

Impact of Carbonaceous Compounds Present in Real-World Diesel Exhaust on NO_x Conversion over Vanadia-SCR Catalyst

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ABSTRACT

Exposure of hydrocarbons (HCs) and particulate matter (PM) under certain real-world operating conditions leads to carbonaceous deposit formation on V-SCR catalysts and causes reversible degradation of its NO_x conversion. In addition, uncontrolled oxidation of such carbonaceous deposits can also cause the exotherm that can irreversibly degrade V-SCR catalyst performance. Therefore carbonaceous deposit mitigation strategies, based on their characterization, are needed to minimize their impact on performance. The nature and the amount of the deposits, formed upon exposure to real-world conditions, were primarily carried out by the controlled oxidation of the deposits to classify these carbonaceous deposits into three major classes of species: i) HCs, ii) coke, and iii) soot. The reversible NO_x conversion degradation can be largely correlated to coke, a major constituent of the deposit, and to soot which causes face-plugging that leads to decreased catalyst accessibility. Accelerated procedures are developed to simulate the deposit formation under real-world and to develop mitigation strategies to limit their impact on NO_x conversion and the risk of exotherm.

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1. INTRODUCTION

Vanadia based Selective Catalytic Reduction (V-SCR) catalysts are widely used to meet NO_x emissions over off-road diesel engines in North America and both on- and off-road diesel engines in Europe and rest of the markets [1]. Even though their counterpart, Cu-zeolite SCR catalysts, offer higher NO_x conversion at lower temperatures, sulfur poisoning of Cu-zeolite leads to a decrease in NO_x conversion and desulfation (deSO_x) temperatures in excess of 500°C which are needed to restore its performance [2]. Wide-spread application of V-SCR is found in off-road aftertreatment systems due to their resistance to poisoning by sulfur that eliminates the need for periodic thermal management (TM) for deSO_x [3]. Several aftertreatment systems with V-SCR catalysts operate below 300°C, for prolonged periods, in conditions that are conducive to carbonaceous deposits formation due to the presence of unburned HCs and PM in the exhaust gas. These deposits can lead to NO_x conversion degradation and pose a risk of uncontrolled regeneration and therefore requires periodic controlled burn-off. In this work, we illustrate the impact of real-world carbonaceous deposits on durability and performance of V-SCR catalysts and the operating requirements to mitigate such deposits.

2. EXPERIMENTAL SETUP

Commercial V-SCR catalyst, supported on 300 cpsi cordierite substrate, was used in this study. Cylindrical samples of 1" diameter and 3" length were cored from a larger SCR catalyst element that was exposed to a range of conditions downstream of engine. Separate

catalyst cores were used for each experimental series as high temperature exposure irreversibly remove carbonaceous deposits from the catalyst ([Table 1](#)).

2.1. Engine Experiment

An SCR brick, placed downstream of an engine which was operated with ULSD, was used for analysis. The system was operated for more than 5000 h under real-world conditions. Several 1" diameter and 3" long cores were used from this brick to quantify the amount of carbon and sulfur deposits and for the identification of different types of stored carbonaceous deposits. In order to accelerate the deposit formation, that simulates the real-world deposits, a separate degreened SCR system was exposed to 150 and 240°C with exhaust containing 280 ppm of HCs and 28 mg/m³ PM achieved by a retard timing combined with post fueling.

2.2. Bench Scale Reactor Experiment

Catalyst performance data were collected using a bench flow reactor system with transient measurement capabilities [4]. All the stainless-steel lines used in this setup were temperature-controlled to 190°C in order to minimize the adsorption of H₂O, NH₃, HCs, and sulfur-containing compounds. Water was injected into the heated synthetic exhaust gas through capillaries connected to Teledyne ISCO pumps. The gas feed mixture was fed to the quartz reactor tube placed in a three-zone furnace (Thermo Scientific). The reactor tubes contained multiple thin quartz pre-heater tubes for mixing the gases and preheating the feed mixture. The pre-heated gas mixture was passed to the catalytic monolith wrapped with a high temperature

performance wrap that does not release any carbon or sulfur containing compounds till 900°C temperature exposure. For every experiment, temperatures were measured at the gas inlet, catalyst inlet, and catalyst outlet locations using K-type thermocouples (Omega Electronics). The maximum variation between these three temperatures was within 5°C for the entire temperature range except for the cases with exotherm generated during oxidation of stored carbonaceous compounds. In this work, catalyst inlet temperature is reported as catalyst temperature.

Synthetic exhaust gas was supplied to the catalyst sample with the gas hourly space velocity (SV) of approximately 20 kh⁻¹. Low space velocity was deliberately chosen to minimally disturb the face-plugging and soot in the cannels by the flow and pressure across the sample. A base feed mixture containing 10% O₂, 7% H₂O in N₂ was used for temperature programmed oxidation with 5°C/min till 550°C to identify and quantify the carbonaceous species. The maximum temperature used in the experiments was kept below 550°C. In the reactor feed gas CO₂ was not used in order to facilitate accurate measurement of its concentration during oxidation process. Composition of reactants and products including base feed gases (H₂O), SCR related species (NO, NO₂, N₂O, and NH₃), carbon containing components (CO and CO₂), and sulfur containing compounds (SO₂ and H₂SO₄) were analyzed using Multigas 2030 FTIR (MKS) with the gas cell temperature maintained at 191°C.

Table (1). Catalysts and experimental conditions in this study

Catalysts	Washcoated V-SCR (300/5) cores after HCs and PM exposure under real-world conditions a. Core A: Temperature programmed oxidation up to 550°C b. Core B: Progressive performance recovery with and without (after physically removing) the face-plugging c. Core C: Performance recovery using progressively increasing temperature d. Core D: Performance recovery using NO ₂ and temperature Washcoated V-SCR (300/5) cores after HCs and PM exposure at Core E: 150°C for 2, 4, 8, 16, 32, 64 h Core F: 240°C for 2, 4, 8, 16, 32, 64, 96 h
Base Feed Gas	10% O ₂ , 7% H ₂ O, N ₂ , SV=20 kh ⁻¹
SCR Feed Gas	NO=200 ppm, NH ₃ =200 ppm at 220°C in baseline feed
TPO (Core A)	100 to 550°C with 5°C/min Ramp followed by 1 h at 550°C
C removal w/o NO ₂	Baseline feed, T = 225 – 550°C
C removal w/ NO ₂ (Core D)	NO _x = 800 ppm, NO ₂ /NO _x = 0.1, 0.5, NH ₃ /NO _x = 1, in baseline feed
Sequence of Experiment (Core E and F)	
1. As received performance	Heat the core in SCR feed up to 220°C and measure SCR performance at 220°C
2. After 400°C	Heat the core in base feed gases at 400°C for 30 mins and measure SCR performance at 220°C
3. After 550°C	Heat the core in base feed gases at 550°C for 30 mins and measure SCR performance at 220°C

3. RESULTS AND DISCUSSION

3.1. Performance of Degreened V-SCR

NO_x conversion over V-SCR, catalyst treated at 550°C for 4 h in base feed mixture, was measured at 40 and 20 kh⁻¹ and shown in Figure 1. The NO_x conversion shown Figure 1 will be used as a reference for describing the degradation and the extent of recovery upon various treatments of the carbonaceous deposited V-SCR catalysts.

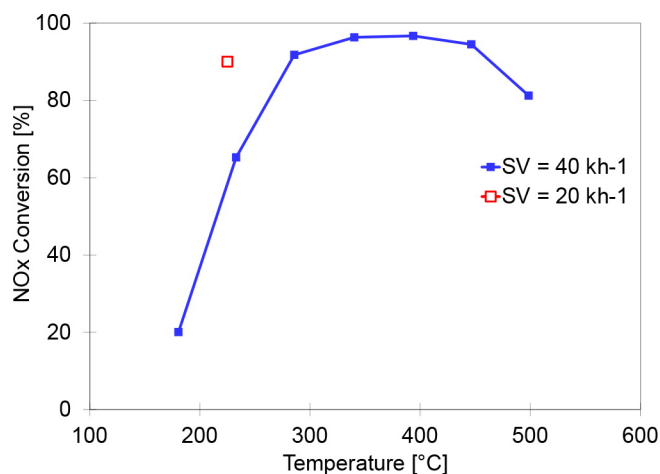


Figure (1). NO_x conversion over V-SCR in presence of 200 ppm NO and 200 ppm NH₃ at 40 and 20 kh⁻¹.

3.2. Assignment of Species in Carbonaceous Deposits

Under real-world engine conditions the V-SCR catalysts, especially without upstream DOC, get exposed to carbon containing compounds, HCs and PM, present in the engine exhaust. Upon such prolonged exposure at low temperatures, both HCs and PM get deposited on the catalyst. The nature and the amount of the carbonaceous species is expected to vary with temperature, time and SV. A temperature programmed oxidation (TPO) technique is used to identify the nature and quantify the amount of carbonaceous deposits.

The CO_x (CO + CO₂) evolving upon the TPO of carbonaceous compounds, that were deposited upon exposure of V-SCR catalyst (core A) to real-world conditions, are shown in Figure 2. Three distinguishable CO_x profiles were observed and can be assigned to different groups of carbonaceous species. The CO_x i) below 250°C is associated with the oxidation of adsorbed HCs, ii) in the range 250-450°C to coke and iii) above 450°C due to soot (partly present as face-plug, optical picture a in Figure 2) oxidation. The HCs and soot are the result of incomplete combustion of diesel fuel in the engine cylinder which gets transported to the downstream SCR catalyst and part of those eventually gets deposited on the SCR catalyst. The incoming HCs also get transformed into coke when exposed to a prolonged time and temperature on V-SCR catalysts systems [5]. The coke is characterized by higher carbonaceous content (low H/C ratio) as compared to parent HCs, which has H/C ratio around 1.8) and oxidized at relatively higher temperature of 250°C to 450°C.