

Detection, Origin and Effect of Ultra-Low Platinum Contamination on Diesel-SCR Catalysts

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ABSTRACT

This paper discusses the poisoning of a selective catalytic reduction (SCR) catalyst by trace levels of platinum originating from an upstream diesel oxidation catalyst (DOC). A diesel aftertreatment system consisting of a DOC, urea based SCR Catalyst and a DPF was aged and evaluated on a 6.4 liter diesel engine dynamometer. The SCR catalyst system consisted of an Fe-zeolite catalyst followed by a Cu-zeolite catalyst. After approximately 400 hours of engine operation at varied exhaust flow rates and temperatures, deactivation of the SCR catalyst was observed. A subsequent detailed investigation revealed that the Cu catalyst was not deactivated and the front half of the Fe-based catalyst showed severe deactivation. The deactivated portion of the catalyst showed high activity of NH_3 conversion to NO_x and N_2O formation. The cause of the deactivation was identified to be the presence of trace Pt contamination. The contamination level was less than 0.002wt% that could not easily be detected by a conventional X-ray fluorescence (XRF) method. The detection of trace Pt was made at first using a newly developed ethylene hydrogenation reaction method. The reaction system was built in-house for measuring the conversion of ethylene to ethane at room temperature over a catalyst monolith core. The system allowed the detection of Pt metal below 0.001wt%. The presence of Fe, Cu, or Ni did not interfere with the ethylene hydrogenation technique. The sublimation of Pt from an upstream DOC onto Fe-based catalysts was demonstrated experimentally in the laboratory using the new technique. In the aftertreatment system studied, the Fe catalyst acted as a buffer to trap Pt sublimed from the upstream DOC shielding the Cu catalyst from Pt contamination. The effect of DOC aging conditions on Pt sublimation and subsequent Pt contamination on the downstream SCR catalyst was also investigated.

INTRODUCTION

Urea-based selective catalytic reduction (SCR) is expected to be employed to help vehicles with diesel engines to meet Tier 2 Bin 5 NO_x emissions requirements. In such systems, an aqueous urea

solution is injected into the exhaust gas, where it vaporizes and forms ammonia (NH_3). The NH_3 then selectively reduces NO and NO_2 on the SCR catalyst. Such systems have been shown to be robust and to achieve very high NO_x conversion efficiencies (see, e.g., [1]).

These SCR systems are generally used in conjunction with diesel oxidation catalyst (DOC) located in front of the SCR in the exhaust layout, and a diesel particulate filter (DPF) is also used. The DOC generally contains precious metal such as platinum (Pt) and/or palladium (Pd). We have discovered that the potential exists for the SCR catalyst to be poisoned by trace levels of Pt from an upstream DOC. As this paper will show, Pt is very good at oxidizing NH_3 even when the Pt concentrations on a catalyst are extremely low. This is a potential issue for SCR systems because if the front portion of the SCR catalyst is poisoned with Pt, the NH_3 is consumed and the remainder of the SCR catalyst volume cannot function since there is no NH_3 present.

An SCR system was evaluated on an engine dynamometer with a 6.4 liter diesel engine. The system consisted of a DOC containing Pt, an SCR system consisting of an Fe-zeolite brick in front of a Cu-zeolite brick, and followed by a DPF.

After 400 hours aging and evaluation, the SCR performance reaction deteriorated severely. The SCR catalyst bricks were removed from the aftertreatment system for further studies in laboratory. Evaluation of sections of the SCR catalyst revealed that only the front portion of the leading SCR catalyst suffered deactivation. The deactivated region of the catalyst did not suffer significant loss of surface area as shown by BET testing, thus excluding the collapse of zeolite caused by high temperature hydrothermal conditions [1].

In laboratory evaluation, the deactivated regions of the catalyst showed significant N_2O formation and high activity of NH_3 oxidation to NO_x that led to significant drop in NO_x conversion. The behavior of the deactivated region was inconsistent with damage due to hydrothermal aging. XRF analysis showed no significant difference in elemental compositions between the deactivated and the functional regions of the catalyst.

The aging with typical poisons, e.g. sulfur, could not duplicate the observation of high N_2O formation and significant drop in NO_x conversion (i.e., NO_x increase due to non-selective NH_3 oxidation) [2]. This unique reactivity for NH_3 oxidation was observed on some Pt-containing catalysts (see, e.g., [3]). Thus it was suspected that the loss of activity was due to Pt poisoning on the front portion of the SCR catalyst. However, no Pt was detected for both deactivated and non-deactivated parts of the SCR catalyst by a conventional XRF method with 0.002 wt% detection limit.

This paper discusses the development and application of a method to the detection of ultra-low level of Pt contamination on a deactivated SCR catalyst. The activity due to Pt contamination was confirmed by comparison to the activities over fresh catalysts doped with ultra-low levels of Pt. This paper also reports the successful duplication of Pt contamination on an SCR catalyst in the laboratory and experimental determination of the cause of Pt contamination.

EXPERIMENTAL

BASIS OF NOVEL PLATINUM DETECTION METHOD

In order to determine the presence of Pt at or below 0.002wt%, a technique was developed within Ford based on hydrogenation of ethylene (C_2H_4) to ethane (C_2H_6). On precious metal surfaces, the rate of the hydrogenation is very fast [4]. The rate for Pt is at least 1 to 10 C_2H_4 molecule/Pt atom per second, also referred as turnover frequency of 1 to 10 s^{-1} . For a typical reaction mixture at 20 ml/min consisting of 2:1 H_2 : C_2H_4 , the turnover frequency corresponds to 5.2 to 52% conversion of C_2H_4 over a 5g catalyst sample with 0.001wt% Pt and 100% dispersion of Pt. If the Pt dispersion is 1%, the conversion would be 0.052% to 0.52%. The conversion value is still higher than 0.02% for the sensitivity of the employed gas chromatograph with TCD detectors. Therefore, the detection of ultra low level of Pt metal on a catalyst can be achieved by monitoring the activity of ethylene hydrogenation. The other element of precious metal, Pd or Rh, actually has a higher activity than Pt for the hydrogenation of ethylene to ethane. In the current system investigated, Pt is the precious metal used.

The activity of ethylene over a reduced metal surface is usually hundreds or thousands times of that over the same metal after being oxidized. Except for precious metals, the other metal after being oxidized cannot be reduced by H_2 at room temperature. If an SCR catalyst is oxidized first, the subsequently conducted ethylene hydrogenation at room temperature would result in very low conversion of C_2H_4 in the absence of Pt or other precious metals. Based on these principles, a method employing ethylene hydrogenation was developed to detect the presence of Pt below 0.002wt% on a SCR catalyst.

AGING OF DIESEL AFTERTREATMENT SYSTEM

The diesel aftertreatment system consisted of a Pt-containing DOC, a 2-brick SCR system (Fe-zeolite in front of Cu-zeolite) and a DPF, as mentioned in the introduction. The aftertreatment system was installed in an engine dynamometer running a 6.4 liter diesel engine and operated for approximately 400 hours. Ultra low sulfur diesel fuel (8 PPM-wt sulfur) was used. The SCR catalysts were each 20 cm in diameter x 15 cm in length, so that the two SCR bricks provided catalyst volume equivalent to 154% of the engine swept volume (ESV).

The aftertreatment on the dynamometer went through several active DPF regenerations, European Stationary Cycle (ESC) 13-Mode tests and U.S. Federal Test Procedure (FTP) transient tests, so that the exhaust temperatures into the SCR ranged from 200°C to 670°C repeatedly. The DOC bed temperature reached as high as 800°C during active DPF regeneration events.

SAMPLING OF DEACTIVATED SCR CATALYST

When the NO_x conversion activity of the SCR catalyst on the engine dyno was observed to deteriorate, the catalysts were removed and cored for analysis. BET surface area measurements were taken from several sections of the catalyst. Also, 2.54 cm diameter cores were taken from the radial center of both catalysts, as well as at varied radial locations. Each core was cut into several 2.54 cm long sections, so that evaluations could determine the state of deterioration of the catalyst as a function of both radial and axial location within each brick.

EVALUATION OF NH_3 -SCR ACTIVITY

Sample cores were tested with simulated exhaust gas with two different compositions. The first composition consisted of 4.5% H_2O , 5% CO_2 , 14% O_2 , 350 PPM NH_3 and 350 PPM NO , all in balance N_2 to test for NO_x conversion activity. The second composition consisted of 4.5% H_2O , 5% CO_2 , 14% O_2 and 350 PPM NH_3 , all in balance N_2 , to test for NH_3 oxidation in the absence of NO_x . An FTIR was used to measure the gases downstream of the SCR core samples. Evaluations were done at 6.44 standard liters per minute (slm), yielding a space velocity of 30,000 h^{-1} . The samples were evaluated from 600°C to 150°C, from high temperature to low temperature to ensure that any organic material would be burned off of the catalyst at the 600°C evaluation point prior to low temperature testing.

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. Helium gas was passed through the sample inside the tubing at room temperature and then 100% hydrogen. After 10 minutes the reaction mixture

was flowed through bypass of the sample. Once an analysis by G.C. was done, the flow of reaction mixture was diverted into the sample at room temperature. The effluent was analyzed every 7 minutes using the G.C. 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 1 shows the diagram of the reactor system and the reaction gas mixture used. The column used for separation of ethylene and ethane on the G.C. was 2 meter length x 3.2mm diameter packed with Unibeads 2S from Alltech. The column was operated at 40°C using 35 ml/min helium as carrier gas.

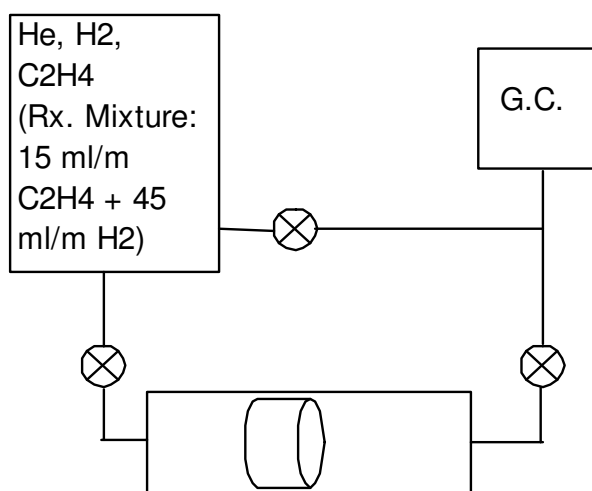


FIGURE 1. Reactor system diagram for ethylene hydrogenation with a catalyst sample inside the quartz tubing

PREPARATION OF DOPED SCR CATALYSTS

Samples of the fresh Fe-SCR catalyst (size of 2.54 cm long x 2.54 cm in diameter) were de-greened at 670°C for 2 hours. The capacity of the sample for adsorbing water was determined at 1.92ml H₂O/g-catalyst. To dope a certain metal on an SCR catalyst sample, a soluble compound of the metal was first dissolved and a measured amount of the solution was adsorbed into the catalyst sample. The final loading of the metal depended on the metal concentration and the volume of the solution used. The maximum volume of solution used in each doping step was no more than that of water-absorbing capacity determined previously. After doping, the sample was usually dried at 55°C overnight and then de-greened at 670°C for 1 hour. The following metal compounds were used for doping: Pt(NH₃)₄(NO₃)₂, Ni(NO₃)₂, Fe(NO₃)₃, and Mn(NO₃)₂.

LABORATORY DUPLICATION OF PLATINUM 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 2. A Pt-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.

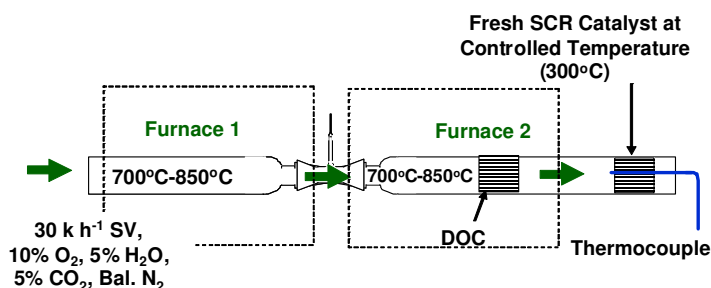


FIGURE 2. Laboratory reactor setup for replicating trace Pt poisoning of SCR catalyst from upstream DOC.

In Figure 2, the gas composition was 4.5% H₂O, 5% CO₂, 14% O₂ and balance N₂. The temperature of the SCR sample was always lower than that of the DOC sample. A typical setup resulted in 300°C at the inlet of the SCR sample with the DOC temperature at 850°C. In this report, most of the experiments lasted for 16 hours. The resulting sample was then de-greened prior to evaluation of NH₃-SCR activity. The de-greening step was intended to have all the samples experiencing the same pretreatment. The sample underwent an additional calcination step at 350°C to 500°C prior to measuring the activity for ethylene hydrogenation.

RESULTS AND DISCUSSION

EVALUATION OF DYNAMOMETER-AGED SCR CATALYSTS

The NO_x conversion performance of the center core of the Fe-zeolite SCR catalyst (front brick) is shown in Figure 3. As noted, evaluations were also performed at various radial locations. The results showed the consistent trend in catalyst performance with that in Figure 3. The first three inches of the front Fe-SCR catalyst suffered severe deterioration in NH₃-SCR performance. The last three inches of the Fe-SCR catalyst showed a slight decrease in the SCR performance. The formation of N₂O increased as the NH₃-SCR performance decreased.