

Impact and Prevention of Ultra-Low Contamination of Platinum Group Metals on SCR Catalysts Due to DOC Design

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ABSTRACT

Diesel aftertreatment systems configured with a diesel oxidation catalyst (DOC) upstream of an urea selective catalytic reduction (SCR) catalyst run the risk of precious metal contamination. During active diesel particulate filter (DPF) regeneration events, the DOC bed temperature can reach up to 850°C. Under these conditions, precious metal (especially Pt) can be volatilized and then deposited on a downstream SCR catalyst. In this paper, the impact of ultra-low contamination of platinum group metals (PGM) on the SCR catalyst was studied. A method based on precious metal volatilization of a Pt-rich DOC at 850°C and under lean gas conditions was employed to contaminate downstream FeSCR and CuSCR formulations. The contamination resulted in poor NO_x conversion (via NO_x remake) and excessive N₂O formation. The precious metal volatilization method was employed to screen various Pt/Pd based DOCs to avoid contamination of the downstream FeSCR. A correlation was developed that showed a reduction in SCR catalyst contamination as the Pt/Pd ratio decreased. The Pd-only DOC showed no impact to NO_x conversion and no increase in N₂O formation. The Pt-rich DOC showed the most impact. DOC formulations with higher Pd content demonstrated enhanced CO and HC light-off stability. The higher Pd content served to stabilize Pt in the DOC formulations. The higher Pd content resulted in less Pt vaporization. This, in turn, reduced the subsequent contamination risk on the downstream SCR. The vaporization of Pd from the DOC formulations was determined to be very low. However, an incipient wetness technique was used to purposely dope Pd on the FeSCR formulation and Pt on the CuSCR formulation. Contamination up to 0.004wt%

Pd was required to alter the NO_x performance by 5-10% on the FeSCR formulation. However, contamination up to 0.008wt% Pt was required to alter the NO_x conversion 5-10% on the CuSCR formulation. A second ethylene hydrogenation method was used on the contaminated SCR catalysts to determine presence of precious metals.

INTRODUCTION

Diesel Oxidation Catalysts (DOC), containing various levels of Pt and Pd, are considered to be a key aftertreatment component in current and upcoming 2010 emission certification requirements for controlling carbon monoxide (CO) and hydrocarbon (HC) emissions. In addition, active diesel particulate filter (DPF) regeneration events needed for soot combustion require that DOC formulations generate large exotherms up to 850°C from engine out hydrocarbons. Recent studies at Ford have shown that ultra-low levels of Pt can vaporize and eventually deposit onto a SCR catalyst situated downstream. In previous work, it has been shown that trace levels of Pt, as low as 0.002wt%, on the SCR catalyst can cause high NH₃ oxidation to NO_x and the excessive formation of N₂O [1].

In this work, two accelerated test methods to replicate Pt contamination over zeolite-based SCR formulations were developed. The first method involved the use of a flow reactor to study the temperature conditions necessary to vaporize Pt from a conventional DOC formulation and the subsequent deposit onto a downstream SCR catalyst. This first method served as a test protocol to screen the impact that various loadings and

combinations of candidate Pt/Pd DOC had on the downstream SCR catalyst. The second method involved the direct deposition of trace levels of Pt by an incipient wetness technique. Both methods were employed to determine the robustness of the latest state-of-the-art SCR catalysts to this type of contamination. The activity impact was accomplished by evaluating the contaminated SCR formulations under the Standard SCR Reaction. To validate the Pt contamination of the SCR catalysts using these two methods, the existence of precious metals was made using a newly developed ethylene hydrogenation reaction technique capable of detecting trace levels.

EXPERIMENTAL

SAMPLE DESCRIPTION

An iron zeolite based SCR formulation (FeSCR), a copper zeolite based SCR formulation (CuSCR) and four different DOC formulations were obtained from several major catalyst suppliers. From previous research, the CuSCR formulation chosen has been shown to have enhanced hydrothermal durability [2]. From full size DOC and SCR cordierite monoliths, cylindrical core samples measuring 2.54cm diameter x 2.54cm length were drilled out. The samples had 400 cells per square inch (CPSI) and 4.5 mil wall thickness.

The DOC total precious metal content varied from 70g/ft³ to 150g/ft³ while the Pt:Pd ratio varied from mostly Pt containing samples to Pd-only samples. The DOC formulations were used to study the indirect contamination of downstream FeSCR catalyst samples due to the volatility of Pt and Pd.

SCR SAMPLE DEGREENING PROCEDURE

Before all precious metal contamination attempts, the FeSCR and CuSCR catalysts samples were first degreened with the feed gas composition and sample conditions described in Table 1. With a total flow rate at 6.44liters/min, SCR samples measuring 2.54cm diameter x 2.54cm length were exposed to 14% O₂, 5%, CO₂, 5% H₂O, and balance N₂. Each sample was prepared with flowing gas and a degreening temperature that was held constant at 670°C for 2 hours. Freshly prepared catalyst formulations often contain residue precursors that may affect the initial performance. As a result, the SCR samples were degreened with this procedure to reduce any possible variability.

Feed Gas Composition	Degreening Conditions
O ₂ (%)	14.0
CO ₂ (%)	5.0
H ₂ O (%)	5.0
N ₂	balance
Flow Rate = 6.44 Liters/min	
SCR Size = 2.54cm diameter x 2.54cm length	
Degreening Temperature = 670°C	
Degreening Duration = 2 hours	

TABLE 1. Feed gas composition and sample conditions utilized to degreen all FeSCR and CuSCR catalysts samples.

EVALUATION OF SCR NO_x CONVERSION ACTIVITY

The evaluation of SCR catalysts was performed on an automated laboratory synthetic gas bench. The flow reactor contained two programmable furnaces. One furnace served as a pre-heater while the second furnace contained the SCR sample housed in a quartz reactor tube.

The NO_x conversion and the amount of N₂O formation over the SCR catalysts were studied using the Standard SCR Reaction (Eq. 1). The standard SCR gas composition is given in Table 2. The NH₃ to NO_x ratio was kept at the 1:1 stoichiometric ratio described in Equation 1.



For all evaluations, the total gas flow rate was held constant at 6.44 liters/min. This resulted in a space velocity of 30,000/hr for the 2.54cm diameter x 2.54cm length sample size used in this study. The samples were evaluated from 600°C to 150°C, from high temperature to low temperature. NO_x conversion was allowed to equilibrate before changing the catalyst temperature to the next level. The inlet gas temperature of the SCR was measured with a thin K-type thermocouple inserted through a channel from the back end of the sample. The analytical gas measurements were performed by a MKS FTIR instrument equipped with a heated sample line. The same instrument was used to measure the concentration of NO, NO₂, N₂O, NH₃, CO₂, and H₂O pre-SCR and then post-SCR.

Feed Gas Composition	STANDARD SCR REACTION
NO (ppm)	350
NO ₂ (ppm)	0
NH ₃ (ppm)	350
O ₂ (%)	14.0
CO ₂ (%)	5.0
H ₂ O (%)	5.0
N ₂	balance

TABLE 2. Feed gas composition for utilized to investigate the sample activity for the STANDARD SCR REACTION.

DOC DEGREENING, AGING, AND EVALUATION

The CO and HC light-off evaluation of all the DOC formulations were carried-out in a typical laboratory flow reactor system set for a space velocity equal to 50,000/hr.

The degreening process employed a 1 hour exposure to the base lean operating conditions with a controlled temperature ramp to 650°C. For the full 120,000 mile aging simulation, all the DOCs were rapidly aged by repeating a 2-mode procedure. The aging reactor, termed 'pulsator', combusted fuel to simulate the typical lean exhaust conditions containing HC, CO, O₂, CO₂, H₂O, and balance N₂. To represent a 120,000 mile equivalent exposure to sulfur and phosphorus, the fuel used in the pulsator was doped with 300ppm sulfur and 20mg/gallon of phosphorus. The 2-mode rapid aging procedure consisted of a low temperature poisoning mode ($T_{\text{outlet}} = 300^{\circ}\text{C}$) and a lean heating mode to simulate a DPF regeneration temperature ($T_{\text{outlet}} = 700^{\circ}\text{C}$). The lean heating mode represented a typical active DPF regeneration with injected HC. The injected HC served to generate a large exotherm over the DOC. Although the target outlet DOC temperature was 700°C, the DOC bed temperature ranged from 800°C to 850°C. To achieve an equivalent 120,000 mile catalyst aging, the duration in each mode and the total number of cycles was controlled to achieve the desired chemical poisoning and high temperature exposure.

LABORATORY DUPLICATION OF PRECIOUS METAL CONTAMINATION

A laboratory flow bench system was set up to simulate the configuration of the DOC and SCR catalysts in the diesel aftertreatment system, as shown in Figure 1. A fresh Pt/Pd-containing DOC sample was placed upstream of the SCR sample. The temperature of the DOC sample was controlled by the heating of a furnace,

while the temperature of the SCR sample was controlled by moving the position of the SCR sample.

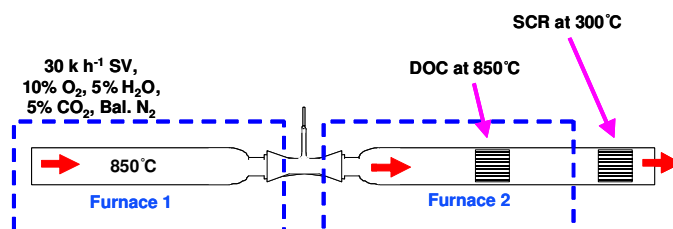


FIGURE 1. Laboratory reactor setup for replicating trace Pt poisoning of SCR catalyst from upstream DOC.

In Figure 1, the gas composition was 5% H₂O, 5% CO₂, 10% O₂ and balance N₂. The temperature of the SCR sample was always lower than that of the DOC sample. The SCR sample was held at 300°C while the DOC temperature was controlled at 850°C. In this report, all of the experiments lasted for 16 hours. The SCR catalyst samples were de-greened prior to this contamination treatment. The de-greening step was intended to stabilize the samples with the same pretreatment. After activity testing, the samples underwent an additional calcination step at 350°C to 500°C prior to measuring the activity for ethylene hydrogenation.

PREPARATION OF DOPED SCR CATALYSTS

Samples of fresh SCR catalysts (each with a size of 2.54cm diameter x 2.54cm length) were de-greened at 670°C for 2 hours. The capacity for adsorbing water was determined at 1.92ml H₂O/g-catalyst on average. To dope a certain metal on an SCR catalyst sample, a soluble compound of the metal was first dissolved in H₂O (purified via Reverse-Osmosis) and a solution of a pre-determined concentration was prepared. Then, the catalyst sample was doped into a crucible containing 1.00 ml solution and was again doped with the other end first into a crucible containing 0.95 ml solution. The final loading of the metal depended on the metal concentration since the volume of solution picked up was fairly constant at about 1.9 ml. After doping, the sample was usually dried at 150°C for 1 hour and then calcined at 400°C for 1 hour. The following metal compounds were used for doping: Pt(NH₃)₄(NO₃)₂, Pd(NH₃)₄(NO₃)₂, and Rh(NO₃)₃.

MEASUREMENT OF ETHYLENE HYDROGENATION ACTIVITY

A sample of 2.54cm length x 2.54cm diameter, after calcination, was placed into a quartz tube that was connected to the reaction gas mixture and a gas chromatograph (GC). Helium gas was passed through the sample inside the tubing at room temperature and then 100% hydrogen. The reaction mixture consisting of ethylene, hydrogen, and helium was flowed through the reactor bypass for 10 minutes to establish baseline signals. Once an analysis by GC was done on the reaction mixture, the flow of the reaction mixture was diverted into the sample at room temperature. The effluent was analyzed every 7 minutes using a GC. The signals of ethylene and ethane were monitored in each analysis. The % conversion of ethylene to ethane was calculated:

$$\frac{(\text{Ethane Signal})}{(\text{Relative Response} * \text{Ethylene Signal} + \text{Ethane Signal})} * 100$$

Figure 2 shows the diagram of the reactor system and the reaction gas mixture used. The column used for separation of ethylene and ethane on the GC was 2 meter length x 3.2 mm diameter packed with Unibeads 2S from Alltech. The column was operated at 40°C using 35 ml/min helium as carrier gas.

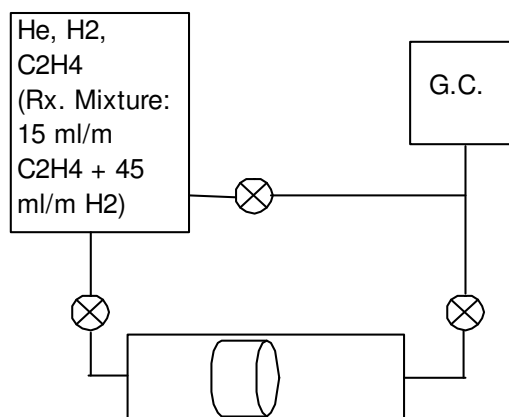


FIGURE 2. Reactor system diagram for ethylene hydrogenation with SCR catalyst inside the quartz tubing

RESULTS AND DISCUSSION

CU/ZEOLITE AND FE/ZEOLITE PLATINUM POISONING BY UPSTREAM DIESEL OXIDATION CATALYST (DOC)

The precious metal contamination over both CuSCR and FeSCR catalyst formulations were duplicated in a laboratory flow reactor system. As outlined in Figure 1, the DOC sample was exposed to 850°C for 16 hours

with a gas composition of 10% O₂, 5% CO₂, 5% H₂O, and balance N₂. For this comparison, the DOC composition had a total Platinum Group Metal (PGM) level of 70g/ft³ at a Pt:Pd:Rh ratio of 20:1:0. To improve the FeSCR performance during vehicle operation, one benefit of high levels of platinum content in the DOC is to improve the oxidization of NO to NO₂. The target SCR sample was placed further downstream and kept at 300°C for each poisoning. A new DOC sample was used for each poisoning attempt. The SCR samples investigated for Pt poisoning by an upstream DOC were termed "contaminated". The SCR samples termed "non-contaminated" were prepared by replacing the upstream DOC with an inactive/uncoated cordierite monolith.

The Pt vaporized from the upstream DOC at 850°C and then condensed on the cooler downstream SCR at 300°C. The SCR samples were carefully labeled to indicate the inlet gas flow direction after the Pt poisoning preparation. From laboratory experiments, it was found that the amount of Pt deposition on the SCR samples varied as a function of length. Higher Pt deposits were observed at the SCR inlet compared to the SCR outlet. For this reason, the subsequent NO_x evaluation experiments of the contaminated SCR samples were performed with the same directional orientation as during the poisoning.

FeSCR Formulation: Standard SCR Reaction

Figures 3A and 3B present the impact of Pt poisoning on the FeSCR NO_x conversion and on the N₂O formation, respectively. At high temperatures, the NO_x conversion of the contaminated FeSCR formulation was severely altered under these test conditions. However, no change in the performance was noted at temperatures under 250°C. The NO_x conversion declined sharply as the temperature was increased above 250°C. In fact, a negative NO_x conversion was observed at temperatures above 470°C. Due to trace levels of Pt contamination, the negative NO_x conversion arose from the undesired oxidation of NH₃ by O₂ to yield NO_x (i.e. NO_x remake). The trace level of Pt deposited on the inlet of the contaminated FeSCR was active enough to compete with the active Fe base metal for NH₃ utilization. Unfortunately, Pt oxidation was mostly active for NO_x remake. As a result, the combination of the feedgas NO_x plus the NO_x remake resulted in a negative overall NO_x conversion.

In addition to NO_x remake, the oxidation of NH₃ by O₂ over Pt contaminated FeSCR catalysts generated significant levels of N₂O (Figure 3B). The formation of N₂O over FeSCR formulations has been reported previously to be much lower than CuSCR formulations [3]. As a result, the much higher levels of N₂O formation by the contaminated FeSCR sample indicated evidence of Pt poisoning. Up to 25ppm N₂O was observed in the 250°C – 300°C temperature range.