

Mitigation of Platinum Poisoning of Cu-Zeolite SCR Catalysts

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ABSTRACT

A typical diesel exhaust emission control system for meeting the US EPA 2010 regulations includes one or more platinum-group metal (PGM)-containing catalysts, located upstream of an SCR unit. However, as was previously reported in literature, under certain operating conditions PGM elements can get transferred onto the downstream SCR catalyst, resulting in the loss of its NO_x conversion efficiency. In the same studies, the effect of Pt poisoning was found to be mitigated by catalyst treatment at 850°C, presumably due to Pt volatilization and migration.

In the present study, we have explored the process of Pt poisoning mitigation, and identified that the recovery can take place at lower temperatures, reducing the risk of hydrothermal damage to the catalyst. We have also proven that the performance recovery, observed upon treatment at 700°C, was induced by Pt sintering, rather than by volatilization, thus minimizing the risk of secondary poisoning via Pt redistribution across the SCR system. These findings pave the way for the practical rejuvenation of zeolite-based SCR catalysts, deactivated through Pt contamination.

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INTRODUCTION

Zeolite-based SCR catalysts have been broadly commercialized in the United States for controlling NO_x emissions from diesel engines, in response to the stringent US EPA 2010 emission regulations. In a typical heavy-duty SCR architecture, a zeolite-based SCR catalyst is located downstream of a diesel oxidation catalyst (DOC) and a diesel particulate filter (DPF). Both the DOC and the DPF contain platinum group metals (PGM), such as platinum (Pt) and/or palladium (Pd), serving to oxidize hydrocarbons, carbon monoxide, and NO.

A comprehensive study by Ford showed that PGM, especially Pt, can get volatilized from DOC and transferred onto the downstream SCR catalyst under high temperature conditions [1,2]. The Ford group demonstrated that even very small amounts of Pt can lead to non-selective NH₃ oxidation by O₂ instead of its reaction with NO_x, resulting in the loss of the overall NO_x conversion efficiency. In the systems with a DPF located upstream of the SCR, the conditions favorable for PGM transfer are most likely to occur during uncontrolled DPF regeneration. While quite infrequent, such events can produce temperatures in excess of 1000°C, more than sufficient for Pt volatilization under the oxidizing atmosphere [3, 4, 5].

The Ford group has further demonstrated that the symptoms of Pt contamination can be reversed by exposing a

poisoned zeolite-based SCR catalyst to 850°C [2]. This recovery was attributed by the authors to Pt volatilization and migration. Unfortunately, the elevated temperatures involved in such a treatment, as well as the possibility of Pt redistribution across the catalyst, entail an elevated risk of secondary damage to the SCR catalyst.

In the present study, we have focused on understanding the nature of the recovery process, by examining three Pt-poisoned SCR catalysts from different field-returned systems, in order to consider the practical possibility of their rejuvenation.

EXPERIMENTAL DETAILS

Samples

Three SCR catalysts belonging to the small-pore Cu-zeolited type, were collected from field-returned AT systems, which have experienced DPF melting events of different levels of severity. These were labeled as SCR A, SCR B and SCR C. The first two catalysts retained their physical integrity. However, the SCR C catalyst has cracked radially ("ring-off" crack), likely due to its exposure to a severe high temperature event in the upstream DPF.

Micro-cores (0.25 inch OD and 1 inch long) were sampled from the inlet face of these SCR catalysts and listed in Table 2. Some of these were submitted for Pt elemental analysis, either in their as-received state, or after heat

treatment at 700°C. In addition, a 6" long micro core (0.25 inch OD) was sampled from the SCR B brick and cut into six 1-inch long pieces, to evaluate axial distribution of Pt across the brick. Pt elemental analysis was performed by Galbraith laboratory (Knoxville, TN) using high-sensitivity ICP-MS.

A micro-core cut from an uncontaminated SCR brick of the same formulation, and degreased at 700°C for 4 hours, was employed as a reference sample.

Experimental Setup and Test Protocol

Key SCR functions of these SCR samples, such NO_x conversion and NH₃ oxidation activity by O₂, were evaluated in a laboratory bench-top reactor. More details about the experimental setup can be found in our earlier paper [6]. Briefly, a sample was loaded into a quartz reactor tube. The gas temperatures were measured before and after the sample by two type-K thermocouples, shielded by sealed quartz tubes. An MKS MultiGas 2030 FTIR was used to monitor the gas composition. All gas sampling lines were maintained at about 150°C to prevent condensation or adsorption of the reactants or products. The key reaction parameters are listed in [Table 1](#).

Table 1. Synthetic exhaust gas composition and flow rate.

Inlet gas species	Concentration
O ₂ , %	10
H ₂ O, %	7
CO ₂ , %	8
NO (when used), ppm	200
NH ₃ (when used), ppm	200
Ar	Balanced
total flow rate = 550 sccm	
Space velocity $\approx 40,000 \text{ hr}^{-1}$	

Catalytic performance of the samples was evaluated using the previously developed 4-step SCR protocol [7]. During such evaluation, the active reagents, 200 ppm NO and 200 ppm NH₃, were switched on and off, as shown in [Figure 1](#), yielding the following information about catalyst functions:

Step 1. NO $\leftrightarrow$ NO₂ oxidation/reduction

Step 2. SCR NO_x conversion, parasitic NH₃ oxidation, selectivity to N₂O

Step 3. NH₃ oxidation by O₂ alone, including conversion and selectivity to NO_x and N₂O

Step 4. NH₃ clean up by NO_x

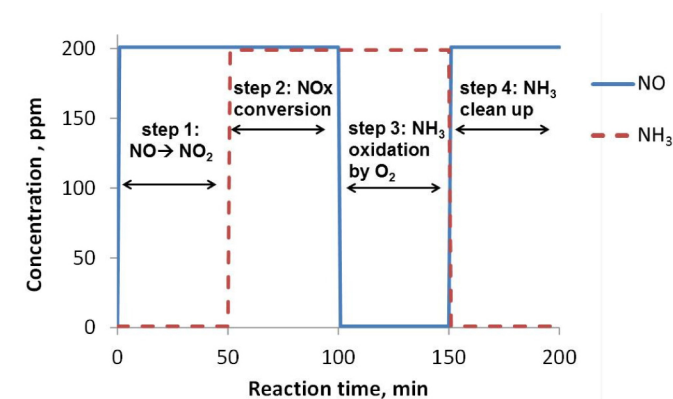


Figure 1. Schematic representation of the 4-step experimental protocol.

The experiments covered the temperature range between 600°C and 250°C, with 50°C intervals. The descending direction of temperature points was chosen so as to ensure the removal of any possible carbonaceous deposit material prior to the performance evaluation.

In some cases, micro-core samples have been also subjected to hydrothermal pretreatment at 600°C and/or 700°C prior to their catalytic testing. During the pretreatments, the inlet gas composition, as listed in [Table 1](#), did not include NO or NH₃. For example, the performance of SCR B#3 sample was evaluated after being progressively exposed to 600°C for 2 hours, 600°C for 6 hours and 700°C for 2 hours, respectively.

Table 2. Summary of micro core samples employed to probe the impact of hydrothermal treatment on key SCR functions.

Brick	Sample	Pretreatment condition	Pt analysis
SCR A	#1	as received	✓
	#2	600°C 2 hours	
	#3	700°C 2 hours	✓
SCR B	#1	as received	✓
	#2	600°C 2 hours	
	#3	600°C 6 hours + 700°C 2 hours	✓
SCR C	#1	as received	✓
	#2	600°C 2 hours	
	#3	700°C 41 hours	✓
Reference	#1	as received	✓
	#2	700°C 4 hours	