

Institute for INTEGRATED CATALYSIS

Advanced Nitrogen Oxide Storage

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Pacific Northwest National Laboratory

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PNA Project Specifically Addresses the "150°C Challenge" through Fundamental Studies of the Active Sites

- THE 150° CHALLENGE 1 FPGM REDUCTION

	ntent (FOA)	We create chemistry	INIVERSITY OF
Slashing PGM in catalytic co	onverters (FOA)	emistry	Y WASHINGTON STATE
D - BASF We create chemistry	Т₩С		THE UNIVERSITY OF NEW MEXICO
SOFIA UNIVERSITY Advanced Storages	Low T CO Oxidation		
	SCR Protocol		
current Durability of SCR catalysts (Cummins)		Multi-functional Devices	K Y M A N E T I C S
CLEERS PNNL Subprogram Goal Complexity for Off-highway PNNL will:treatment (FOA)	CARUS CORPORATION	Advanced JOHN DEERE	l multi-Functional Iter (John Deere)

...provide the practical & scientific understanding and analytical base, e.g., *molecular level understanding of active sites*, required to enable the development of efficient, commercially viable emissions control solutions and *accurate modeling tools* for ultra high efficiency vehicles.

CLEERS Focus Groups USCAR/USDRIVE ACEC team 21CTP partners

ACE118 (Janos Szanyi)

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



Advanced Combustion and Emission Control Roadmap March 2018



Overview



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Timeline

Status: On-going core R&D

FY2021 funding – \$400K



Barriers and Technical Targets

- Emission controls contribute to durability, cost and fuel penalties
 - Low-temp performance is now of particular concern
- Improvements limited by:
 - Available modeling tools
 - Chemistry fundamentals
 - Knowledge of material behavior
- Effective dissemination of information

Partners

- Oak Ridge National Lab: synergies in evaluating both practical and model materials
- BASF: focus on addressing industry-relevant issues





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Milestones:

Complete initial studies of NOx storage function and application to TWCs for	6/30/2021	on track
stoichiometric combustion engines		

Understand the activation, deactivation, and regeneration of Pd/FER

9/30/2021 on track

Approach



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"Science to Solutions"

- Build on our strong base in fundamental sciences to reveal fundamental aspects of the chemistry and catalytic materials in PNA:
 - Institute for Integrated Catalysis (IIC)
 - Environmental Molecular Sciences Laboratory (EMSL)
 - Synchrotron Facilities
- Work closely with our partners and sponsors
 - ORNL (e.g., synergy in PNA)
- BASF (addressing the issues most important to industry)



NMR





Focus on: Improve hydrothermal stability and performance, understand active sites



High NOx uptake capacity

Very high hydrothermal stability



- High concentration of Pd²⁺ ions (titrated by Co²⁺)
- Very high hydrothermal stability
- Accessibility of cations depends on their crystallographic position
- CO adsorption can modulate Pd ion distribution

Technical Accomplishments: 1.7 wt% Pd/SSZ-13: The fraction of -AI-O-Pd²⁺-O-AI sites is maximized by controlled zeolite synthesis to achieve maximum hydrothermal stability







- Using Sr(OH)₂ instead of NaOH in the synthesis gel maximizes the paired Al³⁺ sites in the SSZ-13 structure. In turn, this affords the preparation of Pd/SSZ-13 with maximum number of Pd²⁺ sites.
- Pd/SSZ-13 prepared by the "Sr method" exhibits high NOx storage capacity (NO/Pd²⁺~1) and very high hydrothermal stability, retaining NOx storage capacity under aging up to 900 °C.
- This preparation method can be extended to other zeolite structures as well.

Technical Accomplishments: Cycling of 1.7 wt% Pd/FER: Limited (recoverable) performance degradation after 30 cycles



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220 ppm NOx (200 ppm NO and 20 ppm NO₂), 4000 ppm CO, 14% O₂, 3% H₂O, balanced with N₂ at a flow rate of 300 sccm

In order to address concerns about long-term cyclability/regenerability of Pd/Zeolite PNA, repeated NOx uptake/release + oxidative regeneration is conducted.

- Gradual decline in NOx uptake; performance stabilizes after ~20 cycles. NOx uptake capacity after 30 cycles is ~70% of that in the 1st cycle
- Calcination at 700 °C completely recovers NOx uptake capacity
- Origin of performance degradation? (current FTIR studies will shed light on possible cation movement during cycling and under different exhaust conditions) (long-term cycling experiments are currently ongoing on other PNA materials)

Technical Accomplishments: 0.5 wt% Ru/CeO₂: Highly active PNA and RNA



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NOx uptake and release



 $^{^{\}sim}200$ ppm NOx, 13% O_2, 3% H_2O, 360 ppm CO balanced in N_2. Total flow rate 300 sscm/min.

- Why is Ru/CeO₂ an interesting material?
 - Hydrothermally stable single Ru atoms can be prepared by atom trapping (low cost of Ru!)
 - Single Ru atoms can bind NO (DFT) (PNA) while CeO₂ can store NOx as nitrites/nitrates (RNA)
 - Possible issue: S poisoning
- Single atom Ru/CeO₂ shows high NO_x uptake capacity.
- Two types of NO_x uptake:
 - Passive NO_x adsorption on single Ru ions
 - Reactive NO_x uptake on the CeO₂ support
- Complex NO_x release profile associated both Ru ions and the CeO₂ support
- Efficient NO oxidation on Ru/CeO₂ promotes nitrate formation on the support oxide, and high temperature NO_x release.

Technical Accomplishments: 0.5 wt% Ru/CeO₂: Characterization: TEM/EDS and FTIR







- Very high (atomic) Ru dispersion over the CeO₂
 Ru atoms are uniformly distributed on the CeO₂
- A: nitrosyls on Ru ions in different coordination
- B: The main absorption band converts into one that represent NO-Ru near surface defect on the CeO₂
- **C**: The original nitrosyl band reproduced
- **D**: Nitrates form when $O_2 + H_2O$ are present.

Technical Accomplishments: 0.5 wt% Ru/CeO₂: Hydrothermally stable PNA and RNA



0.5 wt% Ru/CeO₂ resh 0.5 wt% R Aged 0.5 wt% R 250 400 200 150 Gas concentration, ppm NOx 300 600 C 200 NO 100 NO₂ 100 G 20 10 30 50 60 70 Time, minutes

Aging: 750 °C; 10 % H₂O; 10 h

Uptake/release: 220 ppm NOx (200 ppm NO and 20 ppm NO₂), 370 ppm CO, 14% O₂, 3 % H₂O, balanced with N₂ at a flow rate of 300 sccm Uptake: at 100 °C; Release: 10 °C/min from 100 to 600 °C

- No performance degradation after hydrothermal aging at 750 °C in 10 % H₂O stream.
- Both PNA and RNA functions are retained after the high temperature hydrothermal aging.
- The temperature of the maximum rate of CO oxidation coincides with rate of NO desorption.
- After hydrothermal aging the Ru/CeO₂ material retains its high activity for high temperature NO oxidation.

Technical Accomplishments: 0.25 wt% Ru/CeO₂: High stability during multiple uptake/release cycles



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Uptake/release: 200 ppm NO, 2000 ppm CO, 14% O₂, 3 % H₂O, balanced with N₂; flow rate: 300 sccm; Uptake: at 100 °C; Release: 10 °C/min from 100 to 550 °C

- No degradation in NOx uptake release during the 10 cycles studies.
- Stable CO oxidation activity.
- Similar to the Pd-zeolite PNAs, the onset of NOx release coincides with the onset of CO oxidation.
- High NOx/Ru ratio substantiates both PNA and RNA functionality of Ru/CeO₂.
- No loss of Ru during cycling (atom-trapped single atoms are highly stable)

Responses to reviewers' comments from previous year



- Most of the comments from the reviewers last year were supportive and complimentary, especially regarding our approach and technical accomplishments.
- Some comments/recommendations included:
 - 1. "... not much has been done to keep the storage level high with different aging."
 - 2. "... seems like a report on making a few varieties of PNA by changing the zeolites, but it is not much focused toward understanding ..."
 - 3. "The project would benefit from more collaboration with ORNL staff who are also working on PNAs."
 - 4. "...not very relevant... cost of Pd (active metal for PNA) increased a lot in last few years compared to Pt."

PNNL response:

- 1. Preparing new zeolite structures in which the active metal (Pd) cations located in different coordination environment is one of the ways we tackled this problem. Tailoring the Al ion distribution in a given zeolite framework was aimed at improving performance stability by maximizing –Al-O-Pd-O-Al- sites.
- 2. We believe that the results of our extensive spectroscopy and microscopy studies clearly enhanced the understanding how PNA materials operate and guided the development of more active and stable PNAs.
- 3. We are working very closely with our ORNL colleagues on cross testing samples prepared at different labs, and on the effect of HCs on PNA performance.
- 4. New studies on low metal-loaded Ru/CeO_2 materials were conducted to address this concern.



Collaboration and Coordination with other Institutions

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Collaborators/Coordination

- Oak Ridge National Lab: Todd Toops, Josh Pihl, Pranaw Kunal, Sreshtha Sinha Majumdar (sample exchange for performance cross check)
- BASF: Saeed Alerasool, Pascaline Tran, Xinyi Wei, Jeff Hoke (monthly discussion; sample exchange for cross reference studies)
- Sofia University, Bulgaria: Hristiyan A. Aleksandrov, Iskra Koleva and Georgi N.Vayssilov (DFT calculations: adsorbate binding, reaction mechanisms, spectra interpretation)
- CARUS: Ken Pisarczyk, Slava Iablokov and Seth Schugars (discussions on reactive NOx storage; sample exchange)

Acknowledgements

DOE EERE Vehicle Technologies Program: Gurpreet Singh, Ken Howden and Siddiq Khan.



- Understand the PNA/RNA performance of Ru/CeO₂ storage materials under stoichiometric exhaust gas conditions. Poisoning of these storage materials (S, P, etc.).
- Establish structure/performance correlations for zeolite-based PNAs, in particular Pd/FER, by continued spectroscopy investigations.
- Understand performance degradation/regeneration of Pd/FER during long-term cycling/reoxidation.
- Interference with other catalysts such as DOC.



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- Evaluate PNA/RNA performances of Ru/CeO₂ under stoichiometric exhaust gas conditions.
- Understand the mechanisms of possible PNA/RNA degradation (including S poisoning) and provide guidance in mitigating it.
- Understand the activation, deactivation and regeneration of Pd/FER: effects of longterm cycling.

Understand the potential interference and interactions with DOC etc.

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





- Developed a new synthesis method for SSZ-13 zeolite using Sr(OH)₂ in the synthesis gel in order to direct Al ion incorporation into the zeolite framework with maximum number of "Al ion pairs" that led to better stability. (This method can be extended to the preparation of other zeolites as well.)
- Demonstrated superior hydrothermal stability of the Pd/SSZ-13 PNA material prepared by Sr(OH)₂ in the synthesis gel. This adsorber retained its PNA properties up to 900 °C hydrothermal aging.
- Demonstrated long-term performance degradation/reactivation of Pd/FER (~30 % loss after 30 cycles) and initiated FTIR studies to understand the cause of loss in NOx uptake.
- Prepared, characterized and tested hydrothermally stable single atom Ru/CeO₂ materials by atom trapping:
 - High PNA/RNA performance with no NOx uptake degradation during cycling studies.
 - Very stable NOx storage/release performance during 10 repeated cycles and no Ru loss.
 - Low temperature NOx release profile coincides with the onset of CO oxidation.
 - Exhibited high NO oxidation and even some TWC activities at elevated temperatures (>300 °C).



Technical Backup Slides



Technical Accomplishments: Ru/CeO₂: DFT calculations identify the location and oxidation state of Ru and Ru-NO complexes on ceria



												b	
a-10_NO		b-10_l	NO			C-	10_NC)	d-10_N	10		e-10	D_NO
	RuO(NO)/Ce ₂₁ C	$D_{42} E_{rel}{}^a$	BE ^b	Evac	$N_s{}^c$	N _s (Ru) ^d	#(Ce ³⁺) ^e	$q(Ru)^h$	Ru-O	Ru-N	$\overline{\Delta(N-O)^{f}}$	$\nu(N-O)^g$	
	a-10_NO	1.72	-3.11		1	0.8	0	1	184;190	179	2.3	1763	
	c-10_NO	1.42	-2.26		1	0.7	0	1	195;200;204	177	1.4	1824	
	b-10_NO	2.91	-1.03		1	0.7	0	1	185;209;224	177	1.7	1799	
	d-10_NO	1.91	-1.65		1	0.7	0	1	182;190	178	2.7	1733	
	e-10_NO	0.00	-3.00		1	0	1	2	191;212;213; 213; 213	179	1.1	1840	
	e-10_NO_vac_	b 2.08		3.32	1	0	3	2	192;212;212; 214; 215	178	1.2	1832	
	e-10_NO_vac_	a 0.00		1.24	3	0.25	4	2	198;199;202; 204	173	2.4	1788	
	e-10_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 Ce⁴⁺, thus NO⁺ ligand and a Ce³⁺ center are formed, while the formal charge of the Ru remains +2.

0.5 wt% Ru/CeO₂: Stable NO oxidation performance under both dry and wet conditions



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0.5 wt% Ru/CeO₂ is an active and stable NO oxidation catalyst.

NO oxidation performance of 0.5 wt% Ru/CeO₂ is retained under both dry and wet conditions.

Ru/CeO₂: High TWC performance at stoichiometric exhaust gas composition

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- Complete NOx removal above 140 °C (0.5 wt% Ru) and 180 °C (0.1 wt% Ru).
- Highly active WGS and CO oxidation catalysts.