

Durability Assessment of Diesel Cold Start Concept (dCSC™) Technologies

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ABSTRACT

The phase-in of US EPA Tier 3 and California LEV III emission standards require further reduction of tailpipe criteria pollutants from automobiles. At the same time, the mandate for reducing Green House Gas (GHG) emissions continuously lowers the exhaust temperature. Both regulations pose significant challenges to emission control catalyst technologies, especially for cold start emissions. The recently developed diesel cold start concept technology (dCSC™) shows promising results. It stores NOx and HC during the cold start period until the downstream catalytic components reach their operating temperatures, when the stored NOx/HC are subsequently released and converted. The technology also has oxidation functions built in and acts as a diesel oxidation catalyst under normal operating conditions. In a US DOE funded project, the diesel cold start concept technology enabled a high fuel efficiency vehicle to achieve emissions targets well below the SULEV30 emission standards.

In this study, detailed lab assessments of a development diesel cold start concept catalyst were carried out with emphasis on its long-term durability. The catalyst exhibits high NOx/HC storage capacities with high trapping efficiency in the temperature range of 80 to 200 °C. The majority of NOx storage sites can be regenerated at temperatures above 250 °C. The catalyst is thermally durable after 750 °C/100 h/10% H₂O hydrothermal aging, although a noticeable decline of NOx storage capacity is observed after 10 hours aging at 850 °C, or after exposure to a rich atmosphere. The catalyst also has good sulfur tolerance, maintaining high NOx storage capacity even after a 2 g S/L catalyst of sulfur exposure. The long-term durability of the catalyst to hydrothermal aging and to repetitive sulfation/desulfation cyclic aging is also demonstrated on engine/vehicle evaluations. An engine aged catalyst that represents its end of useful life shows clear advantages for cold start NOx/CO/HC emission control on a light-duty diesel truck.

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INTRODUCTION

The US EPA GHG emission standards for light-duty vehicles call for a significant improvement of the fuel economy from 2017 to 2025 model year. During the same period of time, the US EPA Tier 3 and CARB LEV III emission standards require a further reduction of tailpipe criteria pollutant emissions. By 2025, the tailpipe emissions for light-duty vehicles must meet fleet average targets of 163 g/mile CO₂ and 30 mg/mile combined NMOG + NOx (aka. SULEV30 standards). These correspond to approximately a 36% increase of fuel economy from the 2016 model year level and an additional 80% reduction of NMOG + NOx emissions from the federal Tier 2 Bin 5 emission standards at which a majority of the current diesel engine powered light-duty vehicles are certified.

Similarly, for medium and heavy duty vehicles, the US EPA Phase 2 GHG emission standards require a 5.1% fuel efficiency improvement from 2017 to 2027 model year. In addition, CARB is proposing to further reduce the NOx emissions from the current 0.2 g/bhp-hr to be as low as 0.02 g/bhp-hr by 2023.

Diesel engine powered vehicles are more fuel efficient than gasoline vehicles and can be an effective solution to meeting GHG emission standards. Controlling the tailpipe emissions of diesel vehicles to meet

the stringent SULEV 30 or 0.02 g/bhp-hr NOx targets is challenging. Although the emission control systems currently installed on diesel vehicles are effective and reach high conversions, the exhaust temperature has to be above the operating temperature of the catalysts, which is typically above 200 °C. At temperatures below this, especially during the cold start periods of a vehicle operation, these catalysts are relatively ineffective. In fact, the cumulative tailpipe emissions of NOx and HC from a typical Tier 2 Bin 5 vehicle already exceed the SULEV 30 standards in the first 200 seconds of the FTP75 testing cycles. Continuous advancement in diesel combustion control to improve the fuel economy of diesel vehicles will naturally reduce the exhaust temperature further. This trend increasingly stresses the importance of low temperature emission control.

The diesel Cold Start Concept (dCSC™) technology recently developed by Johnson Matthey offers a potential solution to mitigate the low temperature emissions [1, 2]. The catalyst contains storage materials to trap NOx and HC at temperatures below 250 °C, as well as diesel oxidation catalytic (DOC) components to oxidize HC/CO/NO once the exhaust temperatures are high enough. During the cold start period of a vehicle operation, the NOx/HC emissions are captured on the storage materials while the downstream catalytic assemblies, such as SCR, SCRf® and DPF catalysts, reach their

operating temperature. Once the exhaust temperatures are above about 250°C, the stored NO_x/HC are thermally released from the storage materials. While a major portion of the HC and a small portion of the NO_x are converted by the diesel cold start catalyst itself during the releasing process, the rest of the HC/NO_x released from the cold start concept catalyst are reduced by the downstream HC oxidation and NO_x reduction catalysts. Once warmed up, the DOC components in the cold start concept catalyst perform their conventional functions: oxidizing HC/CO to CO₂; converting NO to NO₂ to enhance the passive soot oxidation in the filter and NO_x reduction efficiency of the downstream catalysts; and generating exotherm for filter regeneration or desulfation of downstream catalysts.

In a US DOE funded project, Cummins Inc., partnering with Johnson Matthey Inc. and Nissan Motor Co., evaluated the diesel cold start concept catalyst in combination with SCR[®] and SCR catalysts in an emission control system on a developmental fuel efficient light-duty truck to meet the tight SULEV 30 emission targets. The project demonstrated 0.01 g/mil (NO_x +NMOG) tailpipe emissions under FTP75 testing cycles, which is well under the SULEV 30 standards, while achieving 60% fuel economy improvement from the 2010 baseline [3].

The diesel cold start concept technology was also evaluated on heavy duty diesel engines to explore the potential of improving NO_x conversions. A comparative study was conducted for two systems, (DOC + SCR[®] + SCR) and (dCSC[™] + SCR[®] + SCR), under various conditions with different control strategies [4]. In all cases, the system with a diesel cold start concept catalyst showed clear advantages during the cold start period of the engine operation, resulting 3-4% overall NO_x reduction efficiency increase under HDD FTP testing cycles.

Although all the evaluation work of the diesel cold start concept catalysts in the previous studies was conducted on hydrothermally aged samples, details about the long-term durability of the catalysts have not been reported. In this study, a systematic evaluation was conducted on a laboratory reactor to assess several key aspects of a development diesel cold start concept catalyst. This includes: NO/HC/CO storage, release, and conversion properties; NO_x storage temperature profiles; the minimum temperature required to thermally regenerate the catalyst; the long-term hydrothermal stability of the catalyst when exposed to different temperatures; the stability of the catalyst to simulated exhaust feeds with different O₂ concentrations; the sulfur tolerance of the catalyst. In addition, engine aging was also conducted to verify the long-term sulfation and desulfation stability and the end of useful life durability of the catalyst.

EXPERIMENTAL

Catalysts

The diesel cold start concept catalyst used in this study was a development formulation. It contains multiple components including storage materials for trapping NO_x/HC at low temperatures during the cold start period and oxidative components for CO/HC/NO oxidation during the warm-up and normal operation conditions. These ingredients were incorporated into a catalyst washcoat and

applied onto monolithic substrates with a cell density of 62 cell/cm² (or 400 cpsi) and a wall thickness of 0.1 mm (or 4 mil). The total PGM loading of the catalyst was Pt = 24 g/ft³ and Pd = 96 g/ft³ (or 1:4:0/120). For comparison purposes, a typical zeolite-containing DOC with a PGM loading of Pt = 14 g/ft³ and Pd = 56 g/ft³ (or 1:4:0/70) was used as a reference catalyst for engine evaluation.

Hydrothermal Aging

Core samples of 2.54-cm diameter x 7.62-cm length were taken from a full size monolith catalyst and hydrothermally aged in a tubular furnace.

In one set of experiments, cores samples were aged in a flow of 10% H₂O mixed with air in a wide range temperature range (650 to 900 °C) for different durations (2 to 100 hours) to clearly determine the long-term durability as well as the temperature limitations of the catalysts. Table 1 summarizes the time-at-temperature matrix used in this study. It is worth noting that the 650°C/2h aged sample is also labeled as a degreened catalyst.

Table 1. Matrix of time-at-temperature for the hydrothermal aging in a flow of 10% H₂O/air

Temp. (°C)	Hydrothermal Aging Duration (hours)				
	2	10	25	50	100
650	x	x	x	x	x
750	x	x	x	x	x
800	x	x	x	x	x
850	x	x	x		
900	x	x			

In another set of experiments, cores samples were aged in a flow of 10% H₂O mixed with different levels of O₂ and balanced with N₂ to assess the stability of the catalyst under different gas mixtures to simulate automotive exhaust conditions at various air-to-fuel ratios. The aging temperature and duration were kept at 650 °C and 2 hours, while the O₂ concentration in the feed was decreased from 20% to 0.5% and 0%, respectively during these tests. To further explore the stability of the catalyst under rich conditions, another set of aging was carried out under similar conditions but in a flow of 10% H₂O + 1% CO + N₂ balance. This corresponds to a 0.5% O₂ deficiency, and will be labelled as “-0.5% O₂” in the Results section.

Laboratory Reactor Evaluation

Performance of the aged core samples was evaluated in a laboratory reactor. Synthetic gas mixtures were prepared by adjusting the mass flow of the individual gas components. The total gas flow rate was maintained at 21.2 L/min, resulting a Gas Hourly Space Velocity of 30,000 h⁻¹ (GHSV =30,000 h⁻¹).

To evaluate the NO_x/HC/CO storage, release, and conversion activities of the catalysts, the aged cores were first pre-heated to 500 °C in a flow of 10% O₂ + 5% CO₂ + 5% H₂O + N₂ balance and held at the temperature for 5 minutes. This treatment is intended to remove any adsorbed compounds from the catalysts. The cleaned catalysts were subsequently cooled to a lower temperature set point, 125 °C for most examples, under the same feed gas mixture. Once the

temperature was stabilized, 200 ppm NO, 200 ppm CO, and 500 ppm decane (on a C_1 basis) were added into the above feed gas to mimic a typical exhaust mixture during cold start conditions. The catalysts were exposed to this feed gas for 10 minutes to ensure full saturation of the storage sites. This method enabled the measurement of the NOx storage capacity of the catalysts at this temperature. Thereafter, the temperature was increased linearly to 500 °C, a target desorption temperature, at a ramping rate of 80°C/min in the same feed gas. NOx, HC, and CO concentrations at the outlet of the reactor were recorded during the whole test.

To evaluate the impact of storage temperature on the NOx storage capacity, experiments with different temperature set points at 80, 100, 125, 150, 175, 200, 225, and 250 °C were conducted following the same procedures as mentioned above.

To determine what the minimum target thermal regeneration temperature is required to fully desorb the stored NOx on the catalyst, separate sets of experiments were conducted by varying the desorption temperature set point while maintaining the adsorption temperature at 125 °C. In the first run of each set of the experiments, the catalyst was first cleaned at 500°C to measure its NOx storage capacity. In the subsequent temperature ramps the target desorption temperatures were decreased to 400, 350, 300, or 250 °C, respectively, in each different set of experiments. Within the same set of experiments at a given target desorption temperature, the storage and release tests were repeated 4 times to determine if the catalyst can be regenerated to a stable NOx storage capacity.

Sulfur tolerance properties of the catalyst was evaluated with a 650 °C/2 h/10% H₂O degreened sample on the same laboratory reactor. The catalyst was sulfated at 350°C by introducing 10 ppm SO₂ to the full gas mixture. Different levels of sulfur exposure of 0.5, 1, and 2 g S/L catalyst were controlled by varying the sulfur exposure time. The NOx storage capacities of the sulfur loaded samples were measured after desorption at 350°C.

Engine/Vehicle Evaluation

Two sets of engine/vehicle evaluation experiments were carried out to fully assess the long-term durability of the development diesel cold start concept catalyst under more realistic conditions.

The first set of experiments focused on evaluating the long-term durability of the catalyst to repeated exposure and removal of sulfur. A development diesel cold start catalyst with a volume of 1.6 L was aged in a retort oven at 650 °C with a flow of 10% H₂O/air mixture for 50 hours. The hydrothermally aged catalyst was then mounted on a turbo charged light-duty diesel engine. An SO₂ gas cylinder was connected to the exhaust manifold at the pre-turbo location of the engine to enable accelerated sulfur exposure. The engine was equipped with in-cylinder post injection capability to trigger active regeneration events and allow for sulfur removal or desulfation of the catalyst.

Sulfur exposure to the catalyst was performed under steady state conditions at a space velocity of ~55,000 hr⁻¹ with the bed temperatures at 350 ± 5 °C. An SO₂ inlet concentration of 50 ± 5 ppm was used to accelerate the sulfur loading step. The target sulfur

exposure level was controlled at 0.5 g S /L catalyst in most cases. Immediately after sulfation, in-cylinder post injection was turned on to increase the catalyst bed temperatures to 610 ± 10 °C for 20 minutes to desulfate the catalyst.

At the beginning of the experiments, the NOx storage capacity of the catalyst was measured before and after one sulfation/desulfation cycle. Thereafter, NOx storage capacity measurements were carried out after every additional 10 repetitive cycles, until a total of 71 sulfation/desulfation cycles were accumulated.

The NOx storage capacity of the catalyst was measured under pseudo steady state conditions on the same engine. First, the catalyst temperature was ramped to ~375 °C and held for 10 minutes to desorb any stored NOx in the catalyst. Next, the engine was shut down but the engine dynamometer was switched to a motoring mode with cold air passing through the catalyst to rapidly cool it to ~100 °C. This approach prevents additional exposure of the catalyst to NOx during the cooldown step. Thereafter, the engine was turned on and set to a pre-determined speed and load setting that warms up the catalyst to ~135°C. The average space velocity during the NOx storage capacity test was ~19,000 hr⁻¹. The NOx storage capacity of the catalyst was calculated for the duration while the instantaneous NOx storage efficiency was maintained at ≥ 80%.

The aforementioned procedure was repeated 8 times (to complete a total of 71 sulfation/desulfation cycles). Finally, the catalyst was exposed to 5 g S/L catalyst to evaluate its sulfur tolerance. The NOx storage capacity of this sulfur-loaded catalyst was measured without performing the sulfur removal step.

The second set of experiments focused on assessing the simulated end of useful life durability of the catalyst. Two full size bricks, with a total volume of 4.3L, of the development diesel cold start concept catalysts were loaded in series on a light-duty diesel truck engine (which is different from the one used for the sulfur testing) and aged for 230 cycles with total aging time of 200 hours. Each of the aging cycles consisted of three modes: a low load operation with a target exhaust temperature of 275 °C, a heavy load operation with a target exhaust temperature of 450 °C; and a high temperature operation with exhaust pipe fuel injection to generate target catalyst outlet temperatures above 650 °C for DPF regeneration and desulfation events. The exhaust gas compositions were maintained under lean conditions during the entire aging. A total of 230 of the aging cycles is considered to be representative of the end of useful life durability requirement for the catalyst in terms of thermal exposure. The histogram of the catalyst bed temperatures (1" to the outlet faces) recorded for the two bricks during the entire aging cycles are summarized in Fig. 1.

After engine aging, the two catalyst bricks were loaded in the exhaust system (replacing the OEM DOC catalyst) of a 2011MY light-duty truck equipped with a 6.7 L diesel engine. After pre-conditioning by a FTP75 + US06 run, NOx/HC/CO emissions before and after the diesel cold start concept catalyst were recorded under FTP75 cycles. The engine aged parts were compared with an additional set of diesel cold start concept catalysts which was over-aged in air at 750 °C for 2 hours. In addition, a set of DOC catalysts with the same volume but