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Characterizing Light-Off Behavior and Species-Resolved Conversion Efficiencies During In-Situ Diesel Oxidation Catalyst Degreening

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ABSTRACT

Degreening is crucial in obtaining a stable catalyst prior to assessing its performance characteristics. This paper characterizes the light-off behavior and conversion efficiency of a Diesel Oxidation Catalyst (DOC) during the degreening process. A platinum DOC is degreened for 16 hours in the presence of actual diesel engine exhaust at 650°C and 10% water (H₂O) concentration. The DOC's activity for carbon monoxide (CO) and for total hydrocarbons (THC) conversion is checked at 0, 1, 2, 3, 4, 6, 8, 10, 12, and 16 hours of degreening. Pre- and post-catalyst hydrocarbon species are analyzed via gas chromatography at 0, 4, 8, and 16 hours of degreening. It is found that both light-off temperature and species-resolved conversion efficiencies change rapidly during the first 8 hours of degreening and then stabilize to a large degree. T₅₀, the temperature where the catalyst is 50% active towards a particular species, increases by 14°C for CO and by 11°C for THC through the degreening process. The shapes of the conversion versus DOC inlet temperature curves are preserved. With respect to species-resolved hydrocarbons, conversion efficiency is always highest for acetylenes, followed by olefins, aromatics, non-methane paraffins, and methane.

INTRODUCTION

With ever more stringent emissions standards, DOC's are being used in the abatement of hydrocarbon, carbon monoxide and the soluble organic fraction (SOF) of particulate matter (PM) from diesel exhaust since the early 1990's [1, 2]. In addition to the application as clean-up catalysts, DOC's are also being used as heating-devices in active regeneration of diesel particulate filters (DPF) or lean NO_x traps (LNT) [3, 4, 5, and 6].

Nitric oxide (NO_x) emissions, however, are generally not reduced by the DOC. Measures to reduce engine-out NO_x and PM, such as homogeneous charge compression ignition (HCCI) or premixed compression ignition (PCI) strategies, tend to increase CO and hydrocarbon emissions [7]. Additionally, improvements in the fuel efficiency of the diesel engine tend to reduce exhaust gas temperatures, which impose great challenges to traditional diesel oxidation aftertreatment devices [1].

While DOC's may have very attractive performance characteristics when brand new, their activity deteriorates over time. Many researchers have studied catalyst decay and conditions leading to such [8, 9, 10, 11, 12, 16 and 17]. The most common causes for catalyst decay are thermal deactivation, poisoning, fouling, attrition and mechanical failure [3, 4, 13, and 14]. Exposure to high temperature in the presence of water vapor causes thermal deactivation due to sintering of precious metal sites. The initially highly dispersed precious metal atoms coalesce into larger agglomerates. In its most severe form, thermal deactivation causes phase transformation of the washcoat, thus reducing the specific surface area and eventually eroding the supporting monolith. Poisoning is the deactivation of the catalyst by chemical reactions of the catalytically active material with species present in the feedgas. Fouling or masking in turn is the mechanical deposition of material onto the catalyst which blocks access to the catalytic sites. While poisoning is a discriminating process, i.e. only specific species are affected, fouling is a non-discriminating process. Finally, attrition is a mechanical phenomenon in which catalytic surface area is lost due to abrasive forces such as high fluid velocities or mechanical break-away.

Some of the catalyst deactivation may be reversible and the catalyst can regain activity with proper treatment. It has been shown that coking, a form of fouling, for example, may be reversible by heat-treatment of the catalyst [1]. Washing a catalyst in alkaline solutions has proven to be effective in removing phosphorous from the catalyst and restoring its activity [8]. Thermal deactivation, however, is an irreversible process [8].

It has been shown that catalyst activity deteriorates severely in the first few hours of operation when exposed to high temperatures [5, 12, and 15]. This effect is even more pronounced in the presence of water vapor [16]. It is thought that thermal deactivation due to sintering causes the very rapid initial catalyst decay. When catalysts are studied, it is therefore necessary to degreen the fresh catalysts, i.e. stabilize catalytic activity prior to assessing the DOC performance. Degreening can be either performed hydrothermally (in an oven in the presence of water vapor) or in-situ in an engine test-cell. In-situ degreening more closely reflects what a catalyst actually experiences in the field and is therefore preferred.

While several studies have been published exploring the long-term (500-1000 hrs) performance characteristics of DOC, relatively less emphasis has been placed on exploring the initial degreening process. Therefore the goal of the present study is to investigate the effect of in-situ thermal degreening on DOC performance and the effects on hydrocarbon species conversion during the degreening process. Starting with a green catalyst and monitoring its characteristics at regular operating intervals, we can realistically assess both the length of time required to reach stable operation, as well as the expected light-off activity and performance of the degreened DOC.

EXPERIMENTAL SETUP

All tests are run in an engine – dynamometer test cell. The engine is a 1.7 liter high-speed diesel engine (HSDI) equipped with a common rail fuel injection system, variable geometry turbo charger (VGT), cooled exhaust gas recirculation (EGR) and an intake throttle. The compression ratio of the engine is 16:1. Engine specifications are listed in Table 1. Low-sulfur Swedish diesel fuel is used in this study to avoid possible sulfur poisoning of the catalyst. Fuel properties for Swedish low-sulfur and 2005 US#2 diesel are given in Table 2.

Degreening Setup

Figure 1 shows the catalyst setup for degreening. First the engine exhaust is passed through a heating DOC, and then through a clean-up catalyst and finally into the DOC to be degreened. Exhaust gas temperatures are measured before and after each catalyst. Standard emissions are analyzed before and after each catalyst with an AVL CEBII emissions bench. The entire catalyst setup is wrapped in 25 mm thick fiberglass insulation to

reduce heat loss. When the oxidation catalyst is tested for activity, the heating DOC and the clean-up catalyst are removed, and the DOC is mounted approximately 1 m downstream of the turbine outlet, at the location where the heating DOC is shown in Figure 1.

Oxidation Catalyst Specifications

A model catalyst with 400 cells per square inch (CPSI), a volume of 1.24 Liters, an alumina washcoat, and 7.7 g/ft³ platinum (Pt) loading is used in this study. This lightly loaded catalyst formulation is chosen to better control and characterize the light-off behavior. The monolith measures 144 mm in diameter and 76.2 mm in length. A stainless steel housing is used to support the monolith. Temperature and exhaust gas samples are taken 120 mm upstream and 120 mm downstream of the DOC. The catalyst bed temperature is measured 25 mm from the front face of the substrate.

Table 1: Engine specifications

Engine Type	Diesel Engine
Number of Cylinders	4
Displacement (L)	1.7
Compression Ratio	16.0:1
Valves / Cylinder	4
Number of Cams	2
Fuel System	Common Rail Direct-Injection
Turbocharger	VGT
EGR Valve	Poppet-style Control Valve
Intake Throttle	Flapper Style

Table 2: Diesel fuel properties

	Swedish Diesel	US Diesel #2
Cetane Number	51.6	49.6
Sulfur Cont. (ppm wt.)	12	500
LHV (MJ/kg)	43.48	42.91
AFR Stoichiometric	14.74	14.46
Density (kg/m ³)	810	840
T50 (°C)*	224	257
Molecular C:H:O ratio	C ₁ H _{1.966} O _{0.000}	C ₁ H _{1.771} O _{0.000}

* Temperature at which 50% of the fuel is vaporized

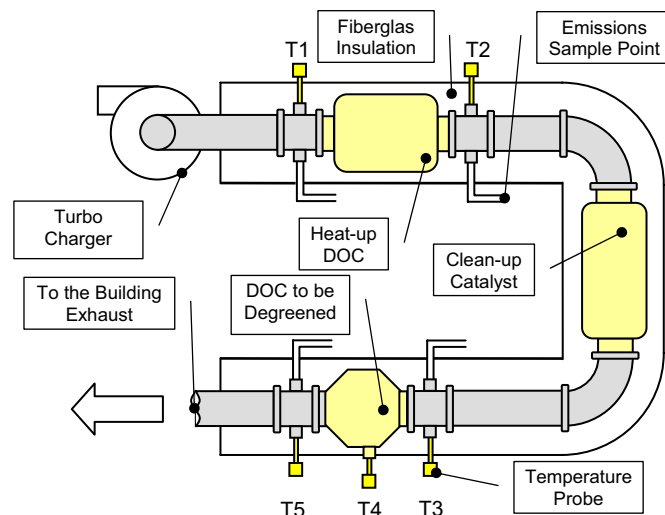


Figure 1: Degreening setup

Hydrocarbon Speciation

Hydrocarbon speciation via gas chromatography (GC) techniques has been successfully developed for gasoline [21, 22, and 23] and more recently for diesel engine exhaust [24, 25, and 26]. Diesel hydrocarbon speciation is more challenging because exhaust hydrocarbons span a much larger range of carbon numbers (C_1 - C_{22+}) and properties.

An exhaust sample cart and a two-GC system were designed to perform diesel exhaust sampling and speciation in this study. The sample cart uses a micro-pump to draw raw exhaust from before or after the DOC; semi-volatile hydrocarbons are adsorbed onto a hydrocarbon trap and light hydrocarbons pass through the trap and are diluted with nitrogen in a sample bag.

The sample bag captures light hydrocarbons (C_1 - C_8) and the Tenax trap captures semi-volatile hydrocarbons ($>C_8$), although an overlap of about 2 carbon numbers exists for each. One GC is used to analyze the sample bag (GC-1) while another GC is used to analyze the Tenax trap (GC-2). Both GCs are Shimadzu GC-17A models with flame ionization detectors (FIDs) that are used to measure hydrocarbon carbon atoms (ppmC₁).

Results from GC-1 and GC-2 are combined to obtain an overall speciation of exhaust hydrocarbons. This method yields more than 210 hydrocarbon species and identifies roughly 70% of carbon mass. More detail on the HC speciation technique can be found elsewhere [28].

RESULTS AND DISCUSSION

DEGREENING PROCEDURE

The fresh (green) DOC is degreened for 16 hours total in the presence of actual diesel engine exhaust. After every hour of degreening the activity of the DOC is checked, which will be discussed later. For degreening, 650°C exhaust gas temperature, 10% H₂O concentration and no HC and CO in the feedgas are specified as target values that the DOC is exposed to. Removing CO and HC from the feedgas avoids localized exothermic reactions in the degreening catalyst. Furthermore, low sulfur and HC concentrations in the exhaust prevent poisoning and masking, thus thermal aging is the sole process deactivating the catalyst. The engine is run at moderate speed and load of 1500 rpm and 600 kPa BMEP with conventional diesel combustion strategy. To raise the exhaust gas temperature, fuel is injected into the cylinder at a crank angle of 90° after top dead center (°ATDC). Little of the chemical energy introduced by the post injection is released; instead, it leaves the cylinder in the form of unburned or partially reacted hydrocarbons and CO. Thus, the exhaust gas temperature downstream of the turbine is about 350°C and large amounts of HC and CO are present as shown in Figure 2 – 4.

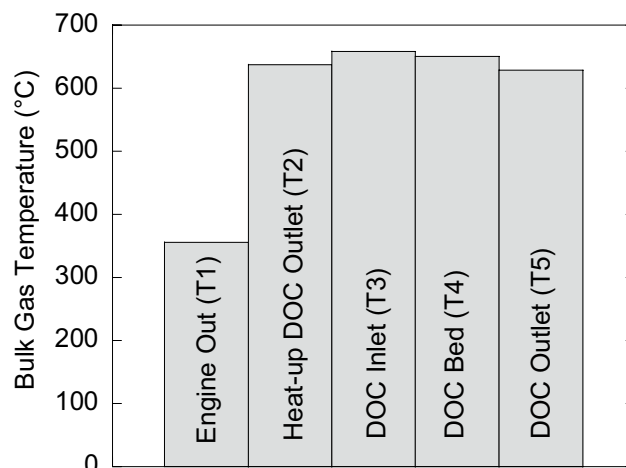


Figure 2: Representative exhaust gas temperatures at various sample locations during degreening

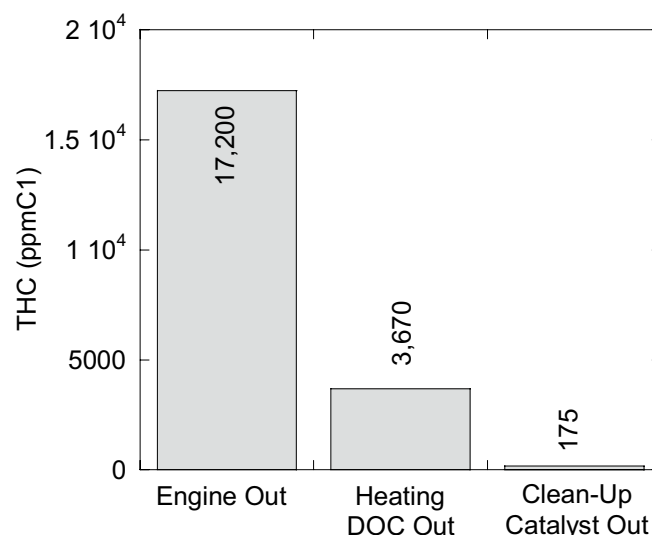


Figure 3: THC concentrations in the exhaust: engine out, heating DOC out, and clean-up catalyst out

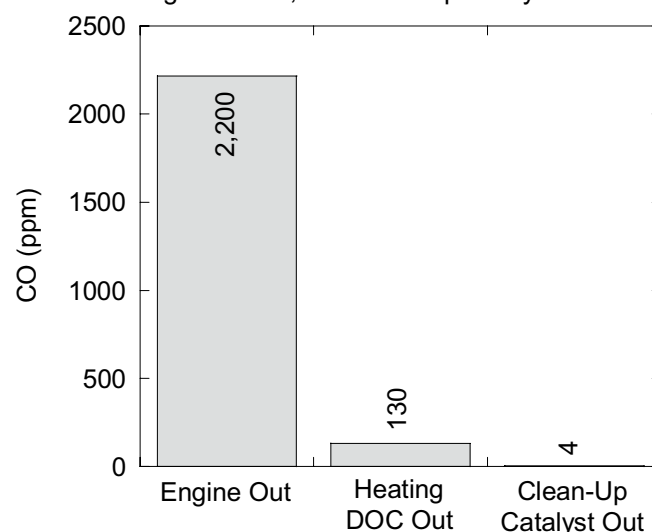


Figure 4: CO concentrations in the exhaust: engine out, heating catalyst out, and clean-up catalyst out

Through the heat-up catalyst, the exhaust gas temperature is increased to about 640°C, and much of the HC and CO is converted to H₂O and CO₂. Even though the proper degreening temperature can be achieved by the heat-up DOC, CO (130 ppm) and particularly THC (3,670 ppmC₁) levels are too high. A clean-up catalyst is therefore placed downstream of the heat-up catalyst as shown in Figure 1. This catalyst, a conventional three-way catalyst (TWC), oxidizes the remaining CO to below 5 ppm and lowers the HC levels to less than 200 ppmC₁ as shown in Figure 3 and Figure 4. Many of the hydrocarbons entering the degreening DOC are found to be methane, which is difficult to oxidize. Besides oxidizing the remaining CO and HC, the clean-up catalyst raises the exhaust gas temperature to the required 650°C.

ACTIVITY CHECK PROCEDURE

Catalyst activity strongly depends on the temperature, and light-off or light-down generally occurs over a very narrow temperature window. To check activity, the engine is run at a particular speed and load at which the DOC is fully lit and conversion efficiencies of CO and THC are determined by analyzing exhaust gas before and after the DOC. Next, the fueling of the engine is reduced, thus reducing exhaust gas temperature. After stabilizing the engine for 5 minutes, exhaust constituents are analyzed pre and post DOC. Repeating this procedure with decreasing loads eventually fully lights-down the catalyst and a quasi-steady state light-down curve is acquired. Examples of such curves for CO and THC are shown in Figure 5. In this case, starting at a nominal engine operating condition of 1500 rpm and 262 kPa BMEP, the fueling is decreased step-wise to reduce the DOC inlet temperature from 250°C to 200°C, which corresponds to 170 kPa BMEP at the same engine speed.

Figure 5 reveals that the catalyst performance depends upon whether the catalytic reaction is undergoing light-off or light-down. The hysteresis between light-off and light-down on Pt is largely attributed to self-inhibition by CO [18 and 19]. At low temperatures, CO strongly chemisorbs to the Pt-sites and thus deactivates the catalyst. As the temperature increases, CO desorbs and the precious metal sites become accessible to O₂, which then removes even more CO by oxidizing it to CO₂. The precious metal sites are now accessible to hydrocarbon species and they are starting to be converted as well. When the catalyst is fully lit, the catalytic surface is

covered with oxygen and CO-inhibition does not occur until lower temperatures. From here on, light-down curves are shown but one must bear in mind that light-off occurs at slightly higher temperatures for this particular catalyst.

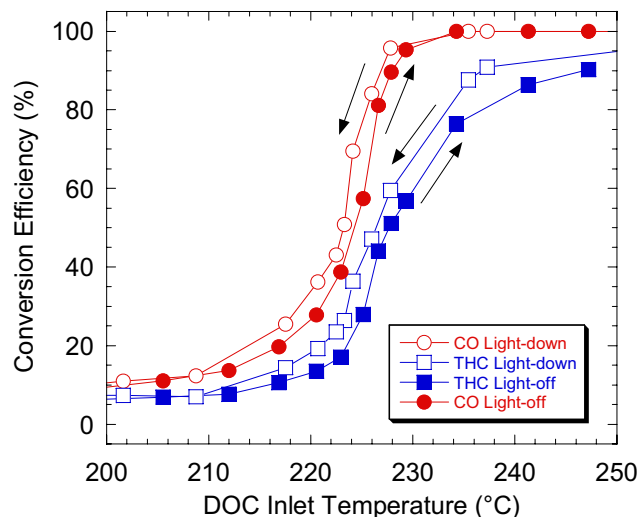


Figure 5: Light-off and light-down curves versus temperature (T3) for CO and THC at M2, 1500 rpm / 262 kPa BMEP nominal

Light-down characteristics of the oxidation catalyst are examined at three engine operating conditions (modes). Table 3 lists the main characteristics for the 3 modes. When the fueling is reduced at any of the nominal engine operating modes, not only does the temperature at the DOC inlet change, but other metrics are affected as well. Changes in SV are shown in Figure 6. When the engine load and the exhaust gas temperature decrease, the space velocity generally decreases as well. However, there are instances where SV increases when engine load decreases. This may be due to the engine control strategy, e.g. changes in the VGT, EGR and injection timing that affect the throughput of the engine.

CO and THC feedgas concentrations are affected when engine load is varied as shown in Figure 7. Both CO and THC concentrations increase when the engine load, and thus the exhaust gas temperature, is decreased. THC increases by 50 – 100%, while CO increases by 0 – 60%. Catalyst light-down can thus not solely be attributed to temperature; SV and species concentration affect the catalyst performance as well.

Table 3: Engine operating conditions and corresponding DOC inlet conditions

Mode	Speed (rpm)	Load	Load (kPa)	SV (hr ⁻¹)	AFR	CO (ppm)	THC (ppmC ₁)	H ₂ O (%)	O ₂ (%)	NO _x (ppm)	FSN (-)	DOC Inlet Temp. (°C)
M2	1500	High	300	50,000	37	650	300	5	13	160	1.5	260
		Low	160	40,000	50	500	500	3.5	16	70	0.7	190
M3	2000	High	230	70,000	40	1,000	900	5	14	60	0.5	270
		Low	110	60,000	60	1,000	1,100	3	16	50	0.2	200
M4	2300	High	420	115,000	35	800	800	5.5	13	100	0.7	330
		Low	110	80,000	60	1,300	1,300	3	16	50	0.1	210

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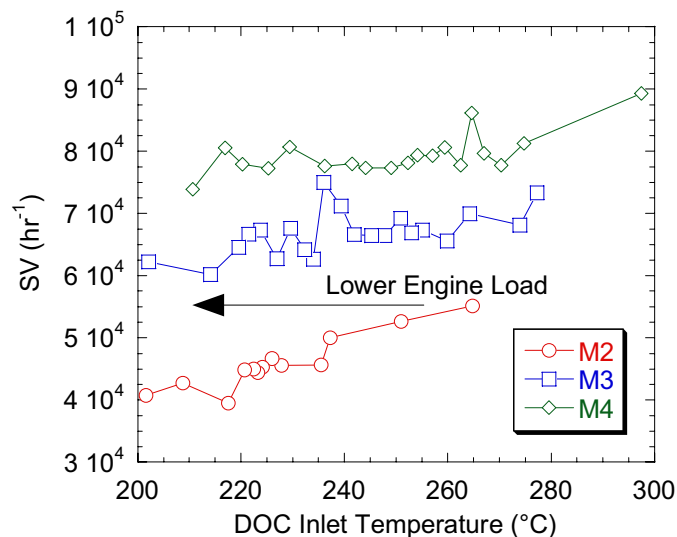


Figure 6: Typical space velocities versus DOC inlet temperature (T3) for engine operating modes M2, M3, and M4

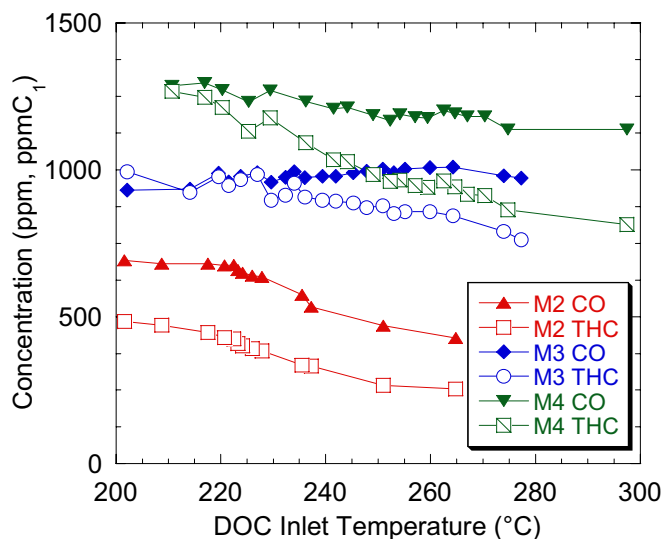


Figure 7: Typical CO and THC feedgas concentrations versus DOC inlet temperature (T3) for engine operating modes M2, M3, and M4

DOC DEGREENING RESULTS

Light-down curves for CO and THC are acquired on the fresh catalyst after 0, 1, 2, 3, 4, 6, 8, 10, 12, and 16 hours of degreening. Figure 8 and Figure 9 show the complete set of light-down curves for CO and THC. They were obtained at engine operating condition M3. Light-down curves are generated for three engine operating conditions, M2, M3, and M4. The engine operating conditions differ, as mentioned earlier, in temperature, space velocity and exhaust gas composition.

Comparing light-down curves at different stages of catalyst degreening reveals that the curves are identical in shape but light-down occurs at higher exhaust gas temperatures as degreening progresses as shown in Figure 8 and 9. Degreening does not affect overall conversion when the catalyst is fully lit. These results are found consistently for CO and THC across the three engine operating modes. The fact that the shape of the curves and the overall conversion are not affected by degreening suggests that only the initial part of the DOC activity is delayed.

In the low temperature regime where light-off begins, it is widely accepted that the conversion efficiency of a catalyst is controlled by chemical kinetics, i.e. chemical kinetics are the rate-limiting factor. At higher conversion efficiencies and temperatures, pore diffusion and bulk gas diffusion are thought to be the rate limiting processes rather than chemical kinetics [2 and 8]. Pore and bulk gas diffusion seem to be unaffected by the degreening process as indicated by the identical slopes and shapes of the light-down curves. This leads to the conclusion that the increase of the catalyst light-down temperature is primarily due to a loss of the precious metal sites, which may be caused by sintering. It is believed that the properties of the Al_2O_3 washcoat, such as specific surface area and pore size, are unaffected by the degreening temperature of 650°C.

During the initial hours of degreening, light-down temperatures increase rapidly and light-down curves are distinctly spaced with little to no overlap. In the later part of the degreening process, however, instances are observed where the catalyst seems to regain activity and light-down occurs at lower temperatures than at some of the cases with fewer hours of degreening. This is attributed to day-to-day and test-to-test variability. The experiments are run in an environment in which ambient temperature and humidity cannot be precisely controlled and thus vary from day to day.

T50, the temperature at which a catalyst is 50% active for a particular species, is a common performance indicator. Figure 10 and 11 show T50 for CO and THC respectively versus degreening time. T50 increases rapidly during the first 8 hours of degreening and then stabilizes. Changes in T50 from 8-16 hours are small and do not exceed measurement uncertainty. T50 CO light-down is shifted by 14°C through the degreening process for all three operating modes.

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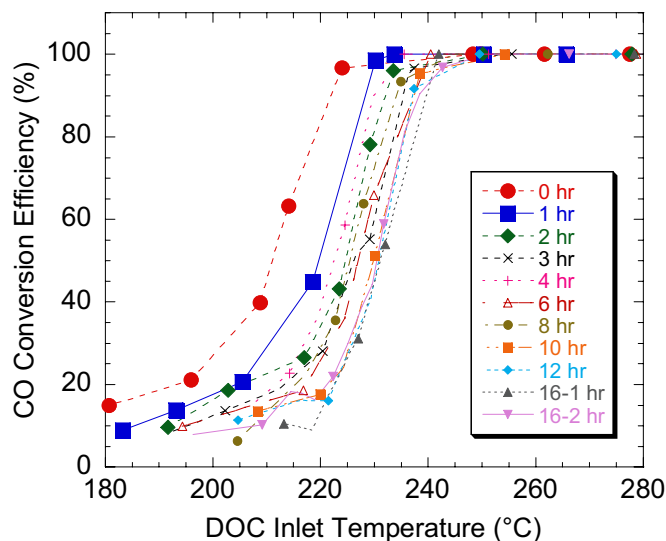


Figure 8: CO light-down curves at 0, 1, 2, 3, 4, 6, 8, 10, 12, and 16 hours of degreening; engine operating mode M3

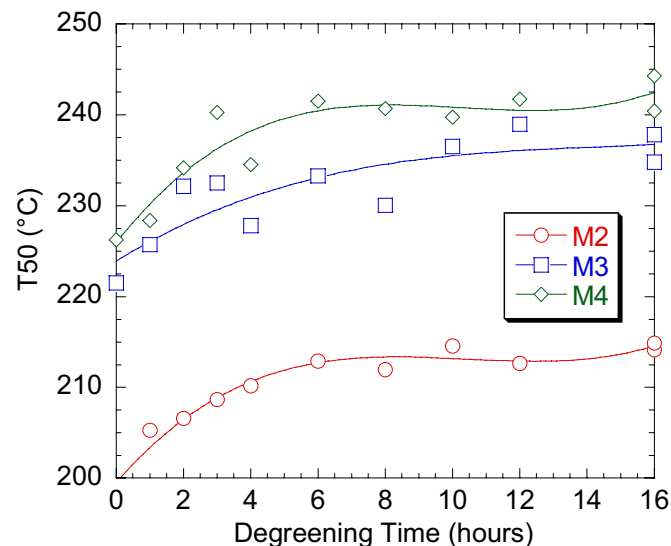


Figure 10: T50 (DOC inlet temperature T3) for CO versus degreening time

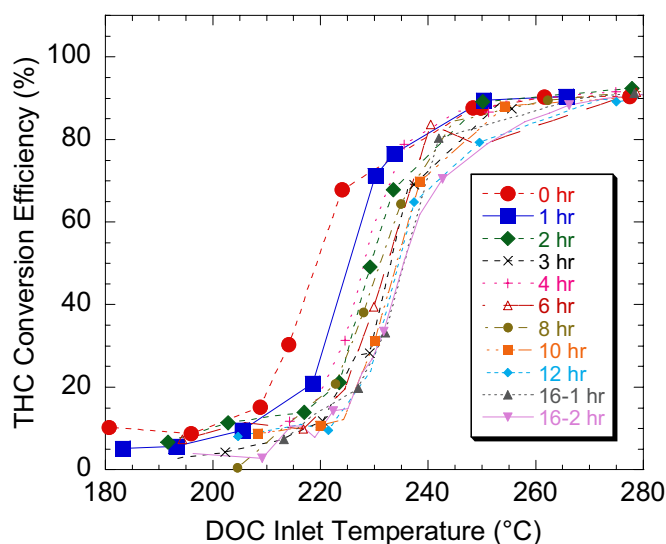


Figure 9: THC light-down curves at 0, 1, 2, 3, 4, 6, 8, 10, 12, and 16 hours of degreening; engine operating mode M3

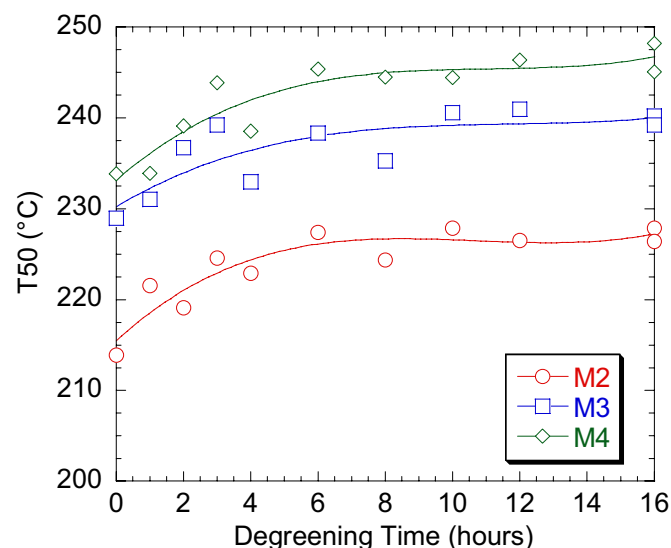


Figure 11: T50 (DOC inlet temperature T3) for THC versus degreening time

At modes 3 and 4, catalyst light-down occurs at higher temperatures as shown in Figure 10, which is probably due to higher space velocities and species concentrations for these cases. Catalyst light-down for THC shows very similar trends. T50 increases rapidly during the initial 8 hours of degreening and then stabilizes to a large degree. Overall, T50 for hydrocarbons shifts by 11°C compared to 14°C for CO. Higher space velocities delay catalyst light-down for M3 and M4 similar to catalyst behavior for CO conversion. The fact that the catalyst activity stabilizes after 8 hours of exposure to 650°C in the presence of actual diesel engine exhaust gas suggests that the platinum dispersion is largely stabilized at this point.

Figure 12 shows the light-down characteristics of the fully degreened catalyst with respect to CO. When the DOC is fully lit, the conversion efficiency reaches 100%. At M2 the catalyst deactivates at a lower temperature and more rapidly than at M3 and M4. In mode 2, conversion decreases from 80% to 20% when the DOC inlet temperature is decreased by 11°C. For M3 and M4 this temperature difference is 13°C. Note that 20 – 50% conversion occurs over the same temperature span for all three cases but 50 – 80% conversion occurs over 4°C for M3 and M4 versus 2°C for M2. CO, THC concentrations, and space velocities are higher for modes 3 and 4; thus CO-inhibition, pore diffusion and bulk gas diffusion may cause the differences in light-down behavior for the 3 operating modes.

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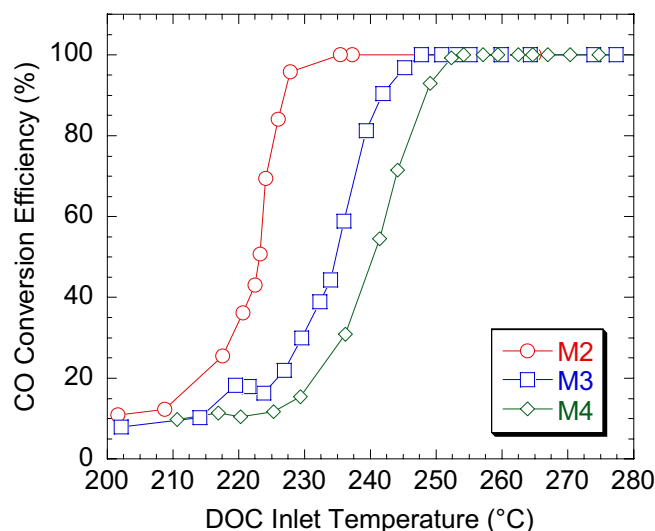


Figure 12: Fully degreened catalyst light-down curves for CO versus DOC inlet gas temperature (T3)

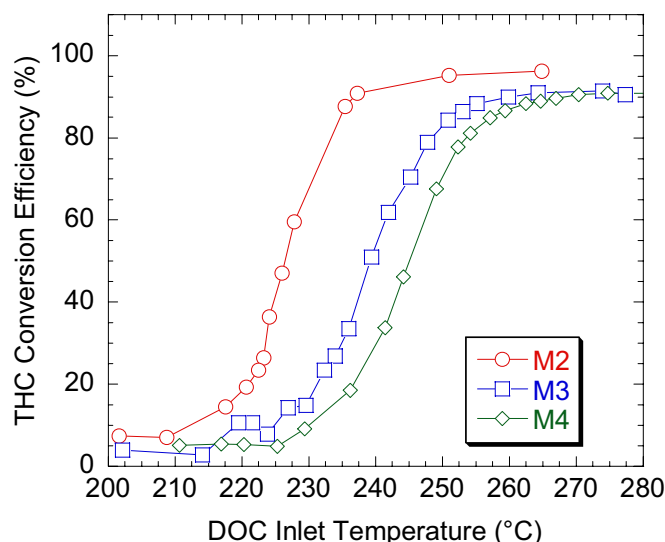


Figure 13: Fully degreened catalyst light-down curves for THC versus DOC inlet gas temperature (T3)

Light-down behavior of the fully degreened DOC with respect to THC is shown in Figure 13. The maximum conversion efficiency is ~95% for M2 and slightly lower (~90%) for M3 and M4. In order to obtain more insight into the catalyst's ability to oxidize hydrocarbons, hydrocarbon speciation was performed during the degreening process.

HYDROCARBON SPECIATION

Engine Operating Condition for HC Speciation

HC samples are taken pre and post DOC at 0, 4, 8, and 16 hours of degreening. Engine operating mode M3 (2000 rpm / 200 kPa BMEP) is chosen as the engine operating condition. As discussed earlier, conversion efficiency of the catalyst in the partially active regime is very sensitive to temperature. It is therefore necessary to accurately repeat and control the feedgas properties

and temperature into the catalyst when the effect of degreening is investigated. Average feedgas temperature is controlled to be within $247.5 \pm 1.5^\circ\text{C}$ and a standard deviation of less than 0.5% over the 5 minute sampling time. The average EGR rate must be within $29.2 \pm 2\%$, and the standard deviation of hydrocarbons at the catalyst inlet must not exceed 5% over the test duration. All HC speciation data shown in the subsequent sections meet the conditions listed above.

Carbon number resolved hydrocarbon concentrations are shown in Figure 14. The four curves represent catalyst inlet and outlet HC species at 0 and 16 hours of degreening. Despite higher HC concentrations at the inlet for the 0 hour test case, lower HC concentrations are found at the exit of the catalyst. This indicates that the HC conversion efficiency of the catalyst deteriorates through the degreening process, which confirms earlier findings. It can be seen that hydrocarbons of all carbon numbers are oxidized through the catalyst except C_1 , which corresponds to methane (CH_4). Throughout this investigation, the methane concentration seems to be largely unaffected by the catalyst.

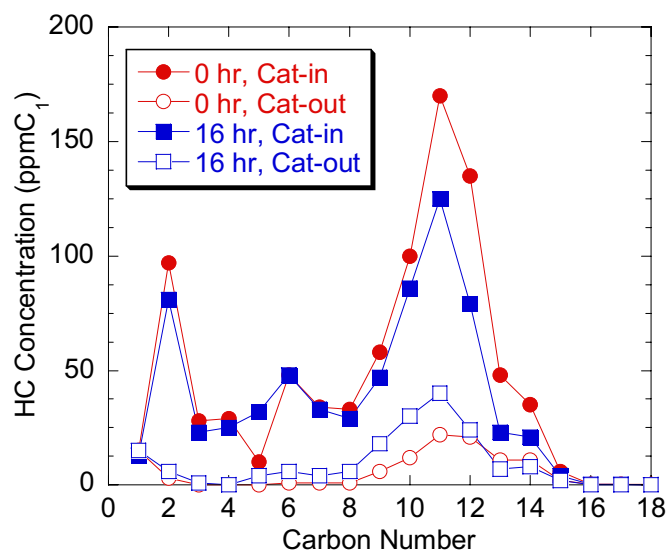


Figure 14: HC species resolved by carbon number pre and post DOC after 0 & 16 hours of degreening (green and degreened catalyst)

THC and CO conversion efficiencies at engine operating mode M3 are listed in Table 4. Note, in this section, THC and HC specific conversion efficiencies are determined via gas chromatography while CO is determined via a chemiluminescence detector (CLD). Conversion efficiency for CO is 100% in all cases. For HC, however, the catalyst shows monotonically lower conversion efficiencies as degreening progresses. Both trends are confirmed by Figure 8 and Figure 9.

Table 4: Conversion efficiency versus degreening time at engine operating mode M3

Time (hours)	CO	THC
0	100%	92%
4	100%	89%
8	100%	81%
16	100%	78%
Feedgas, 0 hr	944 ppm	904 ppmC ₁

Four groups of hydrocarbons commonly found in engine exhaust are acetylenes, olefins, aromatics and paraffins. Acetylenes or alkynes are hydrocarbons with at least one carbon – carbon triple bond; olefins, also known as alkenes, are hydrocarbons with at least one carbon – carbon double bond; aromatics or arenes are HCs with one or more sets of 6 planar carbon atoms; and paraffins or alkanes are fully saturated hydrocarbons.

Table 5: DOC conversion efficiency versus degreening time for Acetylenes + Olefins, Aromatics and Paraffins

Time (hours)	Acetylenes + Olefins	Aromatics	Paraffins
0	99 %	93 %	80 %
4	98 %	87 %	76 %
8	96 %	79 %	66 %
16	92 %	74 %	63 %
Feedgas, 0 hr	168 ppmC ₁	100 ppmC ₁	299 ppmC ₁

Conversion efficiency through the catalyst is found to be highest for acetylenes and olefins, followed by aromatics and paraffins as shown in Table 5. Catalyst activity deteriorates with degreening across all HC groups but

most severely for aromatics and paraffins. It can be seen that the rate of change in conversion efficiency is much higher over the initial eight hours of degreening compared to the later 8 hours of degreening. This suggests that the catalyst is mostly, but not completely, stable after 8 hours of degreening.

Individual major hydrocarbon species from the olefin and acetylene group are given in Table 6. Acetylene and heavy olefins such as 1-butene, 1-pentene and 1-hexene, are found to be among the most reactive hydrocarbons in the DOC. The catalytic converter is 100% active for those species regardless of degreening. Ethene and propene are readily oxidized by the green catalyst but show slightly lower conversion rates through the degreened catalyst.

Selected aromatic species and normal paraffins present in the exhaust are listed in Table 7 and Table 8. The catalyst shows virtually no activity for methane and actually produces methane for the 4, 8 and 16 hour tests as indicated by the negative conversion efficiencies. This may be due to cracking of heavier hydrocarbons by the catalyst where methane is formed as one of the products. The remaining aromatics and olefins show similar trends with catalyst degreening. Oxidation rates through the catalyst decrease rapidly over the initial 8 hours of degreening, and then decrease only a few percentage points through the additional 8 hours of degreening. Conversion of n-tetradecane shows essentially no change with catalyst degreening.

Table 6: DOC conversion efficiency versus degreening time for acetylenes and olefins

Time (hours)	Acetylene (C ₂ H ₂)	Ethene (C ₂ H ₄)	Propene (C ₃ H ₆)	1-butene (C ₄ H ₈)	1-pentene (C ₅ H ₁₀)	1-hexene (C ₆ H ₁₂)
0	100%	99%	100%	100%	100%	100%
4	100%	97%	100%	100%	100%	100%
8	100%	95%	96%	100%	100%	100%
16	100%	93%	94%	100%	100%	100%
Feedgas, 0 hr	22.4 ppmC ₁	74.8 ppmC ₁	25.9 ppmC ₁	14.9 ppmC ₁	4.1 ppmC ₁	4.0 ppmC ₁

Table 7: DOC conversion efficiency versus degreening time for major aromatic species

Time (hours)	Benzene (C ₆ H ₆)	Toluene (C ₇ H ₈)	n-propylbenzene (C ₉ H ₁₂)	1,4-dimethyl-2-ethylbenzene (C ₁₀ H ₁₄)	1,2-dimethyl-3-ethylbenzene (C ₁₀ H ₁₄)
0	99%	99%	97%	88%	89%
4	97%	96%	94%	85%	87%
8	91%	88%	92%	72%	79%
16	87%	85%	90%	66%	75%
Feedgas, 0 hr	18 ppmC ₁	10.3 ppmC ₁	10.4 ppmC ₁	9.3 ppmC ₁	6.3 ppmC ₁

Table 8: DOC conversion efficiency versus degreening time for n-paraffins

Time (hours)	Methane (CH ₄)	n-decane (C ₁₀ H ₂₂)	n-undecane (C ₁₁ H ₂₄)	n-dodecane (C ₁₂ H ₂₆)	n-tridecane (C ₁₃ H ₂₈)	n-tetradecane (C ₁₄ H ₃₀)
0	2%	86%	87%	84%	81%	66%
4	-10%	81%	83%	83%	77%	66%
8	-17%	66%	70%	72%	70%	69%
16	-13%	61%	67%	69%	67%	64%
Feedgas, 0 hr	14.8 ppmC ₁	33.6 ppmC ₁	80.2 ppmC ₁	86.3 ppmC ₁	19.2 ppmC ₁	16.1 ppmC ₁

SUMMARY AND CONCLUSION

A model catalyst was degreened at 650°C and 10% H₂O for 16 hours on a light duty diesel engine. Light-down curves were collected at 0, 1, 2, 3, 4, 6, 8, 10, 12, and 16 hours of degreening. The engine exhaust was analyzed for HC species via gas chromatography and catalyst activity was determined for various HC species at 0, 4, 8, and 16 hours of degreening.

As the catalyst is degreened, the catalyst light-down temperature increases. Light-down temperatures increase rapidly over the first 8 hours and then largely stabilize. T50 increases by 14°C for CO and by 11°C for THC through the degreening procedure. The shape of the light-down curves is not affected by the degreening process. Conversion efficiency of the fully lit catalyst is unaffected by degreening. It is believed that the catalyst performance changes due to coalescence of precious metal sites that have been exposed to high temperature. Thus only the initial part of catalytic activity is shifted towards higher temperatures, but the shape and overall conversion efficiency remains constant.

Hydrocarbons speciation suggests that the oxidation catalyst is not equally active for all hydrocarbon species. The oxidation catalyst is most active for acetylenes, then olefins and aromatics. Paraffins show the lowest activity through the oxidation catalyst. Little to no change in methane concentration is observed through the catalyst. Catalyst activity deteriorates with degreening across all HC groups but most severely for aromatics and normal paraffins.

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ABBREVIATIONS

AFR	Air Fuel Ratio
BMEP	Brake Mean Effective Pressure (kPa)
CO	Carbon Monoxide
CO ₂	Carbon Dioxide
CPSI	Cells Per Square Inch
°ATDC	Degree After Top Dead Center
°C	Degree Celsius
°CA	Degree Crank Angle
DOC	Diesel Oxidation Catalyst
EGR	Exhaust Gas Recirculation
FSN	Filter Smoke Number
H ₂ O	Water
HC	Hydrocarbon (ppmC1)
HCCI	Homogeneous Charge Compression Ignition
Hr	Hour
HSDI	High Speed Direct Injection
ICP	Injection Control Pressure
LHV	Lower Heating Value
Mx (e.g. M2)	Engine Operating Mode (e.g. M2)
NO	Nitric Monoxide
NO _x	Nitric Oxide
O ₂	Oxygen
PCI	Premixed Compression Ignition
PM	Particulate Matter
ppmC	Parts Per Million Carbon Atoms
ppmC1	Parts Per Million Hydrocarbon on a C1 basis
Txx (e.g. T50)	Temperature at which xx% of a particular species is converted (e.g. 50%)
THC	Total Hydrocarbons (ppmC1)
SV	Space Velocity (hr ⁻¹)
VGT	Variable Geometry Turbine