Low Temperature Emissions Control

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U.S. Department of Energy

ACE085
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Project Overview

Timeline

- Started in FY2013
  - Reprogrammed project that was unfunded in 2012
  - Prior project focused on effects of advanced combustion regimes on emissions control (Multi-mode)

Barriers

- From DOE Vehicle Technologies Multi-Year Program Plan (2011-2015)
  - 2.3.1.B: Lack of cost-effective emission control
  - 2.3.1.D: Durability
- Responsive to ACEC Tech Team requested emphasis on low temperature emissions control

Budget

- FY2013: $400k (expected)
- FY2012: $0k

Partners

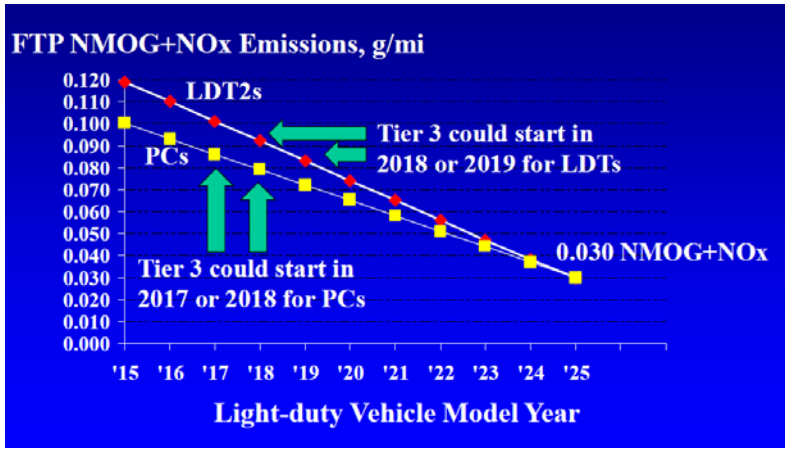
- BES-funded scientists Sheng Dai and Steve Overbury
- Center for Nanophase Materials Science (CNMS) user project

Objectives and Relevance

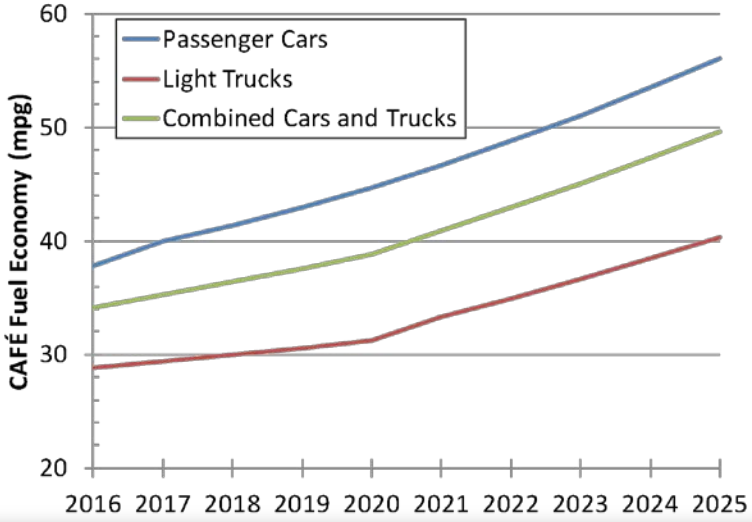
Develop emission control technologies that perform at low temperatures (<150ºC) to enable fuel-efficient engines with low exhaust temperatures to meet emission regulations

- Project aims to identify advancements in technologies that will enable commercialization of advanced combustion engine vehicles
  - Advanced combustion engines have greater efficiency needed to meet CAFE
    - consequently lower exhaust temperatures
  - At low temperatures catalysis is challenging
    - emissions standards harder to meet, getting stricter
- Perform research on strategies to improve low temperature catalysis for emission control
  - Need ~90% conversion at T ≤ 150°C
- Investigate "trap" material technologies that would temporarily store emissions
  - Released and converted later under periodic high temperature conditions

Emissions



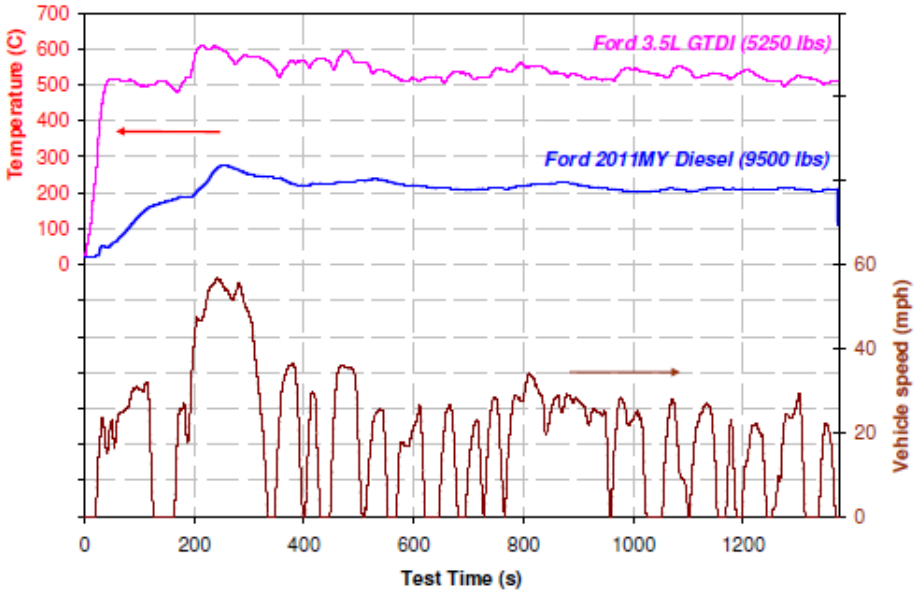
Fuel Economy

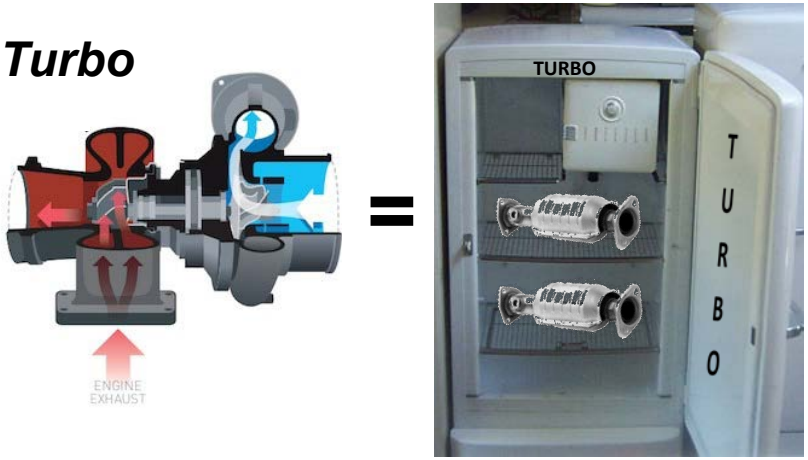


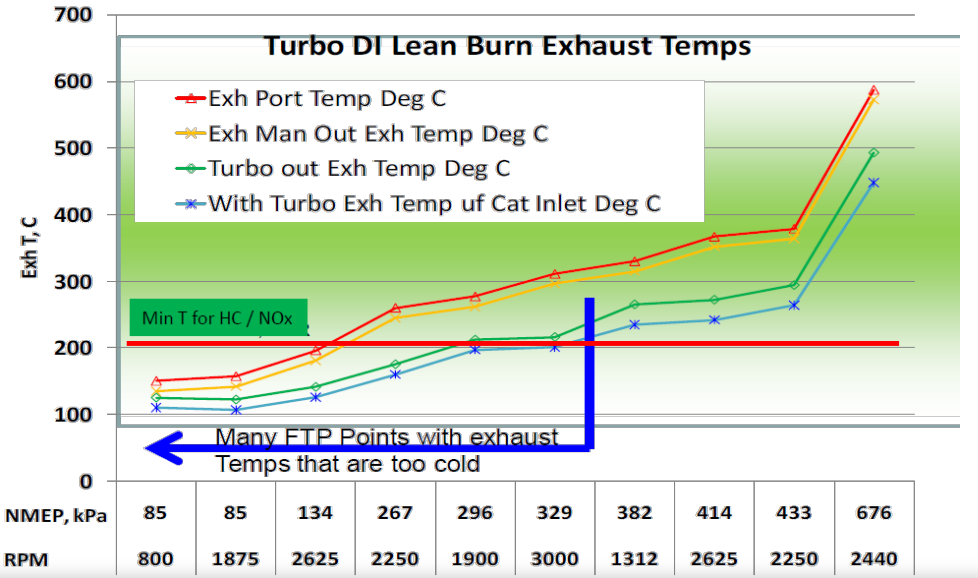
Top: J.Kubsh, "Light-duty Vehicle Emission Standards", 01/10/2013.
Bottom: C. DiMaggio, "ACEC Low Temperature Aftertreatment Program", 06/21/2012.

Improved vehicle efficiency leads to low exhaust temperature

- Advanced combustion modes have greater efficiency and consequently lower exhaust temperatures
- Low temperature exhaust is not simply a start-up problem
- Exhaust temperatures stay low throughout the FTP
- Further improvements in efficiency will be even more challenging for emissions
  - Waste heat recovery (WHR)
  - ACEC: "Turbo = Catalyst Refrigerator"

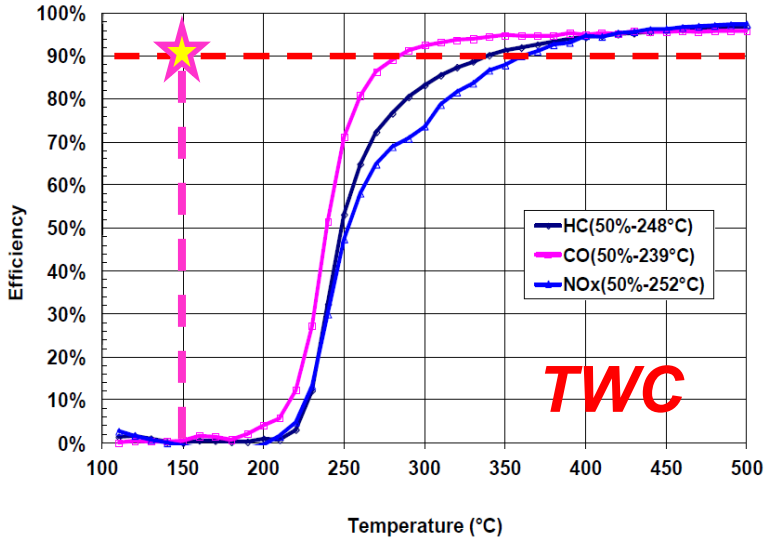


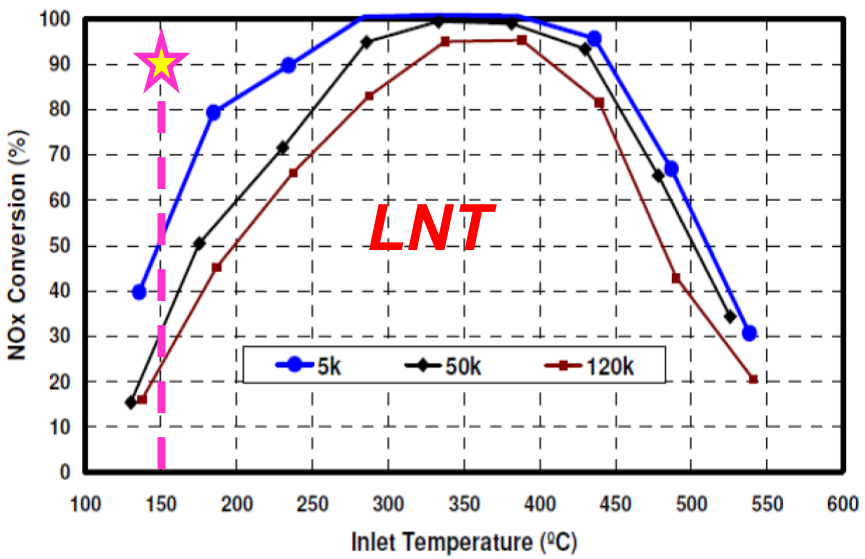


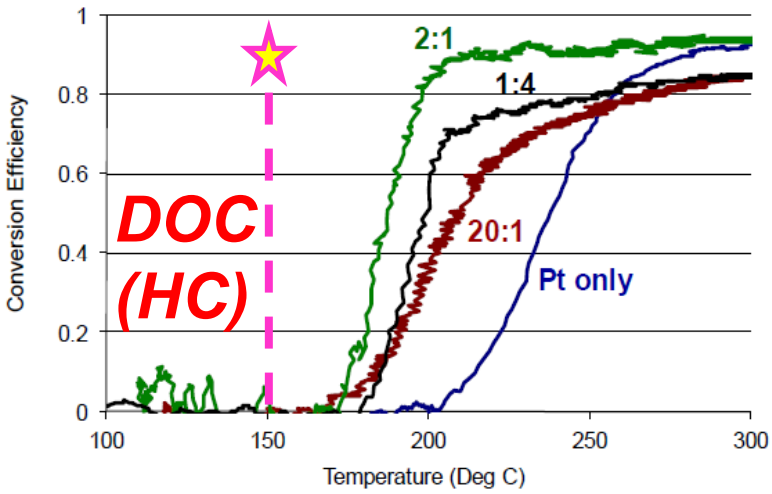


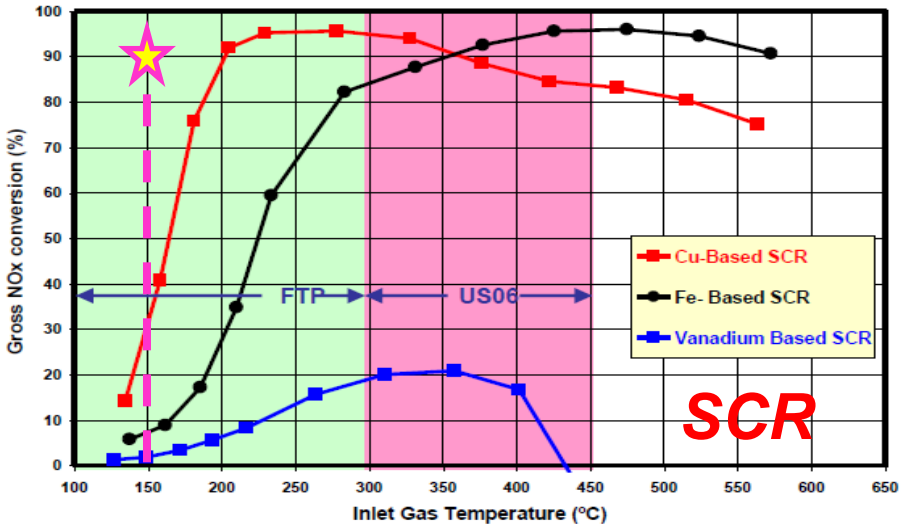
Top: C. Lambert, "Future Directions in SCR Systems", 2012 CLEERS workshop, 05/01/2012.
Bottom: M. Zammitt, "ACEC Future Aftertreatment Strategy Report", 01/10/2012.
Turbo: http://www.autoblog.com/2012/10/03/turbo-sales-to-accelerate-by-80-could-make-up-40-of-global-of/

Current emissions control technologies have limited activity at 150°C







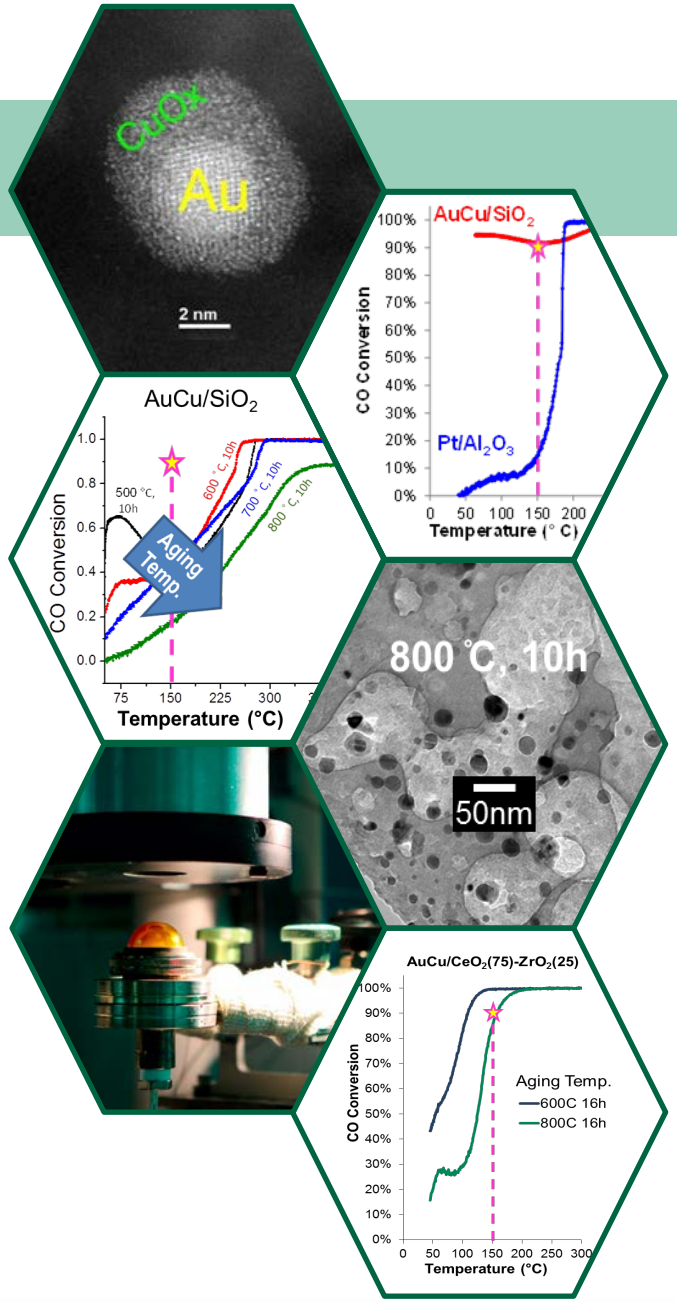


All: M. Zammitt, "ACEC Future Aftertreatment Strategy Report", 01/10/2012.

Approach:

Pursue innovative catalyst technologies to improve low temperature emissions control

- Coordinate with BES-funded scientists to identify catalysts/technologies that have potential
  - Transfer “science” findings to applied settings
- Evaluate promising catalysts/technologies under exhaust-relevant conditions
  - H_2O, CO_2, CO, HC, NOx
- Investigate durability
  - Sulfur, aromatics, hydrothermal cycling
- Characterize catalysts/technologies to understand fundamental behavior and limitations
  - Particularly when performance is being impeded
  - Materials and specific catalyst functionality/chemistry
- Redesign catalysts trying to overcome shortcomings



Milestones

- Previous project scope was aimed at measuring the impact of advanced combustion modes on emissions control
  - Low temperature reactivity seen to be a significant hurdle
- Example completed previous milestones are:
  - Comparison of Cu- and Fe-zeolite Urea-SCR catalyst performance for multimode diesel engine operation
  - Characterization of hydrocarbon oxidation efficiency of diesel oxidation catalyst for low load operation with advanced combustion which results in lower exhaust temperatures
- Current direction is to identify novel/innovative technologies that can be implemented to address the challenges of advanced combustion strategies
- **FY13 Milestone: Characterization of performance and surface morphology for a novel candidate catalyst (September 30, 2013)**
  - *On target*

Collaborations

- Basic Energy Sciences [active]
  - Sheng Dai and Steve Overbury (ORNL)
  - Center for Nanophase Material Science (ORNL)
- Interactions with other fundamental catalysis groups [planned]
- CLEERS [active]
  - Dissemination of data; presentation at CLEERS workshop
- USCAR/USDRIVE [active and future activities]
  - Participation in US DRIVE 2012 Low Temperature Workshop
    - ACEC catalyst sub-team (GM, Ford, Chrysler, PNNL, ORNL)
  - Guidance of critical technology needs

Summary of Technical Accomplishments

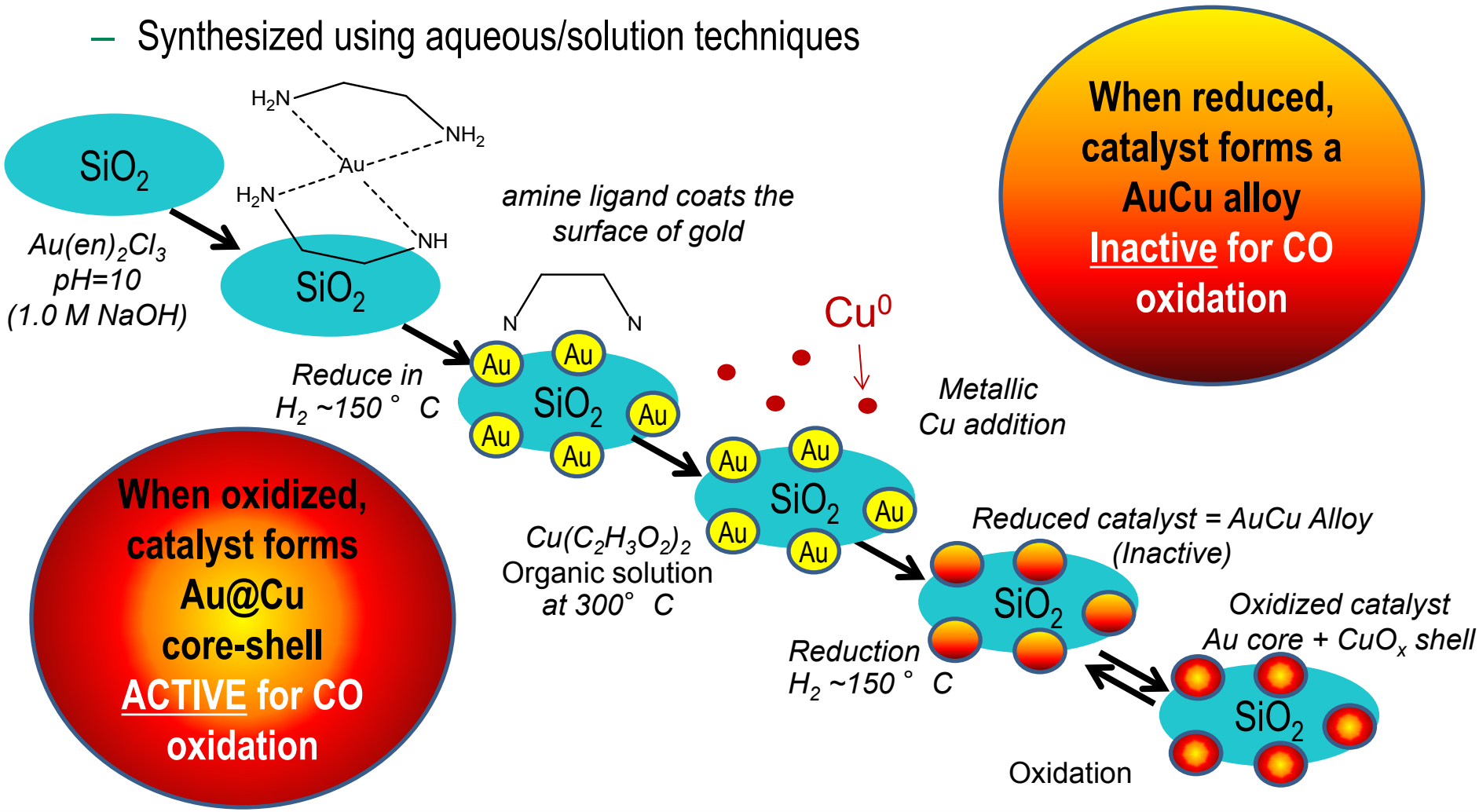
- **Investigated innovative Au@Cu (core@shell) catalyst for oxidation**
  - Copper oxide surrounding Au core shows excellent low temperature CO oxidation behavior
    - In presence of CO_2 and H_2O
  - Inhibition by HC and NOx observed
    - Could be potential CO-cleanup catalyst at tailpipe
  - Durability investigated up to 800°C
    - Performance is good up to 700°C, but falls off 800°C; Sintering observed

- **Demonstrated synergy of mixing of Au@Cu and Pt catalysts and potential to overcome inhibitions**
  - Pt inhibited by CO at low temperature; improved with AuCu
  - Very high NO to NO_2 oxidation observed with mixture

- **Synthesized and evaluated new catalysts using a new support**
  - Improved hydrothermal durability using ceria-zirconia support

Synthesis of AuCu/SiO_2 Catalyst

- Supported Au nanoparticles serve as templates to synthesize small and disperse intermetallic AuCu nanoparticles
  - Synthesized using aqueous/solution techniques

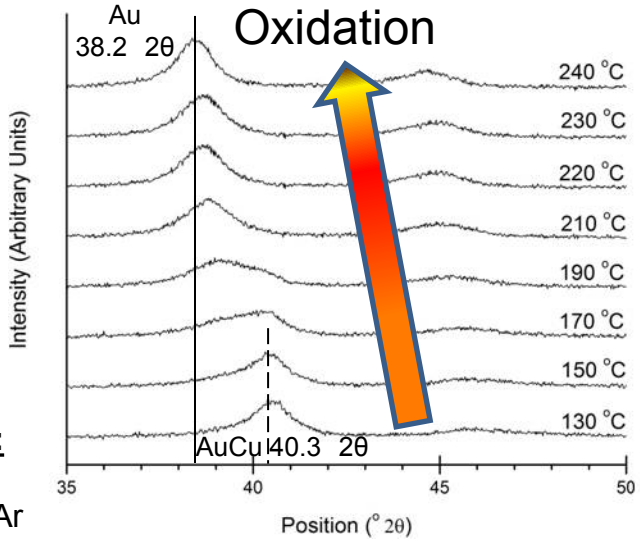


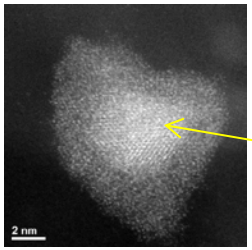
H. Zhu *et al*. *Applied Catalysis A: General* **2007**, *326*, 89-99
Bauer *et al.* Phys. Chem. Chem. Phys., **2011**, *13*, 2571-2581

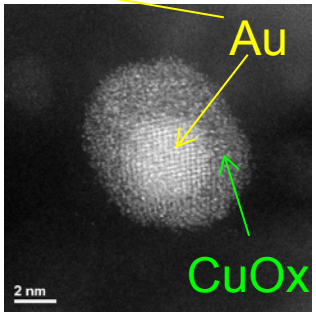
AuCu/SiO_2 catalyst is activated under lean conditions; forms core (Au) shell (CuOx)

- When oxidized, Au core surrounded by amorphous CuO_x shell after heating at 500 °C

Oxidation pretreatment conditions:
Flow Rate = 75 sccm
550°C for 16 in 10% O_2 + 1% H_2O in Ar

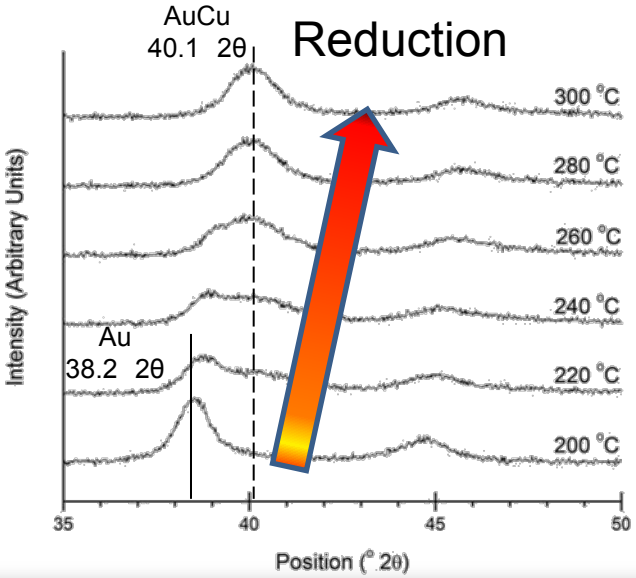


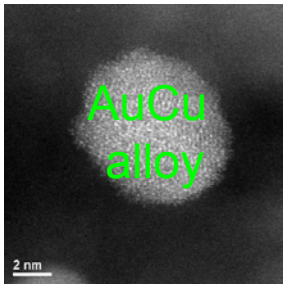




ACTIVE

- After H_2 reduction at 300 °C, AuCu alloy forms
  - Time required to be reduced
  - Brief rich period will not inactivate catalyst



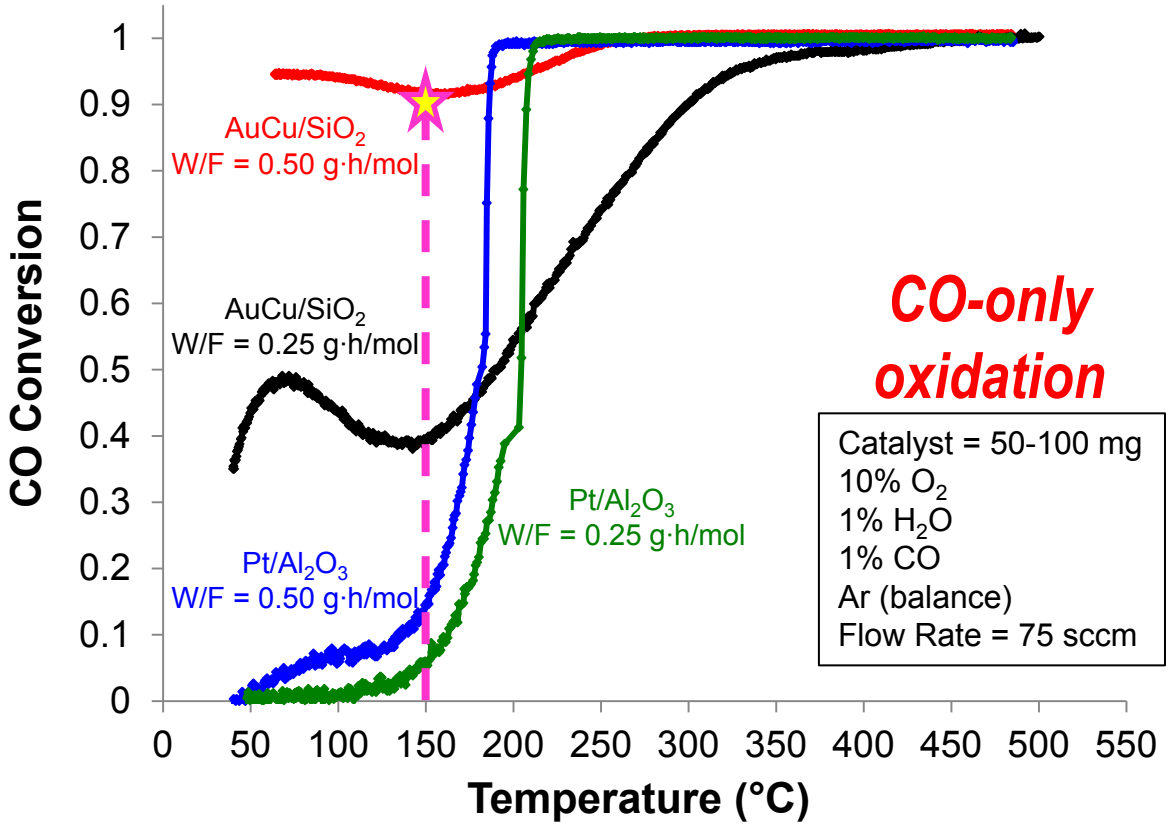


Inactive

$Au@Cu/SiO_2$ catalyst is excellent for low temperature CO oxidation

- $Au@Cu/SiO_2$ shows high activity even at 50°C
  - Reactivity as low as 0 °C
- Similar loadings of Pt/Al_2O_3 catalyst show little activity below 200°C
  - $T_{50\%}$ = 182-205 °C
  - Pt/Al_2O_3 space velocity:

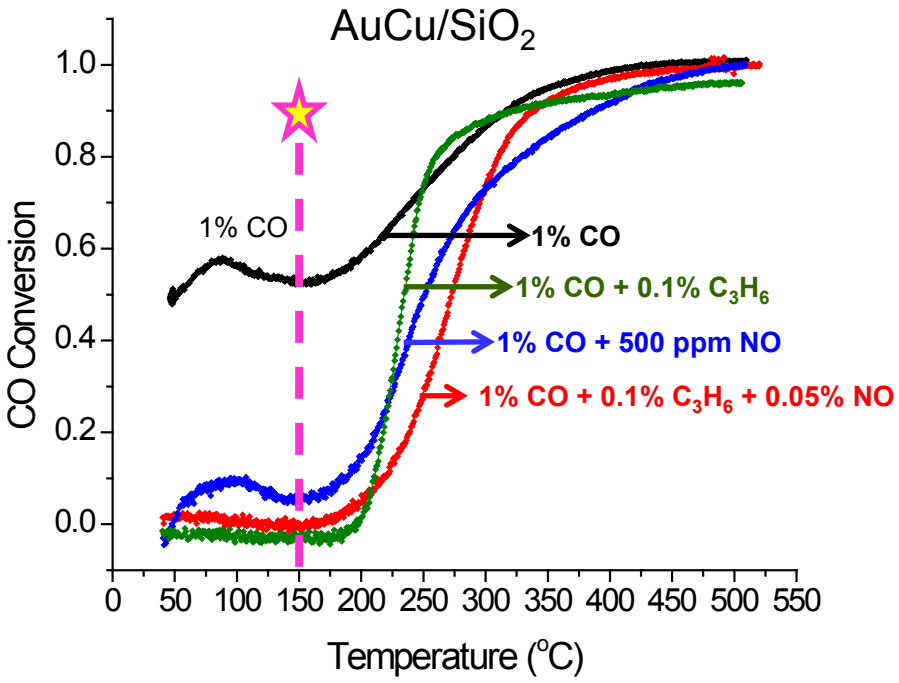
W/F = 0.5 g·h/mol is 27k h^{-1}

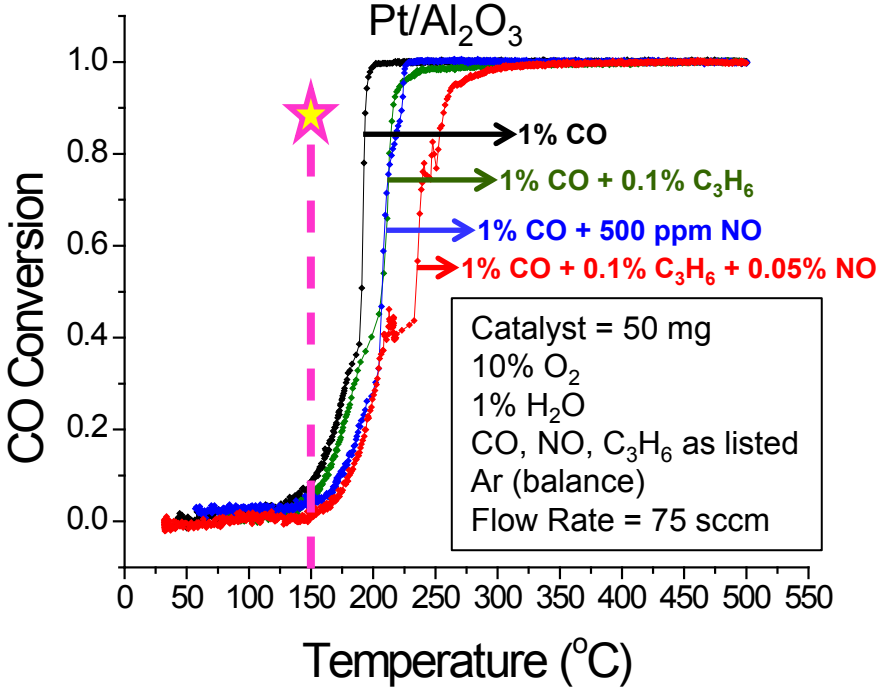


$$W/F = \frac{[\text{weight catalyst (g)}]}{[\text{molar gas flow (mol/h)}]}$$

Low temperature activity is limited in the presence of NO and hydrocarbons

- Strong inhibition by both NO and HC
- Pt/Al_2O_3 displays less impact, but still shows inhibition

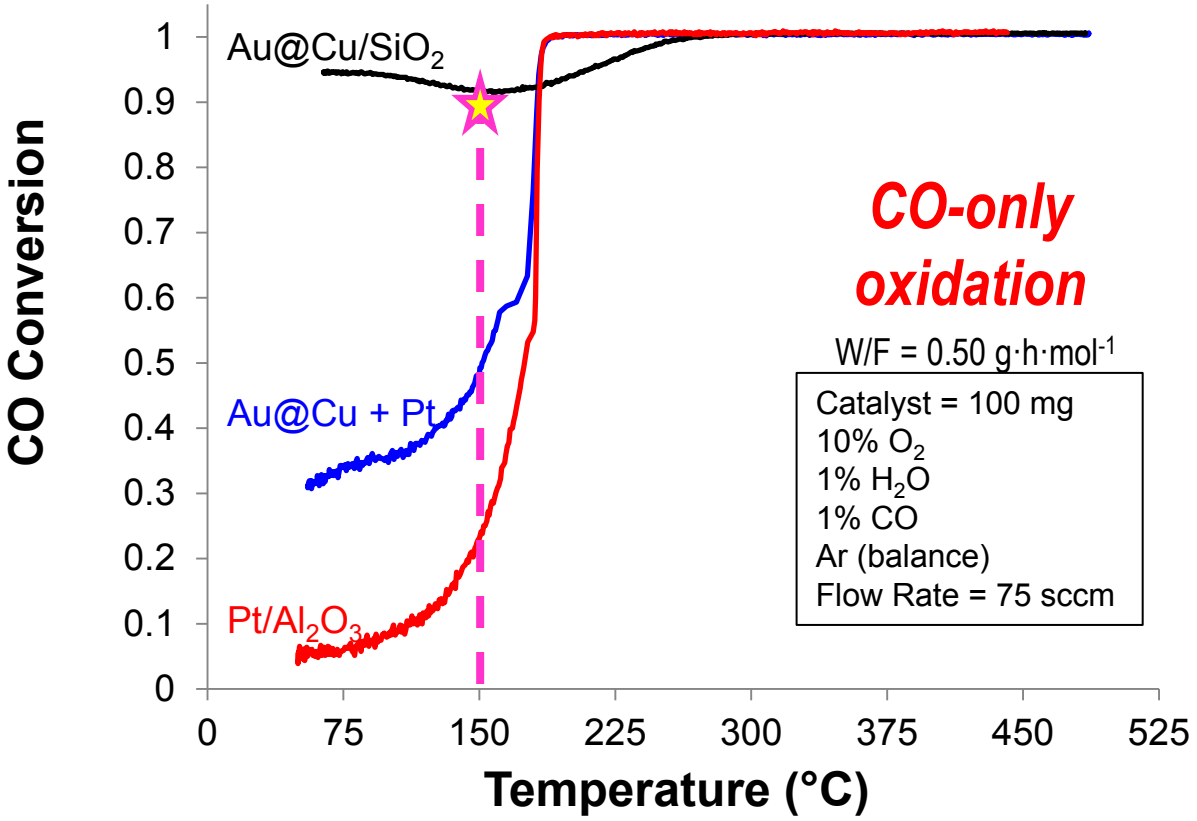




- Opportunity exists as a low temperature CO-cleanup catalyst for Au@Cu
  - Passive SCR approach presented by Jim Parks in prior talk (ACE033) shows CO-only exhaust concerns

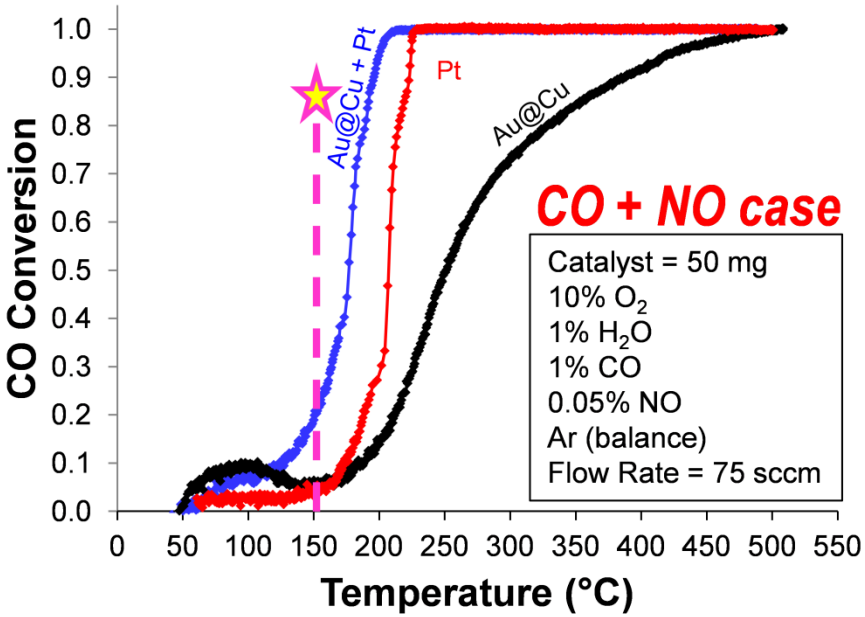
Combination of $Au@Cu/SiO_2$ and Pt/Al_2O_3 studied to explore potential synergies

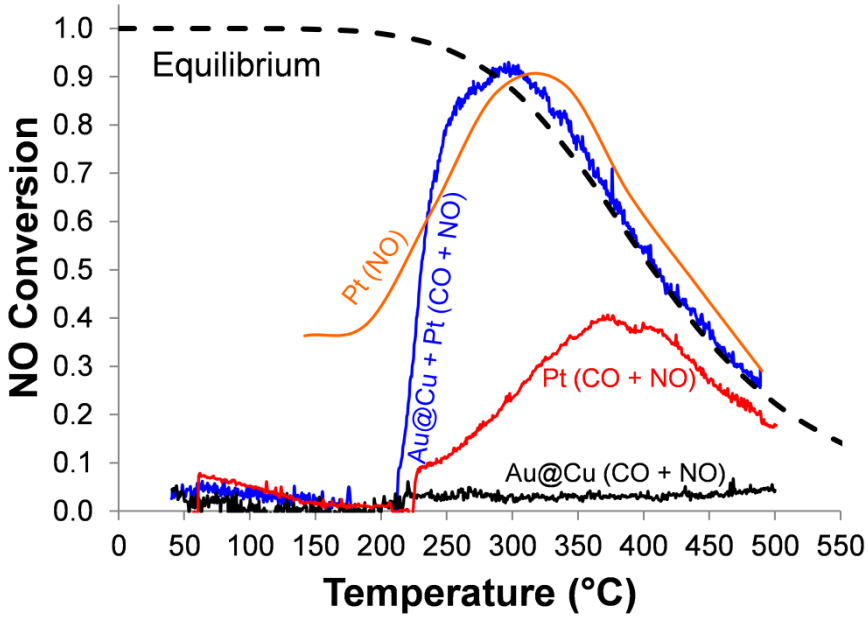
- $Au@Cu/SiO_2$ and Pt/Al_2O_3 were physically mixed together
- CO oxidation activity increases compared to Pt/Al_2O_3
  - but not as high as $Au@Cu/SiO_2$ alone



NO oxidation synergy observed with $Au@Cu/SiO_2$ + Pt/Al_2O_3 physical mixture

- Improved low temperature CO-oxidation in the presence of NO w/ Au@Cu+Pt
  - Better than either individual catalyst
- For Au@Cu+Pt, NO oxidation to NO_2 approaches equilibrium limit at 250°C
- Considerably more active than Pt/Al_2O_3

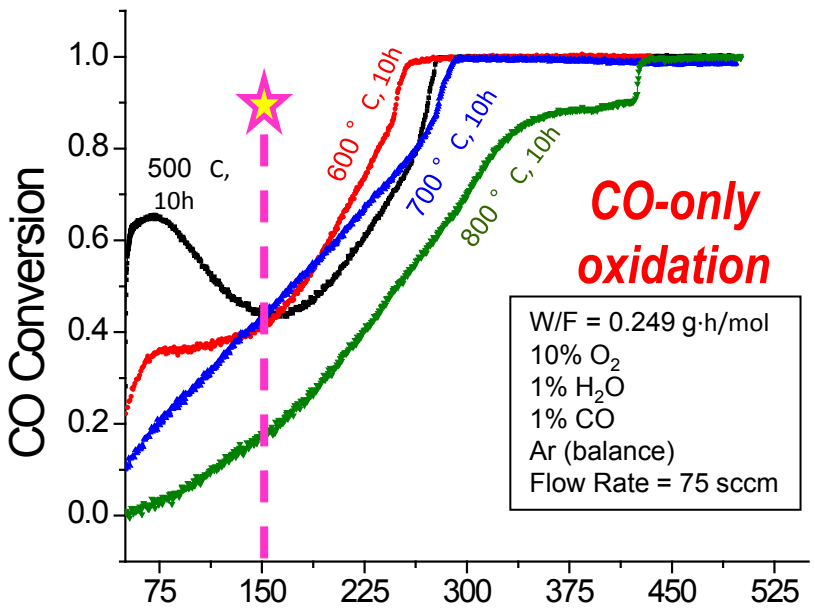


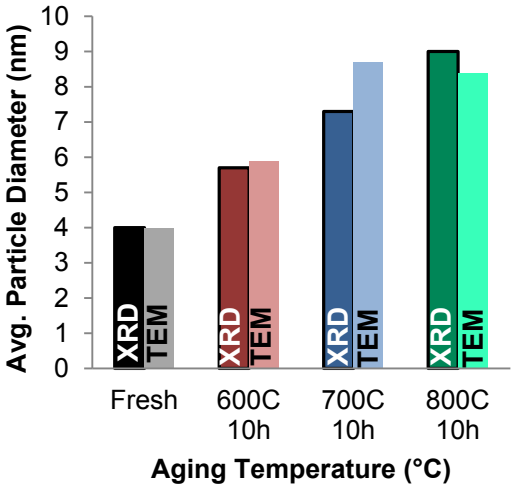


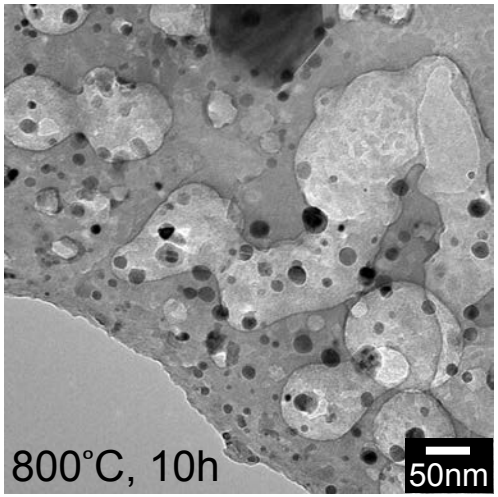
Theory: *1. NO oxidation inhibited by CO on Pt*
2. Au@Cu catalyst oxidizes CO, thus improving NO oxidation

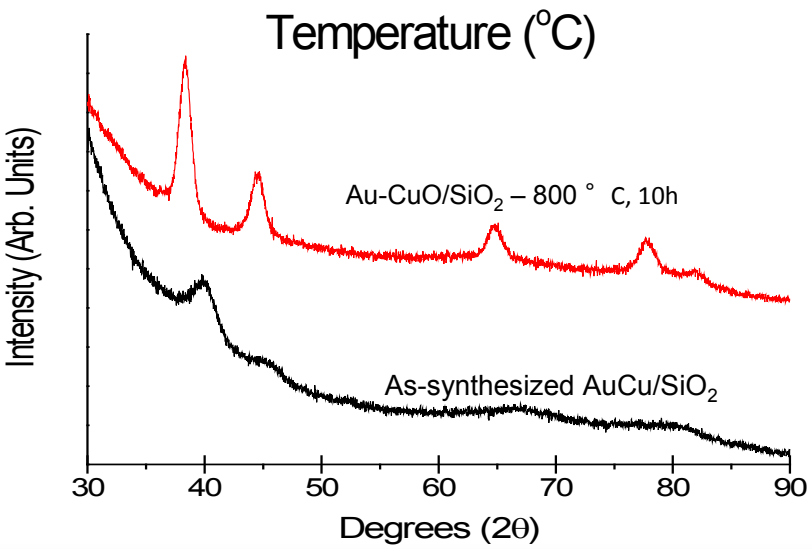
Durability a concern with SiO_2 support

- Au@Cu/SiO_2 aged in 10% O_2 + 1% H_2O in Ar
- Catalyst relatively stable up to 700°C
  - Only very low temperature activity (T< 150°C) diminishes with increasing aging temperature
- Particles grow up to ~25 nm in diameter after thermally aged at 800°C for 10h (8-9 nm avg.)
  - Sulfur also shown to strongly deactivate
- Improved metal support interactions needed







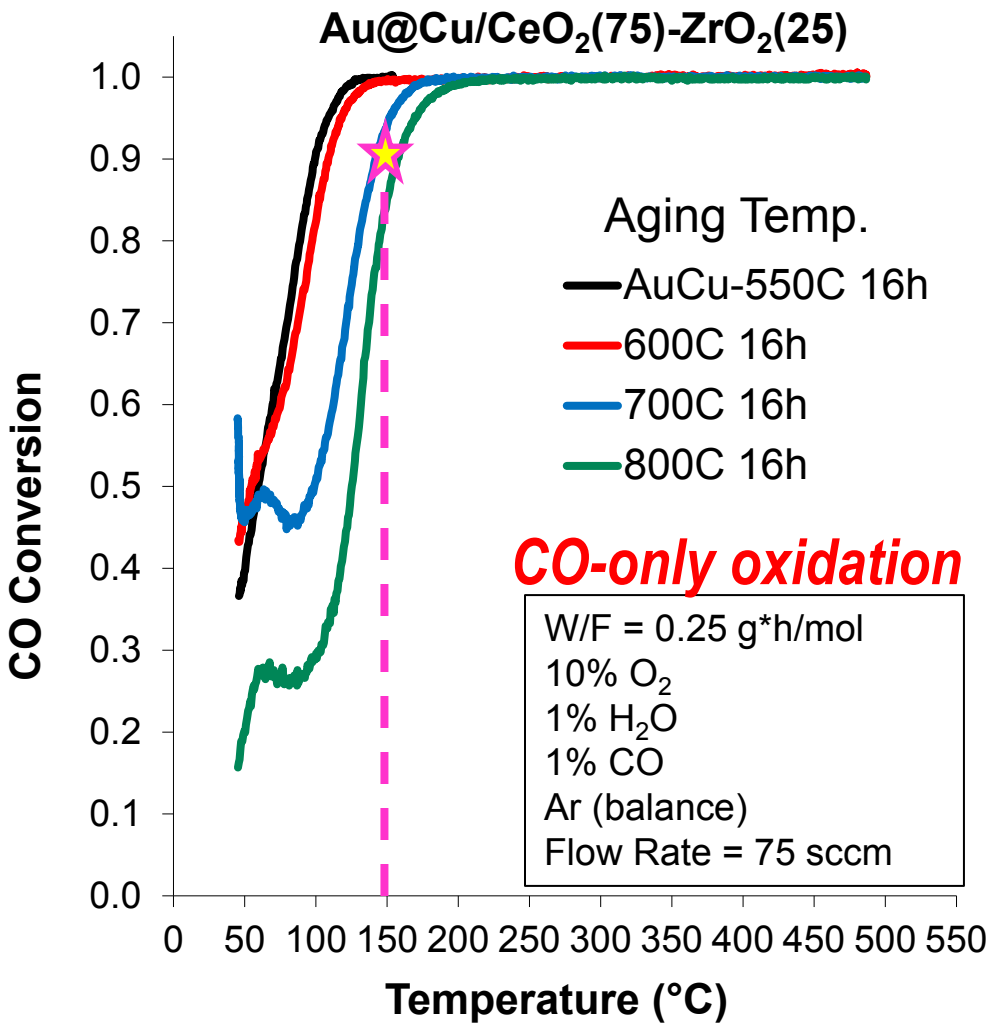


Supporting AuCu catalyst on ceria-zirconia shows improved stability

- Same synthesis procedure as followed as described in slide 10

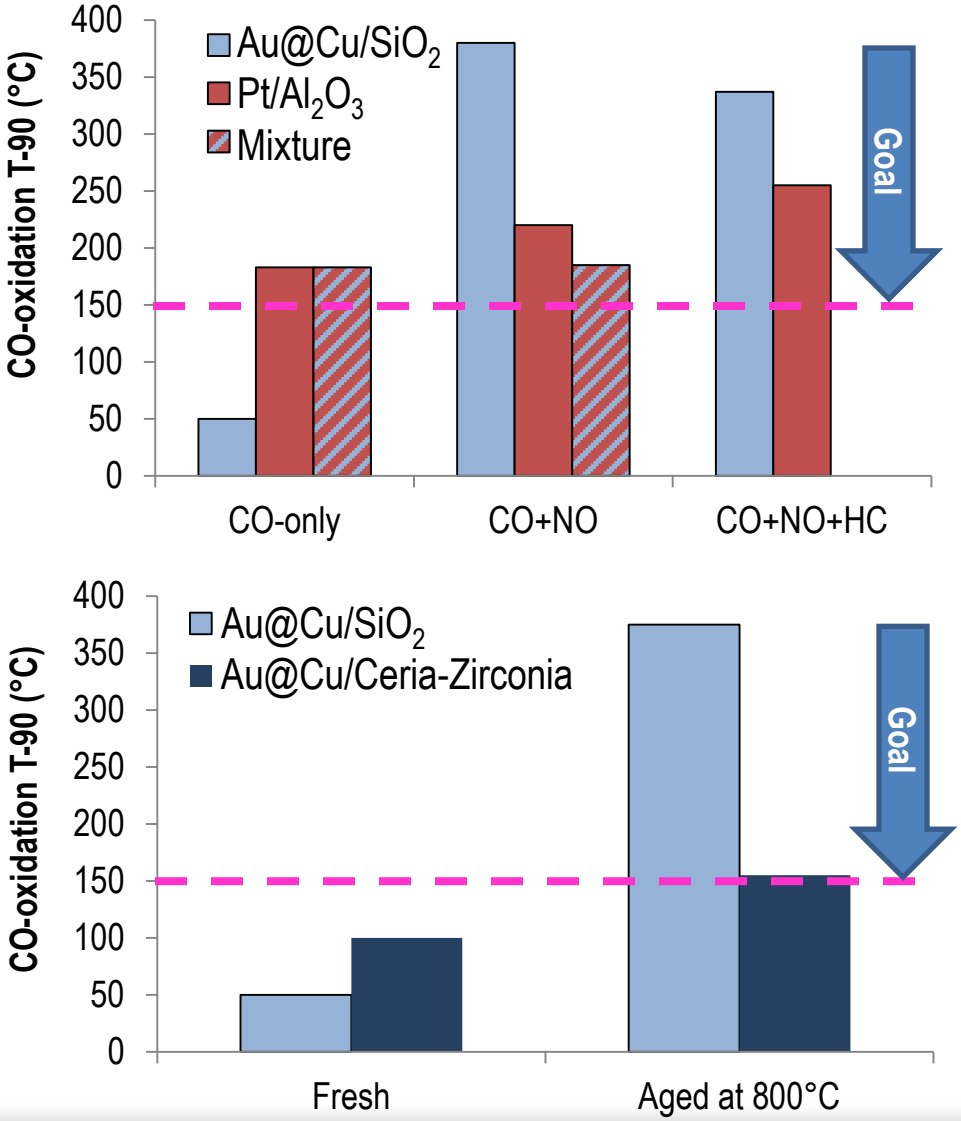
- Even with low weight loading high activity shown with unaged sample
  - W/F = 0.25 g*h/mol
    - SV = ~95,000 h^{-1}; denser than SiO_2
  - $T_{50\%}$ = 60°C
  - $T_{90\%}$ = 98°C

- Activity drops after aging at 800°C, but is still very high
  - $T_{50\%}$ = 125°C
  - $T_{90\%}$ = 155°C



Catalysts studied show promise, but challenges remain

- T-90 compared for each catalyst and condition studied
  - T-90 = temperature where 90% conversion is achieved
  - The lower the better
- 90% Oxidation of HCs and CO at 150°C will continue to be difficult, but exploiting synergies of catalysts show promise
  - Both $Au@Cu/SiO_2$ and Pt/Al_2O_3 show impact from NO and HCs
  - Mixing catalysts results in ~35°C drop in T-90
- Matching active catalysts with the right support shows promise for overcoming durability challenges
  - 90% conv. achieved w/ 800°C aging



Future work

- **Continue investigation on Au@Cu with ceria-zirconia and other supports**
  - Activity in the presence of HC and NO
  - Physical mixture with Pt/Al_2O_3; Pt co-supported on ceria-zirconia
  - Additional supports while studying/characterizing metal support interactions
    - Specifically interested in titania-modified SiO_2 support
      - Discussed briefly last year and this year in CLEERS project (ACE022)
- **Initial focus is on oxidation catalysts, but future efforts will move into trap materials and NOx reduction catalysts**
  - Low temperature NOx and HC trap materials
    - Release at moderate temperatures
  - NOx storage reduction catalysis with low temperature release and highly active reduction chemistry
- **Goal is to move from powder catalysts to washcoated cores and further validation in engine exhaust**
  - Developing washcoating capability

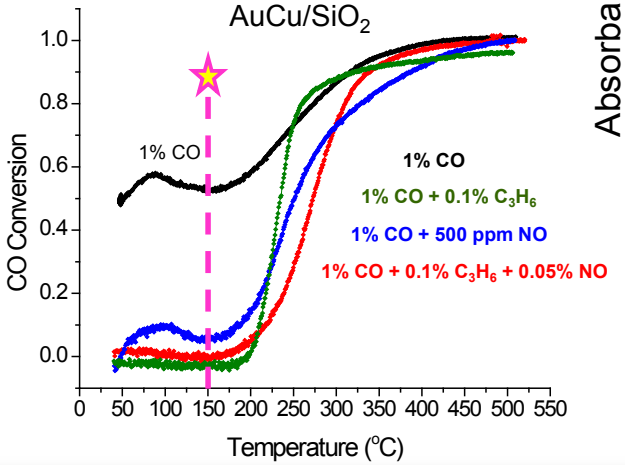
Summary

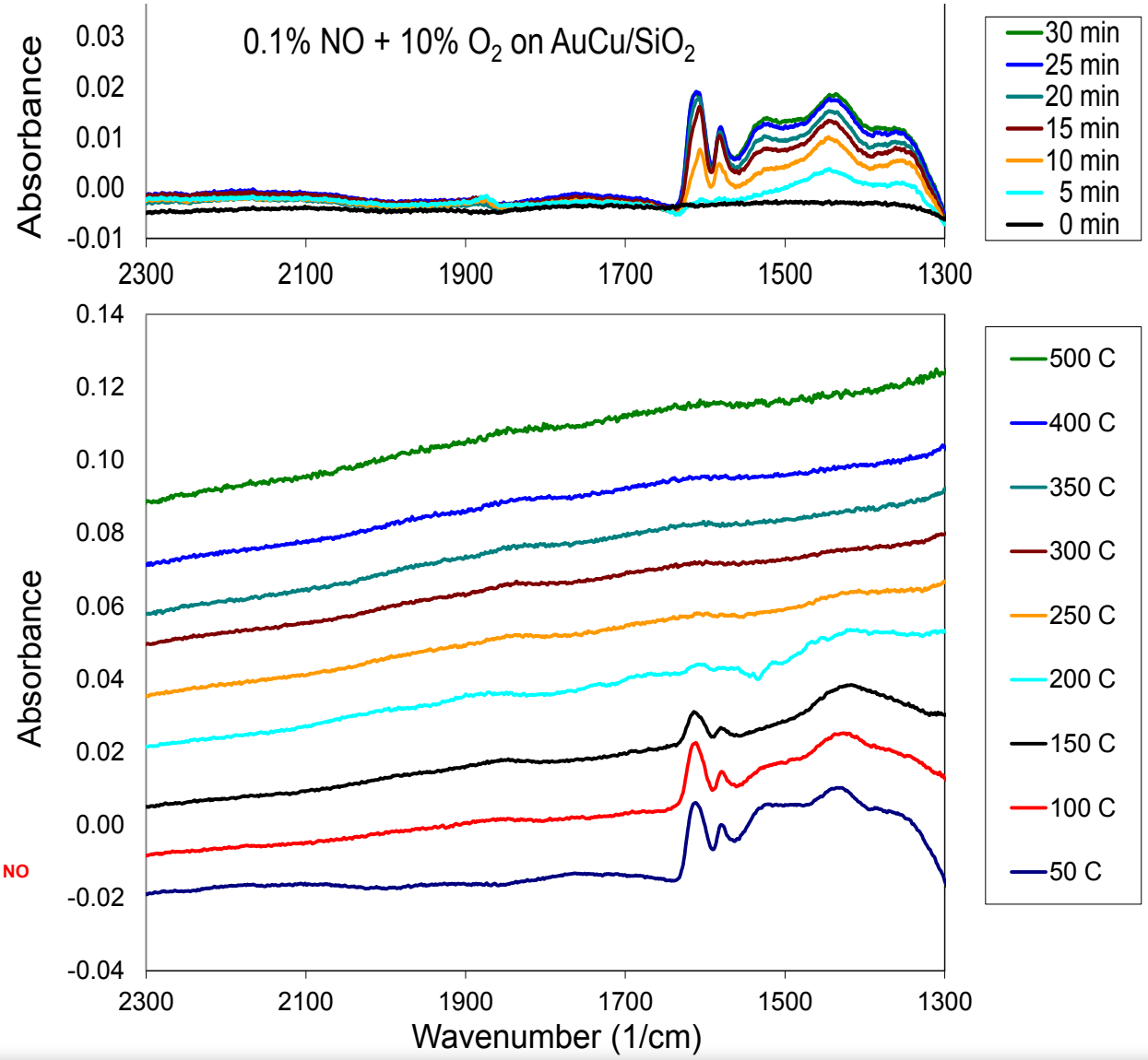
- **Relevance**:
  - Advanced combustion modes have greater efficiency and consequently lower exhaust temperatures
  - Simultaneous increase in efficiency and decrease in allowable emissions necessitates improved emissions control system performance, especially at low temperatures
- **Approach**:
  - Pursue innovative catalyst technologies to improve low temperature emissions control
  - Evaluate performance, investigate durability, characterize materials, identify fundamental limitations
- **Collaborations**:
  - Basic Energy Science scientists, CLEERS, USCAR/USDRIVE
- **Technical Accomplishments**:
  - Investigated activity, durability and material properties of Au@Cu core-shell oxidation catalyst
  - Identified synergistic effects of physical mixture of Au@Cu and Pt catalysts that overcome some of the observed inhibitions
  - Synthesized new catalysts with a range of supports, that significantly improve durability
- **Future Work**:
  - Continue investigation on AuCu with ceria-zirconia and other supports
  - Move into NOx reduction catalysts and trap materials
  - Move from powder catalysis to washcoated cores and further validation in engine exhaust

Technical back-up slides

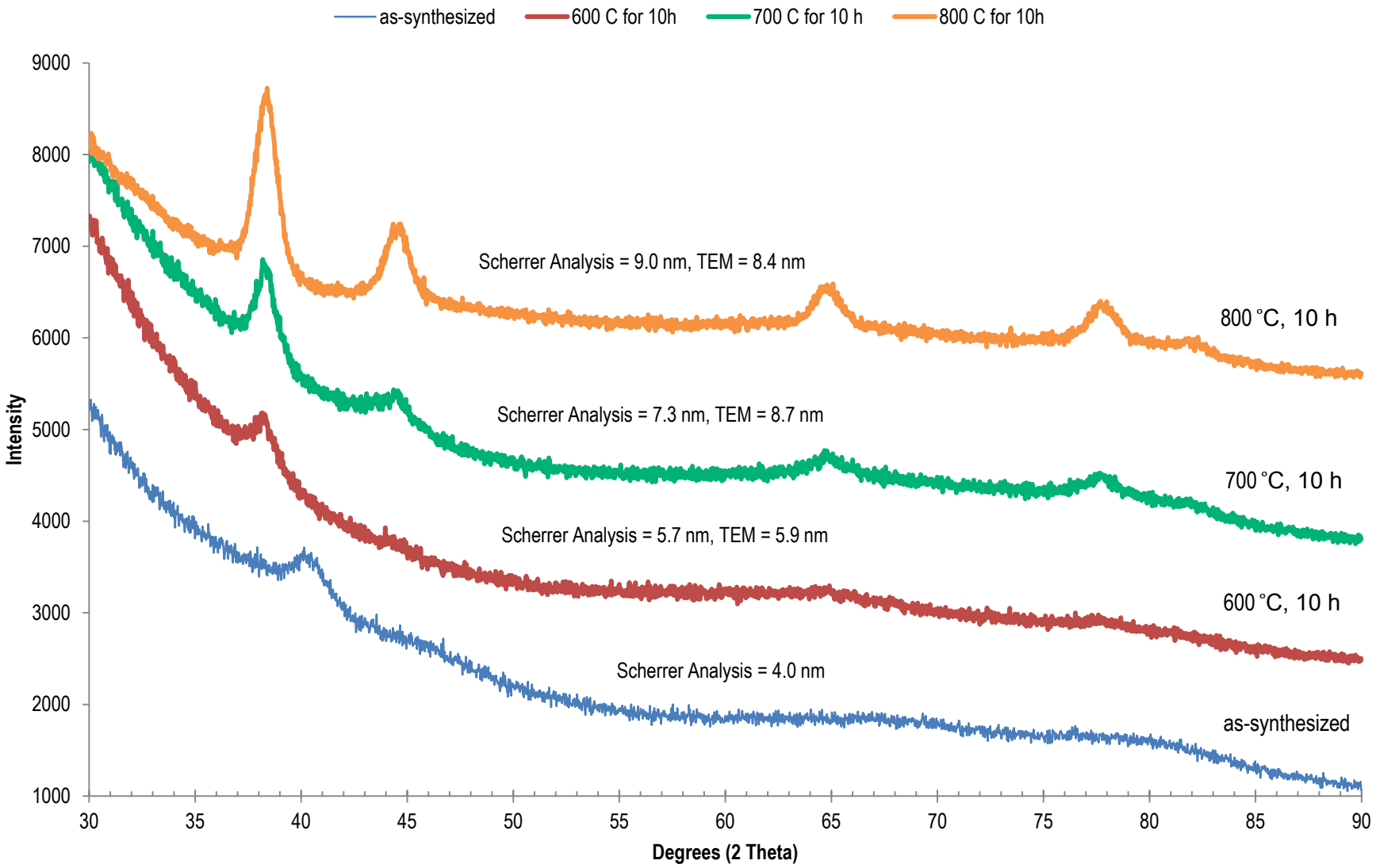
DRIFTS analysis shows NO interactions on catalysts are unstable above 200°C

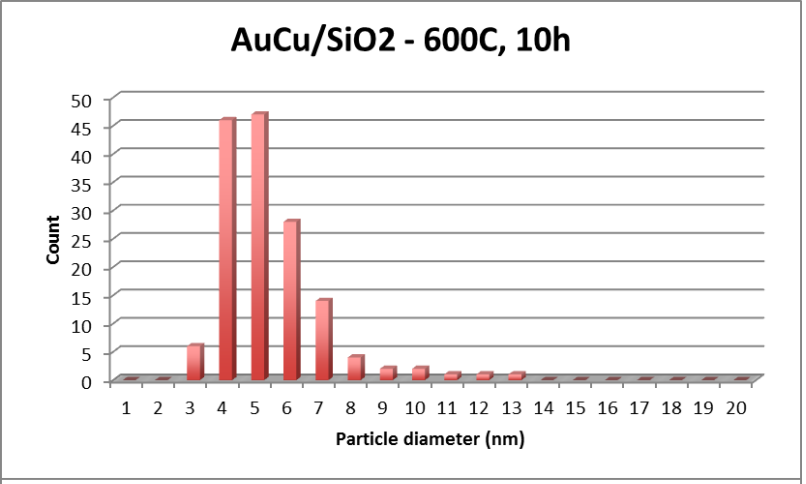
- Evidence of NO adsorbed on $AuCu/SiO_2$
  - Nitrates: 1300-1650 cm^{-1}
  - Chemisorbed on Au; faintly at ~1880 cm^{-1}
- Heating nitrated samples while flowing $NO+O_2$ results in removal at 200°C
  - Coincides with CO-lightoff



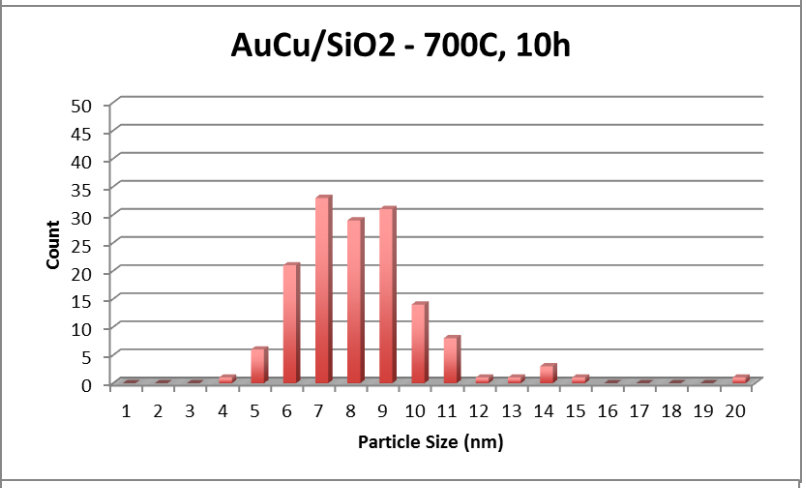


Aging Au@Cu/SiO_2

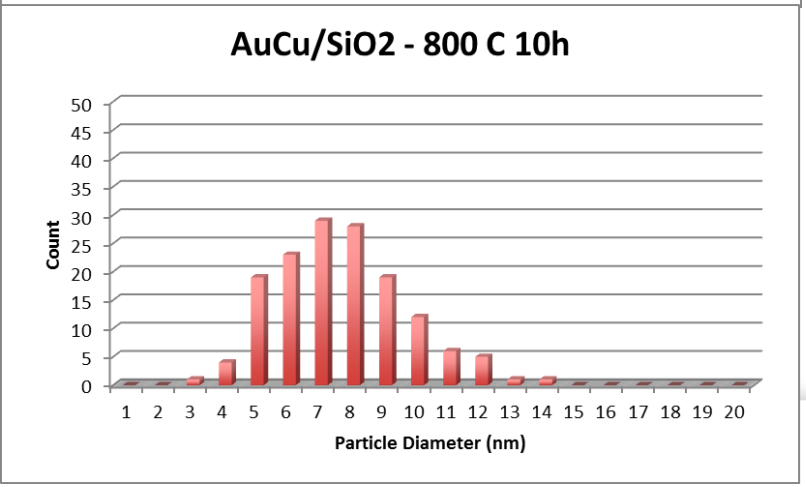




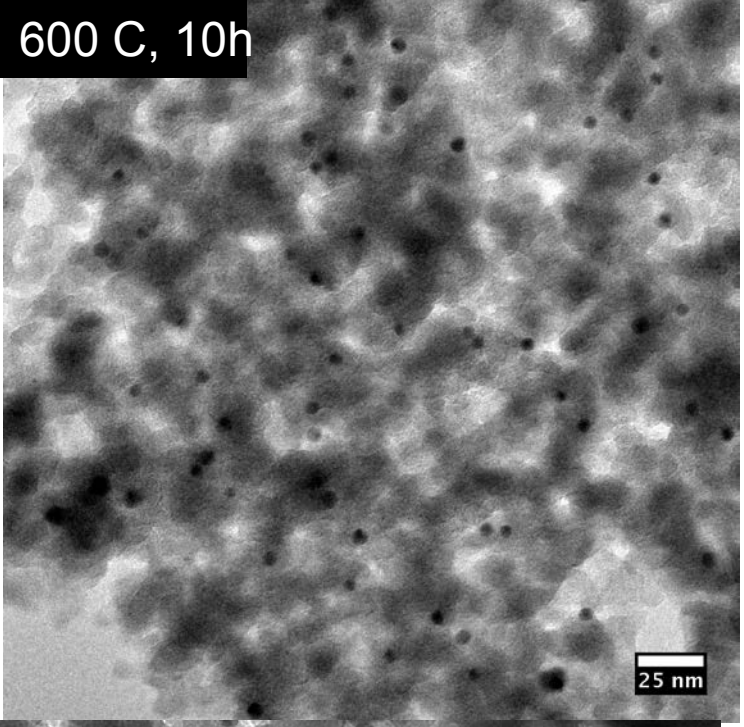
Heated at 600 C for 10 h.

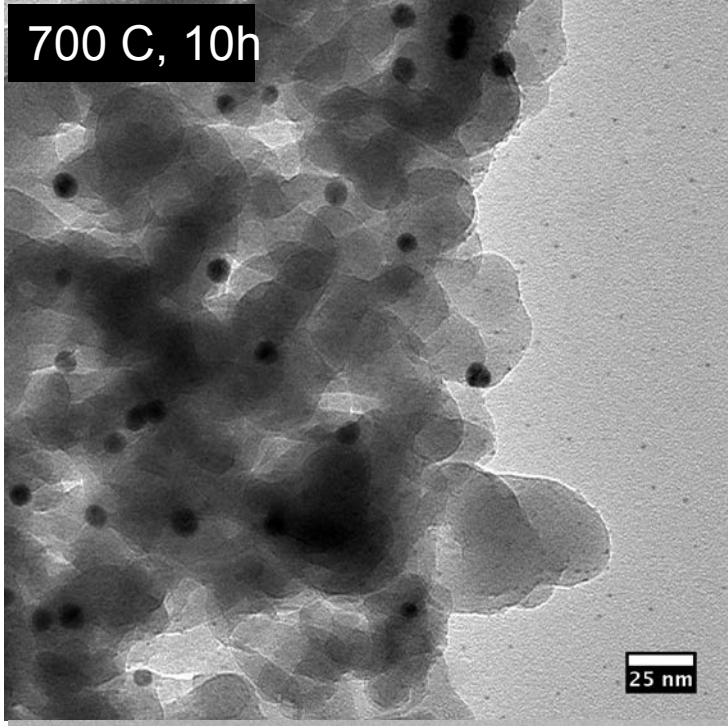


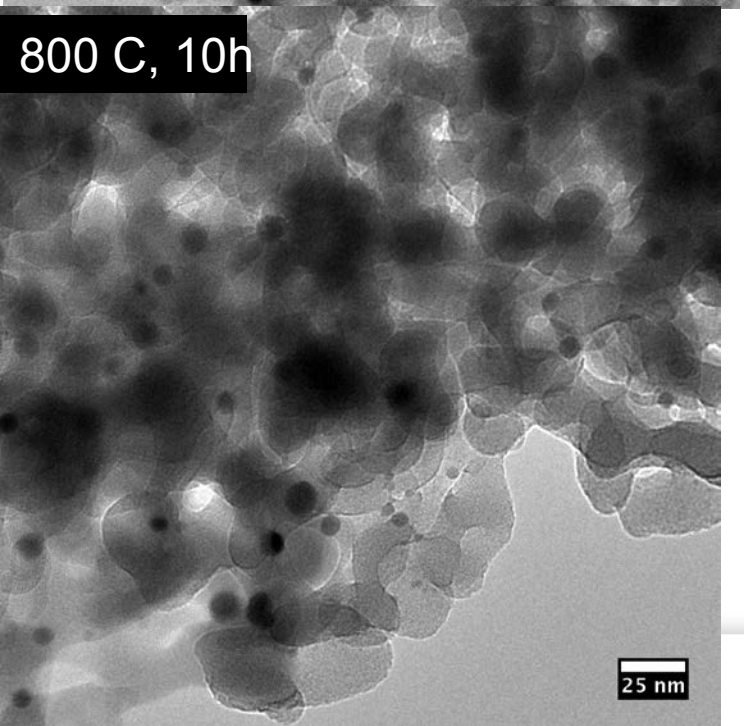
Heated at 700 C for 10 h.

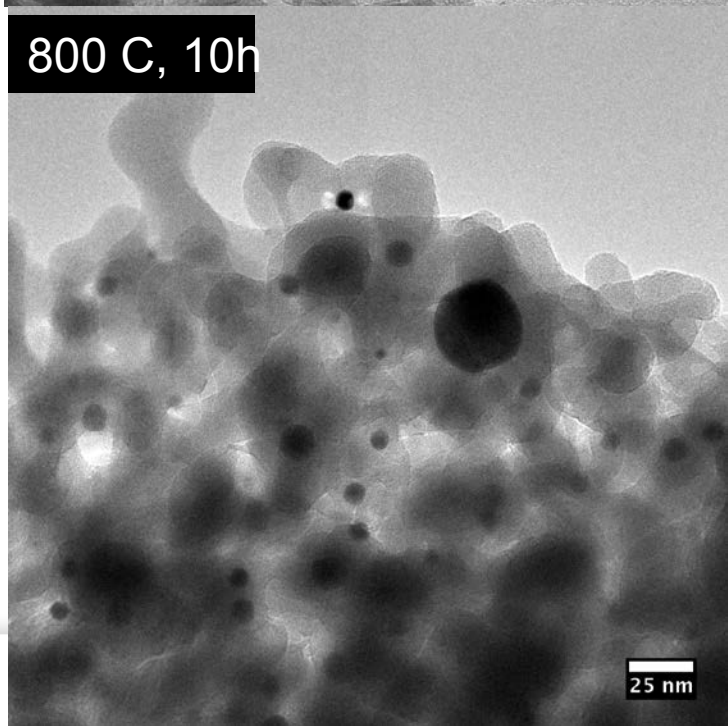


This sample is different from the two above. This sample was from the first Au@Cu batch that was heated 500, 600, 700 and 800 C.


600 C, 10h
25 nm


700 C, 10h
25 nm


800 C, 10h
25 nm


800 C, 10h
25 nm

Au-only catalyst supported on ceria-zirconia also shows good stability

- Even with low weight loading high activity shown with unaged sample
  - W/F = 0.25 g*h/mol
    - SV = ~95,000 h^{-1}
  - $T_{50\%}$ = 50°C
  - $T_{90\%}$ = 94°C
- Activity drops after aging at 800°C, but is still very high
  - $T_{50\%}$ = 103°C
  - $T_{90\%}$ = 182°C