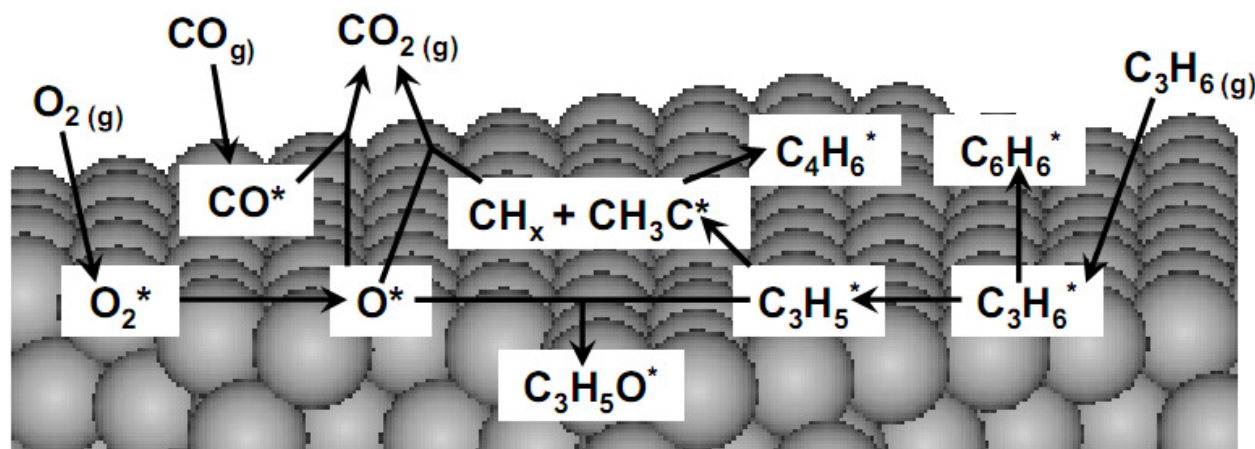


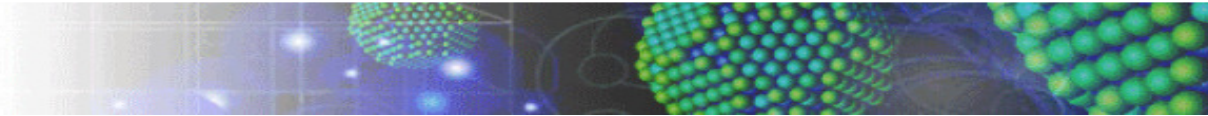
Overcoming Hydrocarbon Inhibition on Pd-based Diesel Oxidation Catalysts with Rational Catalyst Design Approach

Neeti Kapur¹, Jangsuk Hyun¹, Xianghong Hao¹, Bin Shan¹ and Kyeongjae Cho²

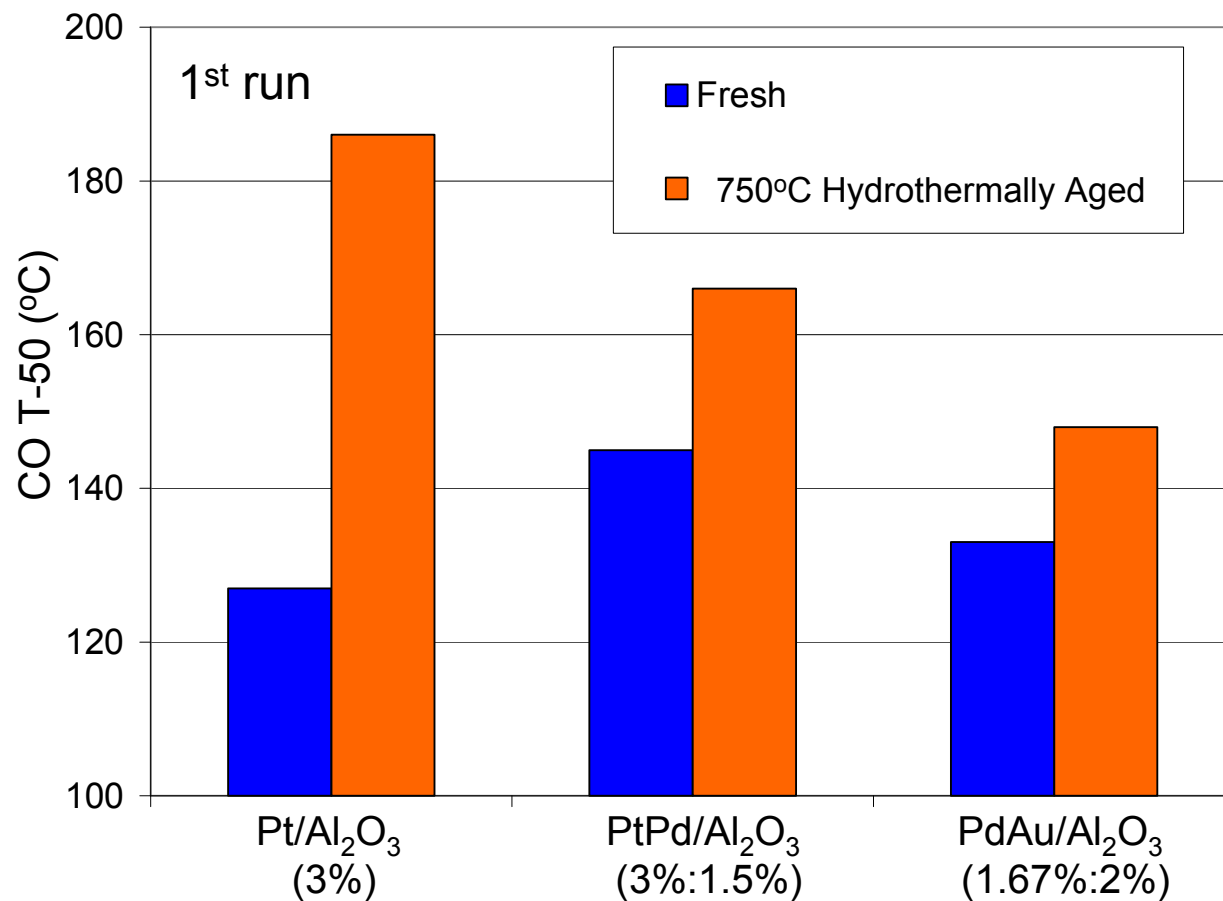
¹Nanostellar Inc., Redwood City, CA

²Department of Material Science and Engineering and Department of Physics, University of Texas at Dallas, Richardson, TX





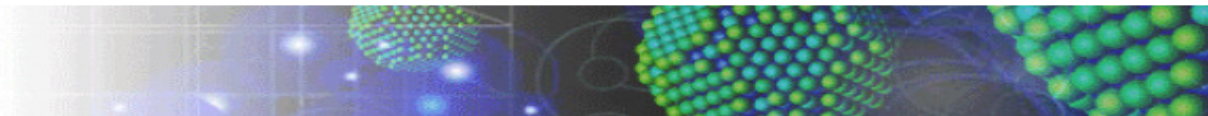
PdAu Catalyst Effective for CO Oxidation



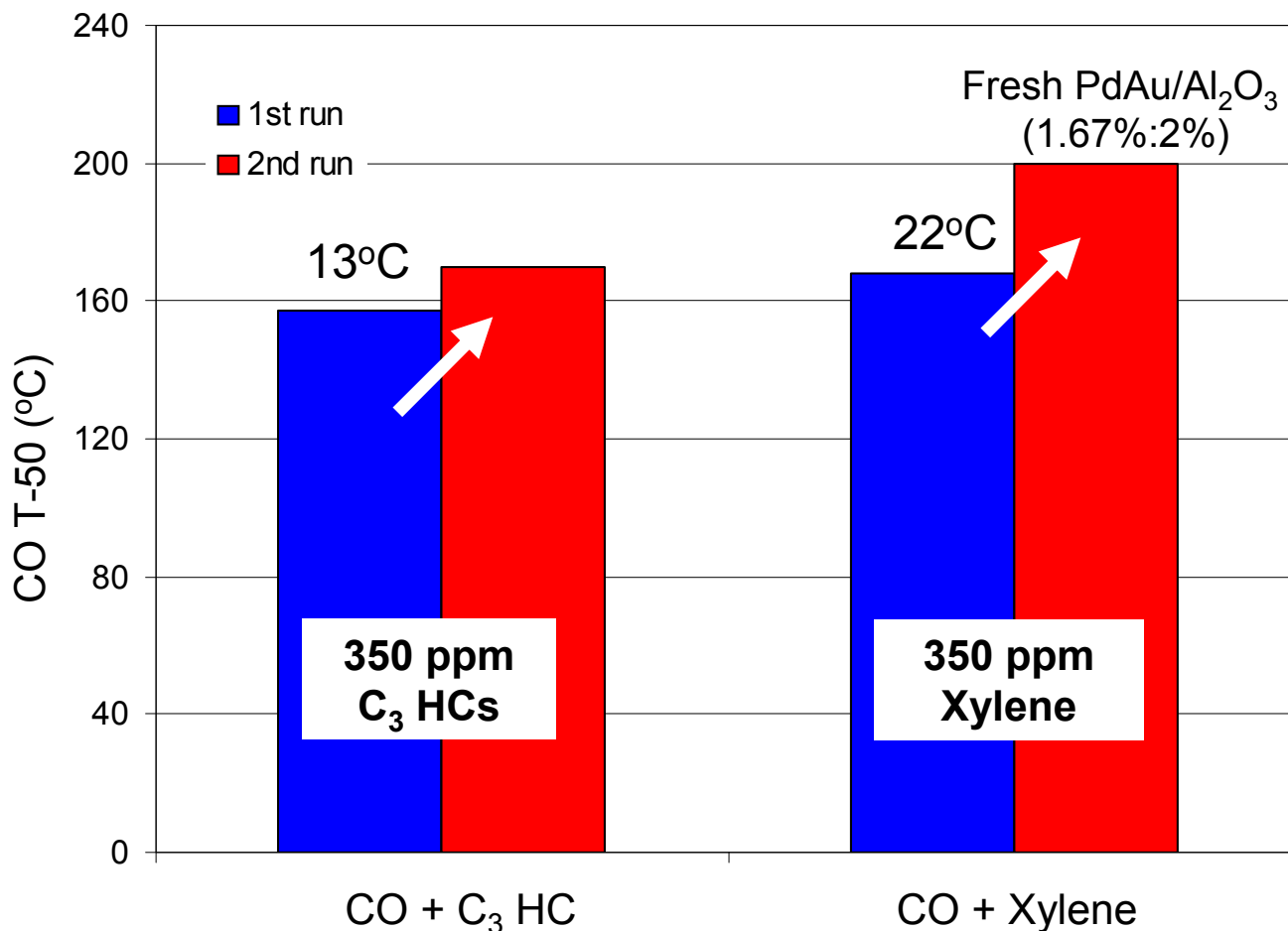
Powder Testing conditions:

1000ppm CO, 245ppm C₃H₆, 105ppm C₃H₈, 450ppm NO, 10%O₂, 10% CO₂ in He

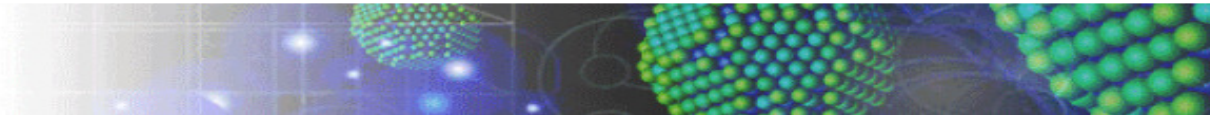
- CO light-off on aged Pt catalyst delayed due to sintering
- PdAu competes well with PtPd & Pt under fresh and aged conditions
- PdAu catalyst shows better hydrothermal stability than Pt & PtPd



Hydrocarbons Inhibit CO Light-Off on PdAu Catalyst



- Engine test show CO oxidation deteriorates more on PdAu than on Pt
- Lab tests show CO light off delayed by 13° (C₃ HCs) and 22°C (xylene)
- HC inhibition effect linked to hydrocarbon species and its oxidation



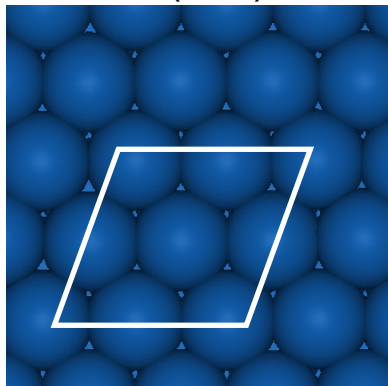
Goals & Methodology

- Mitigate hydrocarbon inhibition for CO oxidation on Pd-based catalysts
 - Mechanistic differences for propylene (C_3H_6) oxidation on Pt and Pd-based catalysts
 - Identify dopants to reduce hydrocarbon interference on Pd & PdAu

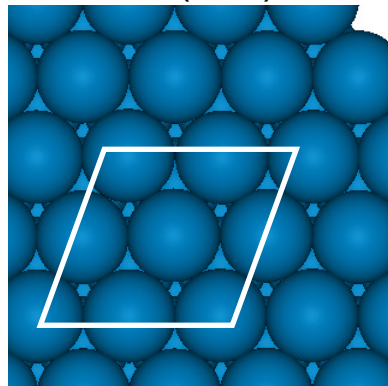
Rational Catalyst Design Methodology

- Light-off performance tests
- Surface characterization techniques (DRIFTS)
- Atomic-scale modeling (Density functional theory)

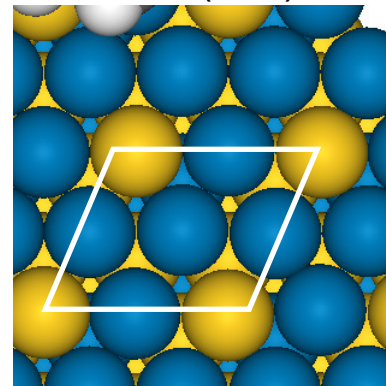
Pt(111)

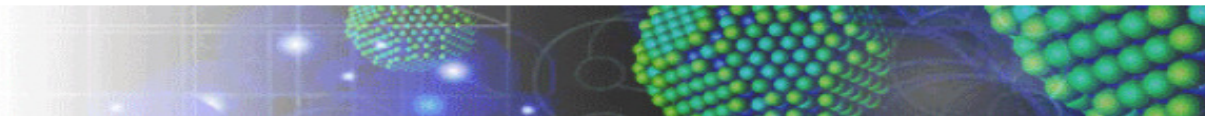


Pd(111)

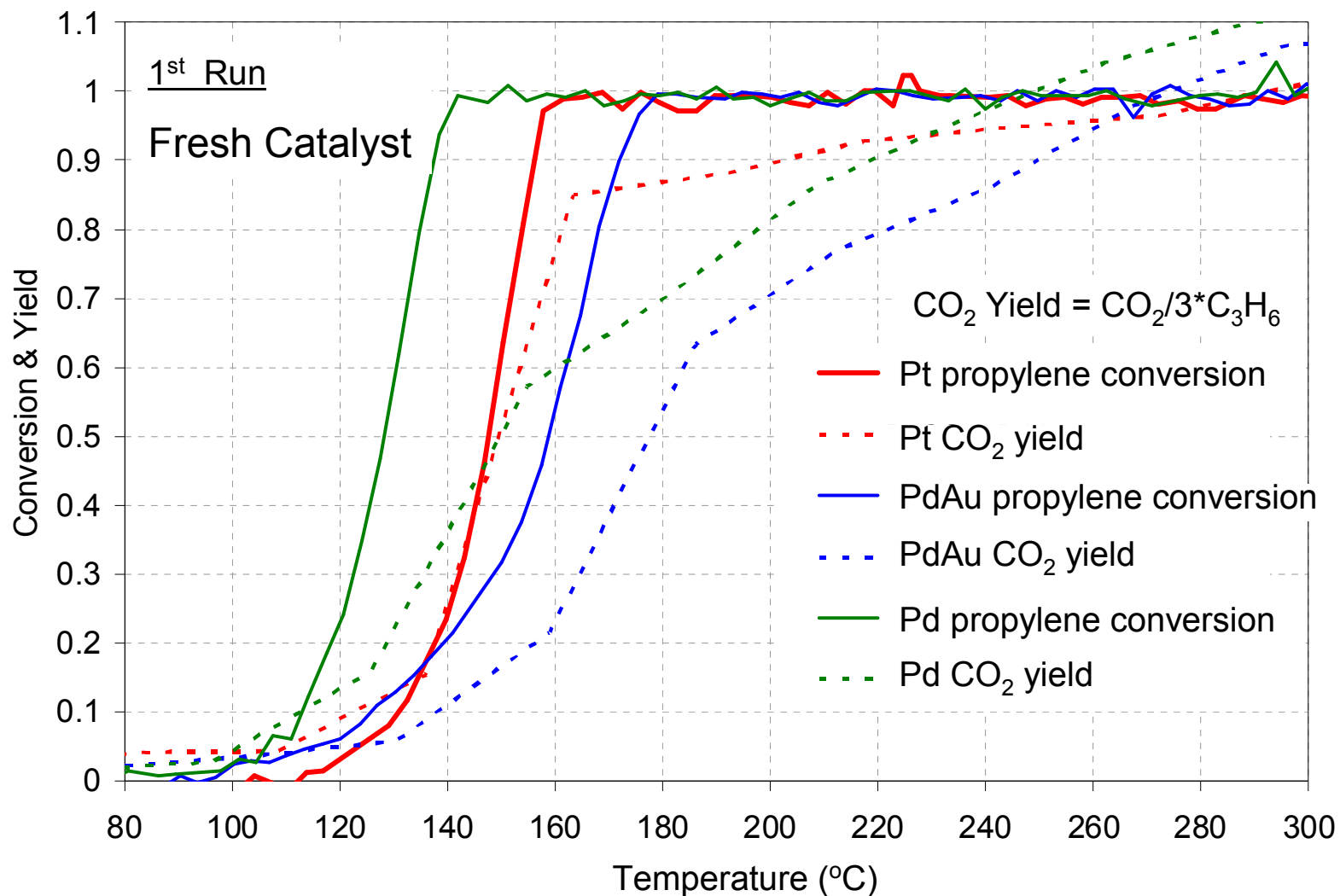


PdAu(111)

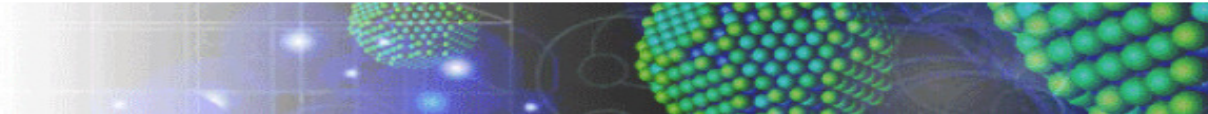




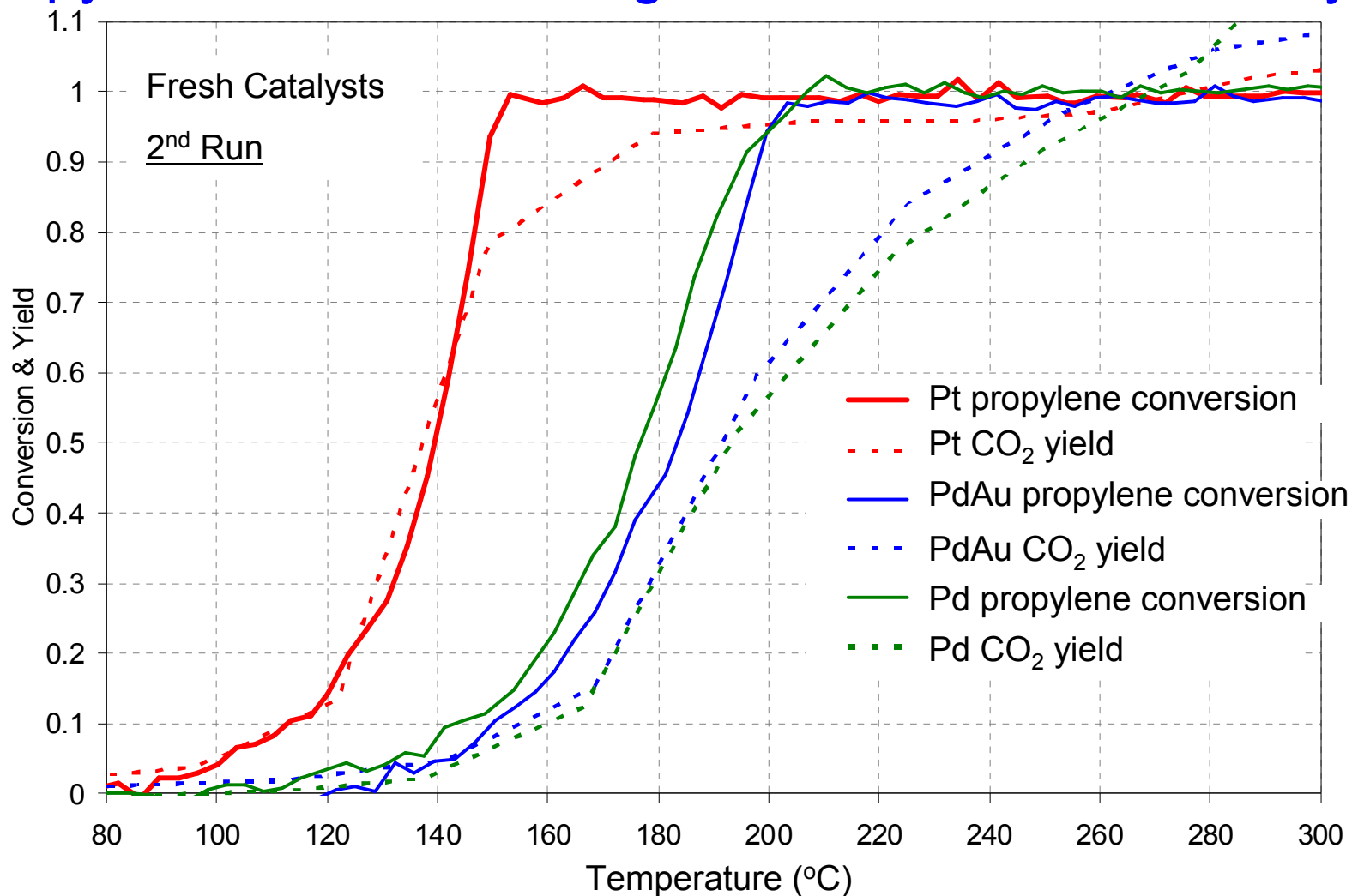
Incomplete Propylene Oxidation on Pd-based Catalysts



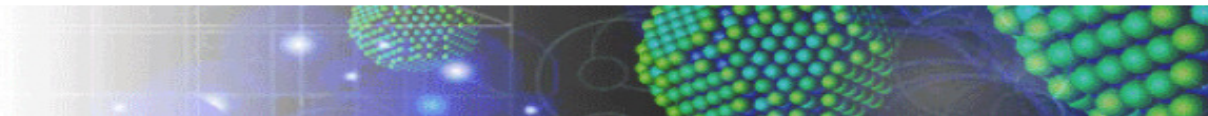
- For the 1st ramp up, propylene light off lowest for Pd
- Comparing propylene conversion and CO₂ yield difference: Pt < PdAu ~ Pd



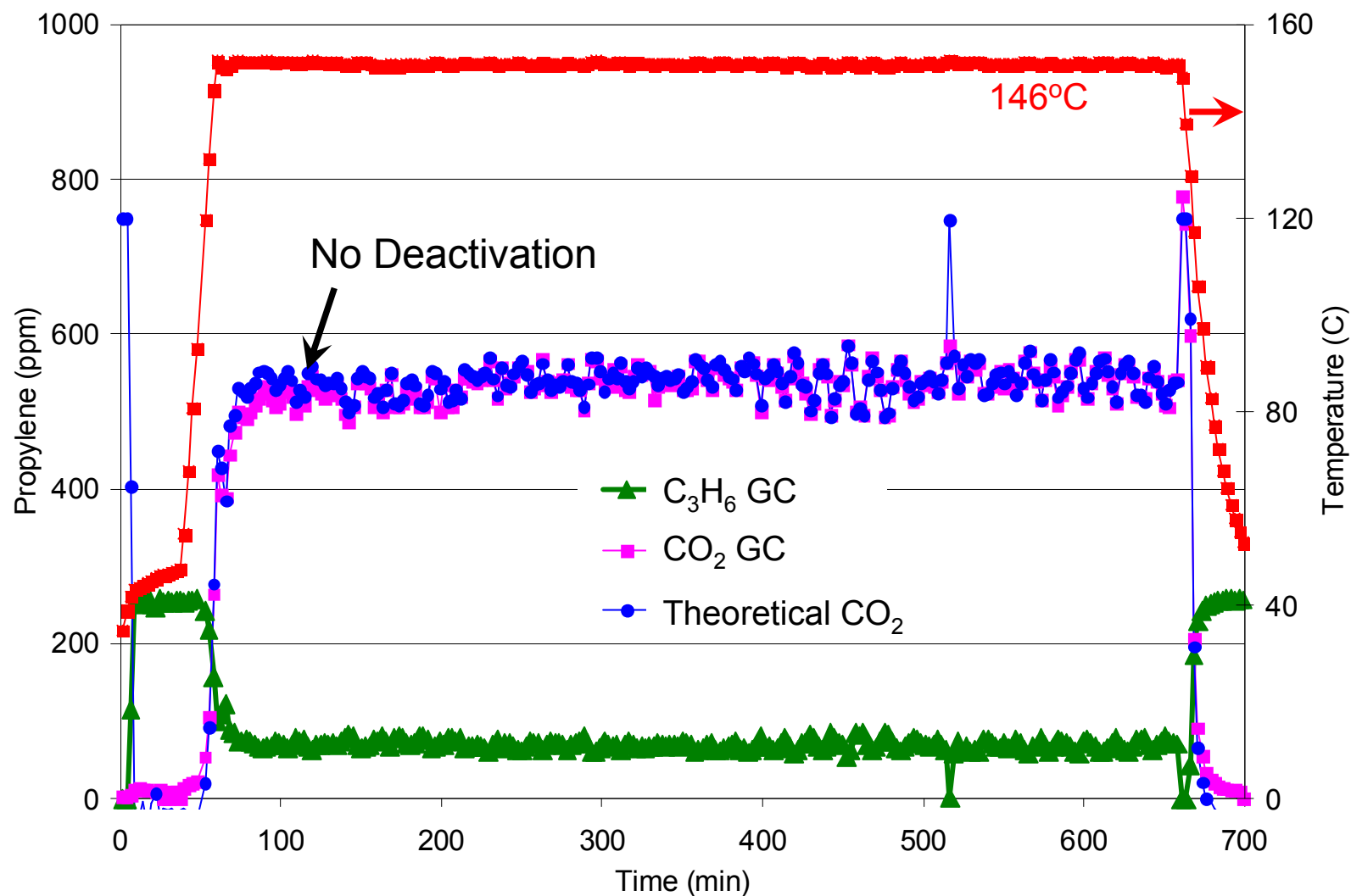
Propylene Conversion Degrades on Pd Over Test Cycles



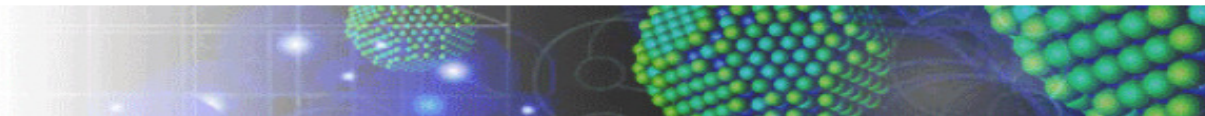
- Maximum light-off performance degradation on Pd (48°C)
- Comparing propylene conversion and CO₂ yield difference: Pt < PdAu ~ Pd



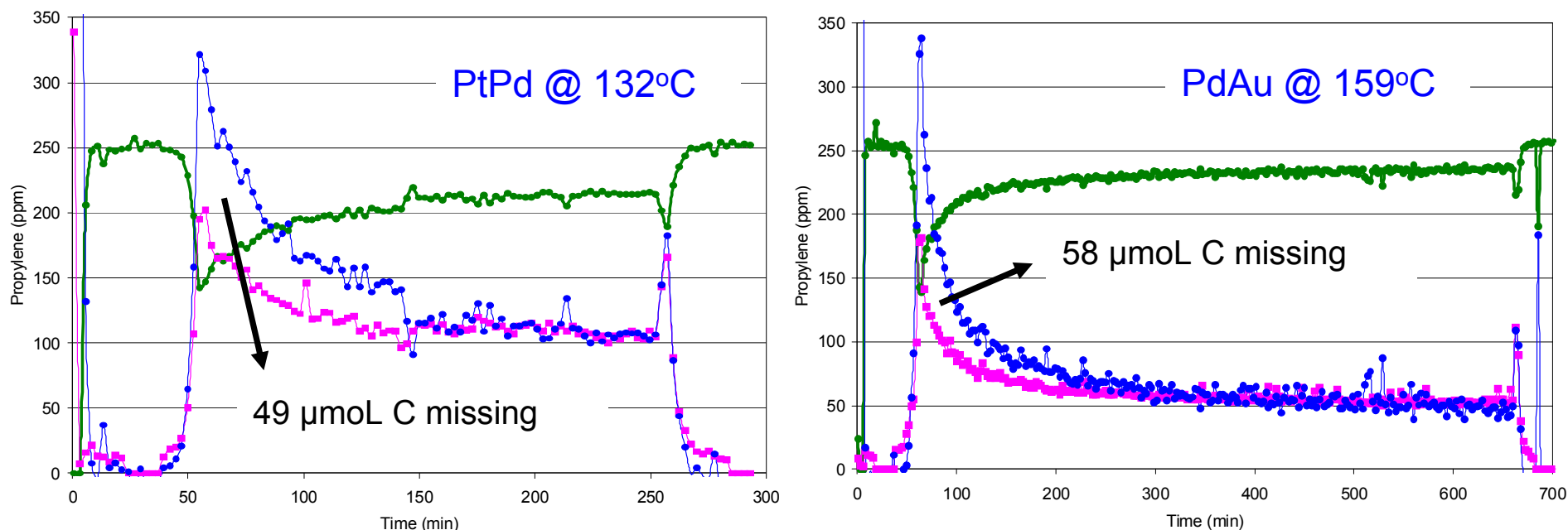
Steady State Propylene Oxidation on Pt



Theoretical CO₂ (100% C₃H₆ conversion to CO₂) agrees well with measured CO₂



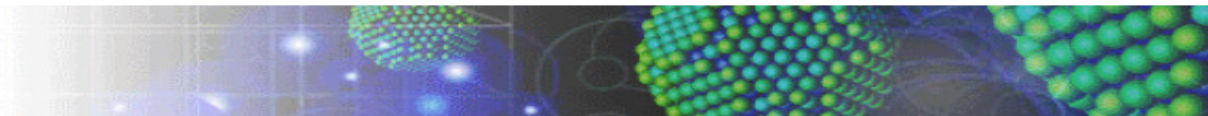
Propylene Oxidation Deactivates on Pd-Catalysts Over Time



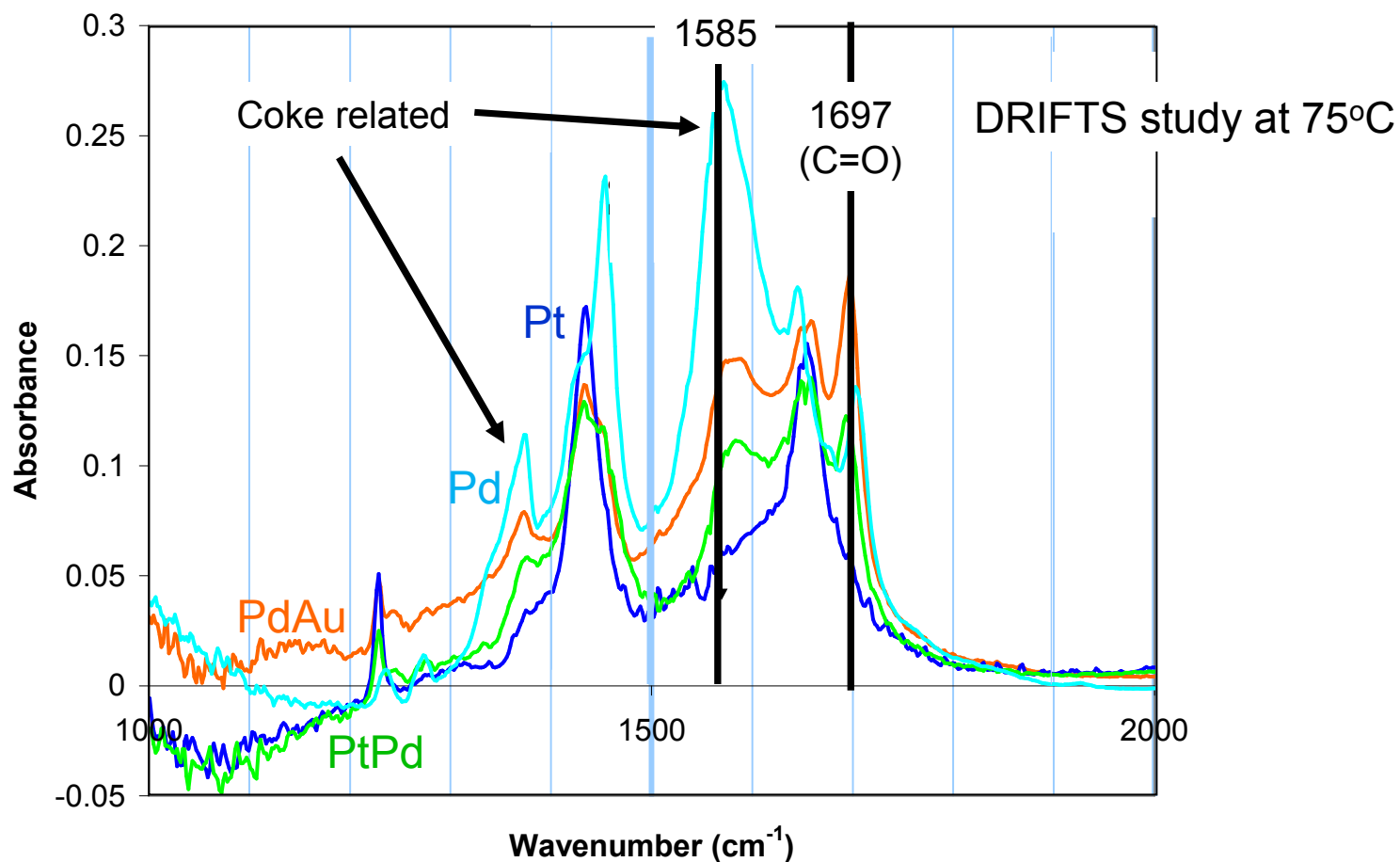
- ▲ C_3H_6 GC
- CO_2 GC
- Theoretical CO_2

- Measured CO_2 less than the theoretical CO_2 for both PtPd & PdAu
- PdAu deactivates for a longer time than PtPd

Oxidation by-products either on the support or blocking reaction sites

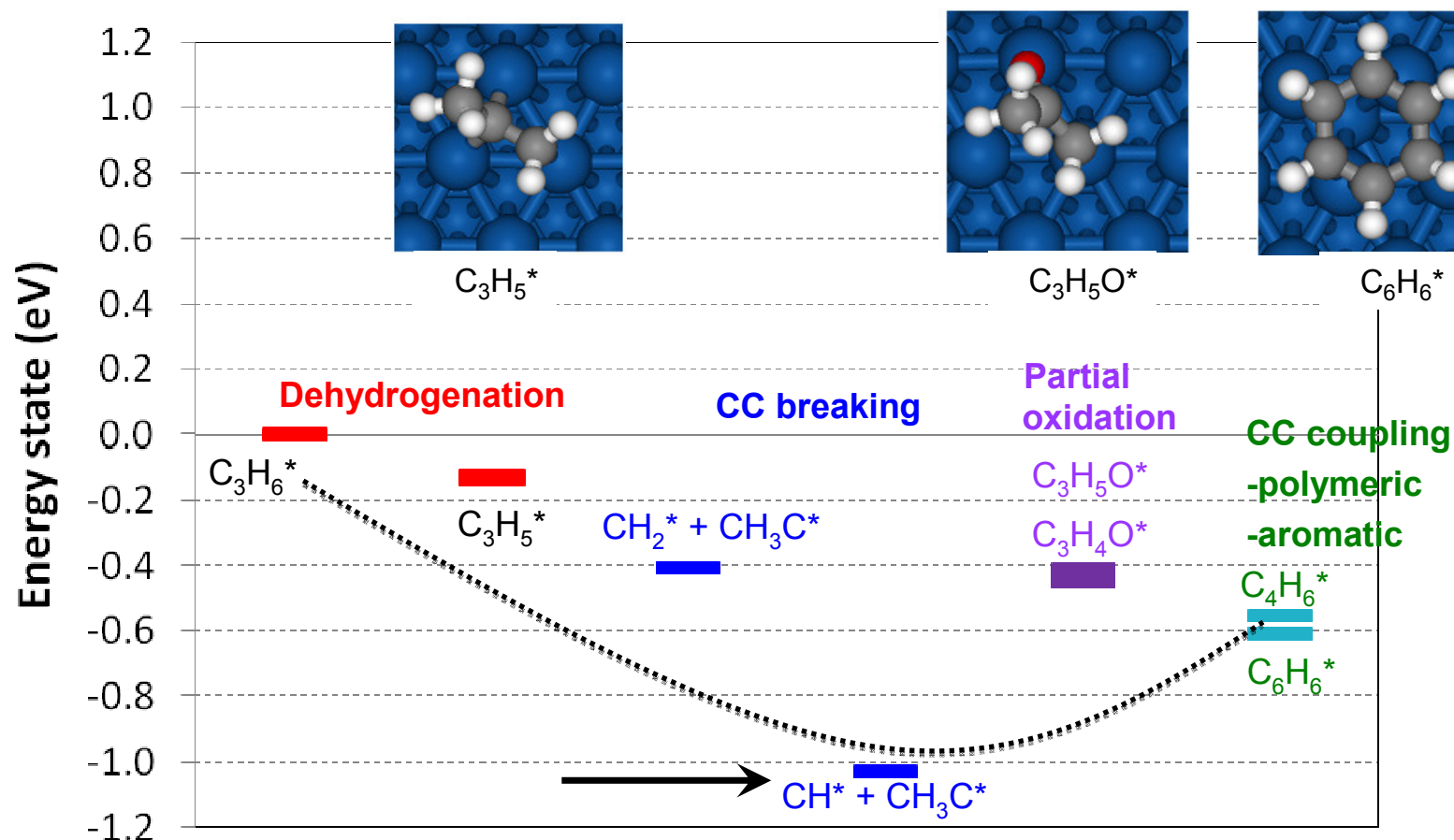


By-Products on Pd sites during Propylene Oxidation

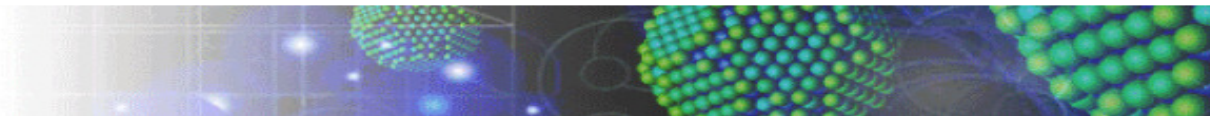


- Pd based catalysts showed significant inhibition effects for CO/HC oxidation unlike Pt
- Inhibition on Pd catalysts linked to presence of C=C vibration ~1600 cm⁻¹ and C=O double bonds ~ 1700 cm⁻¹ → **Coke and coke precursors ?**

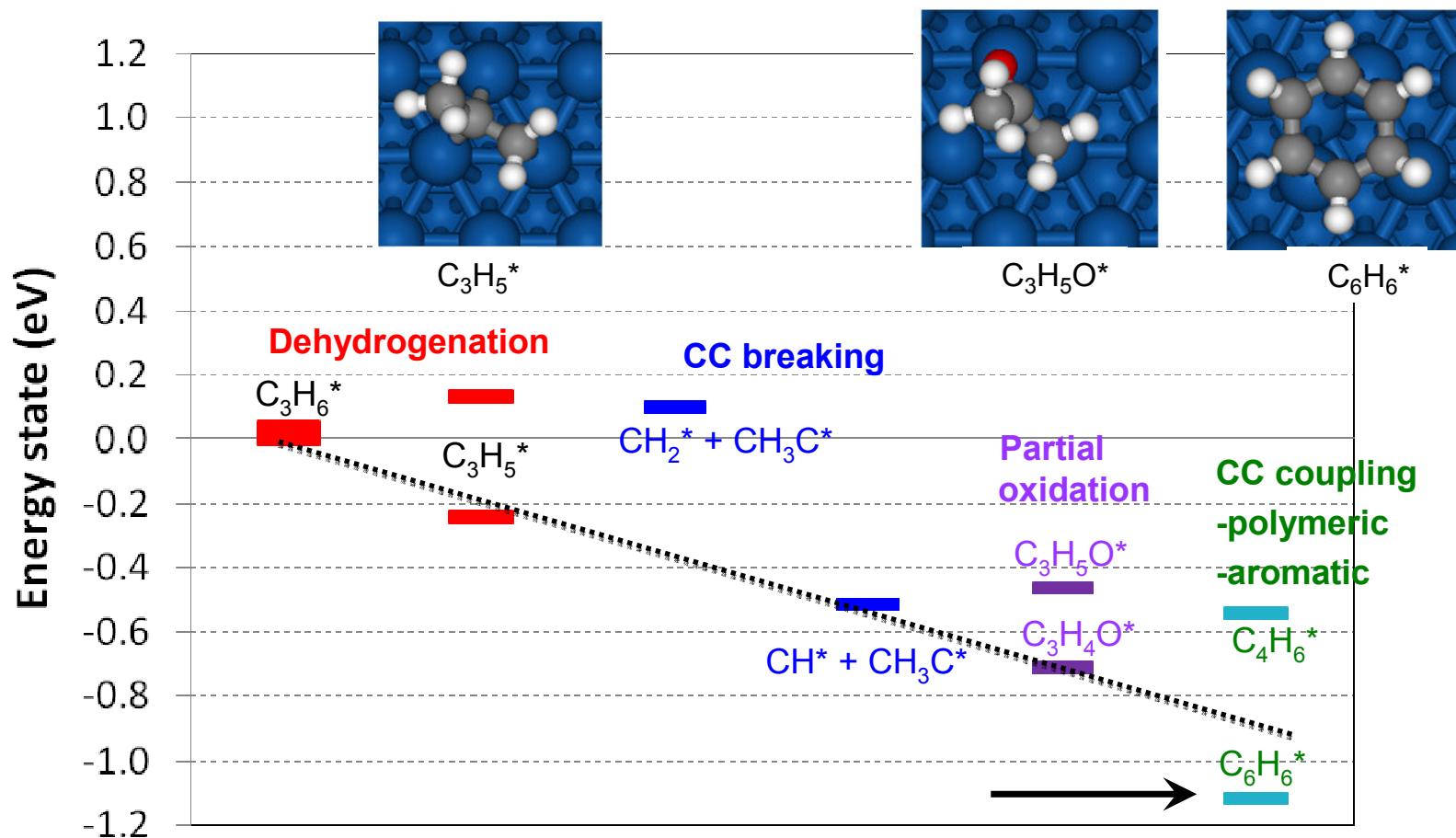
Propylene Decomposition & Oxidation on Pt(111)



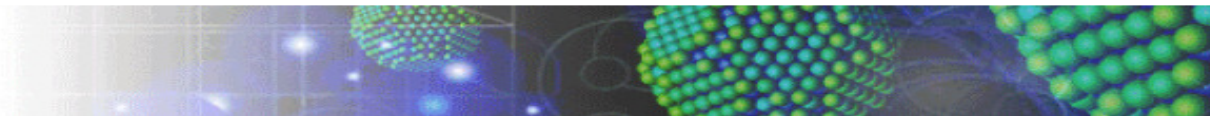
- Using Density Functional Theory to examine propylene decomposition and oxidation products
- C-C scission products (C_3H_4) are more strongly bound on Pt as compared to oxygenates and aromatics



Propylene Decomposition & Oxidation on Pd(111)

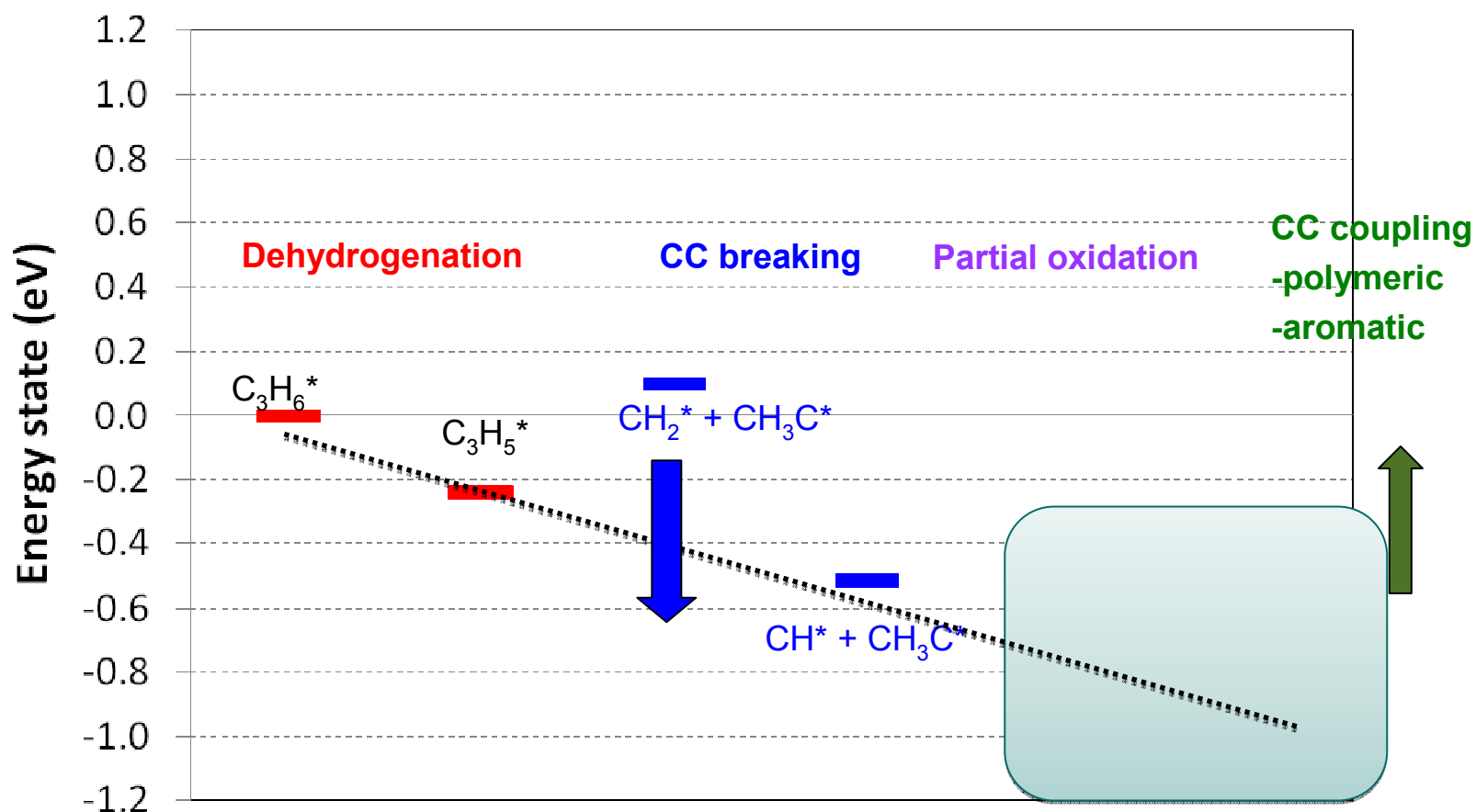


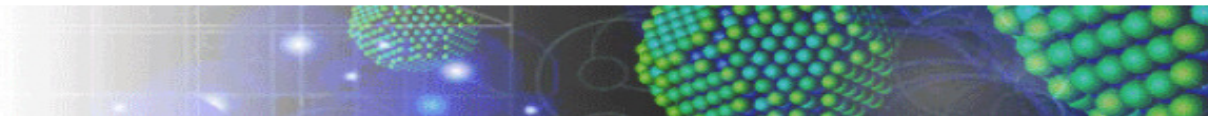
- C-C scission products (C_3H_4) are energetically less favored than partially oxidized species ($C_3H_4O^*$) and polymerized species ($C_4H_6^*$)
- *Formation of aromatic ($C_6H_6^*$) and conjugated diene ($C_4H_6^*$) is strongly preferred on Pd (Coke precursors)*



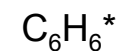
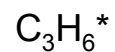
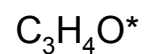
Goal: To develop Pt-like system to overcome hydrocarbon inhibition on Pd-catalysts (Screening Parameters)

- Stabilize small hydrocarbon species
- Destabilize coke precursors (conjugated dienes, aromatics) and oxygenates

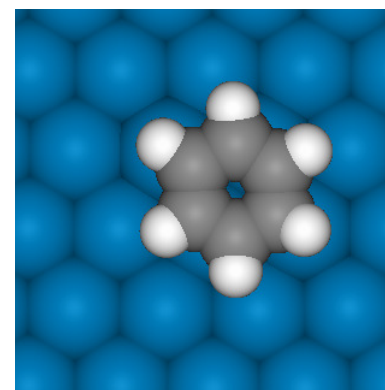
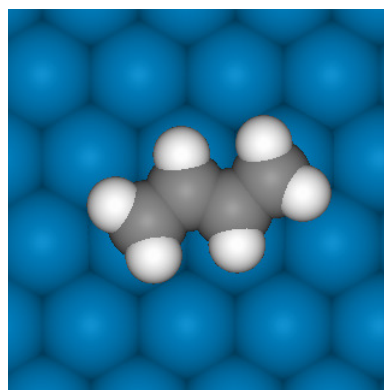
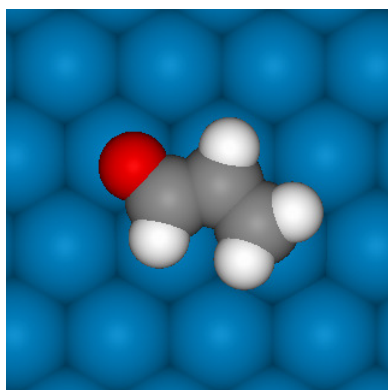




Rational Catalyst Design Approach

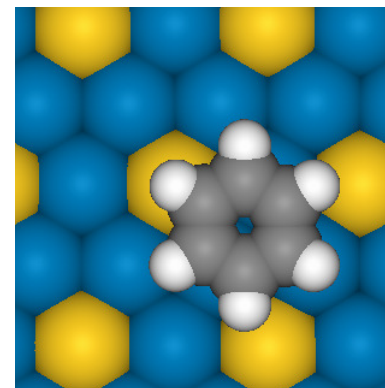
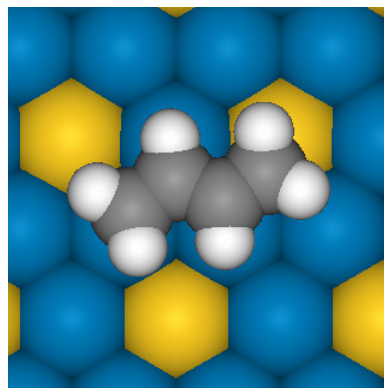
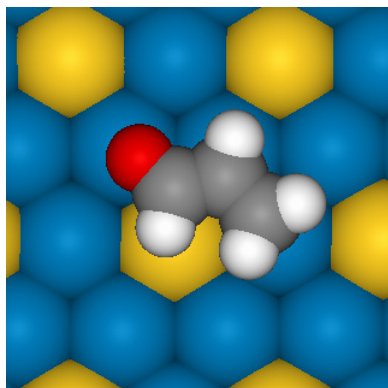


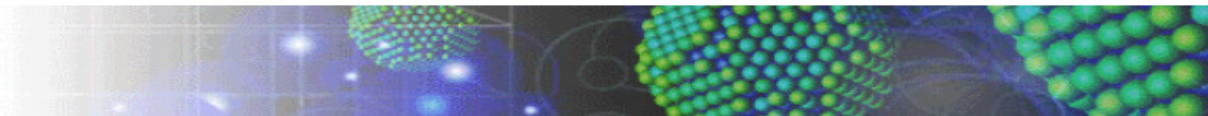
Pd



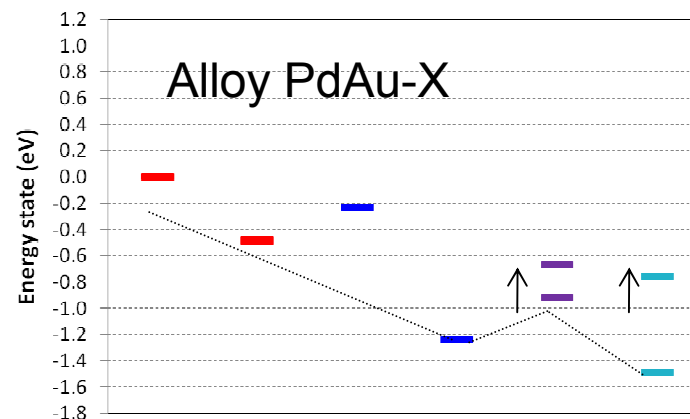
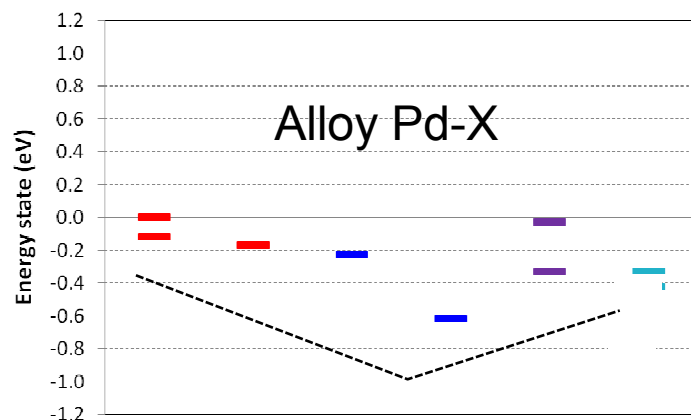
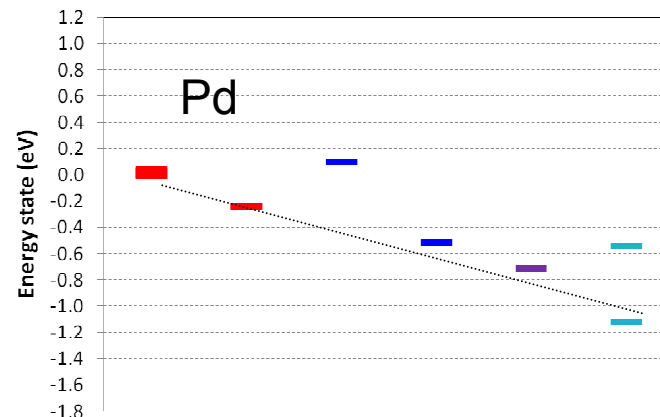
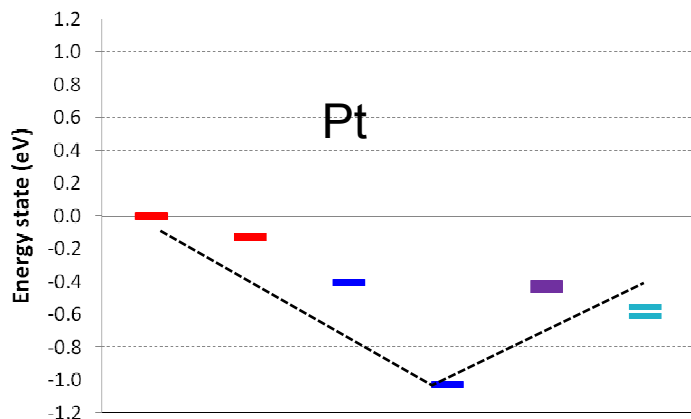
Dilute ensemble to destabilize coke precursors and oxygenates while keeping ensemble favorable towards desired reactions

PdAu





● DFT design: Surface Alloy



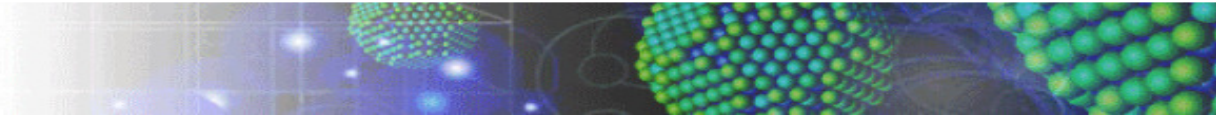
Dehydrogenation

CC breaking

Partial oxidation

CC coupling

- Coke precursors and oxygenates destabilized for PdAu-X
- Pd-X shows Pt-like trend for intermediates



Summary

- CO oxidation inhibited by hydrocarbons during consecutive test cycles on Pd-catalysts unlike Pt linked to hydrocarbon oxidation itself
- Propylene as prototype for gaining insights into oxidation mechanism
 - Pt exhibits stable propylene oxidation performance, oxides propylene completely to CO₂ and no other by-product detected
 - Incomplete propylene combustion on Pd & PdAu, conversion degrades in consecutive runs
 - Light-off performance on PtPd better than Pt, Pd & PdAu but it deactivates over time as well
 - Oxygenate & coke determined as majority by-product on the support and/or accumulated over Pd sites
- Can improve hydrocarbon decomposition by stabilizing small hydrocarbon species and destabilizing aromatic molecules & dienes on catalyst
- Rational catalyst design approach (relative energy of decomposition intermediates) used to identify Pd and PdAu dopants which
 - Favors hydrocarbon scission products over by products
 - Reduced hydrocarbon inhibition & retain CO oxidation performance