

Rational Catalyst Design Applied to Development of Advanced Oxidation Catalysts for Diesel Emission Control

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Diesel Emission Control

Diesel combustion systems are becoming increasingly complex and diverse

- Lower exhaust T and higher CO/HC emissions
- DPF and SCR systems (PM and NO_x control)
- Engine management strategies
- Interplay between mechanical, electronic and catalytic aspects

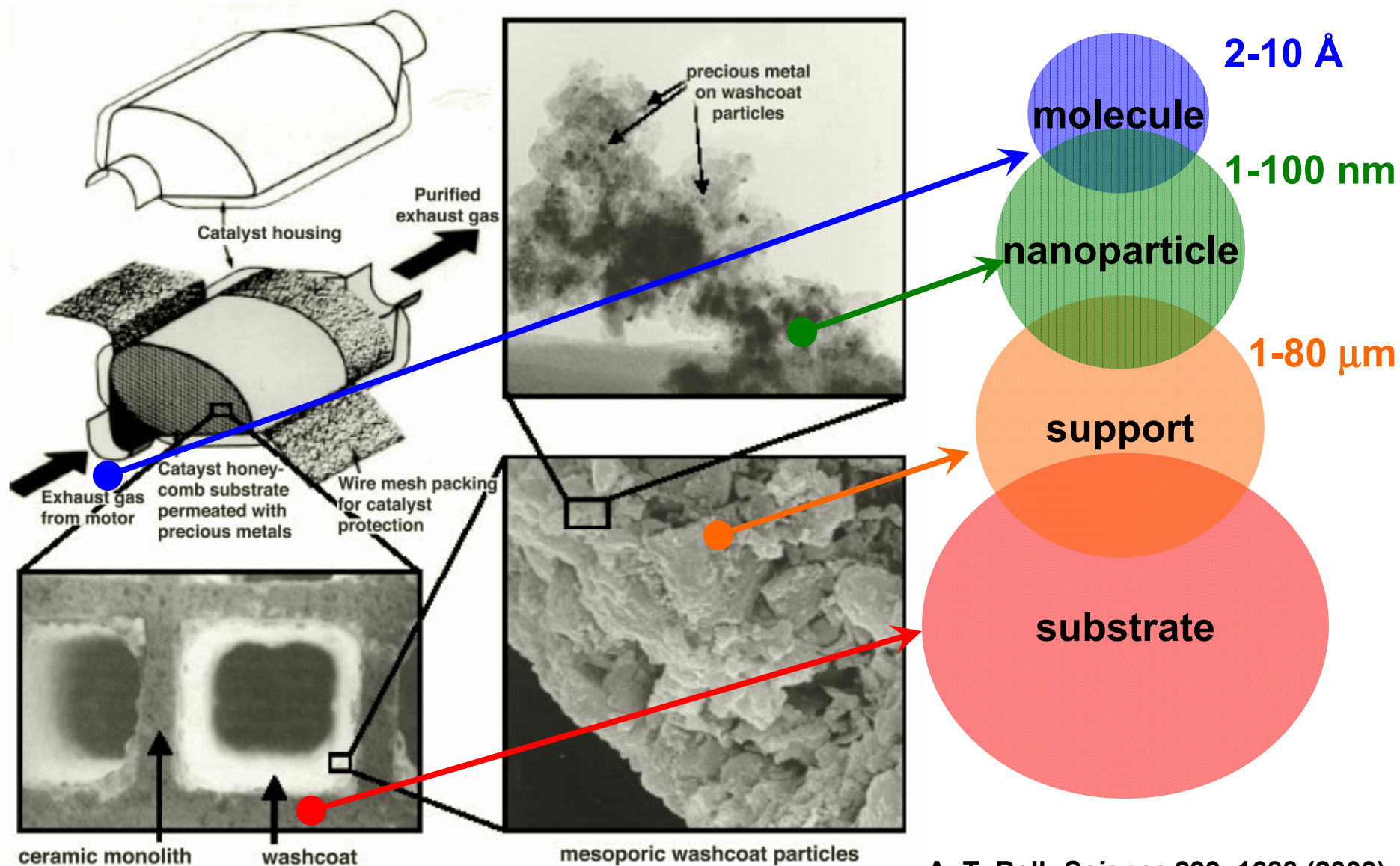
Pt has traditionally been the oxidation catalyst of choice

- Good activity (CO, HC, and NO) + resistance to oxidation and poisons
- Low thermal stability
- Current generations utilize Pd for improved thermal stability
 - This strategy does not significantly alter the intrinsic activity

We have been using our **Rational Catalyst Design (RCD)** methodology, which combines computational and experimental approaches, to identify and put into practice advanced catalytic materials for emission control via modification of the *fundamental surface chemistry* of metal nanoparticles

This presentation will describe the use of our RCD approach to develop Pt-based catalysts with tailored *intrinsic activity* and *thermally stable performance*

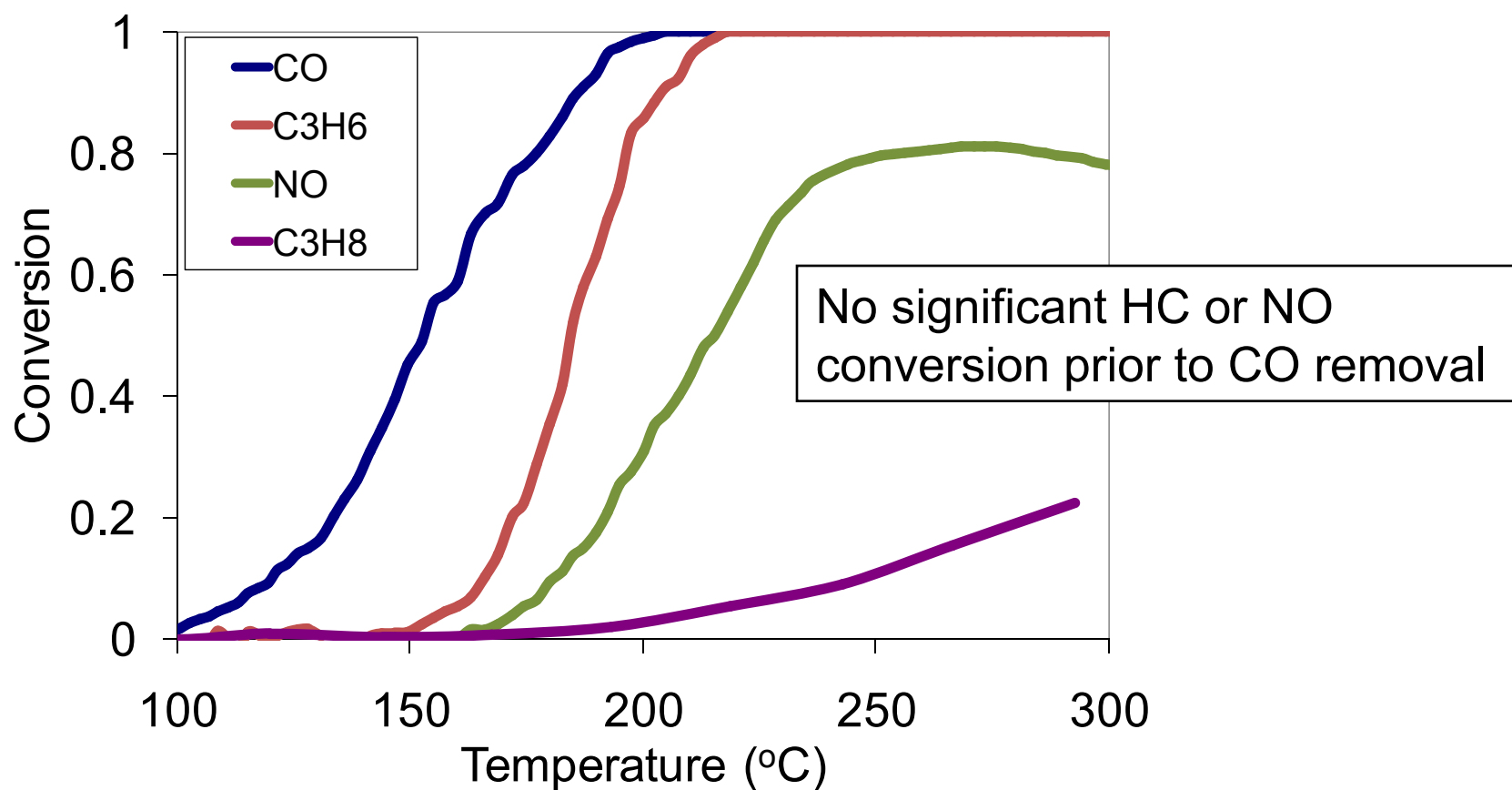
Physical and Chemical Interactions in a Catalytic Converter





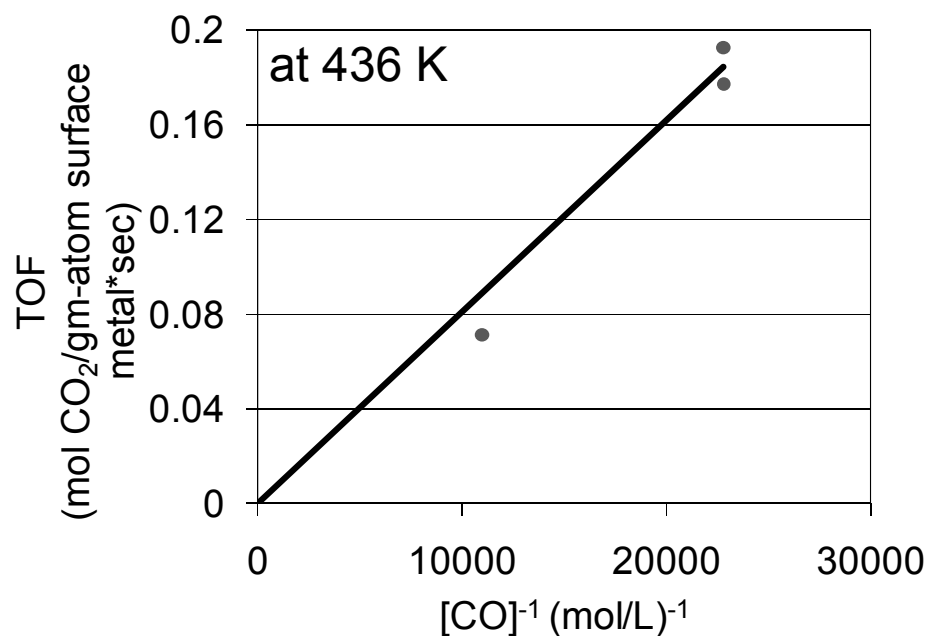
Typical Pt-only Light-off Sequence: The Importance of CO

Development of emission control oxidation catalysts with improved performance starts with a detailed understanding of the CO oxidation reaction mechanism, identification of the limiting step, and use of methods to remove the limitation

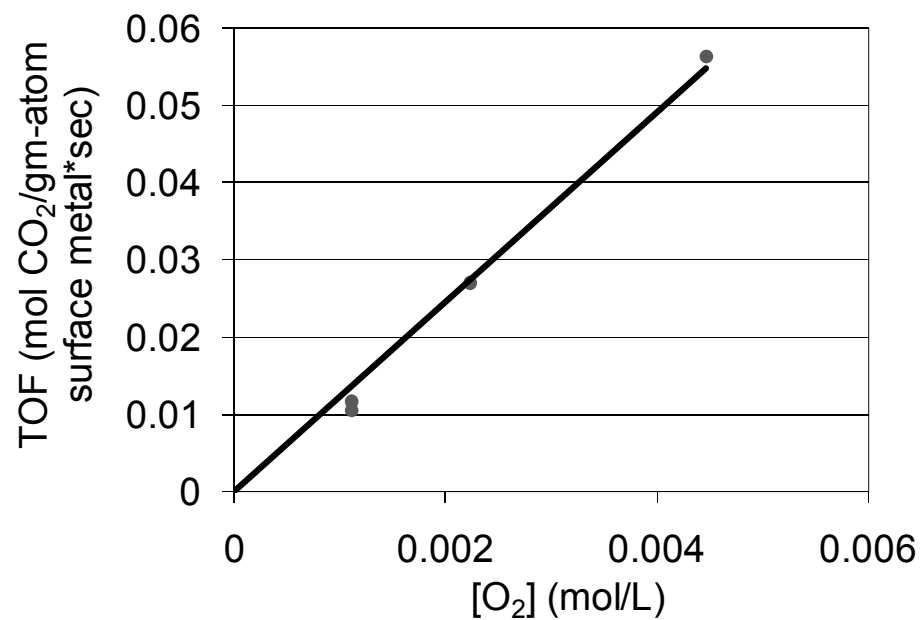


CO Oxidation Kinetics on Pt-only Show CO Inhibition

Variable [CO] + Constant [O₂]



Variable [O₂] + Constant [CO]

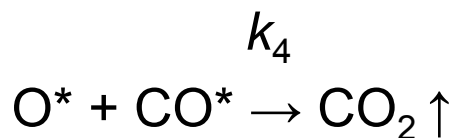
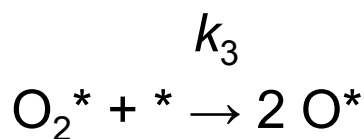
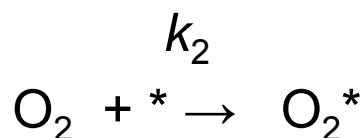
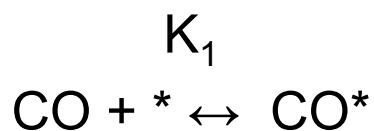


TOF is *inversely* proportional to [CO] TOF is *directly* proportional to [O₂]

Similar to previous work done by M. Boudart, G. Ertl, and others for PGM systems



Elementary Steps for CO Oxidation on Pt



For a CO covered Pt surface, the measured rate is O₂ adsorption (k_2)

$$\text{Rate} = \frac{k_2[\text{O}_2]}{1 + K_1[\text{CO}]}$$

$$\text{Rate} = \frac{A_1 \exp(-E_{a_{\text{app}}}/RT)[\text{O}_2]}{[\text{CO}]}$$

$$E_{a_{\text{app}}} = E_{a_2} - \Delta H_{\text{ads-CO}}$$

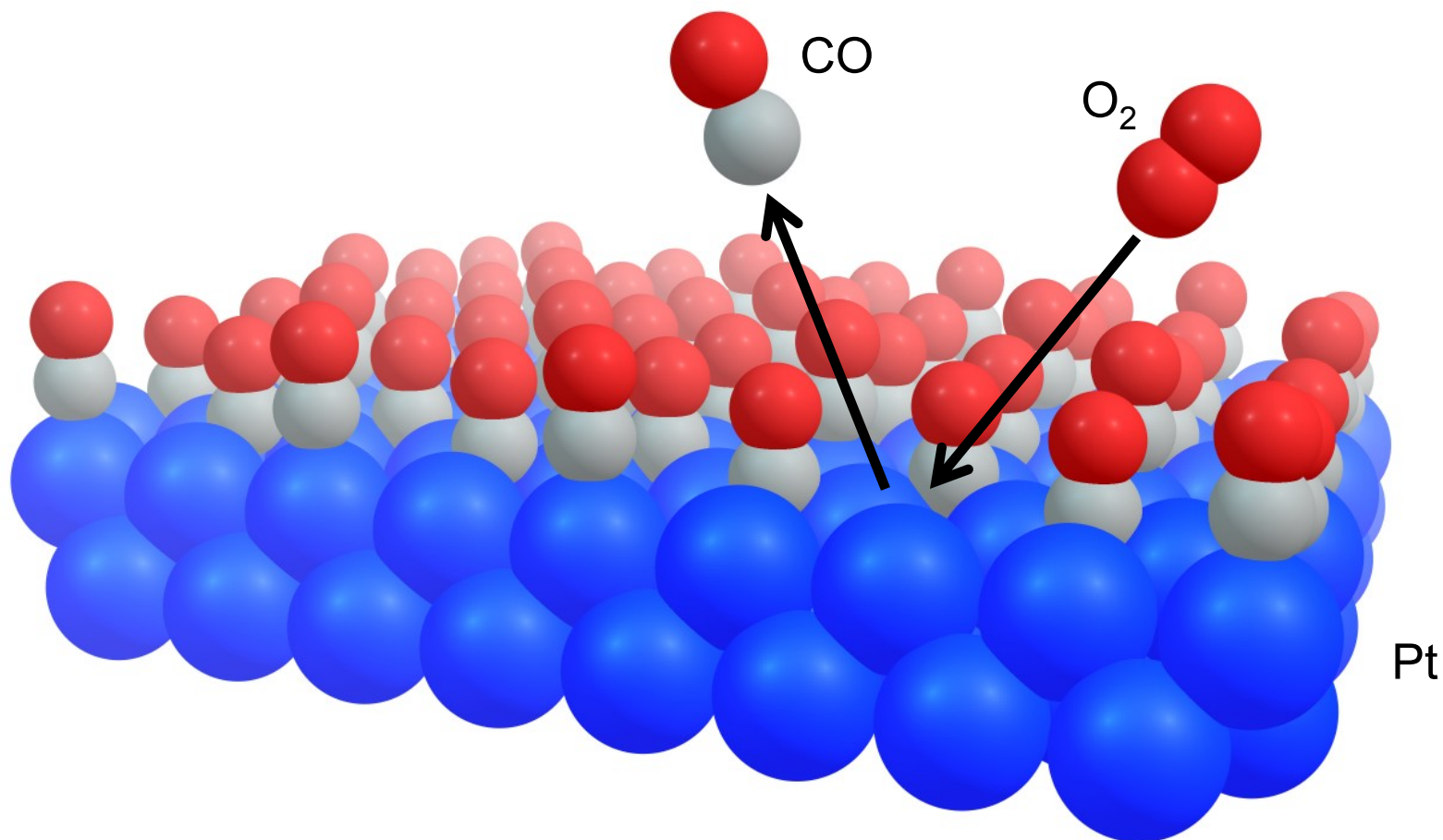
$$\Delta H_{\text{ads-CO}} \sim -75 \text{ kJ/mol (at high CO coverage)}$$

The key to increasing the rate of CO oxidation on Pt is to decrease $\Delta H_{\text{ads-CO}}$, which will allow more facile O₂ adsorption



DFT Calculations: CO Covered Pt (111) Surface

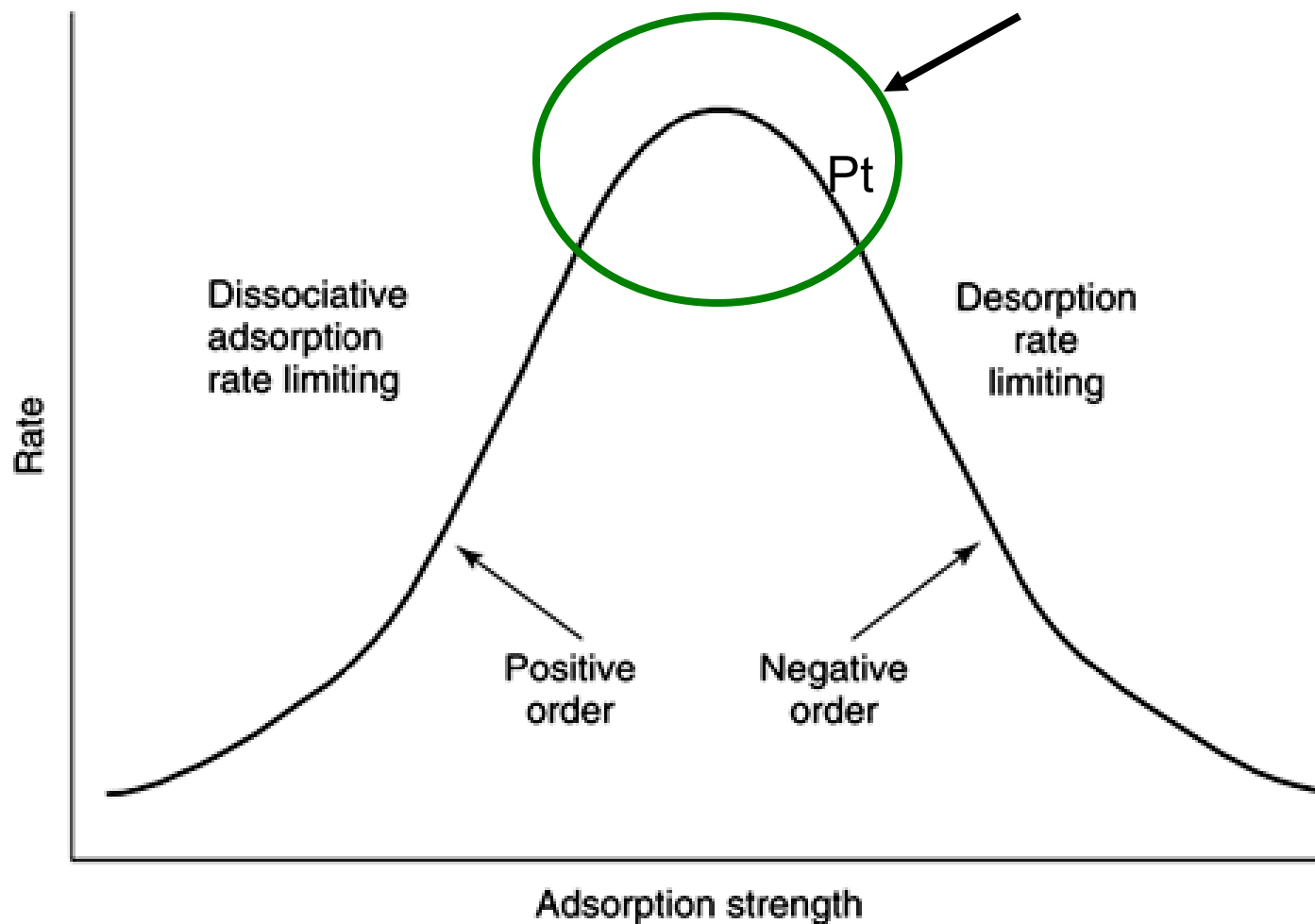
Under typical start-up conditions (low T), CO will dominate the surface and prevent O₂ from finding available reaction sites. Therefore, CO must desorb before oxidation can take place.





Typical Volcano Relationship: Rate vs. Adsorption Energy

Species that are active enough to be practically useful are often found in a very narrow range





Strategy to Modify Intrinsic Pt Activity

Desired characteristics to optimize CO oxidation:

- Lower CO adsorption energy
- Lower O₂ activation energy

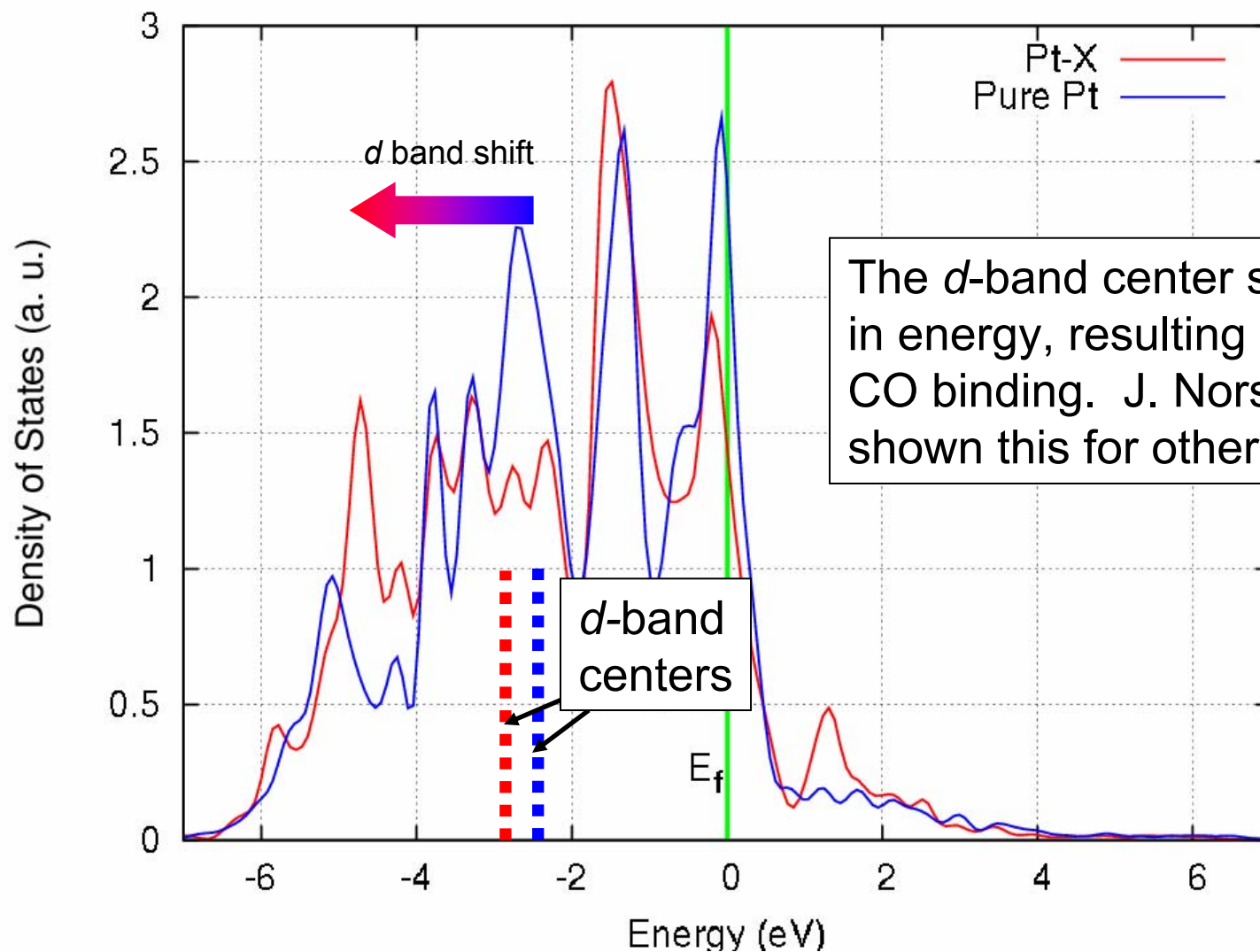
Utilizing quantum calculations, we have examined several potential promoter species (including non-PGM systems) to study their impact on the electronic structure of Pt and CO-surface interactions

Our experimental results will show:

- Modification of reactant adsorption characteristics on Pt
- Dramatic increase of the intrinsic CO oxidation activity
- Demonstration of tunable oxidation performance
- Improved activity stabilization upon thermal treatment
- Practical viability (vehicle tests)



DOS Calculations for Pt and Promoted Pt Show a *d*-band Shift

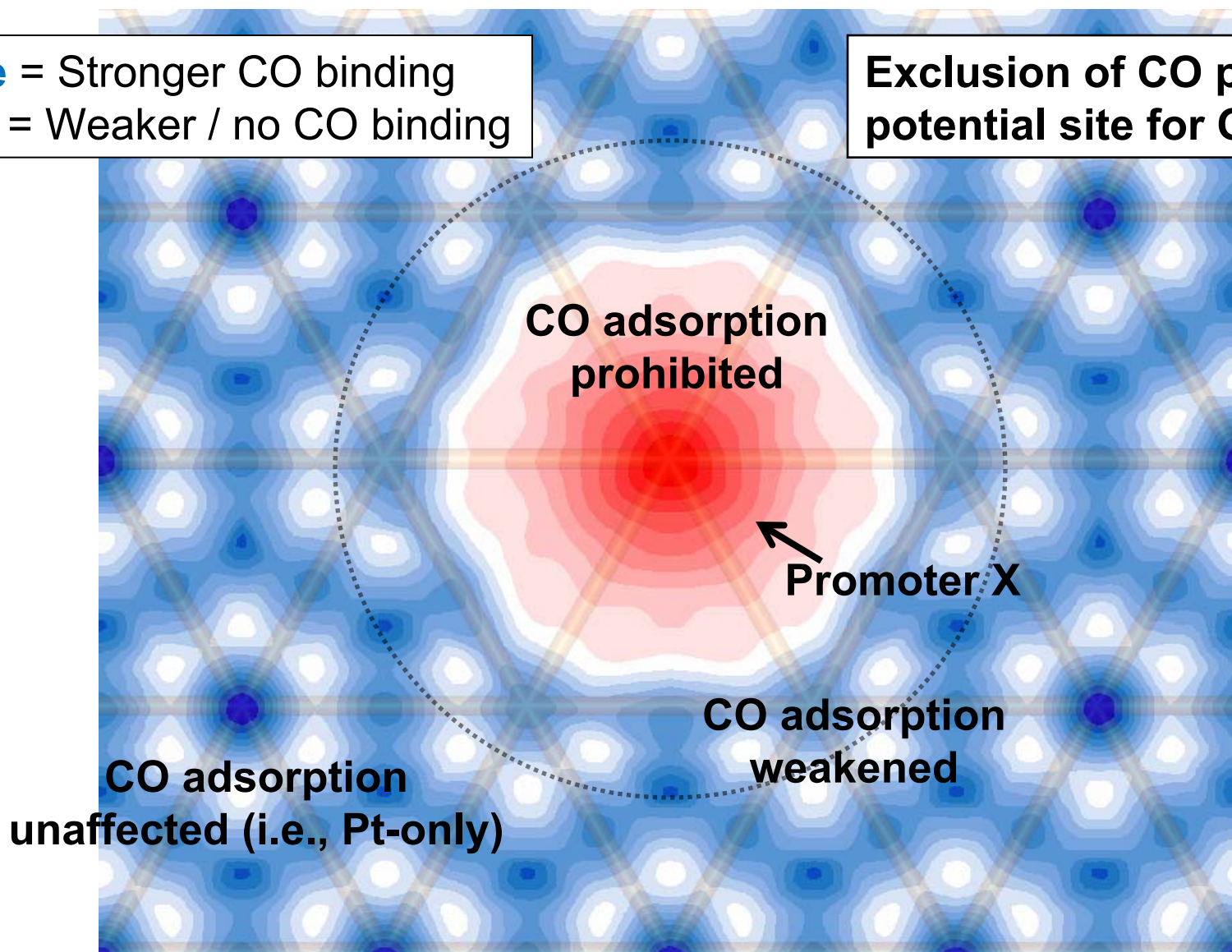


The *d*-band center shifts lower in energy, resulting in weaker CO binding. J. Norskov has shown this for other systems.

CO Adsorption Heat Map for a Promoted Pt Surface

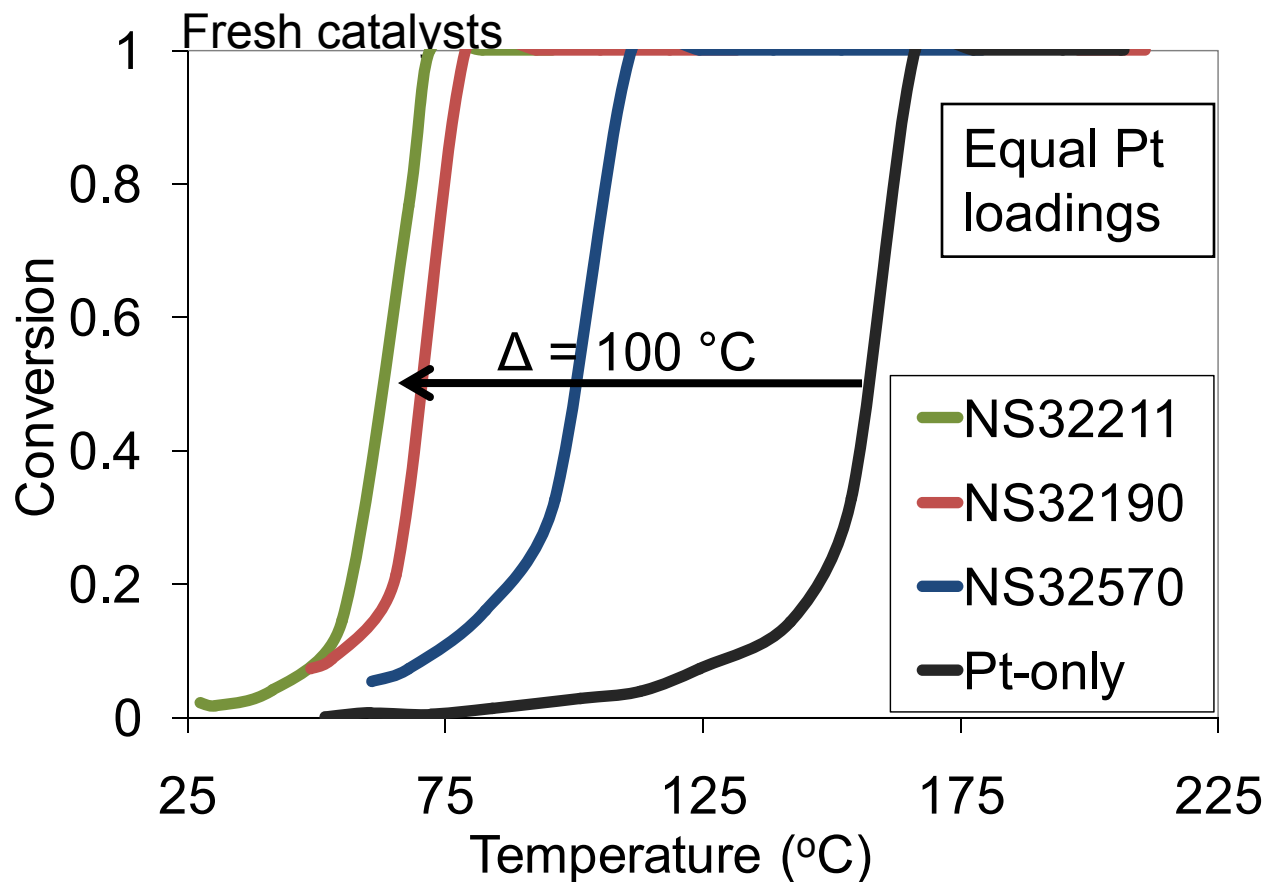
Blue = Stronger CO binding
Red = Weaker / no CO binding

Exclusion of CO provides a potential site for O₂ access



CO Oxidation Tests Show Enhanced Activity for Promoted Pt

Different promoter strategies give dramatic changes in CO light-off temperature

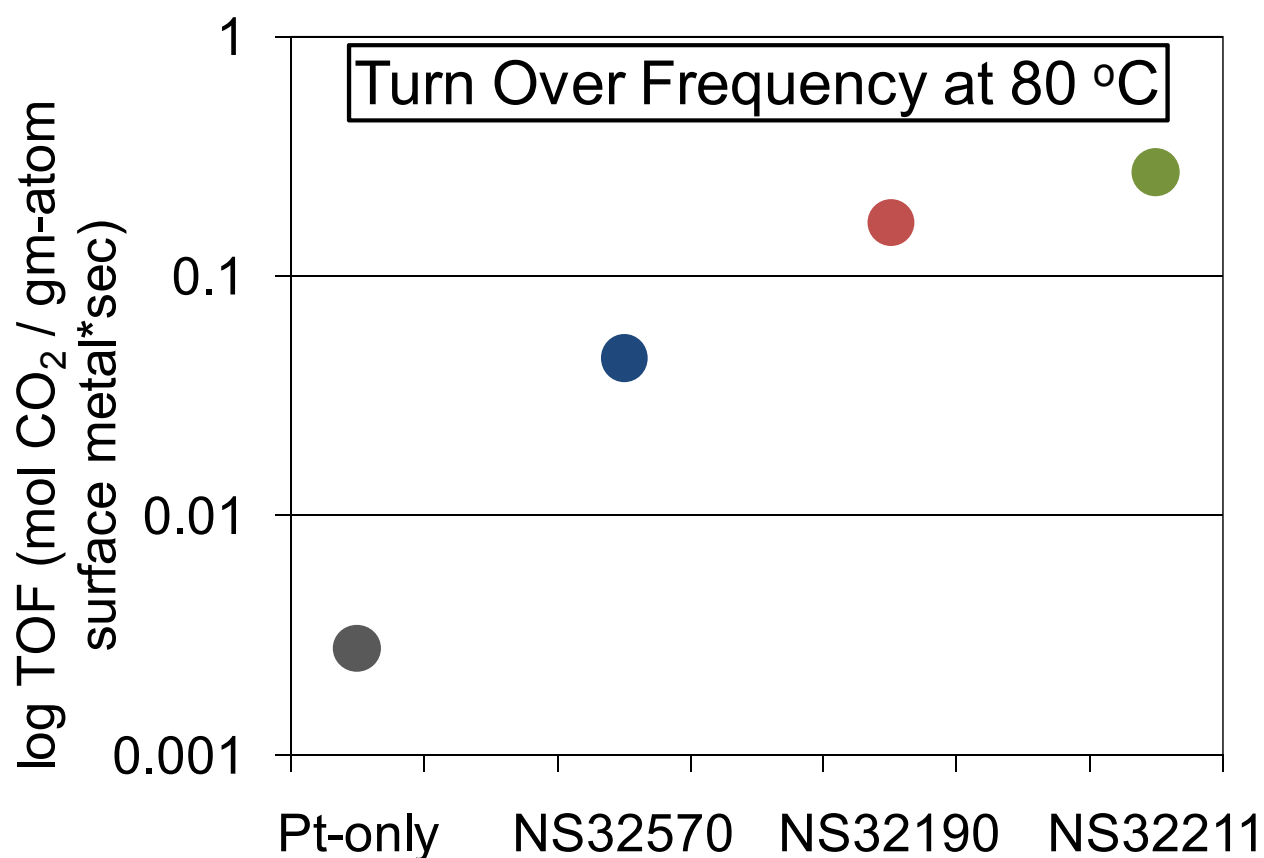


Fixed-bed flow reactor, 10 °C/min, 1000 ppm CO and 10% O₂ (balance He), 10 mg catalyst + 90 mg α-Al₂O₃ (for dilution), 200 cc/min flow rate, GC data
 Fresh = heated in air at 500 °C



Up to 100 X Increase in *Intrinsic* CO Oxidation Activity

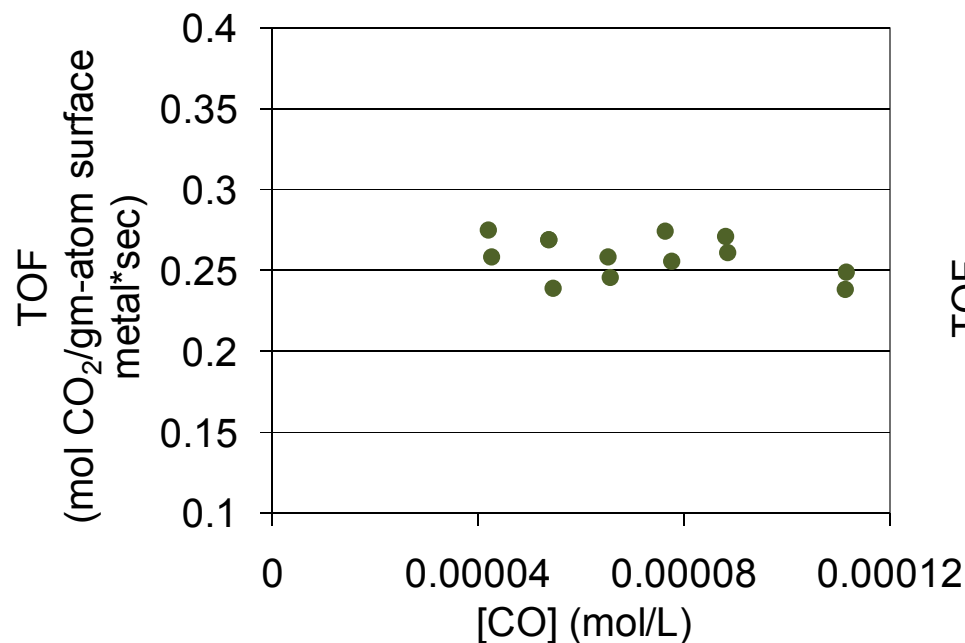
The turn over frequency (i.e., activity per exposed surface site) has been increased by ~two orders of magnitude



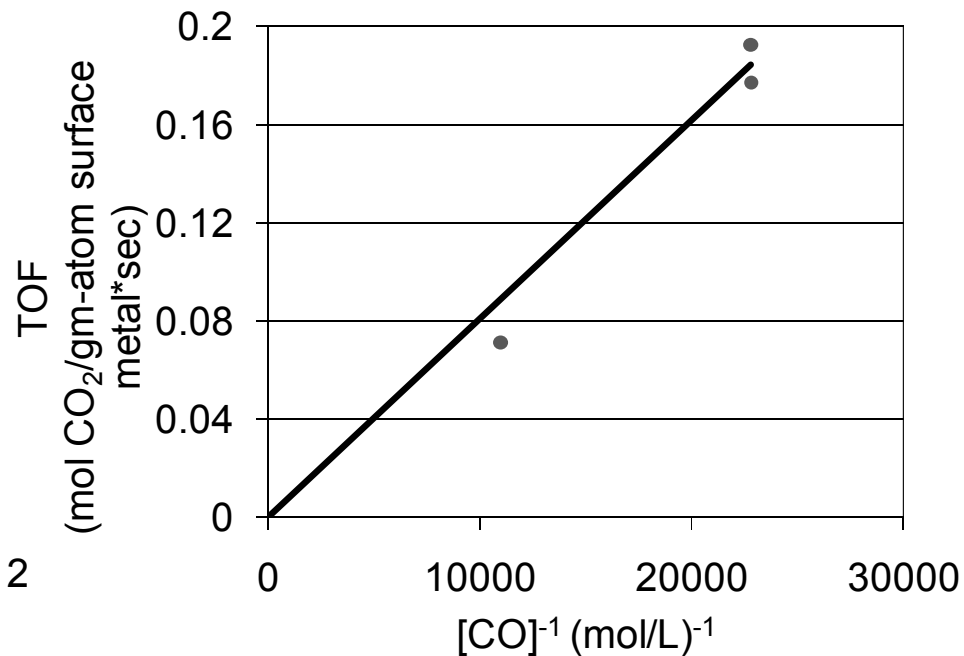


Pt-only vs. Promoted Pt CO Kinetics: CO Inhibition Removed

Variable [CO] + Constant [O₂]



TOF is *independent* of [CO]



TOF ~ 1/[CO]

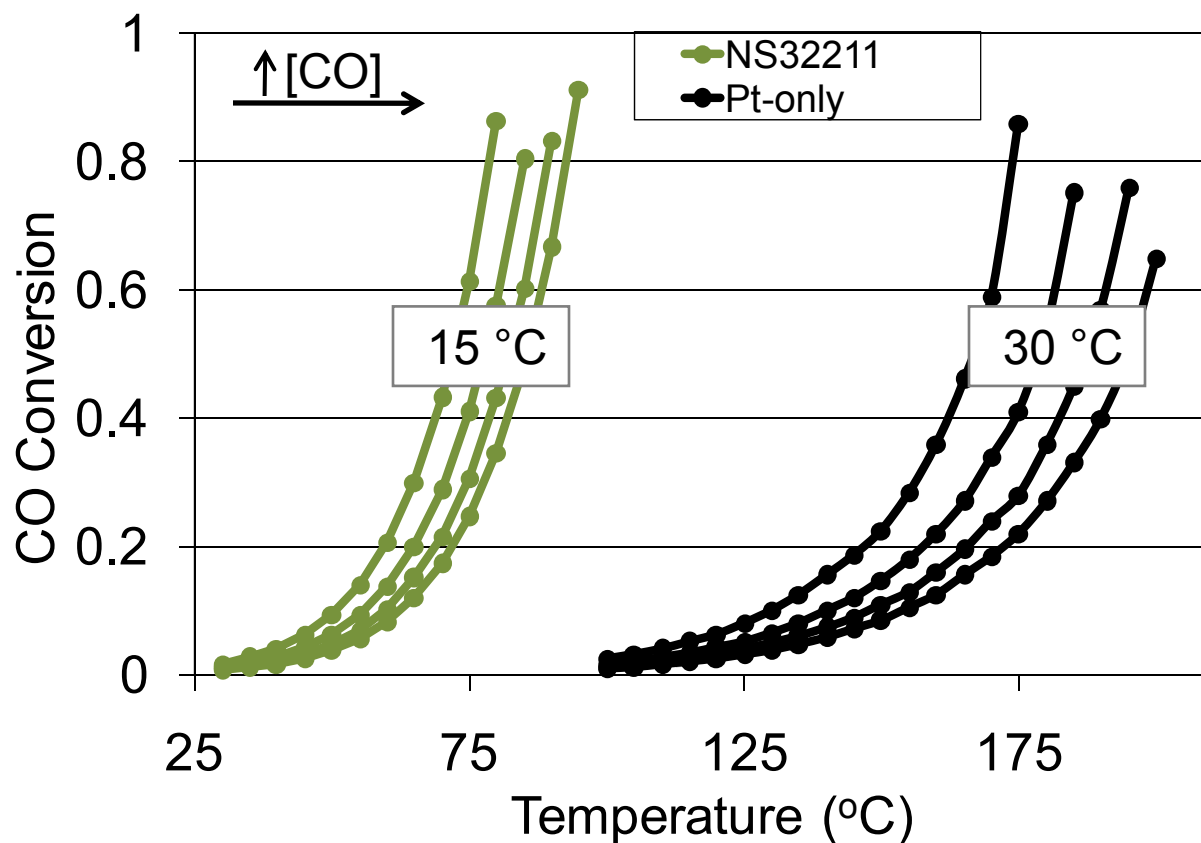
Similar to Pt-only, NS32211 is positive first order in [O₂] (not shown)

➤ Rate_(NS32211) ~ k₂[O₂]

This is consistent with our DFT heat maps showing CO exclusion zones

Calculated CO Concentration Dependence (1000 – 2500 ppm)

Removal of the CO inhibition is desirable for advanced diesel combustion systems having higher engine out CO concentrations



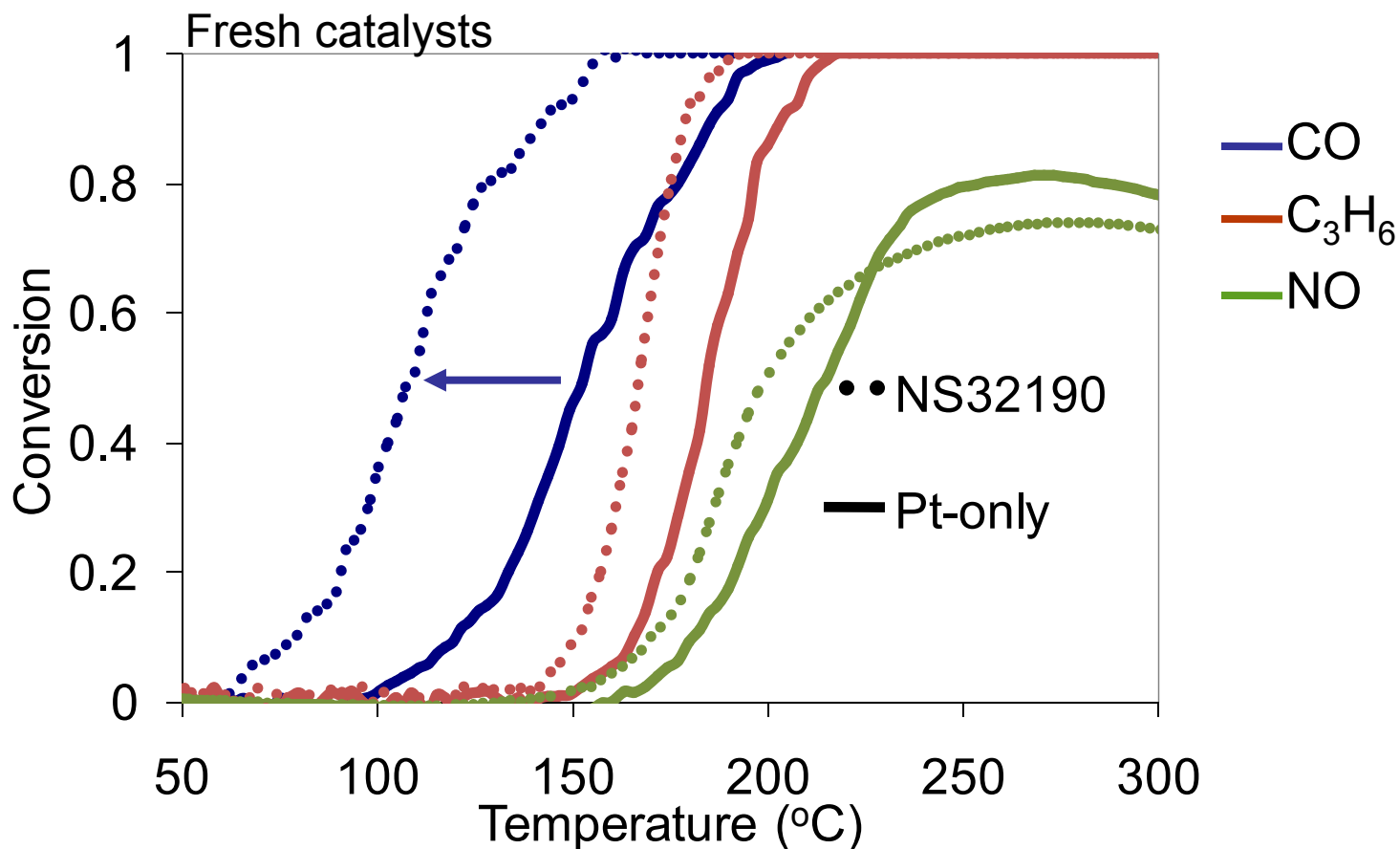
For Pt-only, light-off increases with higher CO mass flow rate *and* decreased reaction rate from higher [CO]

For NS32211, light-off increases only with higher CO mass flow rate (no rate change with [CO])

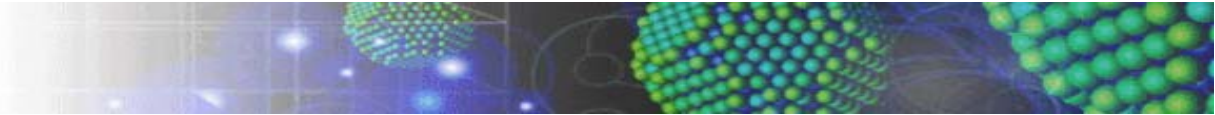
Calculated using 10% O₂



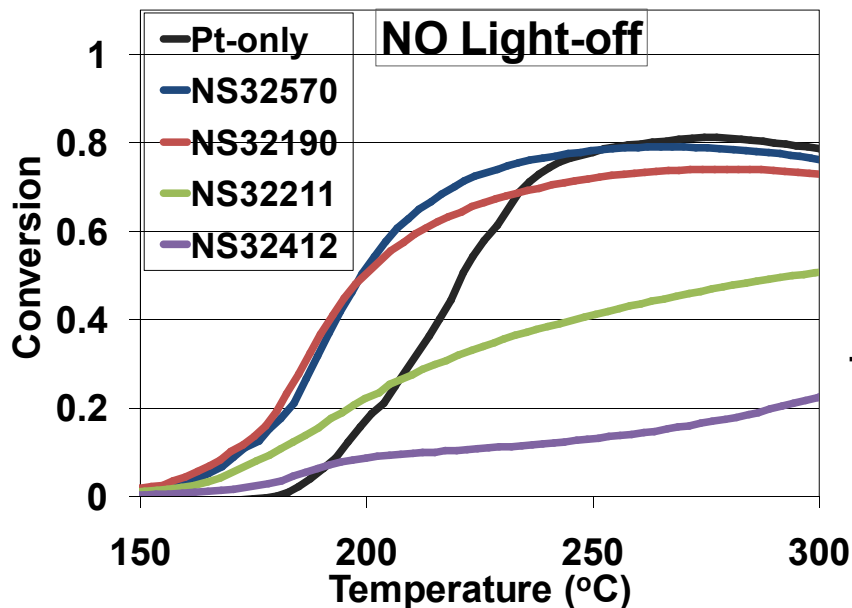
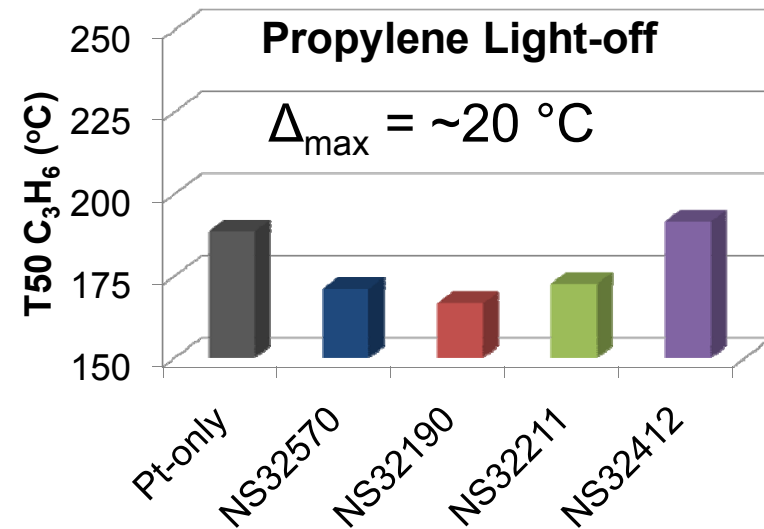
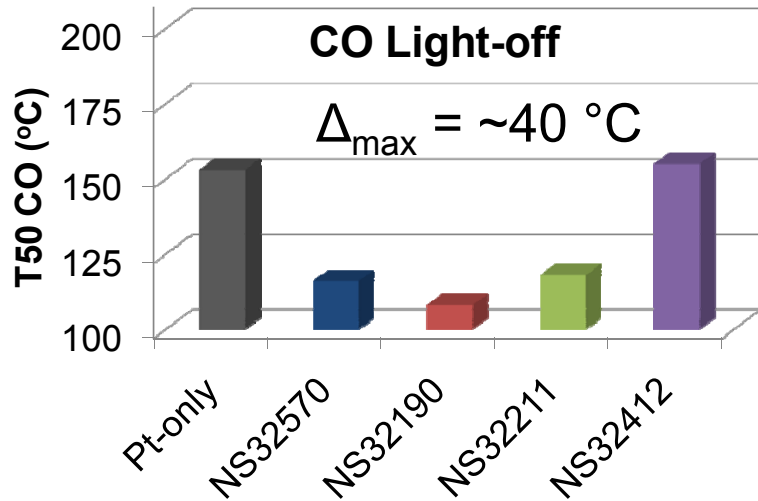
Laboratory Synthetic Exhaust: Pt-only vs. Promoted Pt



Fixed-bed flow reactor, 10 °C/min, 1000 ppm CO, 105 ppm C₃H₈, 245 ppm C₃H₆, 450 ppm NO, 10% CO₂, and 10% O₂ (balance He), 15 mg catalyst + 85 mg α-Al₂O₃, 300 cc/min flow rate, MS and NO_x analyzer data
 Fresh = heated in air at 500 °C



Synthetic Exhaust: Superior and Tunable Fresh Performance



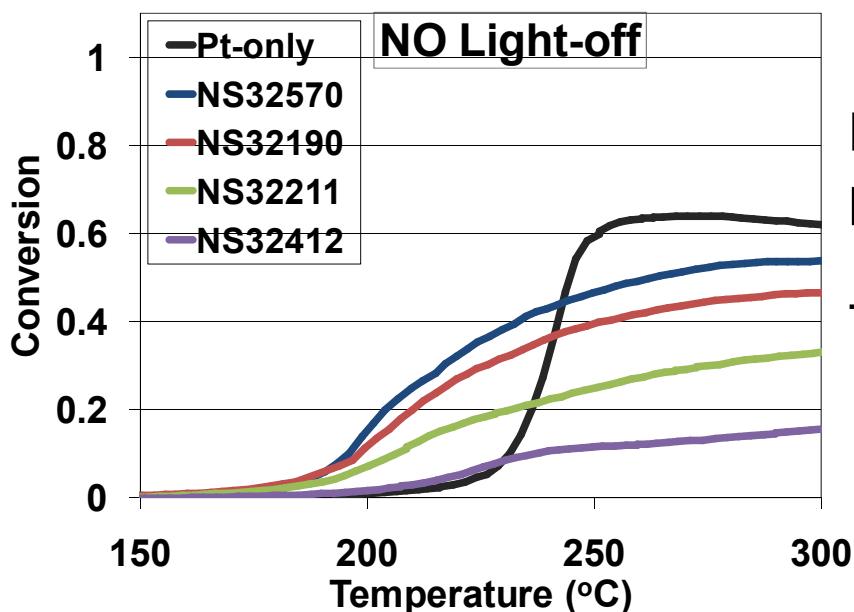
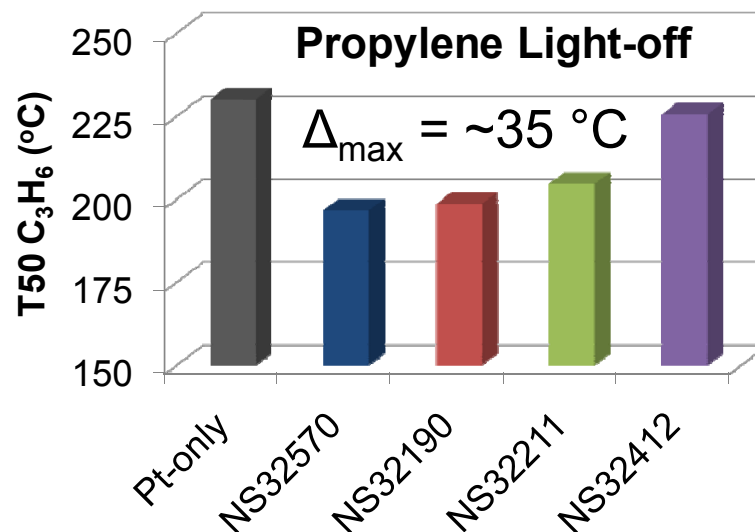
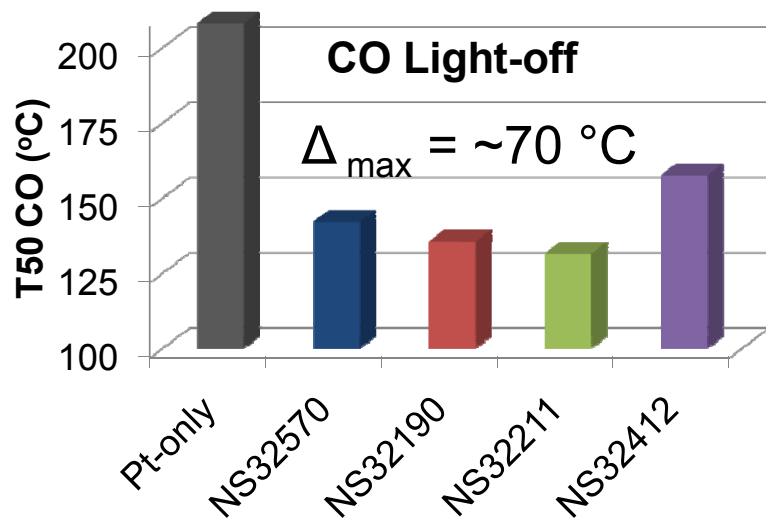
Improved CO + C₃H₆ performance

Enhanced low T (< 200 °C) NO conversion

Tunable maximum NO conversion

Synthetic Exhaust: Increased Performance Gap After Aging

Aged at 750 °C for 20 h with H₂O (10%) in air

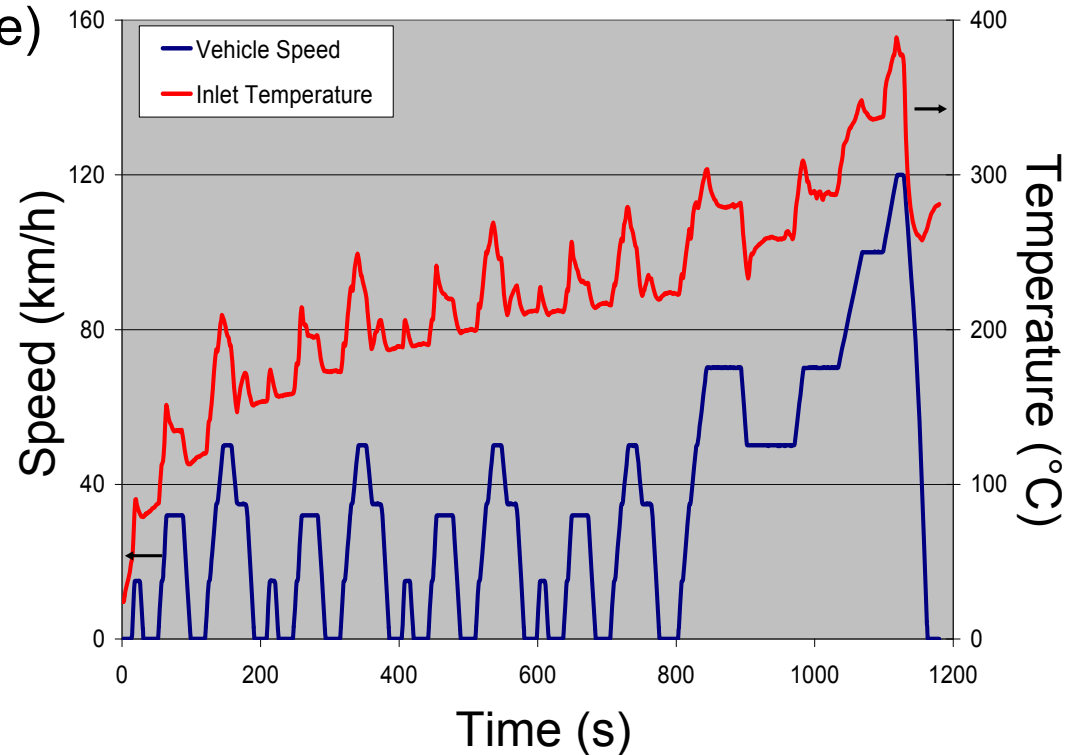


More stable activity → CO + C₃H₆ light-off performance advantage increases

Tunable maximum NO conversion persists

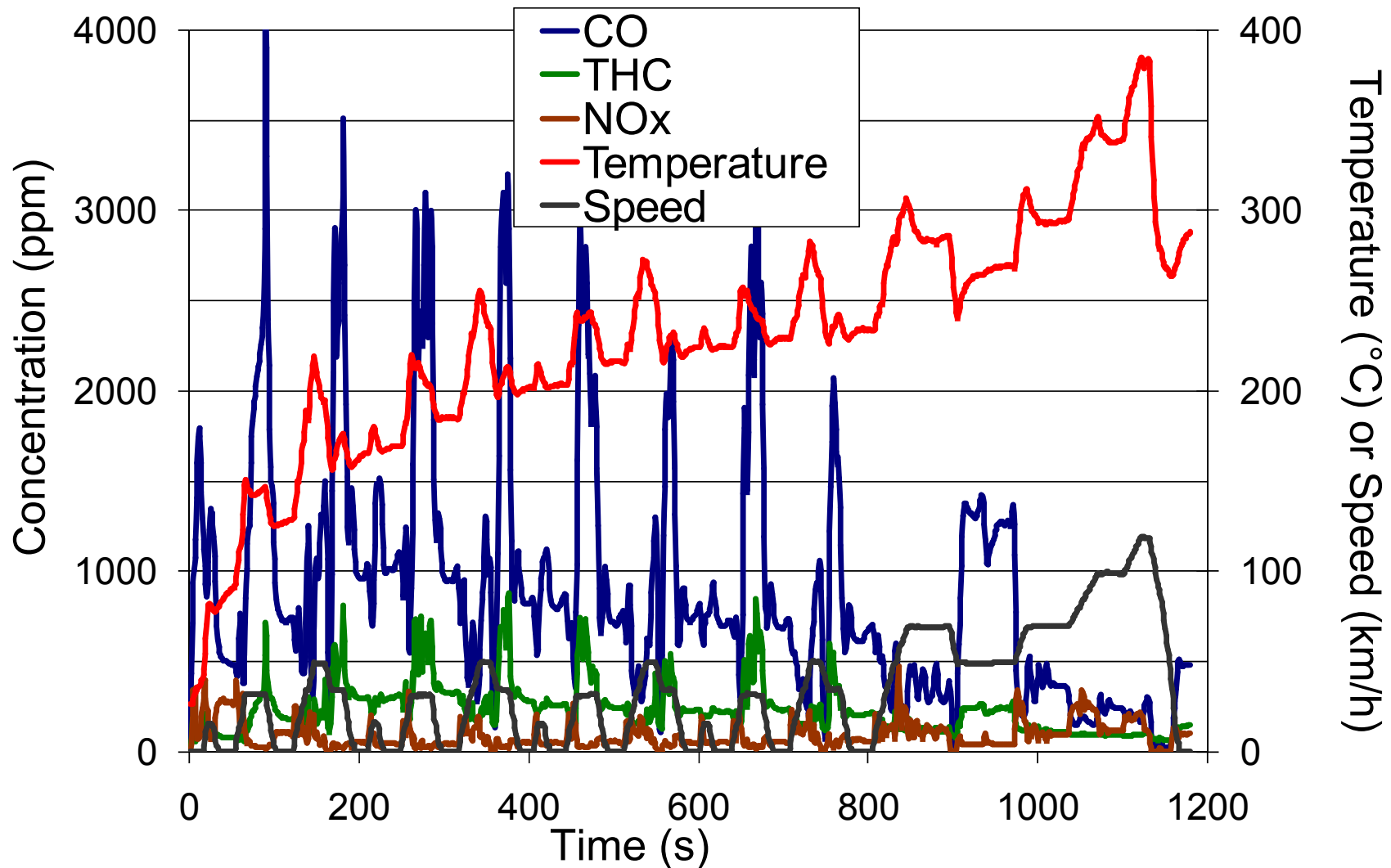
Vehicle Evaluations: Pt-only vs. Promoted Pt

- Vehicle: US LDD (2005 model year)
 - 2.0 L
 - 1 L catalyst (~1/2 OE volume)
 - PGM = 2 g/L Pt
 - Catalyst moved underfloor
- Test: European MVEG →
- Ultra-low sulfur fuel (<15 ppm)
- Testing done at a certified facility
- Engine Aging:
 - 2 mode cycle with fuel injection
 - Maximum temperature of ~650 °C
 - Aged for 20 h
 - Low sulfur fuel (<50 ppm)



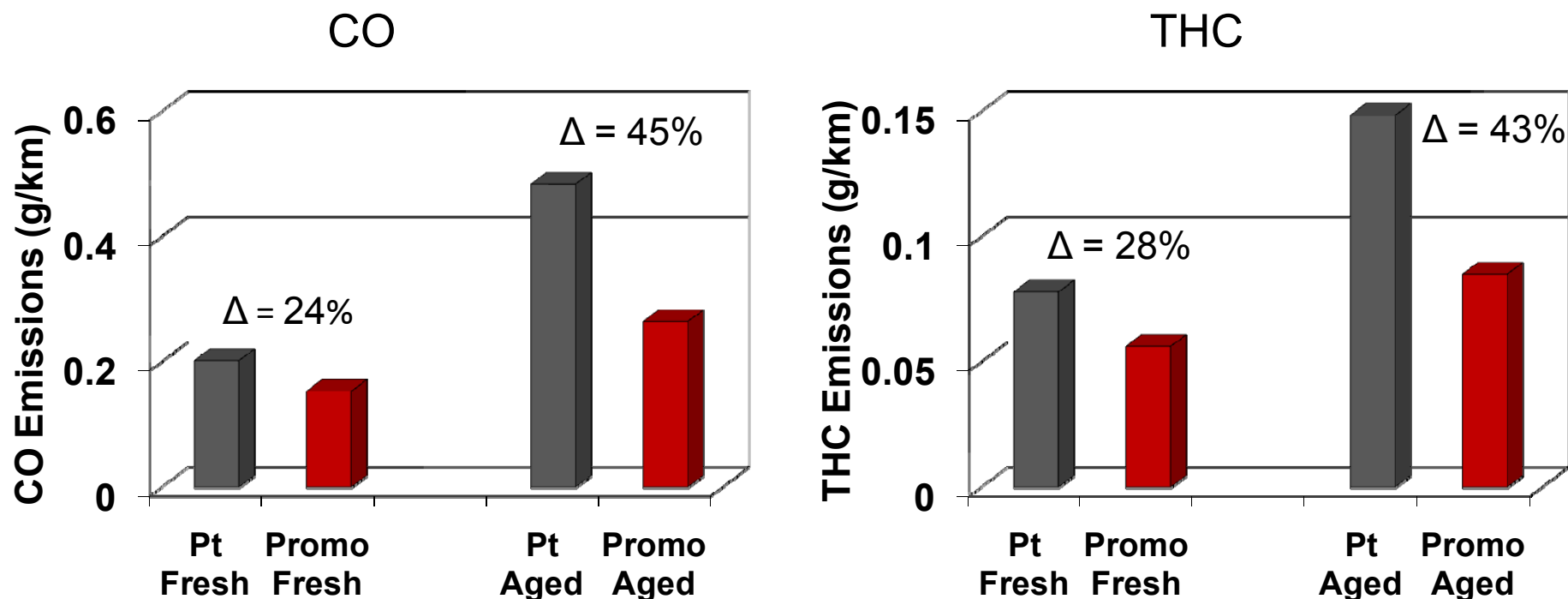
LDD Engine-out Data

[CO] Range: 500 to 3000+ ppm, [THC] range: 100 to 800+ ppm



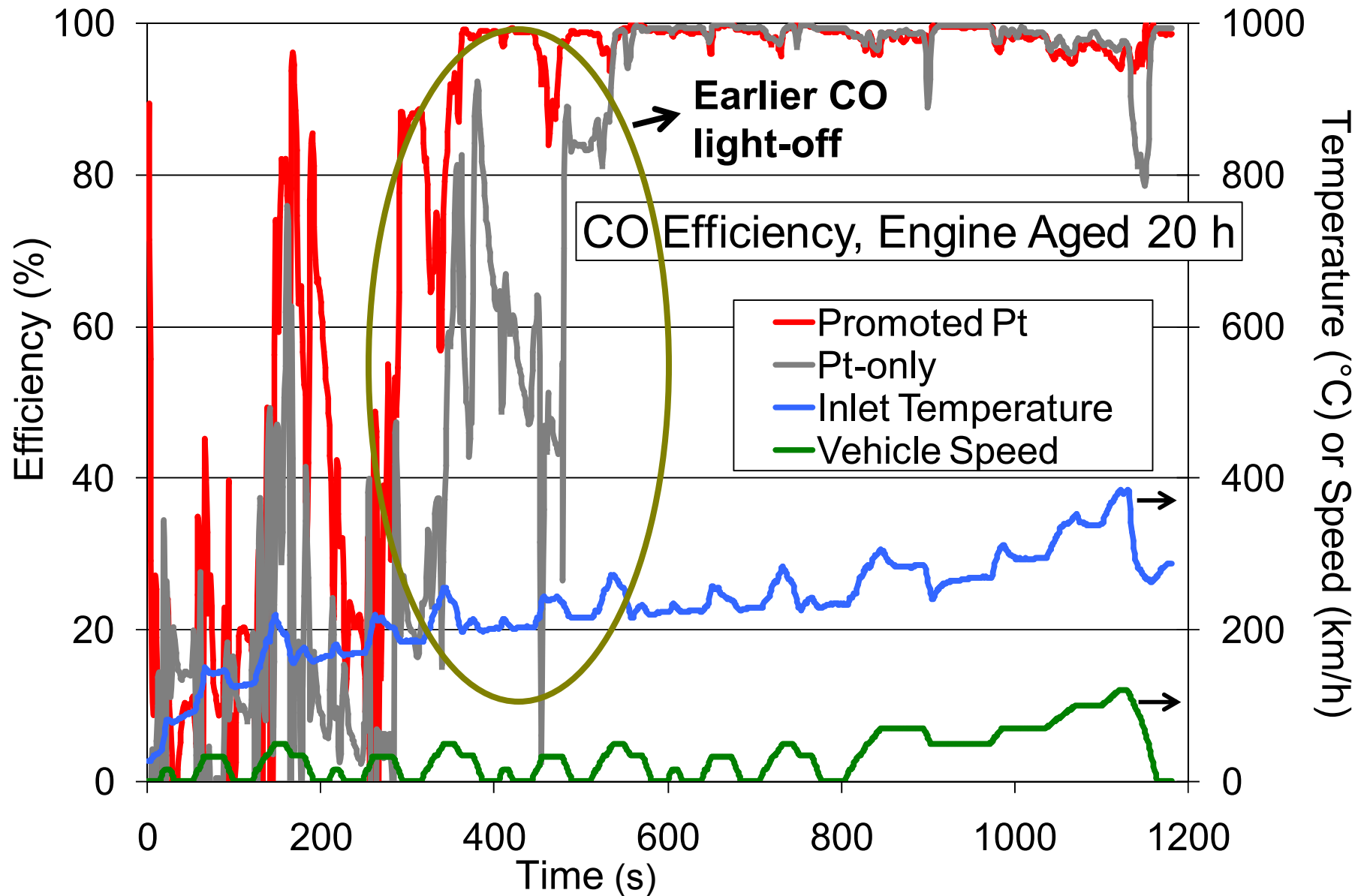
Vehicle Bag Data Show a Significant Advantage for Promoted Pt

24-28% lower fresh emissions and 43-45% lower aged emissions @ 2 g/L Pt

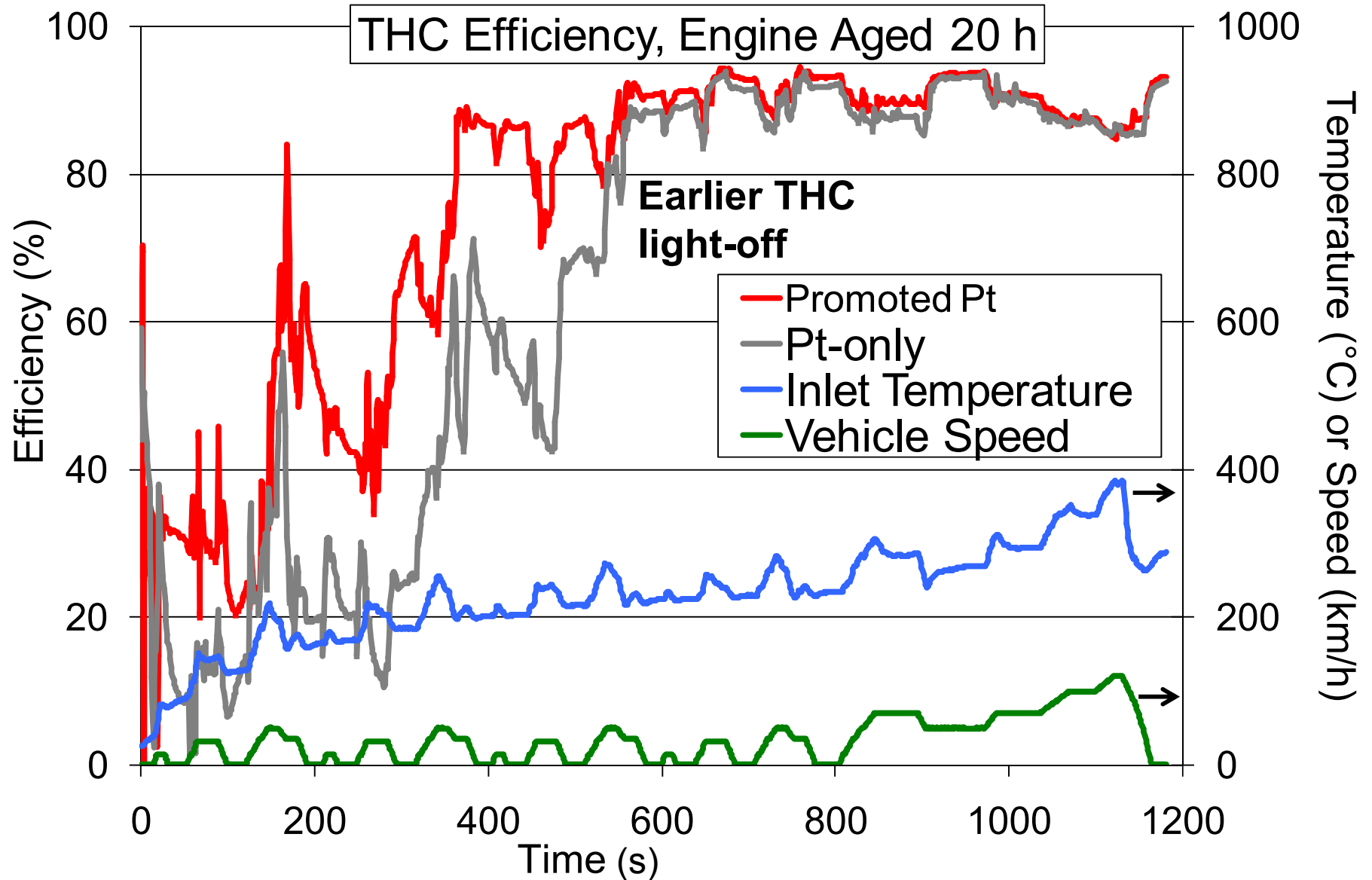


Note: No HC absorption components were added to either system

CO Efficiency Data Show Earlier CO Light-off for Promoted Pt



THC Efficiency Data Also Show Earlier Light-off for Promoted Pt





Summary

- We have developed a new family of Promoted Pt catalysts that have superior low temperature activity, performance stability, and tunable NO conversion
- These materials provide significant opportunity for metal cost savings and performance enhancement in advanced diesel combustion systems
- Rapid progress was facilitated by use of Nanostellar's Rational Catalyst Design methodology → Combining computational and experimental resources to enable advanced material discovery



Acknowledgements

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