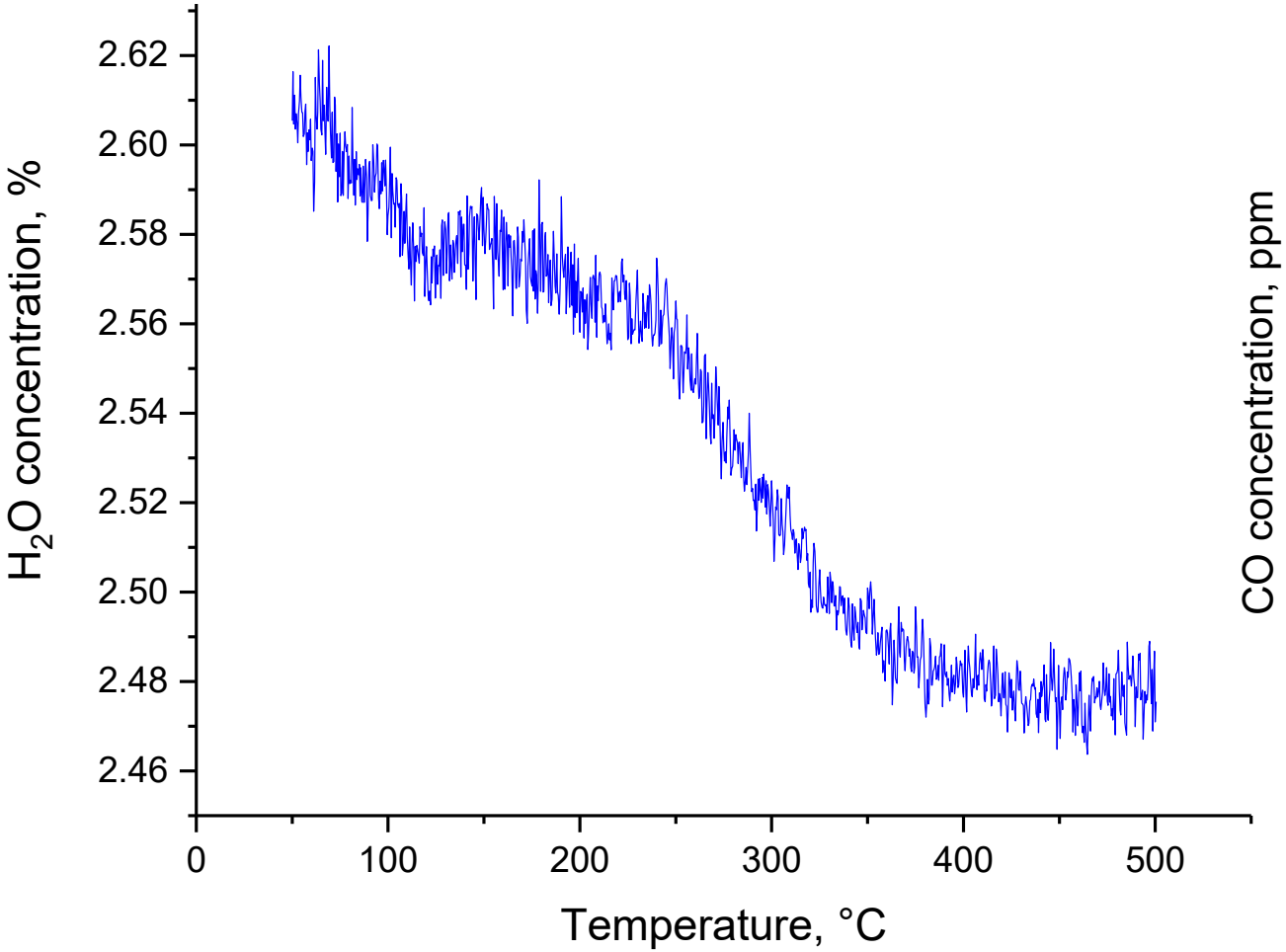

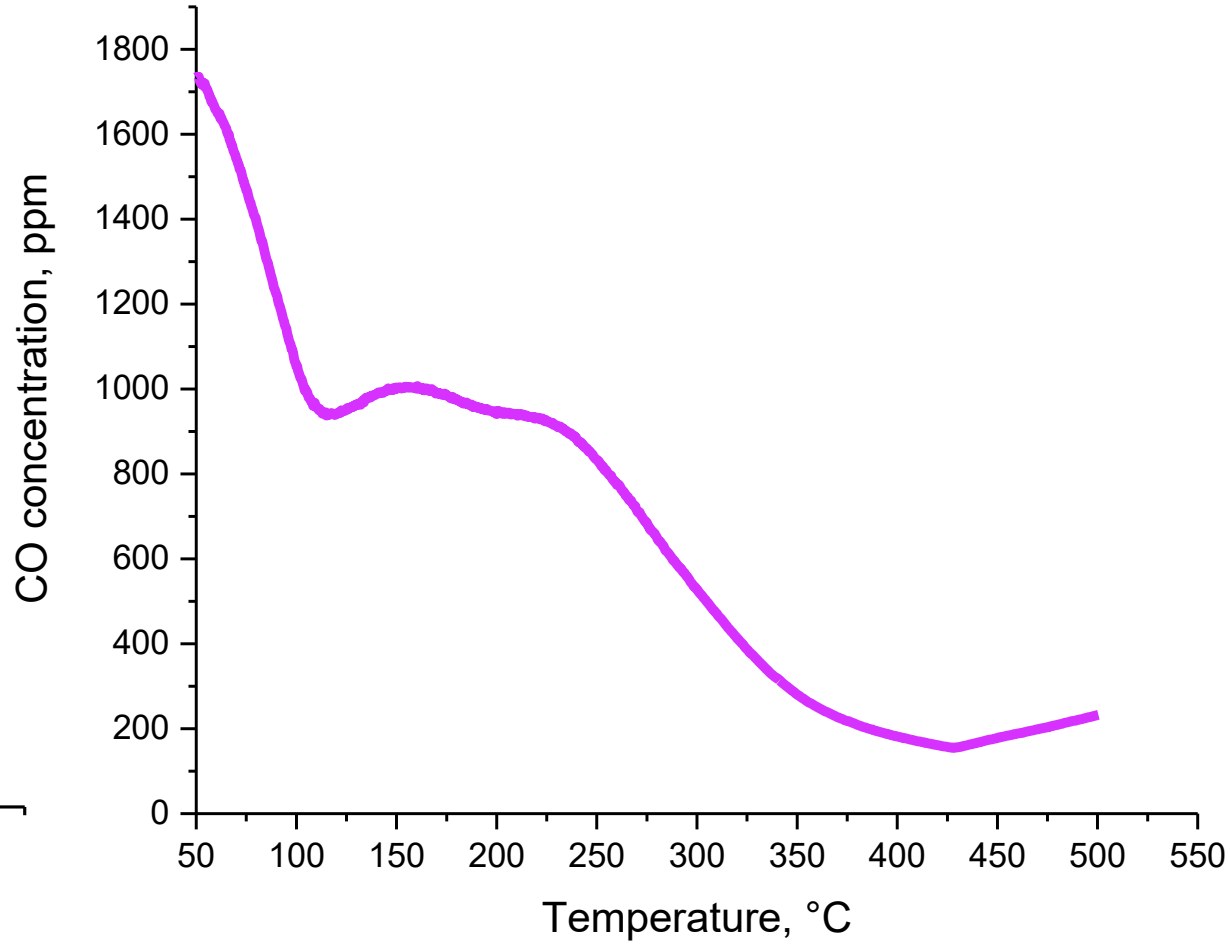

120 mg catalyst 0.1Rh/CeO_2. Total flow 300 ml/min. Concentrations: 460 ppm NO, 1750 ppm CO, (~2.6 % H2O), balanced with N_2. GHSV ~ 150 L/g*hr, ramp rate 2K/min

Infra-red studies show reactivity of Rh_1/CeO_2 at sub-ambient temperatures: Rh1/Zeolite unreactive

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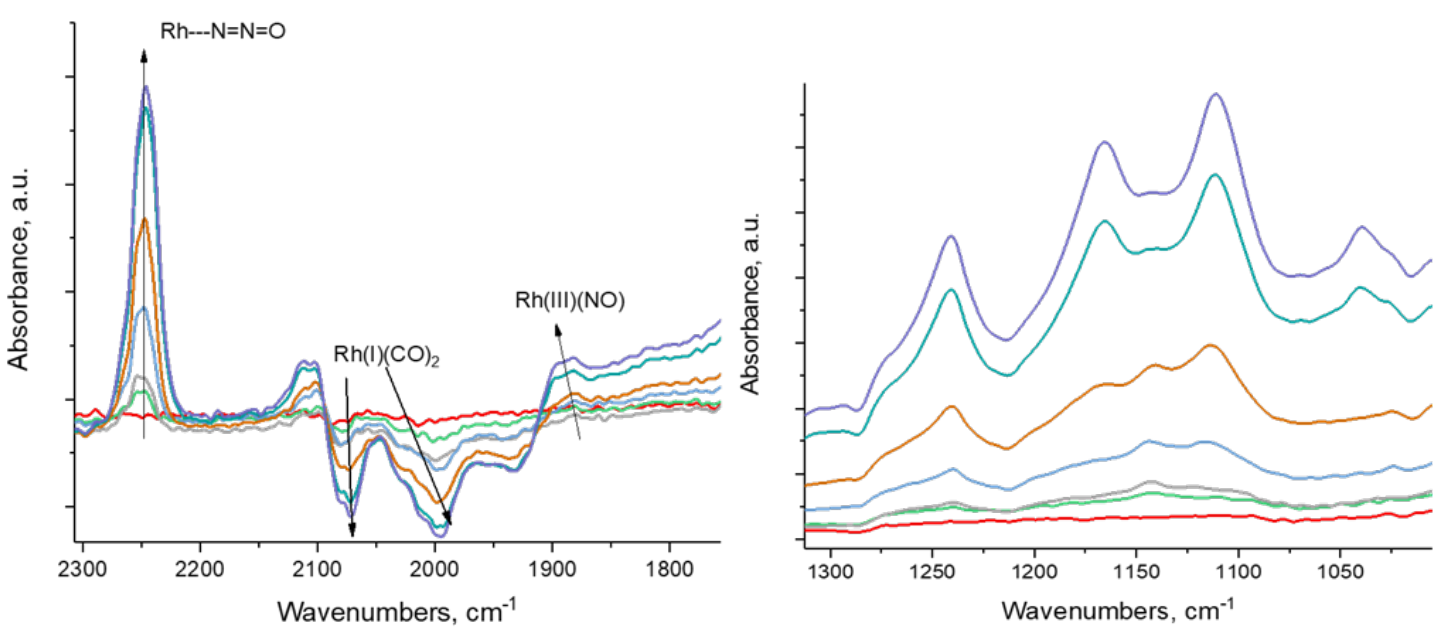
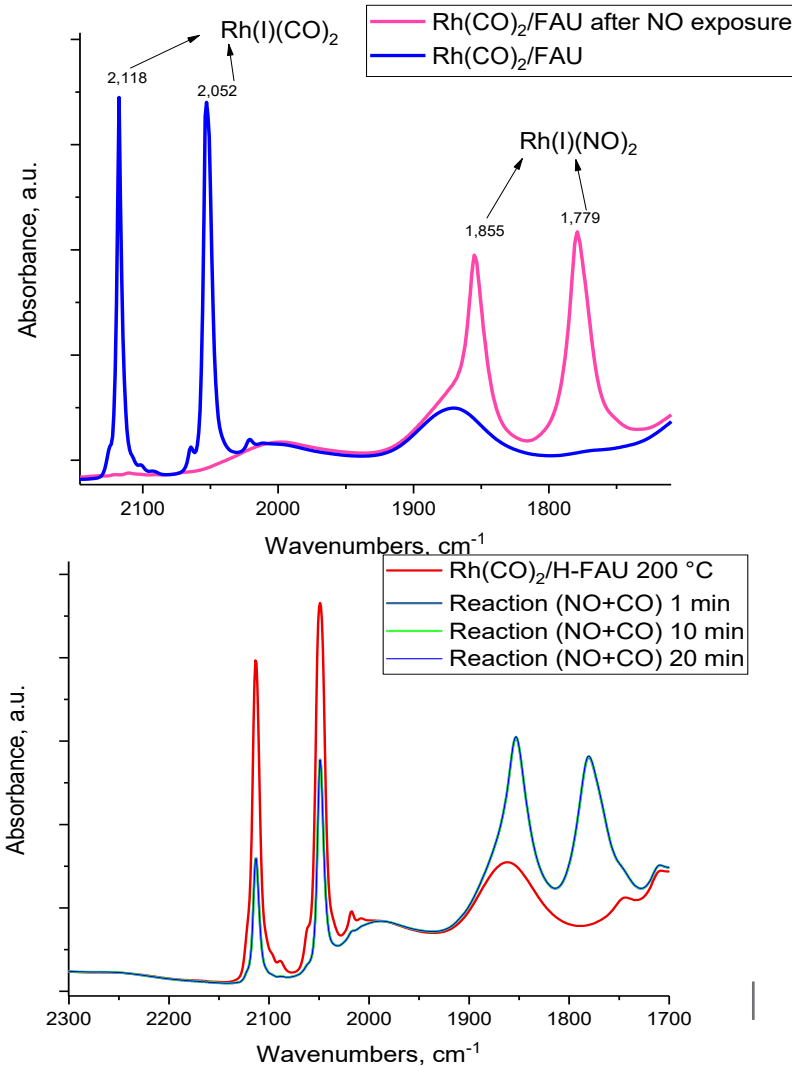
Difference IR spectra during reaction of 0.5 wt% $Rh(I)(CO)_2/CeO_2$ with ~1 Torr NO at ~240 K (1.5 hours). Reaction occurs even at this low-temperature: $Rh(I)(CO)_2$ bands go down, simultaneously N_2O linearly coordinated to Rh center evolves. Hyponitrite bands evolve below 1,200 cm^{-1}

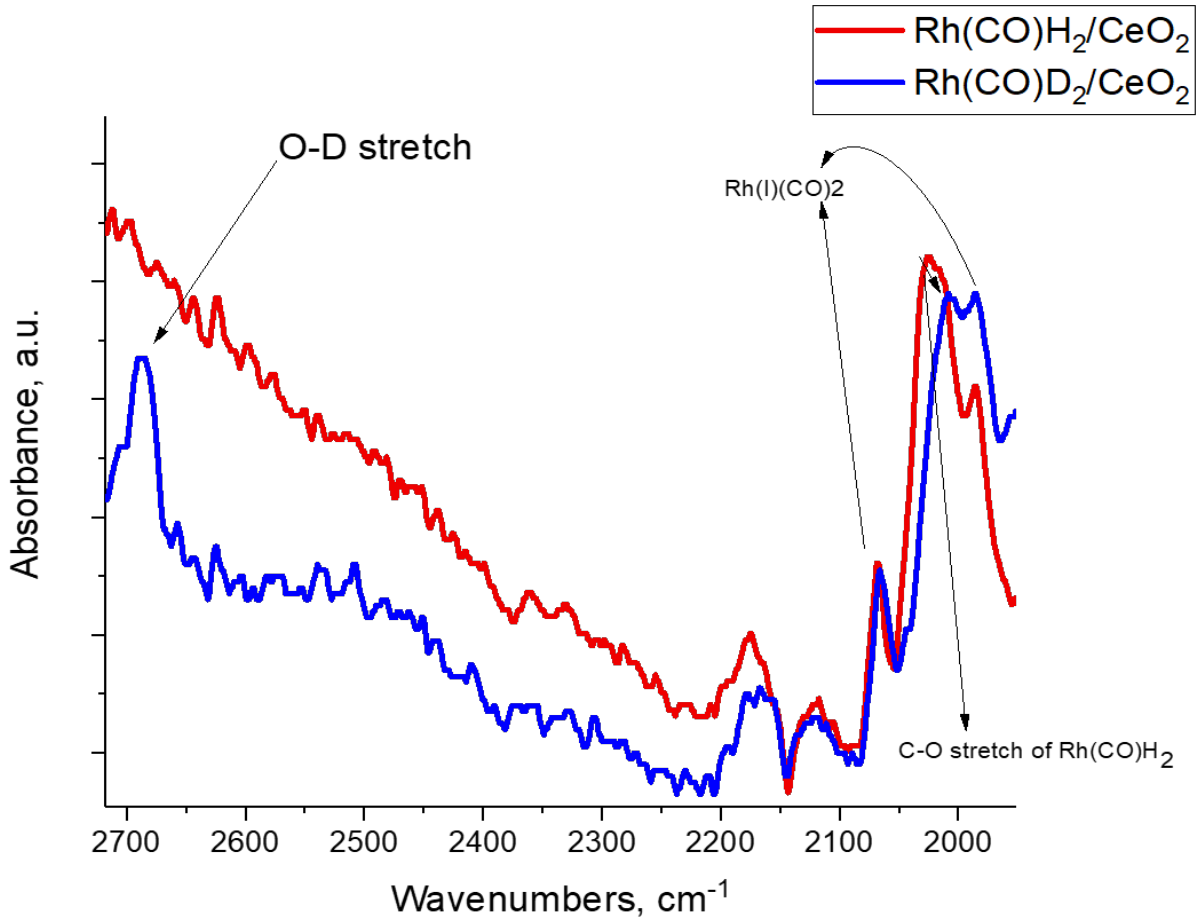


- $Rh(I)(NO)_2$ observed
- Highly electropositive Rh(I) on zeolite unreactive
- Less electropositive Rh(I) on ceria more active
- Reaction occurs even at sub-ambient temperatures at a very low rate

0.5 wt% $Rh(CO)_2$/H-FAU zeolite: $Rh(NO)_2$ formation: unreactive for NO reduction with CO



Trapping intermediates (Rh hydride) with IR provides a pathway to modeling the system



Red spectrum:0.5 wt% $Rh(CO)_2/CeO2$ after interaction with ~ 50 Torr H_2 at 120 ºC.
Blue spectrum: After exposure of $Rh(CO)H_2$/Ceria to 50 Torr D_2.

- Isotopic infra-red experiments provide insight into the nature of Rh(CO)Hx intermediates
- We show the formation of hydrides on Rh/Ceria
- Rh-H species may contribute to ammonia formation