Hydrocarbon fouling of Cu- and Fe-zeolite SCR catalysts in conventional and advanced diesel combustion modes

Vitaly Y. Prikhodko, Josh A. Pihl, Samuel A. Lewis and James E. Parks *Oak Ridge National Laboratory* 

> 2011 CLEERS Workshop April 19-21, 2011



Gurpreet Singh and Ken Howden Vehicle Technologies U.S. Department of Energy



## **Overview**

- Lean-burn engines improve fuel economy and decrease CO<sub>2</sub> emissions but
  - » Conventional combustion produces high levels of nitrogen oxides (NO<sub>X</sub>) and particulate matter (PM) emissions
  - » Removal of  $NO_X$  is troublesome under fuel-lean environment
  - » Technologies for removing  $NO_X$  and PM emissions from lean-burn engine exhaust include lean  $NO_X$  trap (LNT), selective catalytic reduction catalyst (SCR) and diesel particulate filter (DPF)

## - Advanced combustion regimes can simultaneously reduce engine out $\rm NO_X$ and PM emissions while maintaining thermal efficiency

- » Most are categorized as low temperature premixed combustion: homogeneous charge compression ignition (HCCI) and premixed charge compression ignition (PCCI)
- » The goals of advanced combustion modes are to maximize engine fuel efficiency and minimize emissions (which also improve system fuel efficiency by reducing fuel penalty associated with regeneration of exhaust after-treatment devices)

### PCCI often generates higher CO and HC emissions

» Zeolite-based SCR catalysts are adversely impacted by HC in the exhaust stream (SAE2008-01-1030, SAE2010-01-1170)



## 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
  Catalysts Fouled in Engine Exhaust
  - » 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



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
    Exhaust

Schematic of engine exhaust slipstream for catalyst exposure to hydrocarbons

#### 4 Managed by UT-Battelle for the U.S. Department of Energy

## Conventional PCCI

Engine Out NO <sub>X</sub>	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

Engine Condition: 1500 rpm, 2.6 bar BMEP

### GM 1.9-liter CIDI



for the U.S. Department of Energy

### SCR performance was characterized on a bench flow reactor

### Bench flow reactor conditions

- » Inlet: 350 ppm NO<sub>X</sub> + 350 ppm NH<sub>3</sub>, 14% O<sub>2</sub>, 4.5% H<sub>2</sub>O, 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







### HC were extracted and analyzed by GC-MS

 Hydrocarbons were extracted from a loaded sample using 50/50 hexane/ acetone solution in a microwaveassisted extractor



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





## **NH**<sub>3</sub> storage is not affected by stored HC

- Integrated results for total moles of NH<sub>3</sub> 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<sub>3</sub> stored on Cu-SCR as expected



### *NH*<sub>3</sub> stored during stabilization step (prior to ramp)

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

### HC/soot fouling impacts 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
  - » HC fouling reversible at high T (~ $500^{\circ}$ C).



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

- During temperature ramp, HCs, CO, and CO<sub>2</sub> 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<sub>2</sub> peak for Cu-zeolite
- Much more HC on Fe-zeolite



#### C species release during temperature



## More total C (HC and CO+CO<sub>2</sub>) trapped on Fe-zeolite

- Integrated results for total moles of HC and CO+CO<sub>2</sub> 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<sub>X</sub> performance results

### C species release during temperature ramp





## 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<sub>2</sub> release results)
  - » Shift to lighter, more volatile HC in PCCI
- No apparent difference is observed between Cu- and Fe-SCR



### HC (paraffins) distribution

## **Evidence on formation of nitro (-NO<sub>2</sub>) compounds**

- Nitropyrene (carcinogenics to humans) was observed on a surface 100of a catalyst
  - » Nitropyrene is a by-product of combustion: nitrated pyrene emitted in a 50diesel engine
  - » Formation of nitropyrene on the surface of Cu-SCR
    - Cu is a known catalyst for formation of nitropyrene from nitric acid and pyrene



### • Nitropyrene was observed on a surface of 3 out of 4 core samples

» <u>Additional experiments are needed</u> to determine whether nitropyrene is formed during combustion and/or Cu facilitates its formation on the surface of the catalyst



## Summary

### • Reversible HC fouling was observed on Cu- and Fe-SCR

- » At low temperatures Cu-zeolite shows more tolerance to HC fouling compared to Fezeolite
- » PCCI HC are more severe for Cu-zeolite
- Differences in HC species had more adverse effect on Cu-zeolite
  - » Pore size differences in Cu- and Fe-zeolites may explain the more adverse effect
  - » Smaller PCCI HC may be able to penetrate further into Cu-zeolite explaining more severe impact on NO<sub>X</sub> performance of PCCI exposed Cu-SCR
- Evidence on formation of nitro (-NO<sub>2</sub>) compounds
  - » Additional experiments are needed to determine whether nitropyrene was formed during combustion and/or Cu facilitates its formation on the surface of the catalyst



## **Questions?**

