Hydrocarbon fouling of SCR during Premixed Charge Compression Ignition (PCCI) combustion

Jim Parks, Vitaly Prikhodko, Josh Pihl, and Sam Lewis
Oak Ridge National Laboratory

DEER 2011
October 3-6, 2011
Detroit, MI

U.S. DEPARTMENT OF
ENERGY

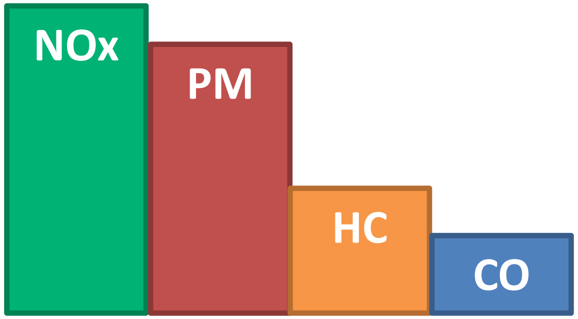
OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

Acknowledgements

- **Thanks to U.S. DOE's Vehicle Technologies Program for funding this study**
  - Program Managers: Gurpreet Singh and Ken Howden

Advanced Diesel Engine Combustion Techniques Present Different Emissions Challenges

Conventional Diesel Combustion



Engine Out Emissions

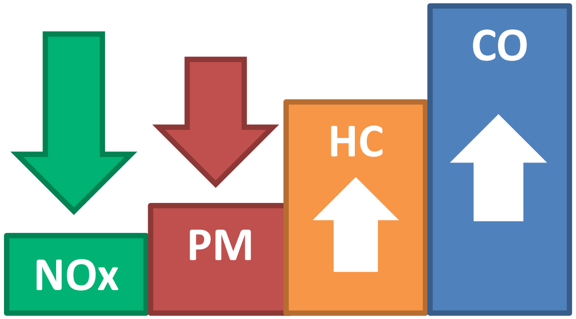
Catalytic Control Options

DOC +

DPF +

SCR or **LNT**

Premixed Charge Compression Ignition (PCCI) Diesel Combustion



Engine Out Emissions

Catalytic Control Options

DOC +

DPF +

SCR or **LNT**

PCCI reduces burden of NOx and PM control on aftertreatment (thereby reducing cost and fuel penalty), but higher CO and HC emissions result

Objective

- **The goal of this study is to investigate the effect of HC emissions from conventional and advanced combustion modes on the performance of the Fe- and Cu-zeolite SCRs**
  - Catalyst cores were exposed to a raw engine exhaust from conventional and PCCI combustion on slipstream setup
    - Cu-zeolite SCR
    - Fe-zeolite SCR
  - Exposed samples were characterized on bench flow reactor
    - SCR performance measured before and after temperature ramp (oxidizing conditions)
  - HC were extracted and analyzed by GC-MS

Catalysts Fouled in Engine Exhaust

Performance Studied on Bench Reactor

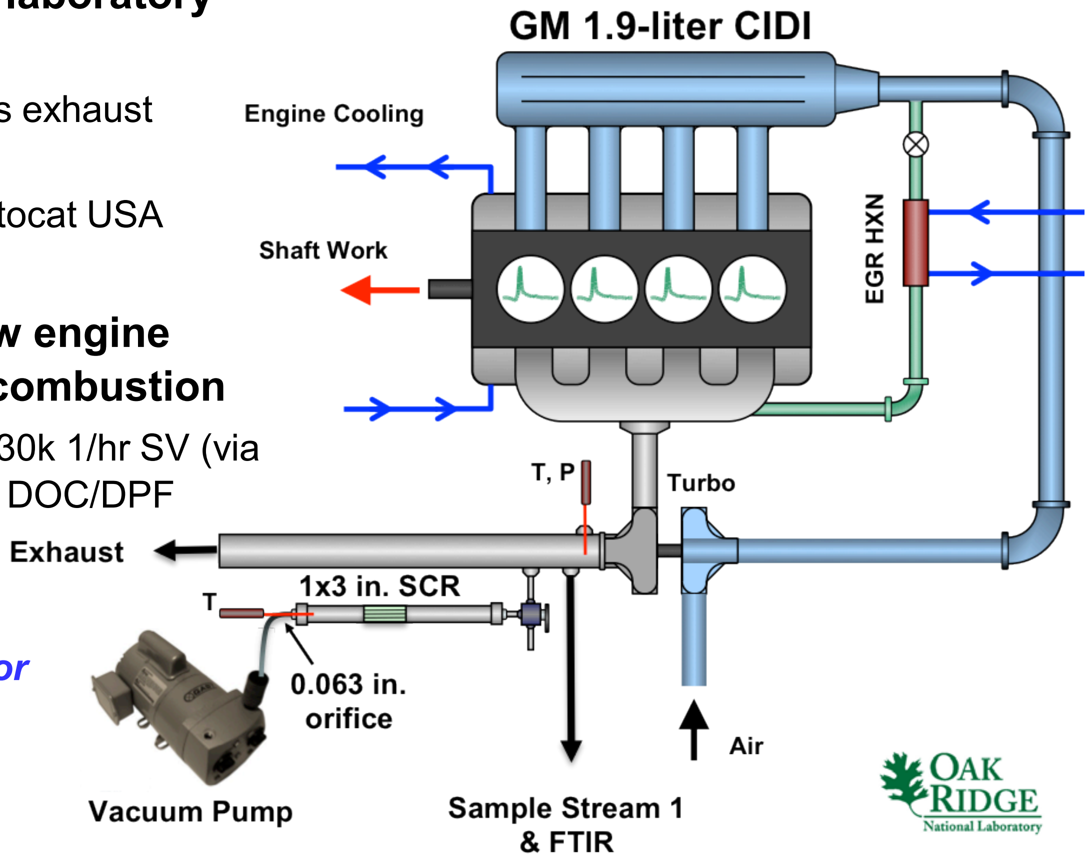
Extracted HC analyzed by GC-MS

Catalyst cores were exposed to a raw engine exhaust from conventional and PCCI combustion on slipstream

- **1.9-liter 4-cylinder GM CIDI**
  - » Variable geometry turbocharger
  - » High pressure common rail
  - » Cooled high-pressure EGR
  - » Full-pass Drivven engine control system
- **1x3 inch sample cores cut from a catalyst brick were hydrothermally degreened in a laboratory furnace for 12hr**
  - » Cu-zeolite SCR from 2010 Ford F-series exhaust system
  - » Fe-zeolite SCR donated by Umicore Autocat USA (CLEERS reference SCR)
- **Catalyst cores were exposed to a raw engine exhaust from conventional or PCCI combustion**
  - » Aggressive conditions: 3 hours, 115°C, 30k 1/hr SV (via Vacuum Pump and 0.063 in. orifice), no DOC/DPF upstream

Engine Condition: 1500 rpm, 2.6 bar BMEP

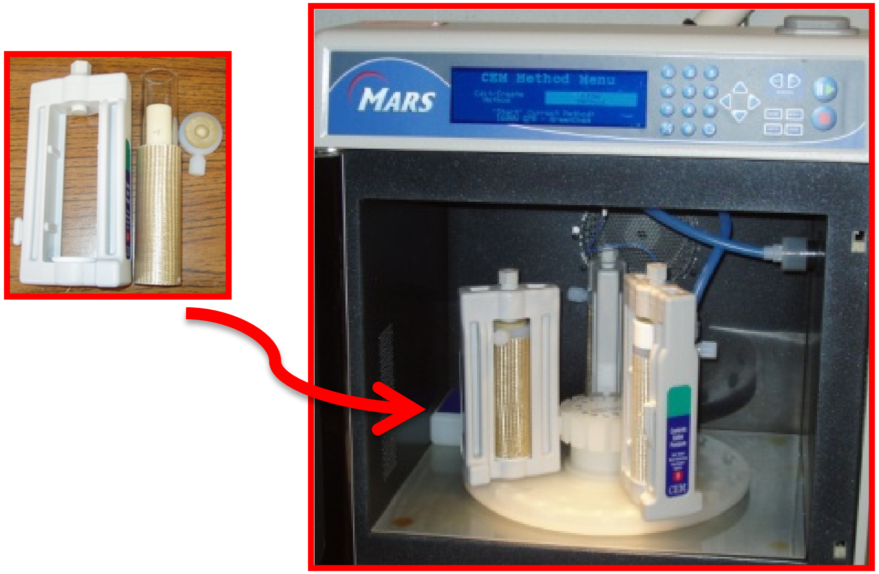
	Conventional	PCCI
Engine Out NO_X	1.02 g/bhp-hr	0.24 g/bhp-hr
Engine Out HC	1.35 g/bhp-hr	2.19 g/bhp-hr
Engine Out CO	3.12 g/bhp-hr	11.70 g/bhp-hr



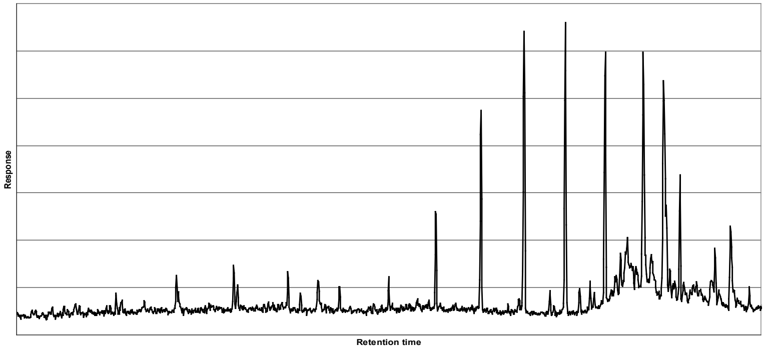
Schematic of engine exhaust slipstream for catalyst exposure to hydrocarbons

HC were extracted and analyzed by GC-MS

- **Hydrocarbons were extracted from a loaded sample using 50/50 hexane/acetone solution in a microwave-assisted extractor**

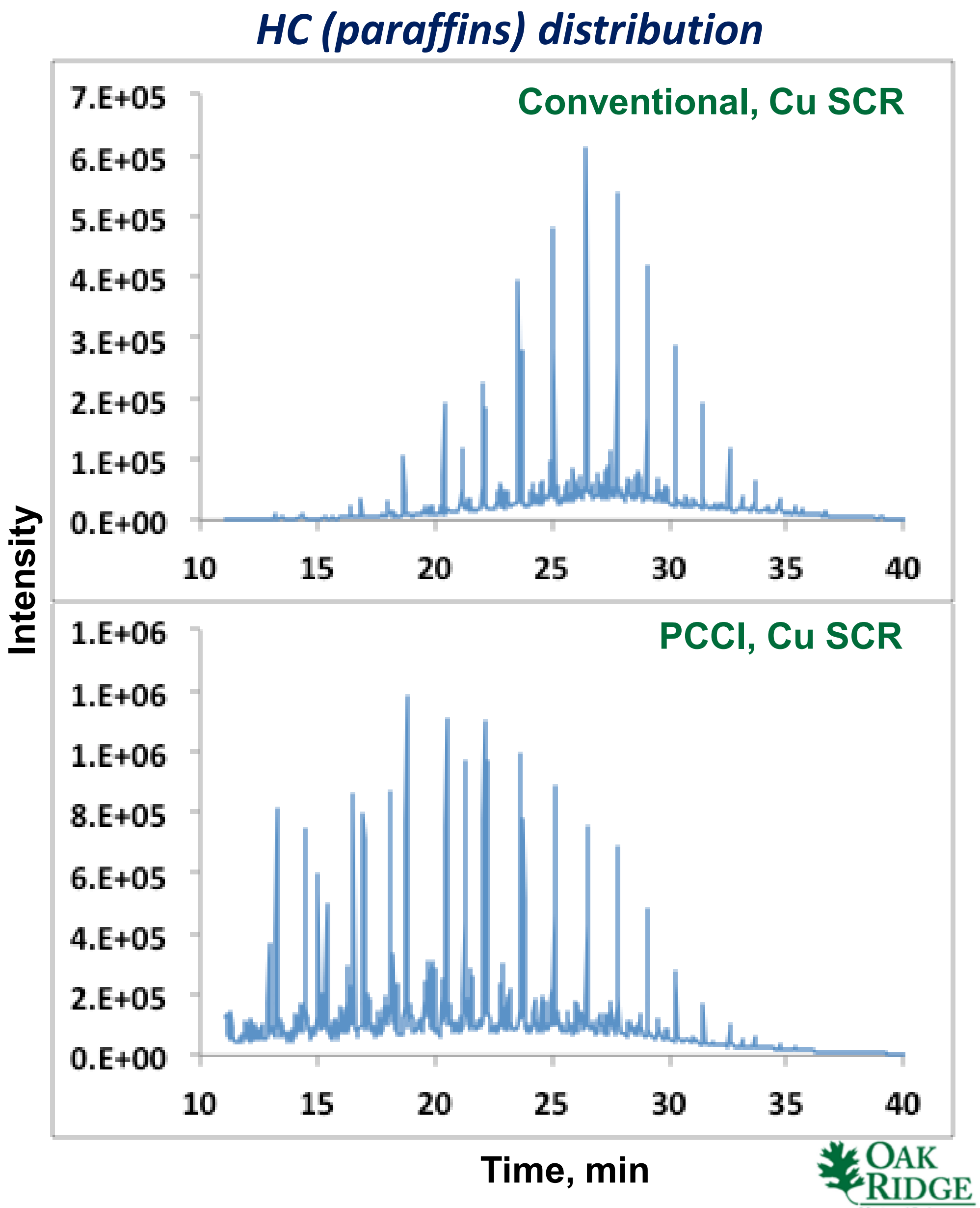


- **Extracts were concentrated, spiked with an internal standard, and then analyzed by GC-MS**
  - Diesel range organic components



Shift to lighter, more volatile HCs in PCCI

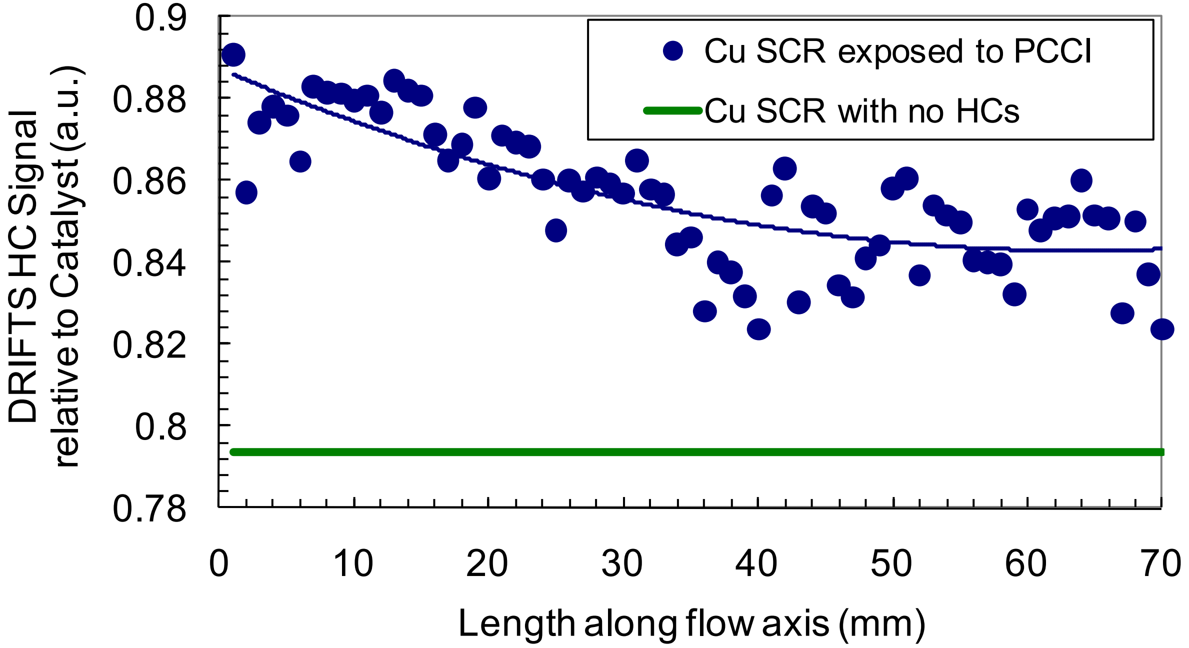
- **Surface HC are different between conventional and PCCI combustion modes**
  - More HC from PCCI exposure (consistent with $CO+CO_2$ release results)
  - Shift to lighter, more volatile HC in PCCI
- **No apparent difference is observed between Cu- and Fe-SCR**

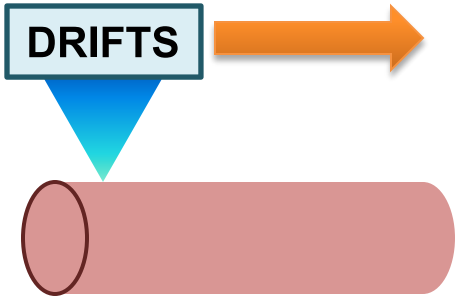


DRIFTS analysis shows distribution of HCs along catalyst

- **DRIFTS detects HC variation along length of catalyst**
  - » DRIFTS=Diffuse Reflectance Infrared Fourier Transform Spectroscopy
- **Under current exposure parameters, HCs observed along entire catalyst length**
  - » Qualitative distribution of HCs may be useful for modeling of HC fouling effects

HC species as function of position along flow axis

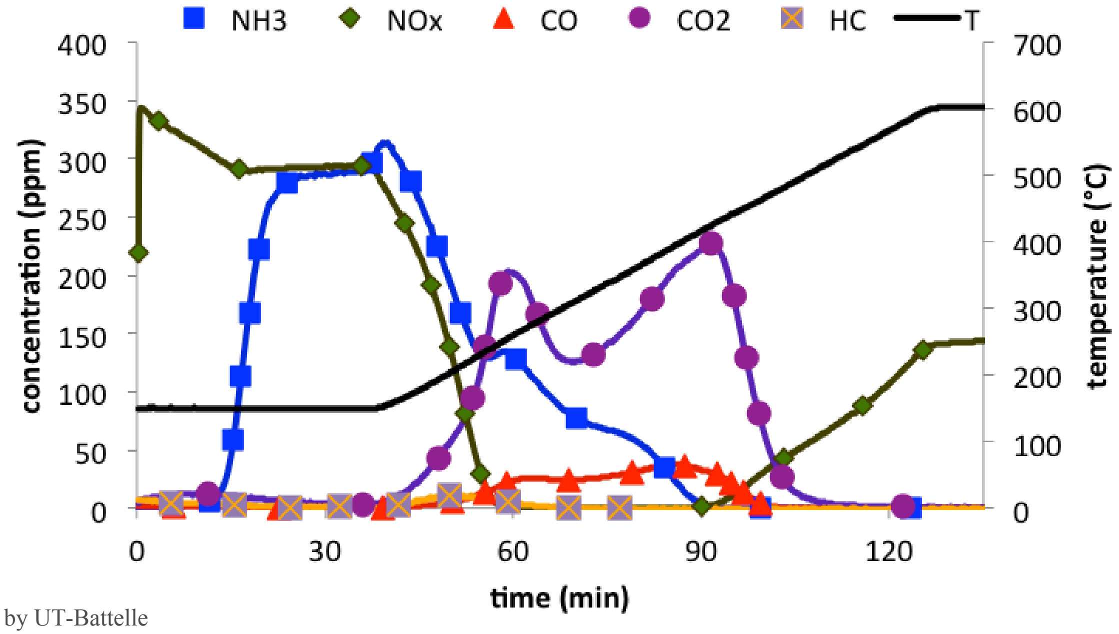




SCR performance was characterized on a bench flow reactor

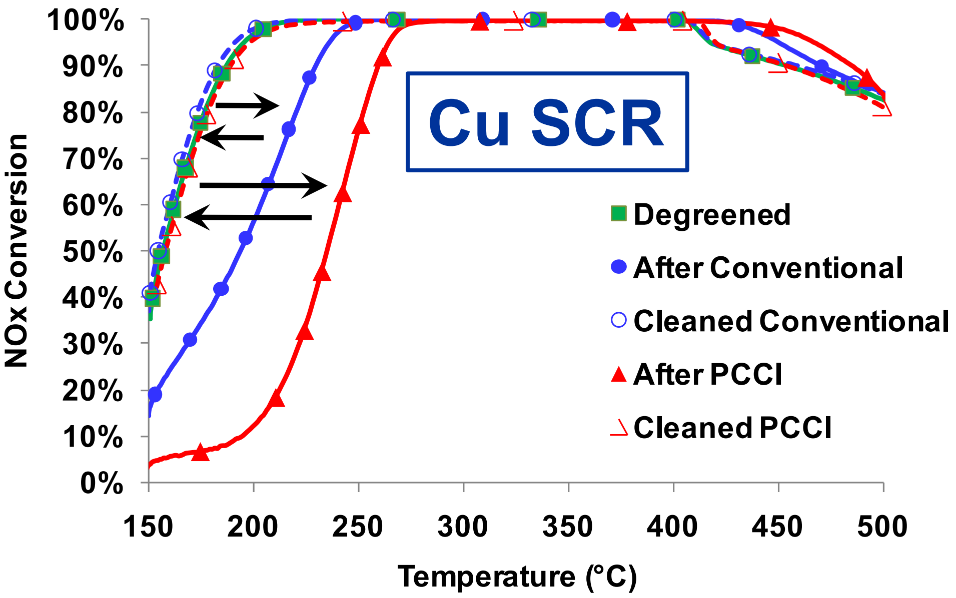
- **Bench flow reactor conditions**
  - Inlet: 350 ppm NO_X + 350 ppm NH_3, 14% O_2, 4.5% H_2O, SV=30K 1/hr
  - Temperature Ramp: 5°C/min, 150-600°C
    - Ramp1: exposed sample (straight from the engine with adsorbed HCs and soot)
    - Ramp2: cleaned sample (cool sample back to 150°C after Ramp1 and repeat ramp)
  - Gas analysis with MKS FTIR

Ramp1: Cu-SCR exposed to conventional combustion exhaust



Cu-zeolite shows more tolerance to HC fouling (vs. Fe-), but fouling from PCCI HCs more severe (for Cu- case)

- **HC/soot fouling impacts mainly low temperature NOx conversion**
  - Fe much worse than Cu as expected
  - PCCI and Conventional similar for Fe
  - PCCI worse than Conventional for Cu
- **Performance loss reversible via higher temperature exposure (see "Cleaned" data plots)**



Engine Condition: 1500 rpm, 2.6 bar BMEP

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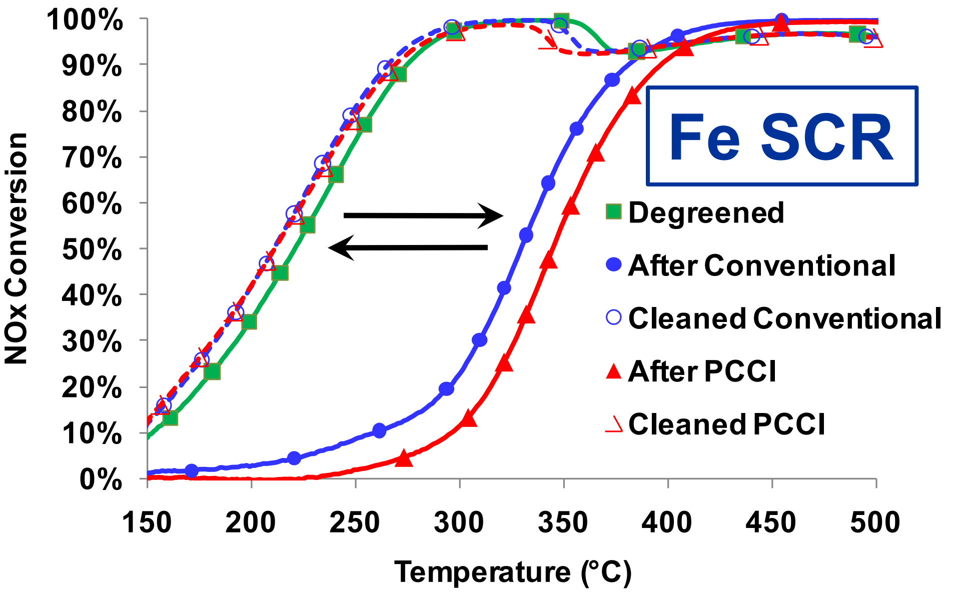
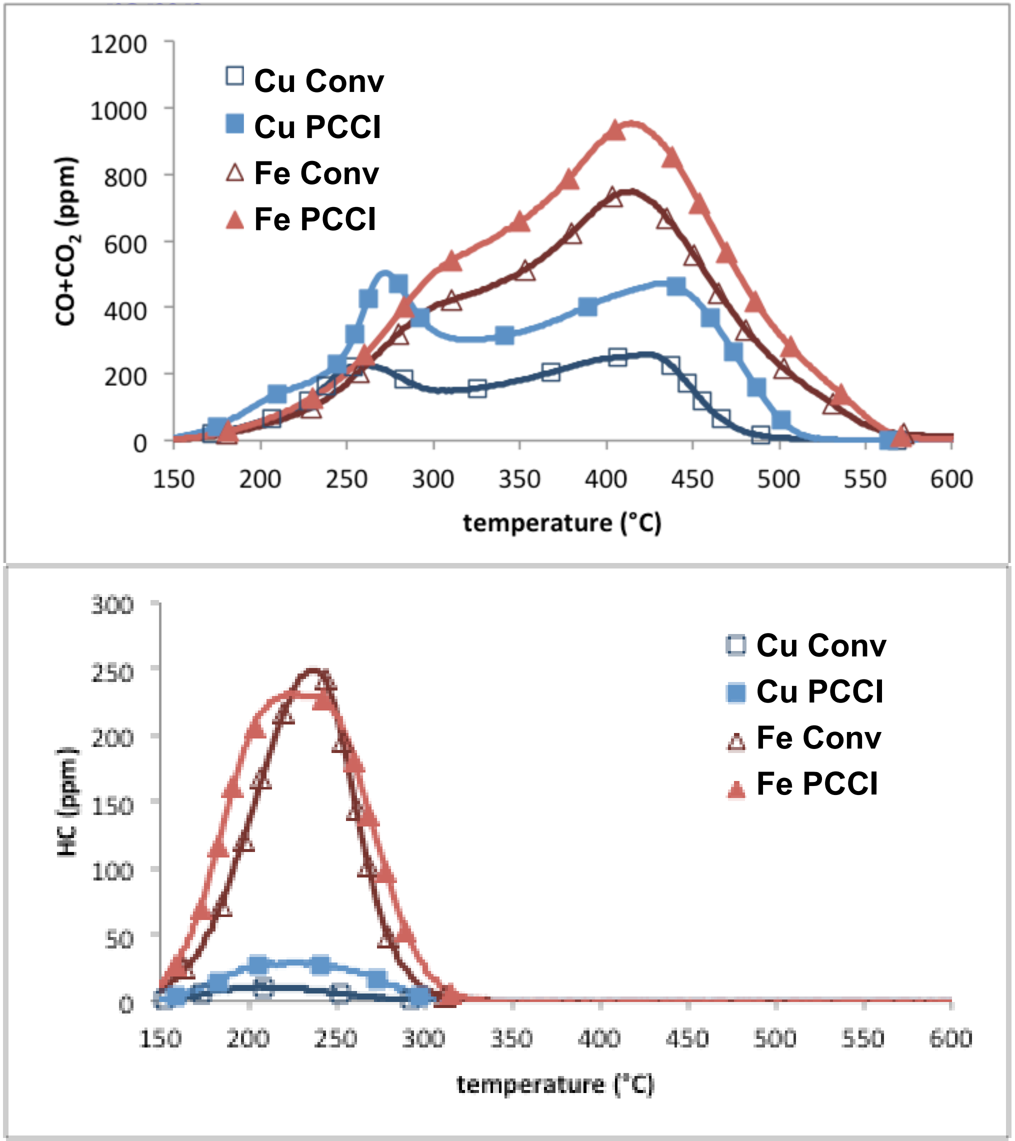
Bench Flow Reactor Conditions:
Inlet: 350 ppm NOx + 350 ppm NH_3 (ANR=1)
SV=30k/hr, 14% O_2, 4.5% H_2O



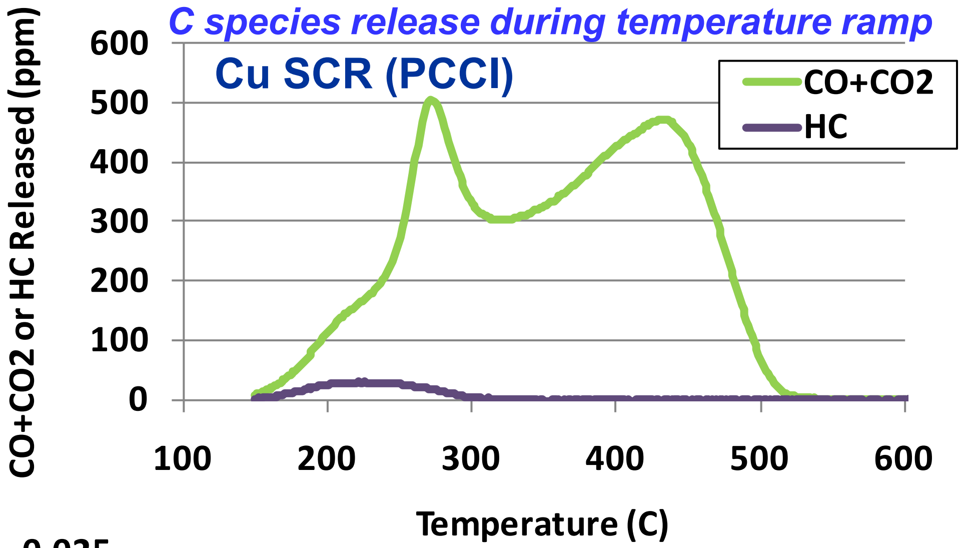
Oxidation and Release of HCs differs for Cu- and Fe-SCR

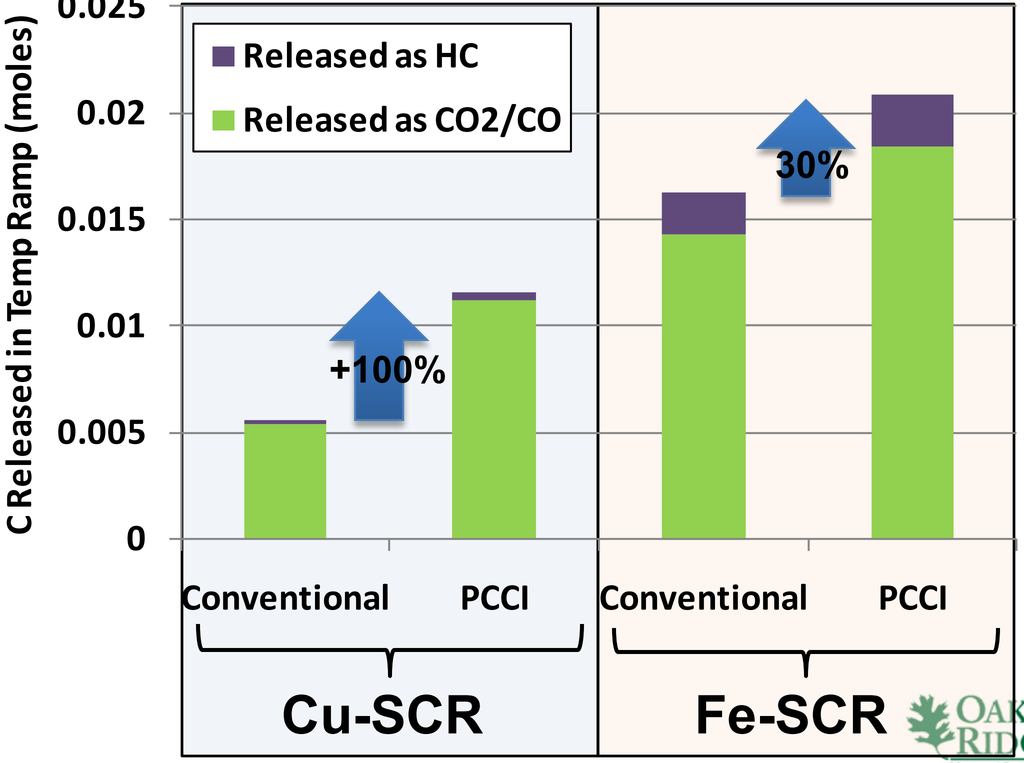
- During temperature ramp, HCs, CO, and CO_2 are released by SCR catalysts
- More C species on surface of Fe-zeolite sample
- More C for PCCI than conventional
- Prominent low temperature $CO+CO_2$ peak for Cu-zeolite
- Much more HC on Fe-zeolite


C species release during temperature

Oxidation and Release of HCs differs for Cu- and Fe-SCR

- **Integrated results for total moles of HC and CO+CO_2 show differences due catalyst formulation and combustion type**
  - » More total C trapped on Fe-zeolite
  - » More total C trapped during PCCI (vs. Conventional)
- **Larger difference in C released from PCCI and Conventional for Cu SCR**
  - » Note that PCCI has higher HC emissions (same exposure time)
  - » C release results consistent with NO_X performance results

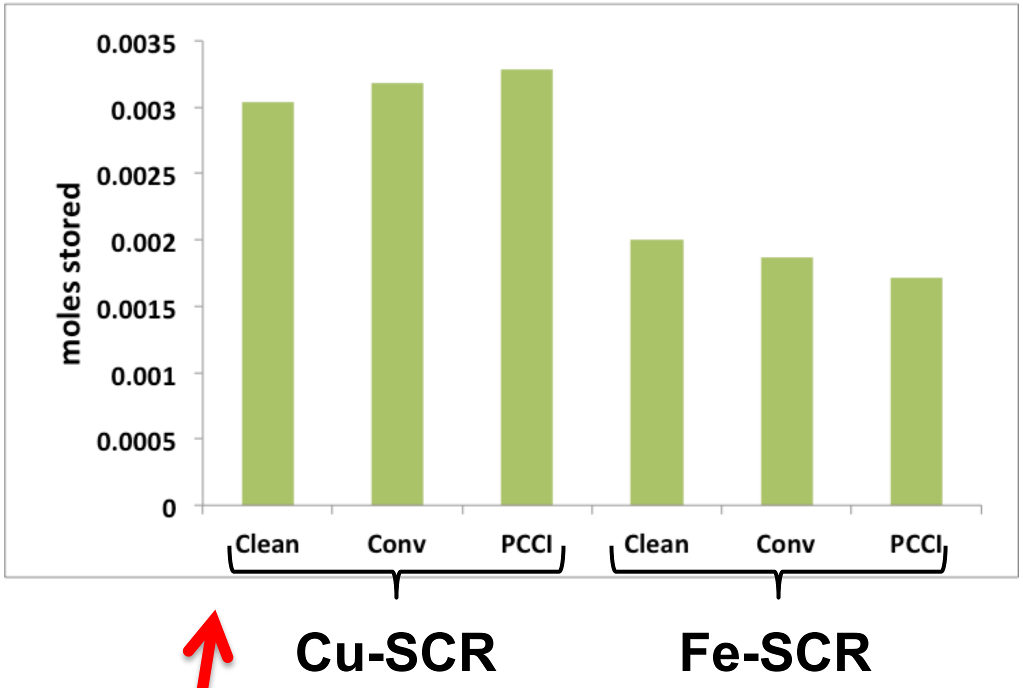


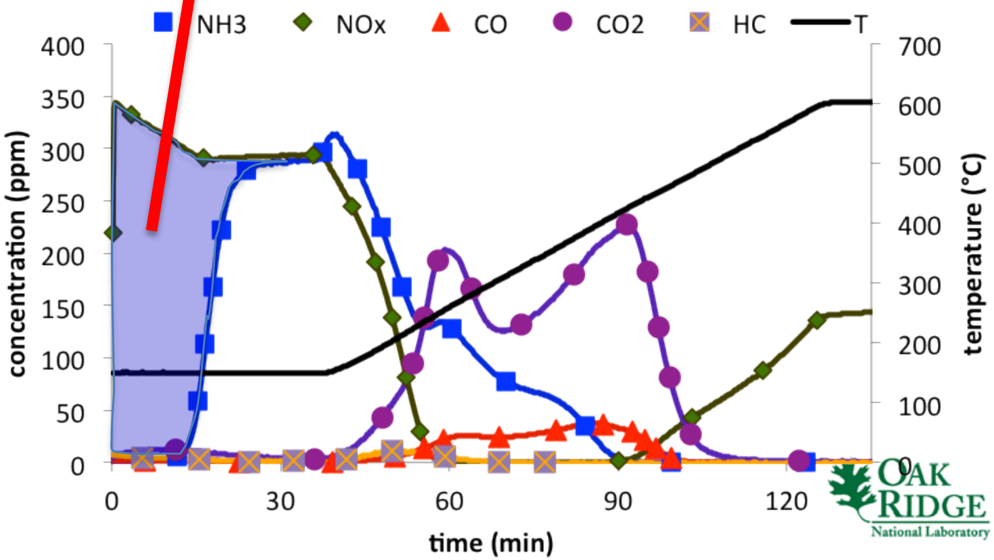


NH_3 storage is not affected by stored HC

- **Integrated results for total moles of NH_3 stored during stabilization step (prior to ramp) does not appear to be affected by HC+Soot present of the surface of the catalyst**
  - More NH_3 stored on Cu-SCR as expected

NH_3 stored during stabilization step (prior to ramp)

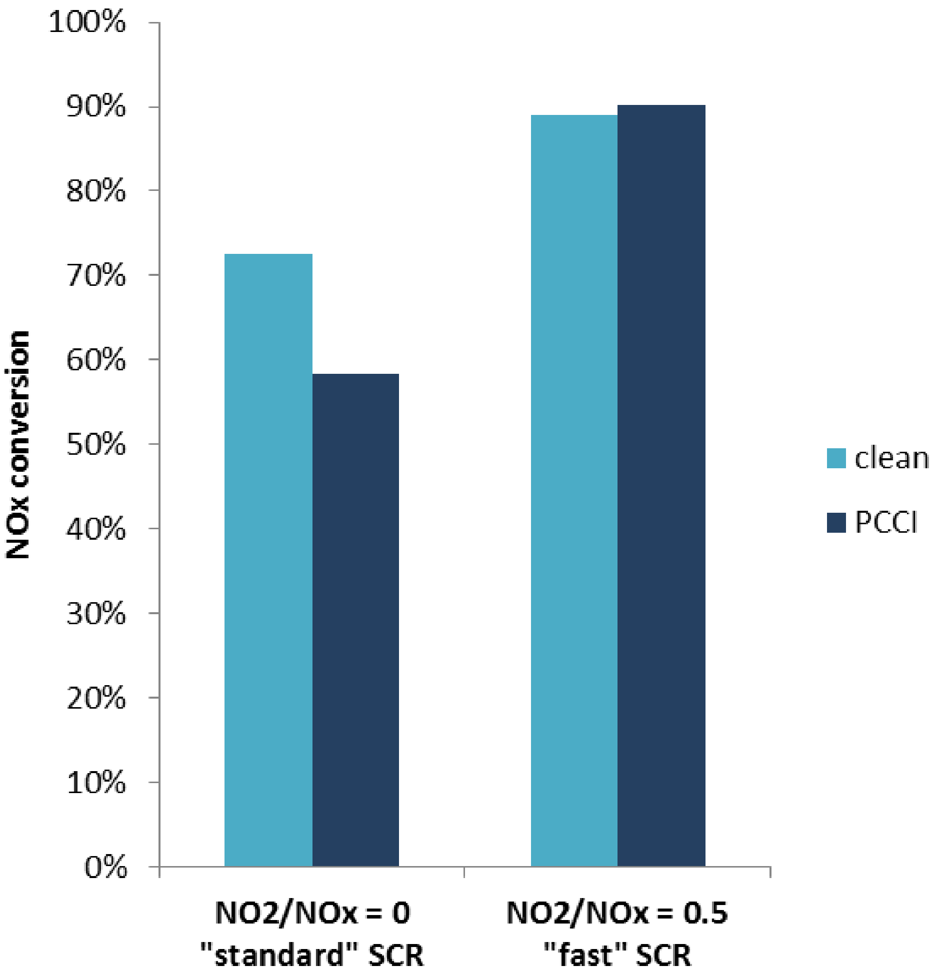




Standard SCR Reaction Impacted More by Fouling

- **Measured steady state NOx conversions for "standard" and "fast" SCR reactions:**
  - » Standard:
  - » $4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$
  - » Fast:
  - » $4NH_3 + 2NO + 2NO_2 \rightarrow 4N_2 + 6H_2O$
- **At 200 C, fouling by PCCI exhaust:**
  - » reduced standard SCR NOx conversion
  - » had no impact on fast SCR activity
- **For temperatures 250 C and above, hydrocarbons desorbed and did affect SCR performance**

Steady state SCR NOx conversions at 200 C



Conclusions

- **Reversible HC fouling was observed on Cu- and Fe-SCR**
  - » Aggressive HC conditions based on low exhaust temperature exposure
- **At low temperatures Cu-zeolite shows more tolerance to HC fouling compared to Fe-zeolite (as expected)**
- **Higher HC levels from PCCI led to more fouling of low temperature performance**
  - » HC fouling effect differences between conventional and PCCI combustion HCs were more noticeable on Cu-zeolite catalyst
- **HC chemistry extracted from SCR cores shows lower molecular weight HCs on SCR from PCCI exhaust exposure (vs. diesel-like HCs form conventional exhaust)**
- **No effect from HC fouling on NH_3 storage capacity was observed**
- **The standard SCR reaction (NO only) was impacted by fouling more than the fast ($NO+NO_2$) SCR reaction**