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LNT + in situ SCR catalyst system for diesel emissions control

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ABSTRACT

An overview is presented of laboratory and vehicle studies conducted at Ford Motor Company on the LNT + in situ SCR catalyst approach to diesel emissions control. Specifically, the paper focuses on results obtained with so-called "2nd-generation" systems developed by Ford's catalyst suppliers since 2007–2008. These systems are characterized by improvements in durability, performance and cost relative to their predecessors. Key features of the 2nd-generation LNT + in situ SCR technology include: (1) lower desulfation temperatures of the LNT, (2) lower LNT platinum group metal (PGM) content than required for LNT-only systems, (3) advanced SCR catalysts of the types used in commercial zeolite-based SCR applications, (4) synergetic coupling of the LNT and SCR catalyst performance to maintain high efficiency after aging, (5) a non-ammonia NOx reduction mechanism over the SCR catalyst in addition to the standard mechanism based on ammonia storage, and (6) improved hydrocarbon oxidation efficiency owing to the SCR catalyst. Taken together, these advances improve the prospect of meeting future emission regulations on light-duty diesel vehicles, but not without considerable challenge to both the aftertreatment system and control strategy for achieving simultaneous low NOx and non-methane hydrocarbon emissions while minimizing fuel consumption.

1. Introduction

Control of NOx emissions from diesel vehicles is challenging because of the difficulty in chemically reducing NOx (preferentially to N_2) under the excess oxygen conditions of diesel exhaust. Two main control technologies have emerged in recent years: lean NOx traps (LNT; also called NOx storage-reduction catalysts (NSR)) [1] and selective catalytic reduction (SCR) [2]. The LNT solves the problem of lean NOx reduction by storing NOx under extended lean conditions and introducing short fuel-rich engine operation to decompose and react the stored NOx by the usual three-way type reactions. SCR, on the other hand, preferentially reacts NOx with a reductant species such as NH_3 despite the large excess of oxygen in the exhaust. LNTs generate NH_3 during the fuel-rich purge events, and SCR catalysts – especially those based on zeolites – store significant quantities of NH_3 under reaction conditions [3]. Hence, combining the LNT with a downstream zeolite SCR catalyst offers a potential means of capturing NH_3 generated by the LNT and using it to convert NOx that slips through the LNT. The combined catalyst approach is variously referred to as an in situ, hybrid, booster, or passive LNT + SCR system, and has been the subject of several patents and publications [4–20]. For brevity, we refer to these systems simply as LNT + SCR in this paper.

The LNT + SCR concept dates back nearly a decade as captured in Ford patents with a priority filing date of October 22, 2002 [4]. Commercially, the concept has been demonstrated on the Mercedes E320 Bluetec vehicle (2007) [21] which utilized relatively high-loaded platinum group metal (PGM) LNTs in combination with an Fe-based zeolite SCR catalyst. Since then, several developments in both LNT and SCR catalyst technology have resulted in improved performance and durability. LNT developments have focused on decreasing the temperature required for trap desulfation, thereby improving trap durability. The main advance in SCR catalyst technology has been the development of Cu-based CHA zeolite SCR catalysts that show excellent low-temperature NOx conversion and selectivity while providing robustness against hydrocarbon and sulfur poisoning, and deactivation in rich exhaust environments [22–25]. These advances form the basis of the 2nd-generation LNT + SCR systems addressed in the present paper. Performance and durability of the 2nd-generation systems far exceed that of both LNTs alone and 1st-generation LNT + SCR systems, and thus potentially open the door to low-emission light-duty diesel vehicles without the need to carry an on-board reductant.

The LNT + SCR publications cited above [4–20] represent a mix of fundamental and applied studies. Most of the fundamental studies have involved model catalysts tested in simple laboratory gas mixtures (often without CO_2 and H_2O) and with hydrogen as the sole reducing species. These studies support the view that NH_3 is formed over the LNT during reducing conditions and some of the NH_3 slips through the LNT to the downstream SCR catalyst where it

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is stored. The benefit of the SCR catalyst is obtained by either oxidizing the stored NH_3 to N_2 or reacting it with NOx that slips through the LNT during lean storage conditions. In this study, we combine results of vehicle and laboratory experiments on fully commercial LNT and SCR catalysts to provide a broader picture of LNT + SCR system function than offered by laboratory studies alone. Although this approach precludes the detailed catalyst characterization afforded by model catalyst studies, it captures the more realistic conditions of the vehicle, especially the dynamic nature of vehicle operation and the broad mix of hydrocarbon species generated on the vehicle. The combined vehicle and laboratory experiments on the same catalyst formulations thus provide unique insight into the LNT + SCR catalyst technology that cannot be obtained from fundamental laboratory or model catalyst studies. Most importantly, the study demonstrates the presence of one or more non-ammonia NOx reduction pathways (in addition to the stored NH_3 mechanism) and also points out the importance of the SCR catalyst in controlling hydrocarbon emissions as well as NOx emissions. Furthermore, the vehicle work shows that both NOx and hydrocarbon emissions can be effectively controlled (and fuel purge penalty decreased) while limiting the amount of NH_3 presented to the SCR catalyst during LNT purge events. Thus, in Ford's exploratory work on this technology aimed at extremely low emissions, purging has focused on maximizing performance of the LNT with the dual aim of minimizing both NOx and HC breakthrough while limiting the fuel consumption required for purging. To these ends, our goal has been to limit rather than promote NH_3 production across the LNT during purge events, yet the SCR catalyst still contributes substantially to overall NOx and NMHC emissions control. Despite the benefits of the LNT + SCR approach, implementing such a technology that requires coordinated and synergetic performance of multiple storage components (i.e., oxygen and NOx storage components for the LNT, and NH_3 and HC storage capability for the SCR catalyst) is a daunting and unproven challenge at the very low emission levels required for future light-duty diesel vehicles in the U.S.

2. Materials and methods

2.1. Catalysts

All catalysts were provided by Ford's catalyst suppliers and consisted of fully formulated LNT or SCR formulations coated on standard cordierite honeycomb monolith bricks. Catalysts are identified only by their generic type (e.g., Cu-zeolite SCR or LNT) and total LNT PGM loadings to protect supplier confidentiality. The LNTs used in this work are primarily newer formulations characterized by desulfation temperatures in the range of 680–745 °C (compared to older formulations, denoted "reference" with desulfation temperatures of 750–800 °C [9]). All of these formulations contain Pt, Pd, and Rh, as well as ceria and barium oxide as principal components. Unless specified, the results from both the lab and vehicle testing were obtained with a low-loaded (85 g/ft^3) LNT formulation.

The SCR catalysts were commercial level monolithic zeolite-based SCR formulations provided either directly by the catalyst suppliers or obtained from a production vehicle. The 1st-generation SCR catalyst was an Fe-BEA zeolite formulation, while the 2nd-generation catalyst was the same Cu-CHA zeolite currently in production on Ford's Super Duty diesel trucks.

2.2. Laboratory experiments

The laboratory setup, instruments, gas compositions, and evaluation and aging procedures are the same as previously reported [9]. The catalysts were 25 mm diameter by 25 mm long cores cut from larger monoliths (cordierite with 400 cells per square inch and 6.5 mil wall thickness). The catalysts were tested in a quartz tube reactor contained in a tube furnace. Gases were blended synthetically (see Table 1 for composition) and fed to the reactor at flow rates corresponding to a volumetric space velocity of 30k h^{-1}, which is representative of driving speeds found in the FTP. Catalyst temperatures were measured at the inlet (6 mm in front of the sample), mid (middle of the 25 mm inch sample core), and the outlet (6 mm after the sample). Experiments with both LNT and SCR catalyst cores utilized 25 mm samples of each separated by a 6 mm gap. All catalyst temperatures reported herein refer to the inlet temperature.

Table 1
Gas compositions used for laboratory catalyst evaluation.

Gas	Lean	Rich
CO	0%	3%
H_2	0%	1%
C_3H_6	0%	5000 ppm C1
NOx	200 ppm	200 ppm
O_2	10%	1%
CO_2	5%	5%
H_2O	5%	5%
λ	1.96	0.92

The laboratory experiments utilized a V&F Airsense chemical ionization mass spectrometer, Midac heated FTIR (4 m cell), and a Horiba Mexa 9100 Hegr gas bench consisting of a chemiluminescent analyzer (NOx, NO), combined flame ionization (THC)/Magneto-pneumatic (O_2) analyzer, and non-dispersive infrared analyzer (CO and CO_2). Gases to the mass spectrometer and analyzer bench were passed through heated sample lines and diluted with N_2 in a ratio of about 1:3 to avoid water condensation. Heated, undiluted "raw" gas was fed to the FTIR. For the majority of testing, a standardized set of gas compositions was used (Table 1). Cycling between rich and lean exhaust conditions was accomplished via solenoid valves (with pressure balancing) at a typical duty cycle of 60 s lean and 5 s rich (60/5).

The laboratory gas compositions are not entirely representative of diesel exhaust. NOx was supplied exclusively as NO, and at a relatively high level (compared to a part-load engine operating mode), so as to better discriminate between catalyst formulations. A 3:1 ratio of CO:H_2 was used. We utilized propylene (C_3H_6) and ethylene (C_2H_4) as HC – typical of light cracked hydrocarbons in diesel exhaust but not representative of larger unburned fuel species.

2.3. Vehicle experiments

Two vehicles were tested with similar configurations of the aftertreatment system. Early work was carried out on a production 2005 model year Land Rover (LR3) diesel vehicle that was Euro 3 emission compliant. This vehicle was equipped with a twin turbocharged, common-rail direct-injected 2.7 L V6 diesel engine. The front drive shaft was disconnected to convert the original all-wheel-drive system to rear-wheel drive for emission testing on a single roll chassis dynamometer. The powertrain control system was originally modified for lean NOx trap aftertreatment system development, but was subsequently adapted for evaluation of the LNT + SCR system as depicted in Fig. 1. Catalyst details are shown in Table 2. Both the LNT and SCR catalyst were hydrothermally aged at 750 °C for 64 h before installation. The vehicle inertia weight was set to 3780 lbs on the chassis dynamometer to simulate the power-to-weight ratio of a light-duty diesel truck. The second vehicle equipped with the LNT + SCR system was a non-production 4.4 L V8 TDI light-duty pickup truck. The inertia weight was set to 5750 lbs on the chassis dynamometer for this vehicle. The catalysts in this truck are arranged in the same order as on the LR3 (DOC plus LNT and SCR followed by catalyzed DPF). The catalyst information on