ACE#169

Greatly Reduced Vehicle PGM Content Using Engineered, Highly Dispersed Precious Metal Catalysts

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Yipeng Sun, Pascaline Tran, **Xinyi Wei** (BASF)
Konstantin Khivantsev, Shari Li, Janos Szanyi (PNNL)
Abhaya Datye (UNM)

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This presentation does not contain any proprietary, confidential, or otherwise restricted information.

Overview

Timeline

- 39-mon project funded by FOA DE-FOA-0002197
- Status:
  - Start date – Oct. 1, 2020
  - End date – Dec. 31, 2023

Budget

- DOE share: $2.5M
  - WSU: $790K
  - Stellantis : $195K
  - BASF: $195K
  - PNNL: $780K
  - UNM: $540K
- Cost share: $625K
  - Stellantis: $325K
  - BASF: $300K

Barriers

- Lack of cost-effective and sustainable emission control
- Durability of emissions control devices

Partners

- WSU
- Stellantis
- BASF
- PNNL
- UNM

BASF We create chemistry

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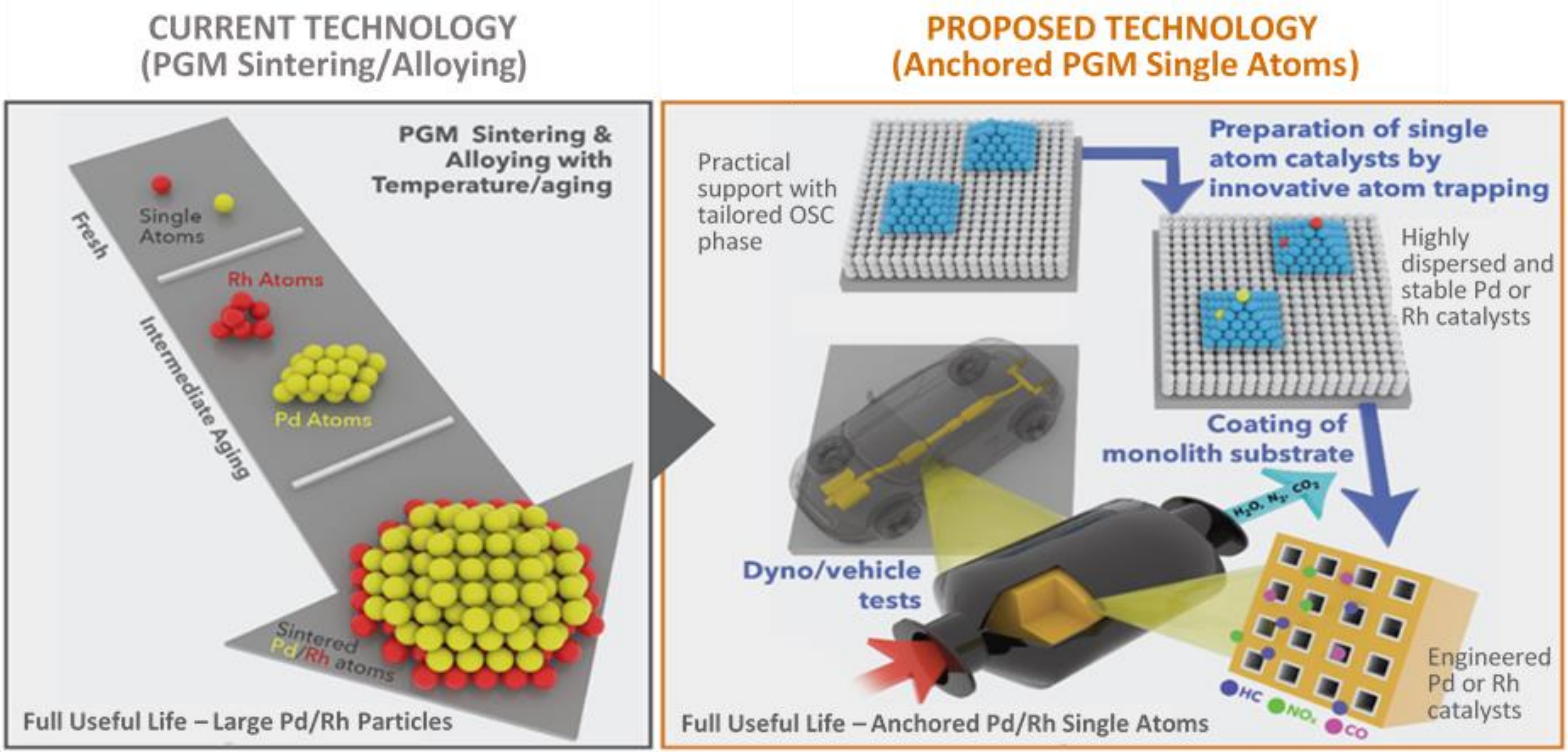
Relevance

- Minimize PGM content in stoichiometric three-way catalyst systems for greater strategic material sustainability and cost competitiveness
- Provide high reactivity at low temperatures (USCAR 150˚C Challenge) to remediate cold start emissions
- Assure Bin30/SULEV30 emissions compliance, which requires near 100% conversion efficiency over the full useful life of the vehicle
  - Mitigate sintering, intermixing, and alloying of the PGM components
  - Minimize the detrimental effect of poisons derived from the fuel and lubricants

Our end goal is to demonstrate vehicle FTP, US06, and HWFE test performance on par with current (SULEV30/20) systems that employ 2x-4x higher levels of PGM.

Approach



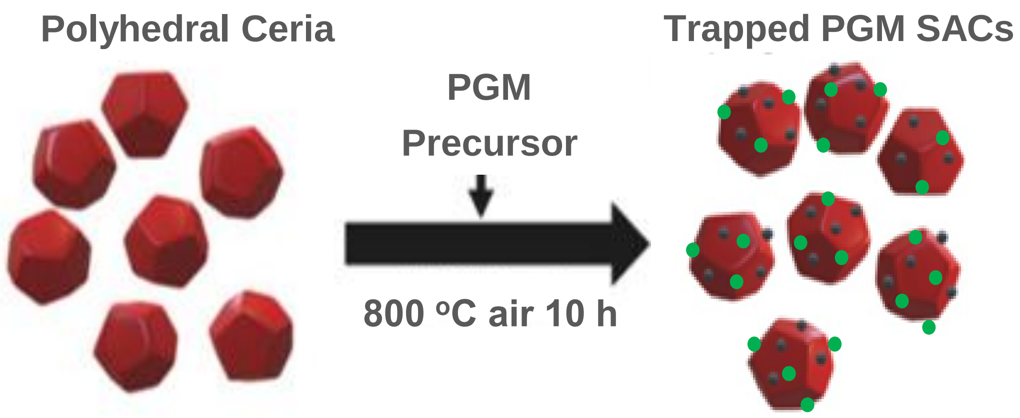
C.K.Lambert, ***Nature Catalysis*** 2019, 2, 554–557
S.B.Kang, S.H.Oh, et al, ***Chem.Eng.J.*** 2017, 316, 631-644

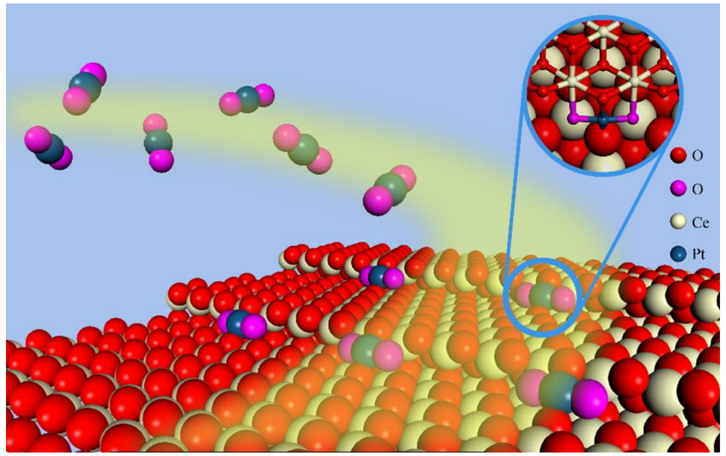
Jones *et al*, ***Science,*** 2016, 353 (6295),150-154; Kunwar *et al*, ***ACS Catalysis***, 2019, 9, 3978-3990; Alcala *et al*, ***Appl.Catal.B***, 2021, 10.1016/j.apcatb.2020.119722

Overcome major limitations of current TWCs (sintering/alloying) by employing atom trapping (*at*SACs) technology to create single atom catalysts.

Technical Accomplishments and Progress

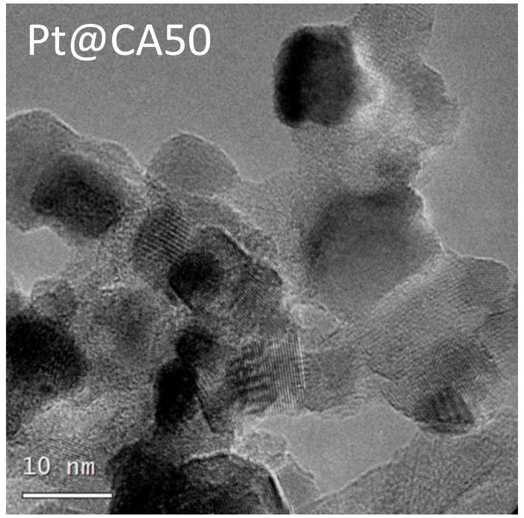
Preparation of thermally stable SACs on ceria containing supports by atom trapping





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

Confirmation of atom trapping on BASF support by HRTEM

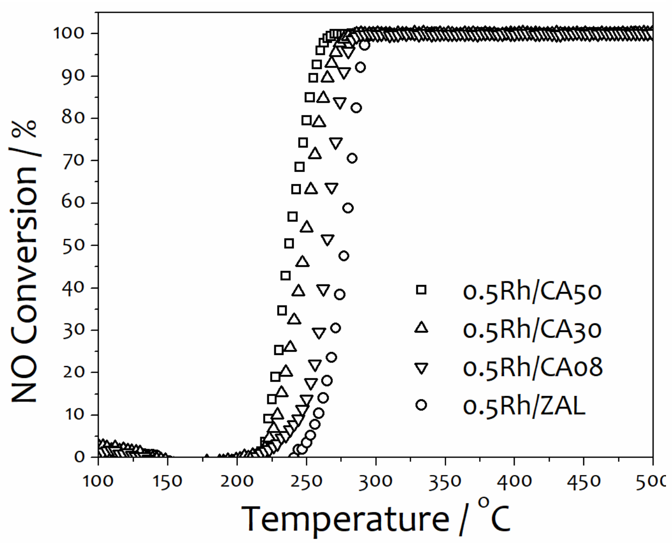


- Initial reference SACs employed four commercially relevant BASF supports, completed full characterization at WSU, UNM and PNNL
- Confirmed efficacy with the lead candidates for atom trapping with Pt
  - SACs inherently more stable at higher temperatures due to the high-temperature preparation process

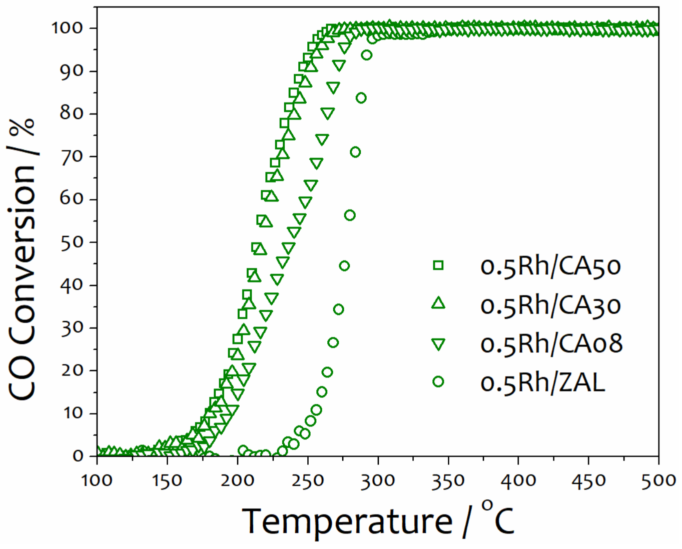
Technical Accomplishments and Progress

Baseline BASF 0.5% Rh catalysts (after hydrothermal aging) in NO reduction by CO

NO Conversion vs Temp



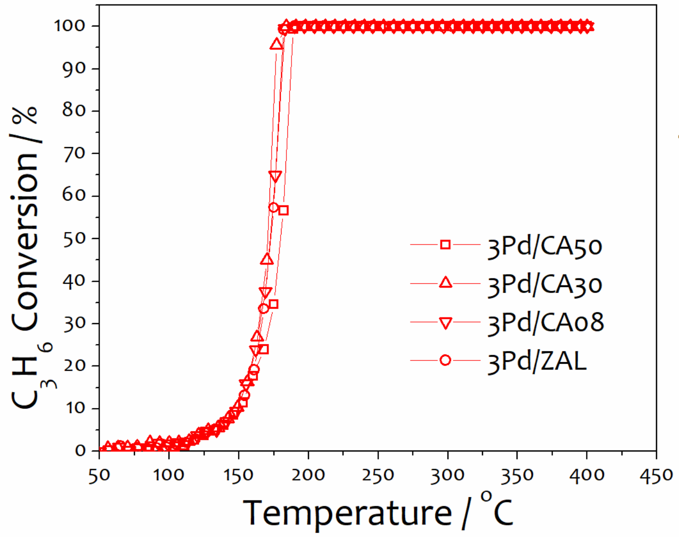
CO Conversion vs Temp



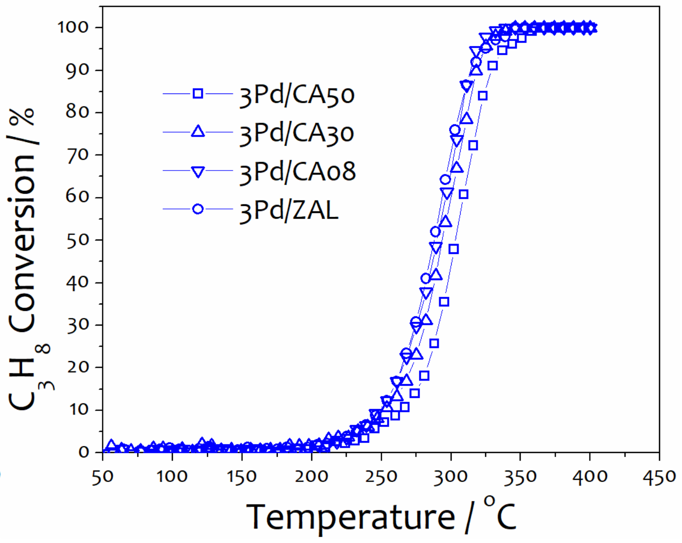
460 ppm NO, 2350 ppm CO, 800 ppm O_2, 4-5 % H_2O, N_2 balance, 150 L/g-h

Baseline BASF 3%Pd catalysts (after hydrothermal aging) in propylene and propane oxidation

Propylene Conversion vs Temp



Propane Conversion vs Temp



125 micron (10mg cat + 20mg carbide), Reduced at 200°C for 1hr in 10%H_2/Ar, 2°C /min, 0.2%propane, 0.2% propylene, 2%O_2, balanced with N_2, GHSV=150 L/g·hr

- Fully characterized and established performance of 8 baseline catalysts (0.5%Rh on 4 BASF supports, and 3%Pd on 4 BASF supports) prepared by BASF under representative hydrothermal aging (de-greening, 800°C, 10% H_2O, 10 hr) and testing conditions

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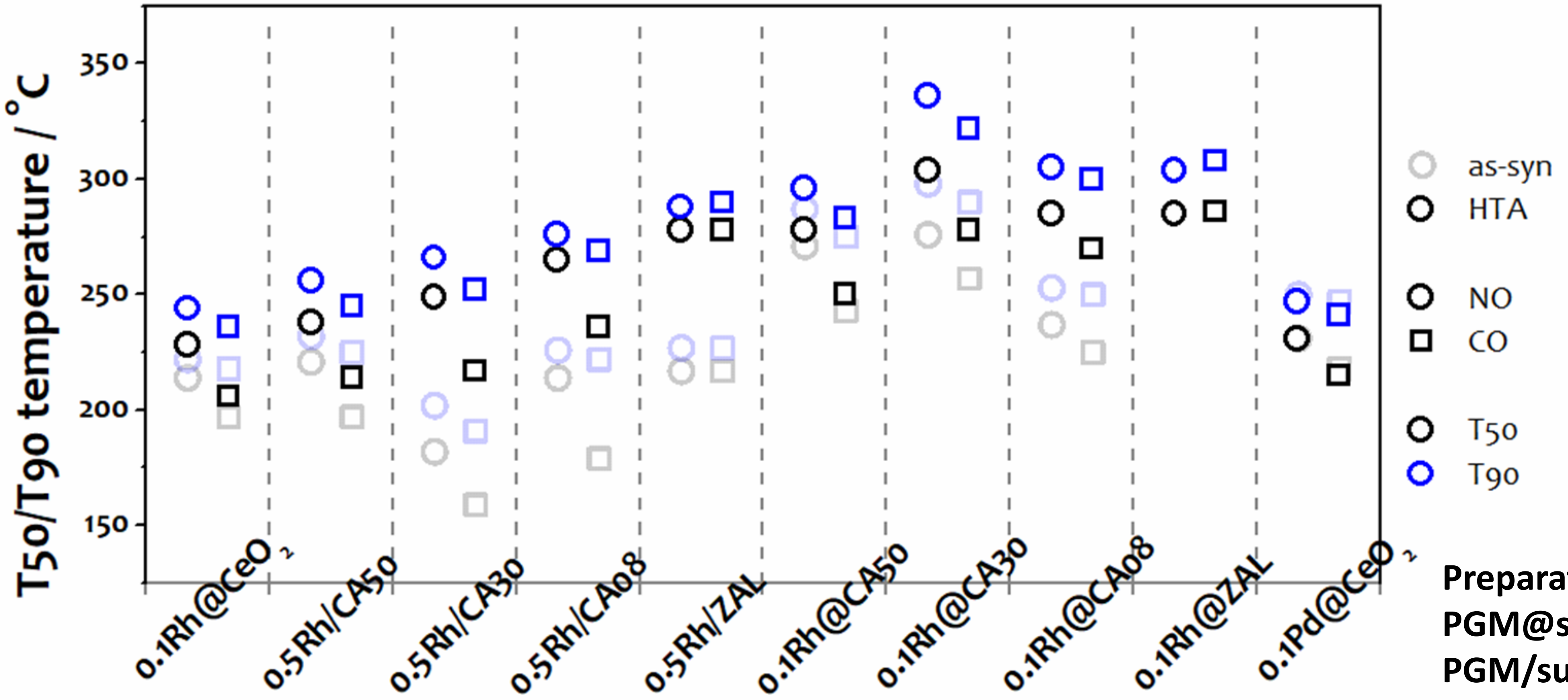
Comparison of single atom catalysts with baseline BASF catalysts in NO reduction by CO (after HTA)



Preparation method:
PGM@support: atom trapping
PGM/support: conventional impregnation

460 ppm NO, 2350 ppm CO, 800 ppm O_2, 4-5 % H_2O, N_2 balance, 150 L/g-h, before and after HTA (800 °C, air, 10 % H_2O, 10 h), using 2nd LOC (stable performance)

- Synthesized atom trapping catalysts with 5x and 2x lower Rh and Pd, respectively, than baseline BASF catalysts
  - Several candidates achieved similar or better T50/T90 NO_X reduction by atom trapping
- Pd SAC NOx performance similar to the best Rh SAC catalysts at equivalent pgm loading!

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Collaboration and Coordination with Other Institutions

Yong Wang (WSU), Project Lead PI
Craig DiMaggio, Quan Do (Stellantis), Co-Lead PI
Pascaline Tran (BASF), Co-Lead PI

Abhaya Datye
(*at*SAC development, TEM characterization)
Yong Wang, WSU
(*at*SAC optimization, *in situ* characterization)
(UNM+WSU)

Janos Szanyi
Konstantin Khivantsev
(USDRIVE protocol test, baseline BASF catalysts, advanced characterization)
(PNNL)

Pascaline Tran
Yipeng Sun, Xinyi Wei
(Washcoat development, modified alumina supports, performance simulation)
(BASF)

Craig DiMaggio
Kiran Premchand
Vencon Easterling
(Design, package, and manufacture of converters, Dyno/vehicle test, cost models)
(Stellantis)

TRL3 **TRL4** **TRL5** **TRL6** **TRL7**

Technology Development — **Technology Transfer/Validation** — **Technology Demonstration**

Commercialization Lead (Quan Do, Stellantis)

Acknowledgements

DOE Vehicle Technologies Program:

Siddiq Khan, Ken Howden, Gurpreet Singh

Proposed Future Research

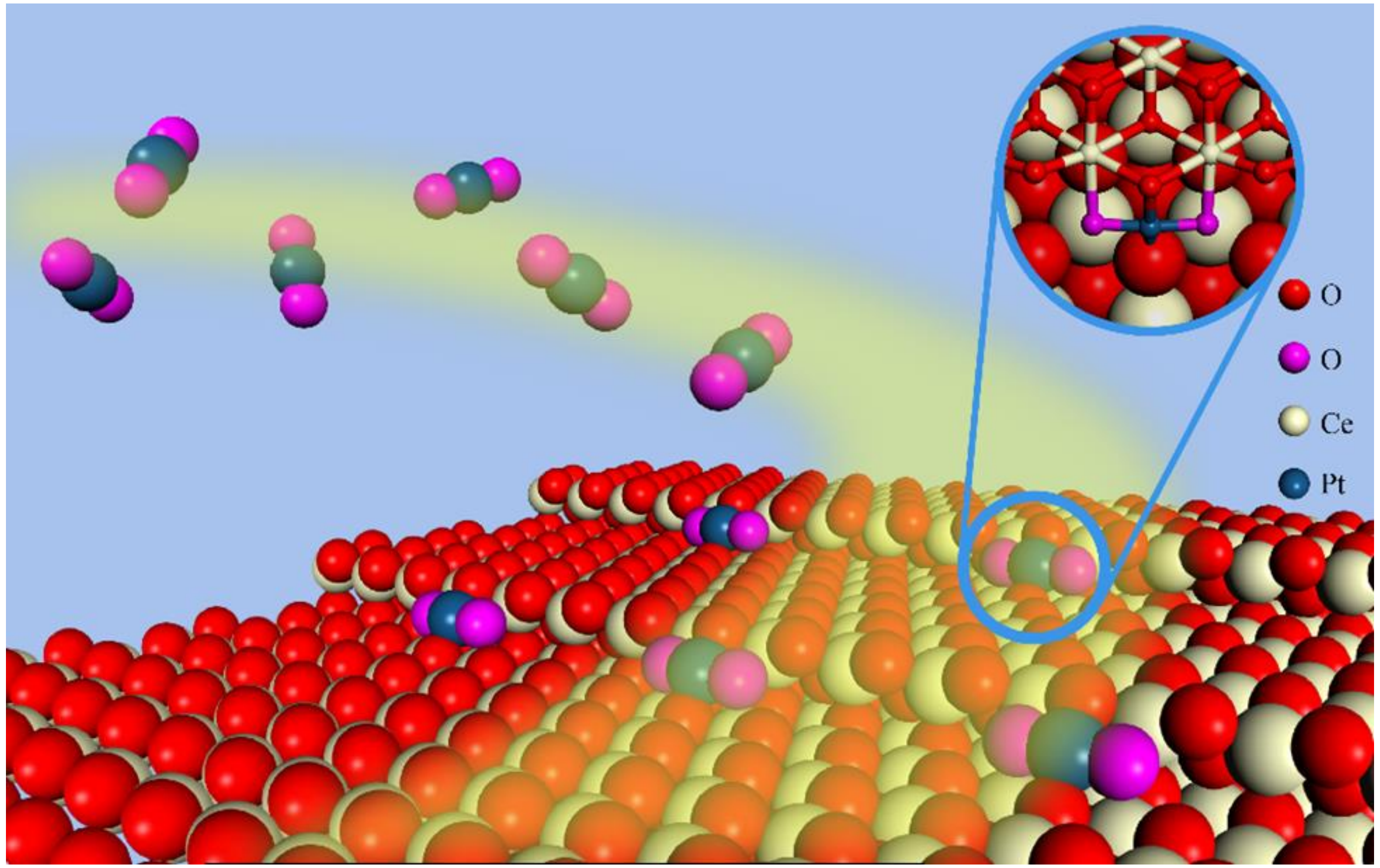
- USDRIVE protocol testing of best performing Pd and Rh SACs:
  - Evaluate the best performing Pd and Rh powder TWCs
  - Evaluate sulfur tolerance using the USDRIVE Test Protocol
  - Compare SAC performance to baseline commercial Pd and Rh TWC catalysts
- Scale up the synthesis of Pd and Rh SACs to >10 grams:
  - Identify the key barriers potentially involved in the scale-up synthesis of *at*SACs
  - Synthesize samples using conventional equipment such as rotary evaporator and nebulizer
  - Perform characterization and activity testing

Summary

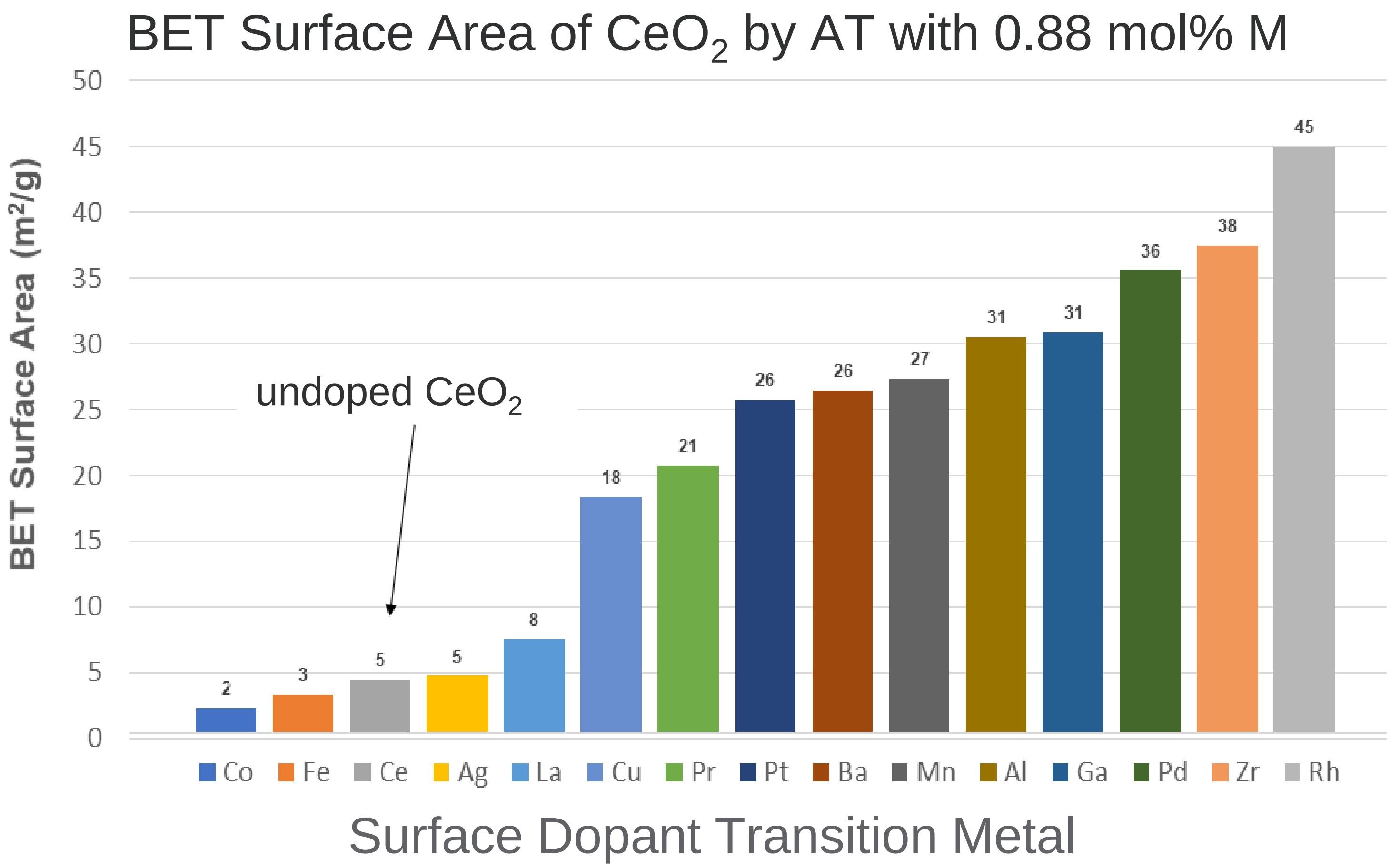
- Selected four representative commercially available supports by BASF, completed full characterization at WSU, UNM and PNNL
  - Confirmed efficacy with the lead candidates for atom trapping with Pt
- Fully characterized and established performance of 8 baseline catalysts prepared by BASF under representative hydrothermal aging (de-greening) and testing conditions
  - Synthesized catalysts with BASF supports via atom trapping with 5x Rh and 2x Pd reduction
  - Achieved similar T_{50}/T_{90} with 5x less Rh for NO reduction by CO, identified alternative Pd catalyst prepared by atom trapping exhibiting similar activities with the baseline catalyst
  - Achieved comparable propane and propylene oxidation reactivity as the best baseline BASF catalyst achieved but with 2x less Pd

Backup Slides

Creating Single Atom Catalysts by Atom Trapping (*at*SACs)



Jones, Xiong, DeLaRiva, Peterson, Pham, Challa, Qi, Oh, Wiebenga, Hernández, Wang, Datye, ***Science,*** 2016, 353 (6295),150-154
Kunwar, Zhou, DeLaRiva, Peterson, Xiong, Hernández, Purdy, ter Veen, Brongersma, Miller, Hashiguchi, Kovarik, Lin, Guo, Wang, Datye, ***ACS Catalysis***, 2019, 9, 3978-3990



Alcala *et al*, ***Appl.Catal.B,*** 2021, 10.1016/j.apcatb.2020.119722)

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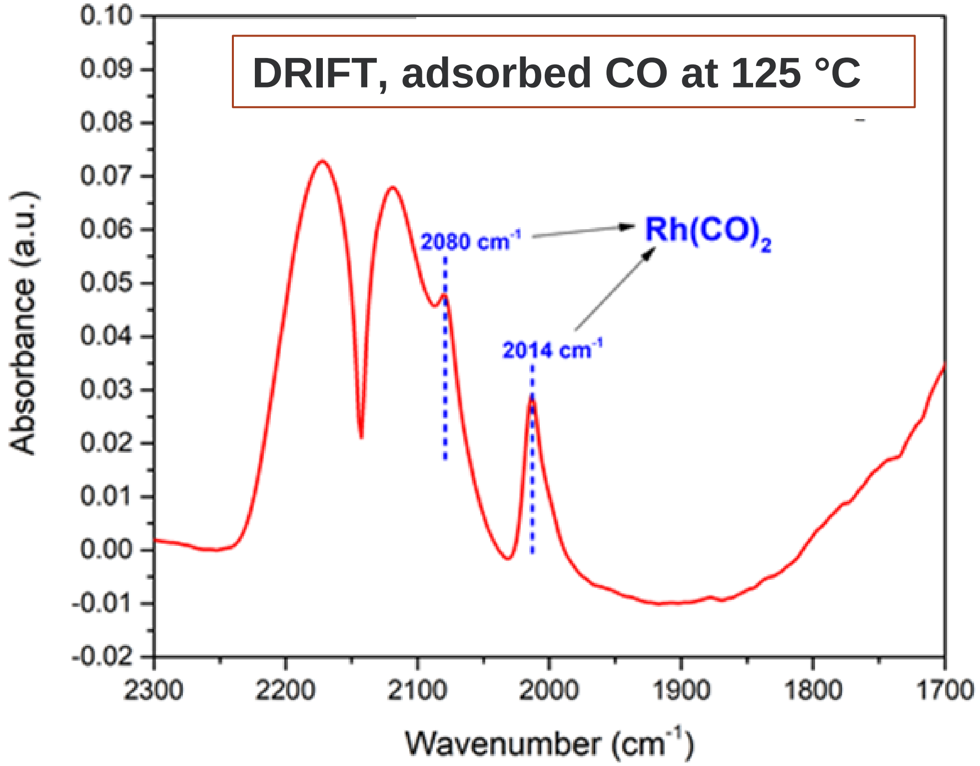
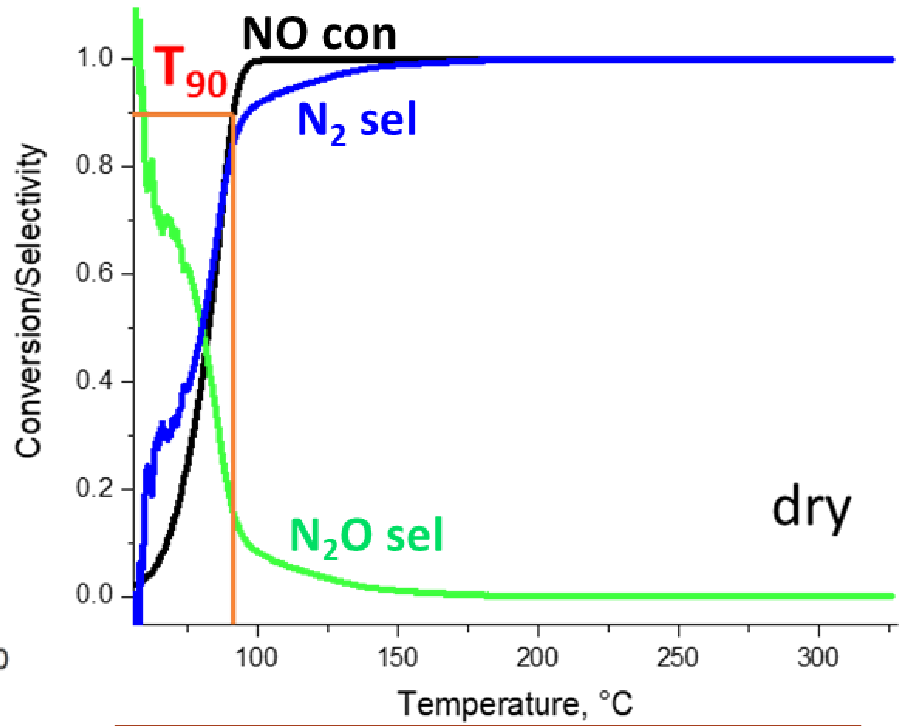
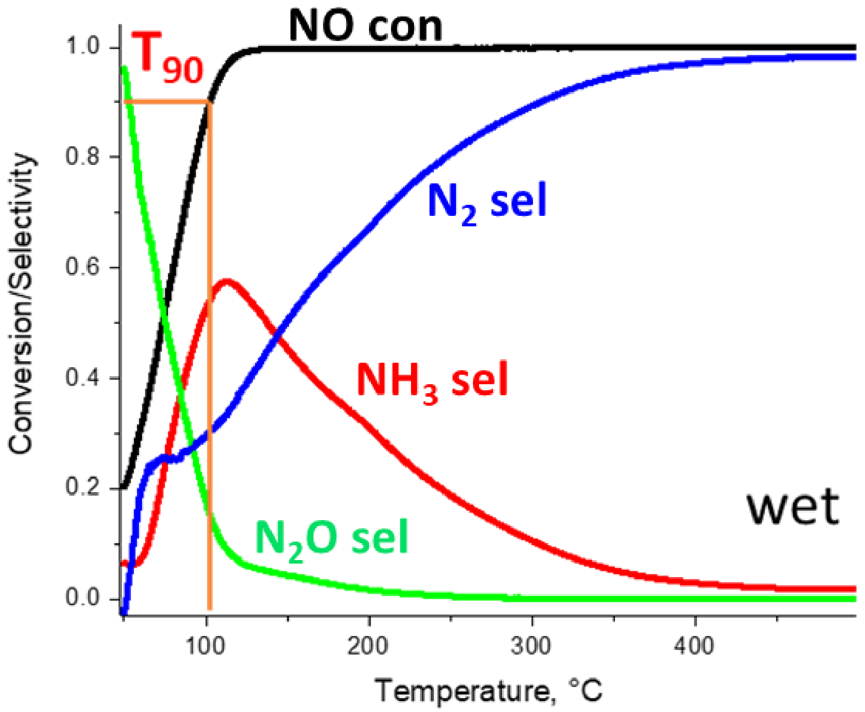
0.1wt% Rh_1/CeO_2 Single Atom Catalyst Is Highly Active for NO Reduction





120mg cat., 460 ppm NO, 1750 ppm CO, balanced with N_2, 150,000 mL·g_{cat}^{-1}·h^{-1}



120mg cat., 460 ppm NO, 1750 ppm CO, 2.6% H_2O, balanced with N_2, 150,000 mL·g_{cat}^{-1}·h^{-1}

Khivantsev, Vargas, Tian, Kovarik, Jaegers, Szanyi, Wang, ***Angew.Chem.Int.Ed.***, 2020, DOI: 10.1002/anie.202010815

- Thermally durable 0.1%Rh/CeO_2 single atom catalyst was synthesized using atom trapping (800°C in air).
- IR confirms all the Rh ions are located in a structurally identical position and are stable even in CO at 125°C.
- Remarkably high NO reduction activities were observed under both dry and wet conditions, with T_{90} of ~85 and ~100°C, respectively → USCAR 150^{o}C T_{90} Challenge Exceeded

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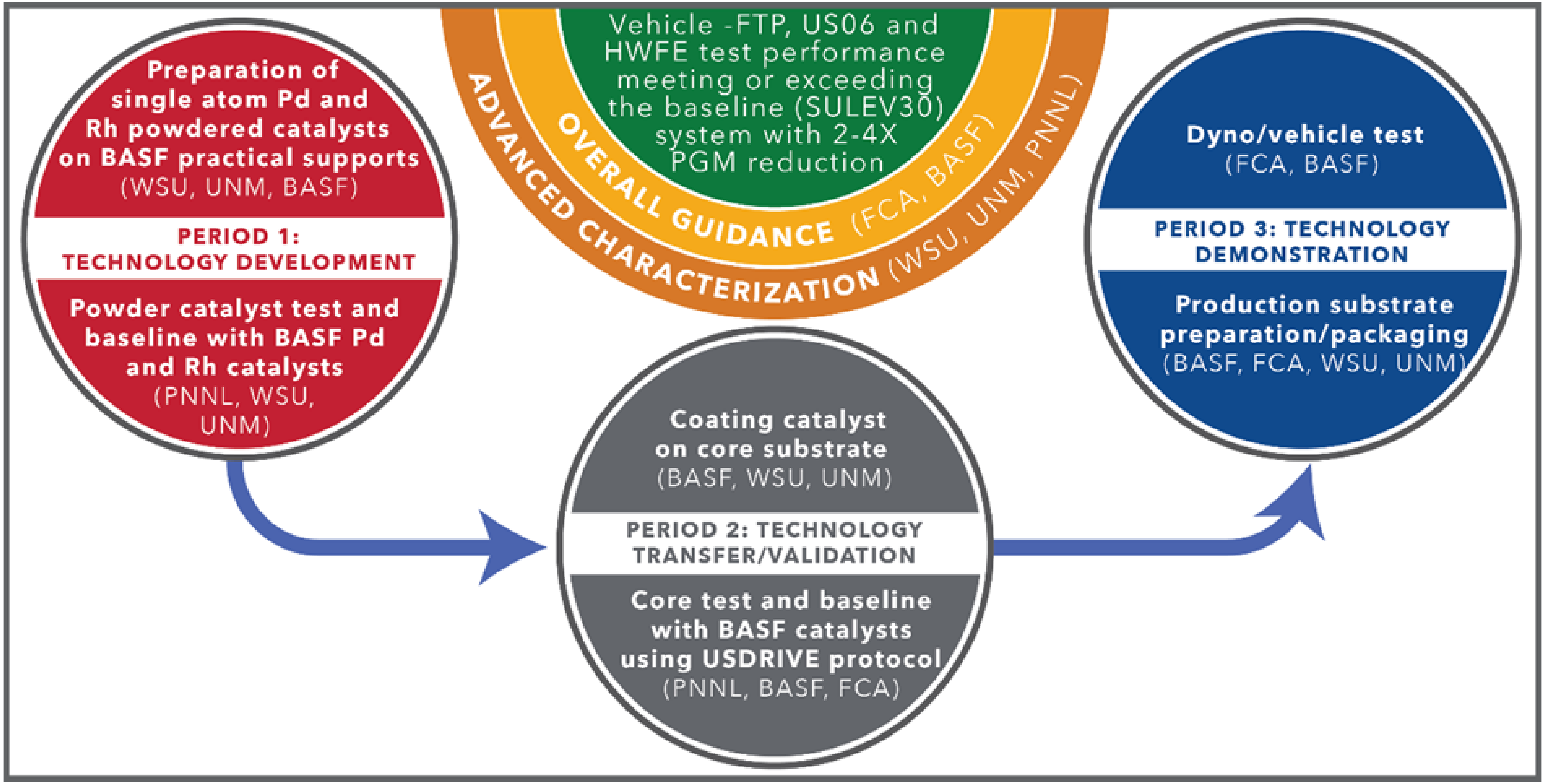
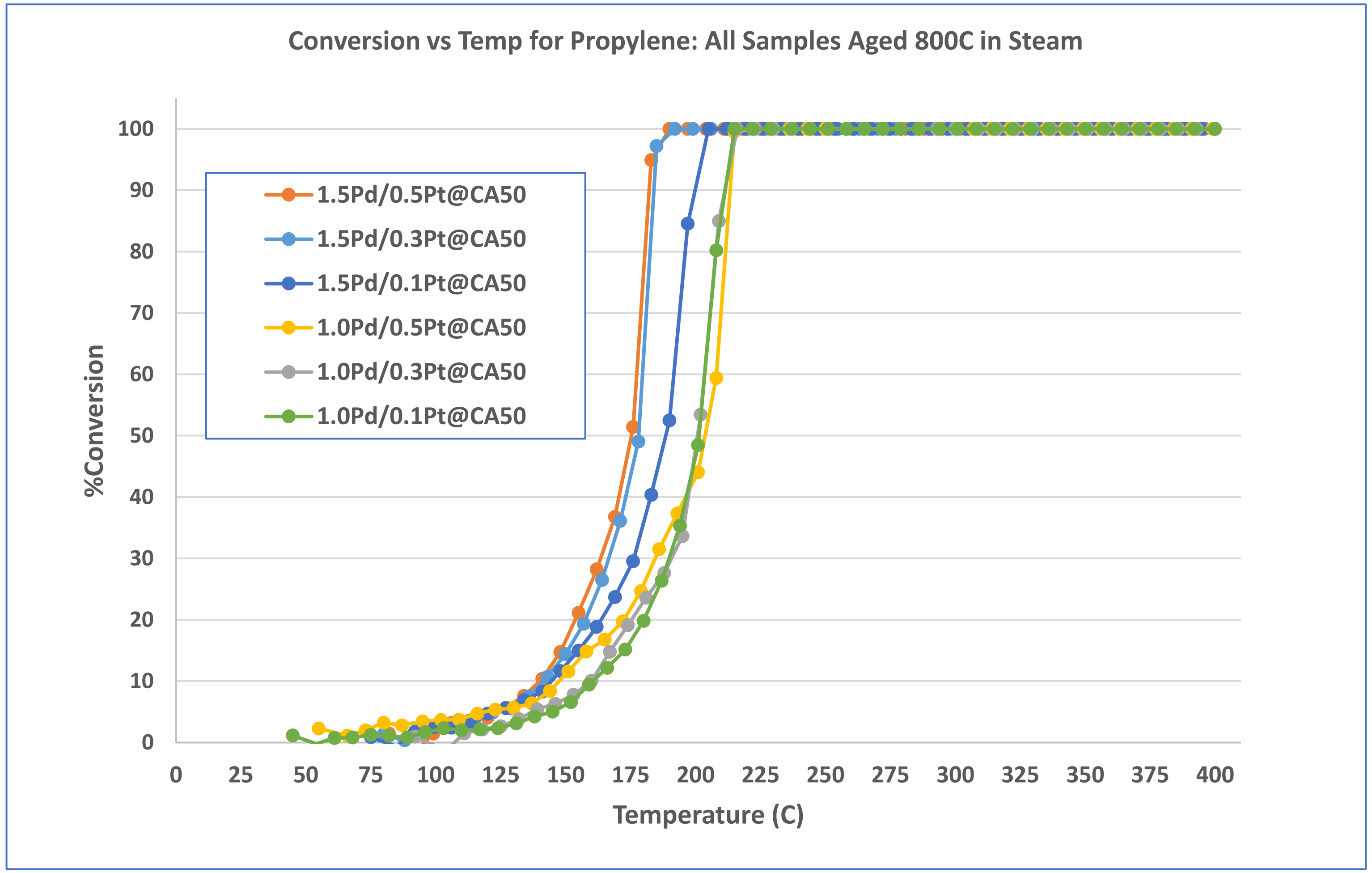
Scope and Overall Objective

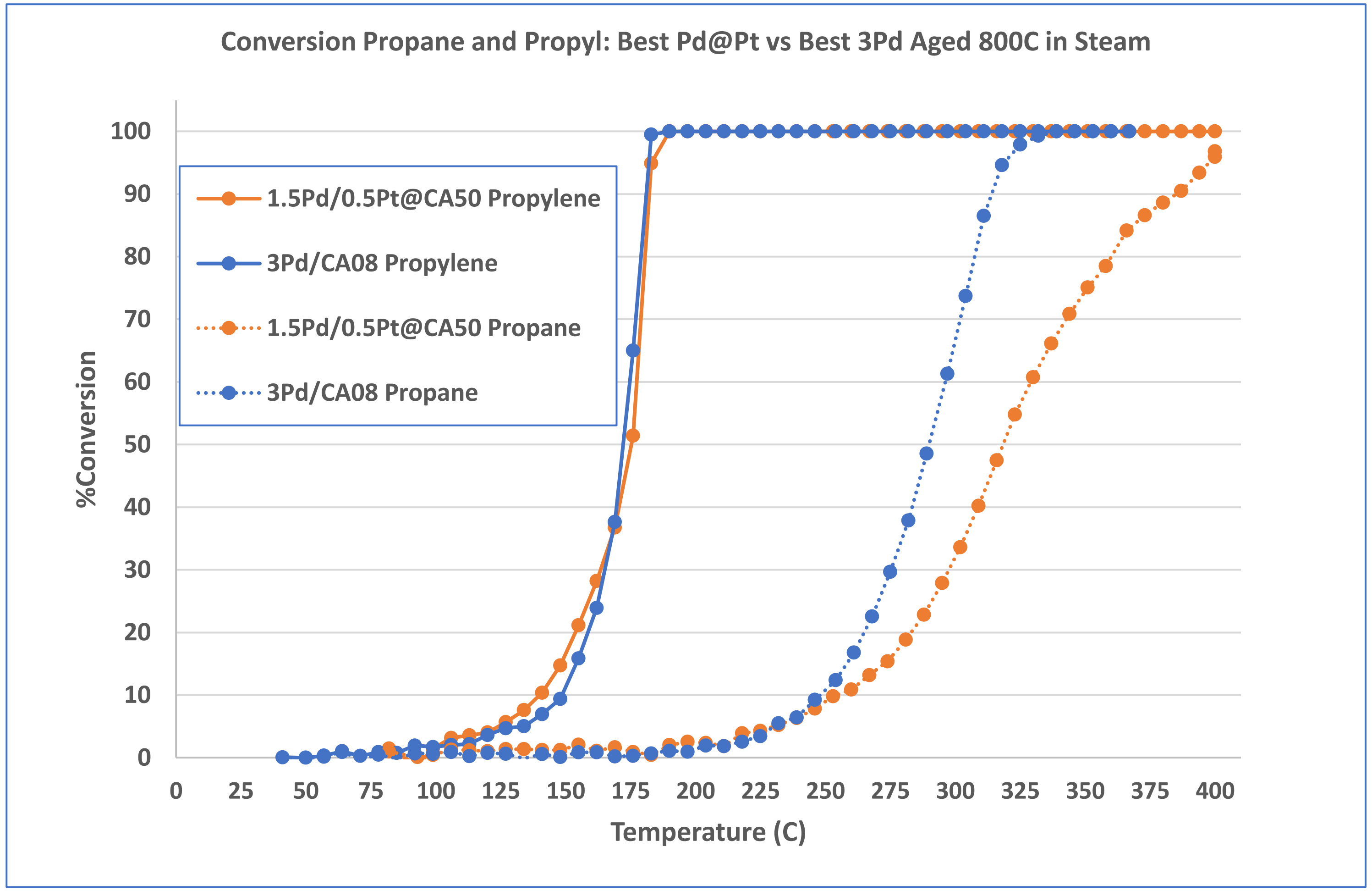


2x Reduced Pd on Atom Trapping Modified BASF Support

Lowest T_{90} (177˚C) achieved with 1.5Pd/0.5Pt@CA50 for propylene oxidation



Comparable propane and propylene oxidation reactivity as the best baseline BASF catalyst achieved with 2x less Pd



125 micron (10mg cat + 20mg carbide), Reduced at 200℃ for 1hr in 10%H_2/Ar, 2˚C /min, 0.2%propane, 0.2% propylene, 2%O_2, balanced with N_2, GHSV=150 L/g·hr

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