

Hydrocarbon Fouling of SCR During PCCI Combustion

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ABSTRACT

The combination of advanced combustion with advanced selective catalytic reduction (SCR) catalyst formulations was studied in the work presented here to determine the impact of the unique hydrocarbon (HC) emissions from premixed charge compression ignition (PCCI) combustion on SCR performance. Catalyst core samples cut from full size commercial Fe- and Cu-zeolite SCR catalysts were exposed to a slipstream of raw engine exhaust from a 1.9-liter 4-cylinder diesel engine operating in conventional and PCCI combustion modes. The zeolites which form the basis of these catalysts are different with the Cu-based catalyst made on a chabazite zeolite which has smaller pore structures relative to the Fe-based catalyst. Subsequent to exposure, bench flow reactor characterization of performance and hydrocarbon release and oxidation enabled evaluation of overall impacts from the engine exhaust. The Fe-zeolite NO_x conversion efficiency was significantly degraded, especially at low temperatures (<250°C), after the catalyst was exposed to the raw engine exhaust. The degradation of the Fe-zeolite performance was similar for both combustion modes. The Cu-zeolite showed better tolerance to HC fouling at low temperatures compared to the Fe-zeolite but PCCI exhaust had a more significant impact than the exhaust from conventional combustion on the NO_x conversion efficiency. Furthermore, chemical analysis of the hydrocarbons trapped on the SCR cores was conducted to better determine chemistry specific effects.

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INTRODUCTION

Advanced combustion techniques for diesel engines are an enabling technology for lower engine out nitrogen oxides (NO_x) and particulate matter (PM) emissions. Lower engine out NO_x and PM emissions reduce some of the burden of NO_x and PM control with active catalyst technologies in the exhaust, thereby, reducing the performance, cost, size and fuel penalty requirements associated with controlling these pollutants with exhaust aftertreatment devices. Many advanced combustion strategies can be categorized as a low temperature premixed combustion. Examples of such strategies are homogeneous charge compression ignition (HCCI), premixed charge compression ignition (PCCI) and reactivity controlled compression ignition (RCCI). In addition to lowering engine out NO_x and PM emissions, these combustion strategies can achieve fuel efficiencies equal to or better than conventional diesel combustion^{1, 2}. However, higher hydrocarbon (HC) and carbon monoxide (CO) emissions often result in these combustion techniques. It has been shown that HC and CO emissions may hamper the performance of the exhaust catalyst technologies, especially at low temperatures^{3,4,5,6,7}. It is, therefore, important to

understand the effects of higher CO and HC on the system components, and to identify strategies for oxidizing these species in order to implement advanced combustion techniques.

SCR catalysts are commonly used to control NO_x emissions from diesel engines. They utilize a catalyst to selectively react ammonia (NH₃) with NO_x in the exhaust stream to form N₂ and H₂O, thereby reducing the overall NO_x emissions from the vehicle. The NH₃ is typically supplied from a urea solution, which hydrolyzes to NH₃ after it is injected into the exhaust. Modern SCR catalysts for automotive applications are commonly zeolites that are ion-exchanged with either Fe or Cu^{8, 9}. Recent advancements in Cu-zeolite SCR catalysts based on chabazite zeolites show improved low temperature NO_x reduction performance as well as greater resistance to thermal aging and hydrocarbon fouling, but their efficacy in the exhaust from advanced combustion has not been established.

In the work presented here the effects of the unique HC emissions from PCCI combustion on the performance of SCR catalysts were characterized. Experiments with the engine operating in conventional combustion were also performed to understand the trends in SCR performance relative to type

and quantity of HC emissions in the exhaust. Two commercial SCR catalysts were studied: a Cu- based chabazite zeolite and a Fe-zeolite; of the two, the chabazite zeolite has smaller pore structure size. Core samples of the catalysts were exposed to exhaust from a multi-cylinder diesel engine operating in both conventional and PCCI combustion modes. Then, bench-scale flow reactor experiments were used to characterize the overall impacts from the exhaust exposure. Furthermore, chemical analysis of the type of HC species trapped on the SCR catalysts was conducted to better understand the chemistry specific trends from the flow reactor experiments. The goals of this study are to (1) quantify the impact of HC fouling on a new Cu- zeolite catalyst relative to an older Fe-zeolite technology and (2) determine if PCCI exhaust fouling has a different impact on the performance of SCR catalysts relative to conventional diesel exhaust. This study builds on previous work in this area at the same laboratory⁷.

EXPERIMENTAL METHODS

CATALYST MATERIALS

The Fe-zeolite was donated by Umicore Autocat USA and has been studied by the CLEERS community¹⁰. The Cu-zeolite was removed from the exhaust system of a Model Year 2011 Ford Diesel Super Duty pickup truck and represents the current state-of-the- art for SCR catalysts in production. Both catalysts came washcoated on square channel cordierite monoliths with cell densities of 400 cells/in². Several core samples (1 in. diameter by 3 in. long) were cut from the front face of the full size catalyst bricks. Prior to use, all catalyst cores samples were degreased for 16 hr at 650°C under flowing humidified air (5% H₂O by volume).

CATALYST EXPOSURE TO ENGINE EXHAUST

The exhaust exposure experiments were conducted with a GM 1.9-liter 4-cylinder diesel engine (Model Year 2007) installed in an engine test cell at Oak Ridge National Laboratory's Fuels, Engines, and Emissions Research Center. The test cell includes a motoring direct current (DC) dynamometer to control engine speed and load, several dedicated emissions analyzers, and a full-pass engine control system (Drivven, Inc.), which enables full control of all engine parameters. All experiments were run with ultra-low-sulfur diesel fuel.

The engine was operated in conventional and PCCI combustion modes. Conventional combustion was achieved by operating the engine with control parameters duplicating the original equipment manufacturer (OEM) electronic control unit (ECU). For PCCI combustion, the fuel rail pressure was increased, the fuel injection timing was advanced, and higher levels of EGR were used. Also, the

pilot fuel injection used in conventional combustion was not used for PCCI. The engine load and speed for both conventional and PCCI combustion were 2.6 bar brake mean effective pressure (BMEP) and 1500 rpm, respectively. This particular operating point is based on a set of conditions developed by an Ad Hoc working group, and represents a low speed cruise condition that vehicles may encounter during the Federal Test Procedure (FTP) driving cycle¹¹. The parameters utilized for both combustion modes are summarized in Table 1, and the resulting emissions from the two combustion modes are summarized in Table 2. The filter smoke numbers reported in Table 2 were collected previously on the same engine at the same conditions as in this study, and they should be representative of the experiments conducted for this study.

Table 1. Engine control parameters for conventional and PCCI combustion at 1500 rpm and 2.6 bar BMEP

	Conventional	PCCI
Main SOI (deg. ATDC)	0.2	-5
Rail Pressure (bar)	570	875
EGR Rate (%)	32	41

Table 2. Engine-out emissions from conventional and PCCI combustion at 1500 rpm and 2.6 bar BMEP

	Conventional	PCCI
NO _x (g/bhp-hr)	1.02	0.24
HC (g/bhp-hr)	1.35	2.19
CO (g/bhp-hr)	3.12	11.70
Filter Smoke Number (FSN)	0.07	0.03

The SCR catalyst core samples were exposed to engine exhaust through a slipstream arrangement. A fraction of the main exhaust from the engine was pulled through the catalyst cores with a vacuum pump downstream of the core. Flow through the core was held constant to maintain a GHSV of 30,000 hr⁻¹ by utilizing a 0.063 in. orifice between the pump and core. This space velocity is representative of conditions expected in vehicle applications. Insulation of the slipstream lines held the catalyst temperature at 115°C and prevented condensation points. Exposure time was 3 hours. There were no other aftertreatment components in the engine exhaust. Typically, a vehicle exhaust system would include a diesel oxidation catalyst (DOC) and/or a diesel particulate filter (DPF) upstream of the SCR catalyst, both of which could reduce HC concentrations in the exhaust stream. Low core temperatures were used in the study to simulate conditions where HCs would not be controlled by the upstream DOC. Taken together, low core sample temperatures, the long exposure time, and lack of upstream aftertreatment components represent very aggressive HC fouling conditions. A diagram with details of the engine test system is shown in Figure 1.

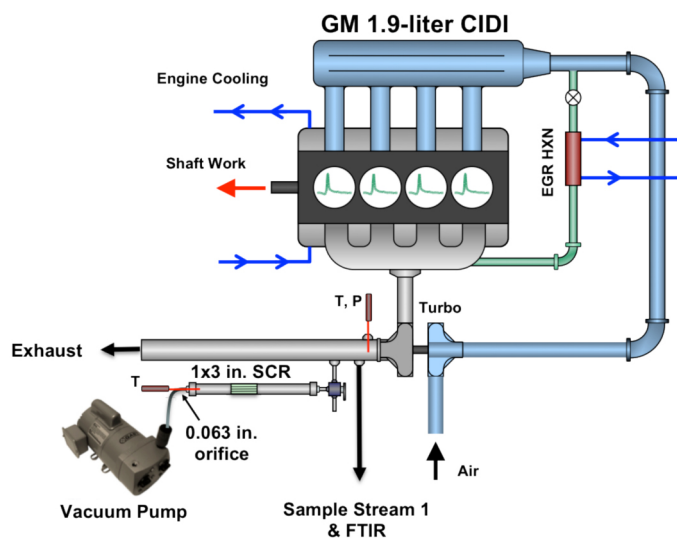


Figure 1. Engine test system diagram

FLOW REACTOR PERFORMANCE EVALUATION

After exposure to engine exhaust, the SCR catalyst cores were loaded into a bench-scale flow reactor for characterization of the impact of HC fouling on catalyst performance. The flow reactor used mass flow controllers to generate simulated exhaust gas mixtures from compressed gas bottles and an HPLC pump for water delivery. Tube furnaces controlled the temperature of the catalyst sample and the inlet gases. Gas concentrations were measured with an MKS Multigas 2030HS Fourier Transform Infrared (FTIR) Spectrometer. Two different types of flow reactor experiments were conducted: temperature programmed SCR, and an isothermal transient gas input protocol.

Temperature Programmed SCR Evaluation

The temperature programmed SCR experiments were used to measure NO SCR performance and HC release/oxidation over a wide temperature range. The reactor flows were set to achieve a gas hourly space velocity of $30,000 \text{ hr}^{-1}$ (based on flows at standard conditions and total catalyst core sample volume). The catalyst sample was initially heated to 150°C under flowing nitrogen. Once the catalyst temperature was stable, SCR experiment flows were initiated: 350 ppm NH_3 , 350 ppm NO, 14% O_2 , and 4.5% H_2O . Inlet CO_2 was omitted from these experiments to enable quantification of HC oxidation. The catalyst sample was held at 150°C until the measured outlet concentrations stabilized; the NH_3 uptake during the step was used to estimate NH_3 storage capacity. Once the gas concentrations were stable, the catalyst temperature was ramped to 600°C at a rate of $5^\circ\text{C}/\text{min}$. After the temperature ramp was completed, the catalyst was cooled back down to 150°C and the entire experiment was repeated to characterize the performance recovery after the HCs were

removed from the catalyst surface during the first ramp. A table summarizing the experimental steps for the temperature programmed SCR evaluation is shown in Table 3.

Table 3. Summary of experimental steps for temperature programmed SCR evaluation

Steps	Description
1	Stabilize at 150°C : NH_3 storage capacity
2	Ramp to 600°C ; NO_x reduction, HC release
3	Cool to 150°C
4	Stabilize at 150°C : NH_3 storage capacity
5	Ramp to 600°C ; “cleaned” NO_x reduction

Isothermal Transient Gas Input Protocol

An isothermal transient gas input protocol was used to further characterize how HC fouling impacted specific functions of the SCR catalysts. The protocol consisted of a series of well-defined inlet gas transients that probe NH_3 uptake; NH_3 oxidation; NO oxidation; SCR reaction rates with NO_2/NO_x ratios of 0.0, 0.5, and 1.0; and surface NH_3 coverage under all three SCR operating conditions. A detailed listing of the gas compositions during the protocol steps is included in Table 4. The isothermal protocol was performed at 200°C based on results from the temperature programmed SCR evaluation. FTIR data was collected during the temperature changes between protocol runs to quantify HC release and oxidation during heating. Flows were set to achieve a gas hourly space velocity of $60,000 \text{ hr}^{-1}$.

CHARACTERIZATION OF HYDROCARBON SPECIES

Microwave-assisted HC extraction with GC-MS

The HC emissions from PCCI are known to differ in chemistry from conventional combustion HC emissions^{12, 13}. In order to better understand the HC composition effects on SCR fouling, the HCs trapped on the SCR cores were characterized with gas chromatography mass spectrometry (GC-MS) techniques. For every SCR core sample analyzed in the bench-scale flow reactor, a second “twin” SCR core sample was exposed to the same exhaust conditions for HC characterization. After exposure, the HCs were extracted from the second core by submersing it in a mixture of hexane and acetone (equal parts by volume) and utilizing a microwave-assisted extraction technique. The resulting extracts were concentrated, spiked with an internal standard, and analyzed by the GC-MS.

Pyrometry Analysis with GC-MS

Temperature specific analysis of HCs desorbed from SCR catalysts was conducted with a pyrometry technique on the GC-MS. A 10 mm single channel section of a catalyst sample was extracted from a HC-exposed SCR and loaded into a Frontier Laboratories LTD multi-slot pyrolyzer (EGA/

Table 4. Gas composition during isothermal transient inlet gas protocol steps

Steps	Description	NO (ppm)	NO2 (ppm)	NH3 (ppm)	O2 (%)	H2O (%)
1	Stabilize	0	0	0	0	5
2	NH ₃ adsorption	0	0	350	0	5
3	NH ₃ oxidation	0	0	350	10	5
4	NH ₃ inventory: NO ₂ /NO _x = 0.5	175	175	0	10	5
5	SCR: NH ₃ /NO _x = 1.0; NO ₂ /NO _x = 0.5	175	175	350	10	5
6	NH ₃ inventory: NO ₂ /NO _x = 0.5	175	175	0	10	5
7	NO oxidation: NO ₂ /NO _x = 0.0	350	0	0	10	5
8	SCR: NH ₃ /NO _x = 1.0; NO ₂ /NO _x = 0.0	350	0	350	10	5
9	NH ₃ inventory: NO ₂ /NO _x = 0.0	350	0	0	10	5
10	Clean: NO ₂ /NO _x = 0.5	175	175	0	10	5
11	NO ₂ decomposition: NO ₂ /NO _x = 1.0	0	263	0	10	5
12	SCR: NH ₃ /NO _x = 1.0; NO ₂ /NO _x = 1.0	0	263	350	10	5
13	NH ₃ inventory: NO ₂ /NO _x = 1.0	0	263	0	10	5
14	Clean: NO ₂ /NO _x = 0.5	175	175	0	10	5

PY-3030D). The sample was then purged with helium for 30 seconds followed by a temperature ramp from 40°C to 200°C under helium flow. The volatile organics were injected onto a Restek Rxi-5ms column (30m, 350µm id, 0.25µm df). The column was kept at 40°C for 3 minutes, then ramped to 320°C at 6°C/min and held at 320°C for 5 minutes. The analytes were analyzed by an Agilent Technologies mass spectrometer, which was scanned from 35 to 550 daltons at a 1 second scan rate. An additional pyrolysis analysis was conducted on each sample by repeating the above procedure with the same experimental conditions with the exception that the sample was rapidly heated to 600°C in 30 seconds before injection into the GC-MS.

RESULTS AND DISCUSSION

TEMPERATURE PROGRAMMED SCR EVALUATION

Figures 2 and 3 show NO_x conversion as a function of temperature for the Cu-zeolite and Fe-zeolite catalysts during the temperature ramp experiments. These results have been presented in a previous study⁷. The Cu-zeolite catalyst shows superior NO_x conversion at the lower temperatures, as expected, in comparison to the Fe-zeolite. Furthermore, the loss in NO_x conversion due to HC fouling is relatively less for the Cu-zeolite catalyst in comparison to the Fe-zeolite catalyst. Performance loss for both catalysts appears to occur primarily in the lower temperature regions. For both catalysts and both combustion modes utilized, HC fouling was reversed by the elevated temperatures experienced during the

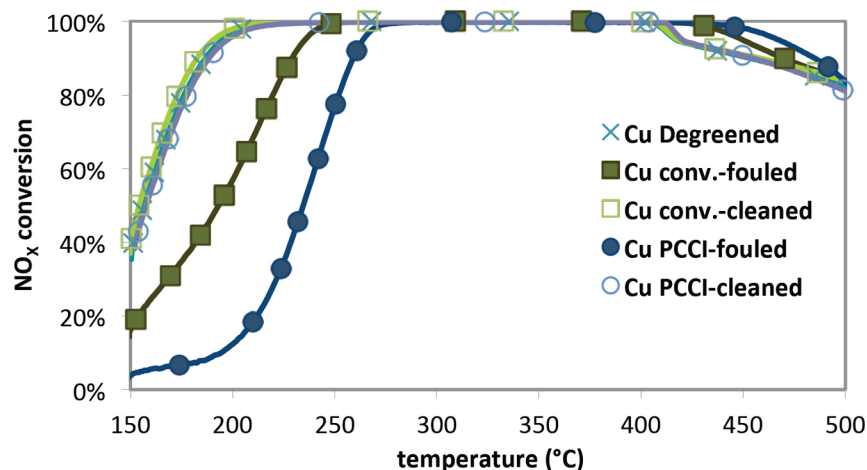


Figure 2. Cu-zeolite NO_x conversion during the temperature ramp for various states of catalyst exposure