

Spatially-Resolved Thermal Degradation Induced Temperature Pattern Changes along a Commercial Lean NO_X Trap Catalyst

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ABSTRACT

The low-temperature performance characteristics of a commercial lean NO_X trap catalyst were evaluated using infra-red thermography (IRT) before and after a high-temperature aging step. Reaction tests included propylene oxidation, oxygen storage capacity measurements, and simulated cycling conditions for NO_X reduction, using H₂ as the reductant during the regeneration step of the cycle. Testing with and without NO in the lean phase showed thermal differences between the reductant used in reducing the stored oxygen and that for nitrate decomposition and reduction. IRT clearly demonstrated where NO_X trapping and regeneration were occurring spatially as a function of regeneration conditions, with variables including hydrogen content of the regeneration phase and lean- and rich-phase cycle times. As expected, lower reductant concentration led to incomplete regeneration, limiting nitrate decomposition to the upstream portions of the sample and therefore isolating NO_X trapping in the front, or upstream, portion of the catalyst. More reductant, via longer regeneration time or higher reductant concentration, resulted in more catalyst being used for trapping, with the length of catalyst involved in trapping a function of the amount of reductant delivered during the regeneration phase. Tests at 200°C and 300°C also demonstrated differences in the amount of catalyst used for

trapping NO_X, related to the efficiency of reductant use during the rich phase, with 200°C showing poorer performance. Tests with the thermally aged catalyst demonstrated the same trends, but with measured differences in the efficiency of H₂ use during regeneration. The temperature measurement results were consistent with all concentration trends, indicating such measures can predict subsequent catalyst activity and be used as a measure of the extent of degradation.

INTRODUCTION

Concern over the impact of vehicle emissions on environmental and human health has led many governments to implement strict emissions regulations [1]. Furthermore, there are also proposed limits on CO₂ emissions, which can be significantly reduced by using lean-burn engines, such as diesel engines. However, the higher concentration of oxygen in lean-burn engine exhaust makes reduction of NO_X to N₂ inherently difficult [2,3].

Three-way catalysts (TWC) have successfully been used for many years to reduce NO_X emissions from gasoline engines, but the oxygen-rich exhaust of diesel engines prevents the use of a TWC for diesel exhaust treatment [2,4,5,6]. Two technologies for diesel engine applications are selective

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catalytic reduction (SCR) and NO_x storage and reduction (NSR) catalysts. SCR systems add a reductant to the exhaust mix, typically ammonia, which selectively reacts with NO_x [7]. NSR catalysts contain alkali or alkaline-earth metals, for example Ba, for NO_x storage via nitrate formation, and precious metals, such as Pt, Pd, and Rh, for NO oxidation and NO_x reduction [1,7,8,9]. Some formulations also contain oxygen storage components such as Ce, which can provide NO_x adsorption sites [7,10,11] as well as thermal stability for the precious metals. During the lean phase, or normal engine operation, NO is oxidized to NO₂, which is then stored in metal nitrate or nitrite form until the adsorption components are saturated or unacceptable NO_x slip is observed [3,4,9,7,12,13,14]. At this stage, the exhaust gas is forced rich in reductant relative to oxygen, inducing surface nitrate decomposition, NO_x release, and reduction to N₂. The rich phase contains reductants such as H₂, CO, and hydrocarbons, with little or no O₂ [7].

NSR catalysts also trap sulphur species, inherent to diesel fuel, and these adsorbed sulphates are more stable than the nitrates. This leads to a decrease in active sites for nitrate formation during NO_x trapping as well as decreased precious metal reduction activity, both caused by sulphur exposure [1,2,4,5,12,14,15,16]. The sulphur species can be removed from the catalyst by occasionally exposing the catalyst to a reducing, very high temperature environment. However this in turn causes thermal deactivation of the catalyst [4,5,7,14,15]. The primary deactivation mechanisms at work during these high temperature exposures are precious metal sintering and agglomeration, the loss of NO_x storage site surface area, and the loss of oxygen storage capacity [3,5,6,8,9,10,11,16].

In this study, infrared thermography (IRT) was used to create temperature maps of the catalyst surface during reaction. IRT in catalysis was first used to study temperature patterns during H₂ oxidation over Pt/Al₂O₃ by Schmitz et al. [17]. This study showed that variation of active site geometry at the microscopic level led to temperature variation at the macroscopic level. Other catalysis researchers have found IRT useful as well [18,19,20,21,22,23,24,25,26]. Luss and colleagues have used the technique to study the temperature behavior of a catalyst during various oxidation reactions, finding non-uniformity in catalyst and oscillating reaction rates as factors in the formation of non-uniform hot spots [18,19,20,21,22]. Qin and Wolf compared the effect of feed fluctuations on model Pt/Al₂O₃ and Rh/SiO₂ samples and a commercial catalytic converter sample. They noted that while the model samples resulted in temperature oscillations with feed perturbations, the monolith did not. They also observed that oscillation behavior changed with precious metal loading, with higher activity attained at locations with higher metal loading [24]. As the temperature of the solid is

monitored instead of the gas phase temperature, IRT can be used to observe transversal reactor hot spots and temperature fronts due to reactions. Hot spots can cause undesired effects such as non-uniform reactions and catalyst deactivation [20,26]. In this study, a commercial NSR catalyst sample was evaluated before and after thermal aging by examining oxygen storage capacity, NO_x trapping and reduction, and propylene oxidation over the catalyst using IRT and outlet gas concentration measurements.

EXPERIMENTAL METHODS

REACTOR SETUP

A custom designed reactor for IRT was used in this study. A detailed description of the reactor can be found in previous work [26]. The reactor included a sapphire window that was transparent to the IR radiation for the IR camera. Thermocouples were located at the reactor inlet and the front and back of the catalyst for calibrating/validating the IR camera data, but were not routinely used to observe temperature changes in the catalyst. The reactor feed of simulated exhaust gas, comprised of component gases supplied by Praxair and controlled by Bronkhorst mass flow controllers, was combined upstream of the reactor and passed through a preheater before entering the reactor. Water was passed through an evaporator and introduced just before the preheater. The outlet gases were analyzed by an MKS 2030 FT-IR at an acquisition rate of approximately 2 Hz. Inlet and outlet lines were insulated and heat-traced to prevent water condensation.

The NSR catalyst sample, provided by Johnson Matthey, was a 3 in. × 0.125 in. rectangle and 3 in. in length with a wall thickness of approximately 0.45 mm and a cell density of 300 cells per square in. The gas flow rate was 10 L/min, corresponding to a space velocity, based on monolith volume, of 32,500 hr⁻¹. A FLIR Merlin Mid InSb MWIR (Mid-Wave InfraRed) camera was mounted vertically above the reactor and imaged the flat surface of the catalyst through the sapphire window. A 50 mm lens, also supplied by FLIR, was used in these studies. The camera used has a focal plane array consisting of a 320 × 256 array of detectors, i.e. 320 × 256 temperature points are measured, providing a measurement resolution of 0.3 mm. The energy data collected by the camera was converted to temperature using ThermoCAM Researcher software made by FLIR Systems Inc. The data are stored as a sequence of frames that make up a movie file, each frame an IR image comprised of a matrix of temperature values 320 points in length and 256 points in width. The catalyst itself was 246 points in length and width. Images were recorded at a rate of 10 frames per second. The data were extracted from the movie file along a line 1.5 in. from each side of the sample, similar to what would approximate the radial center position referred to for cylindrical samples, at seven equally-spaced points along the length. The same

experiment sets were run on fresh and thermally aged catalyst samples. Aging was performed in a laboratory oven at 750°C for 5 hours in lab air atmosphere.

OXYGEN STORAGE CAPACITY EXPERIMENTS

Oxygen storage capacity (OSC) was assessed to identify the amount of reductant consumed by surface oxygen. OSC was tested at 200°C and 300°C using CO oxidation by cycling between a CO-containing stream and an oxygen-containing stream, and the difference in total effluent CO between the test with the catalyst and reactor bypass was taken to represent total stored oxygen. The lean-to-rich cycle time was 100/80 seconds, with the lean gas composed of 10% O₂ and 5% CO₂ and the rich gas 5% CO₂ and 1% CO, both with balance N₂.

NO_x CYCLING EXPERIMENTS

Different gas mixtures are required for the lean and rich phases of the NSR cycle; these were created in separate manifolds and controlled by a pneumatic solenoid valve. Lean-to-rich timing, starting temperature, and hydrogen (reductant) concentration were varied. Cycling experiment conditions are listed in [Table 1](#). The experiments were run with and without NO in the inlet to isolate the effects of OSC and NO_x-related reactions. The three cycle timings tested were 100 sec. lean with 5 sec. rich (100/5), 150 sec. lean with 5 sec. rich (150/5), and 100 sec. lean with 10 sec. rich (100/10). The lean phase was composed of 10% O₂, 5% H₂O, 5% CO₂, and either 0 or 300 ppm NO. The rich phase consisted of 5% H₂O, 5% CO₂, and the indicated concentration of H₂. N₂ gas was the balance in both phases. The catalyst was cleaned for 15 minutes at 500°C with a gas composition of 5% CO₂, 5% H₂O, 1% H₂, and balance N₂ before each set of experiments to remove any remaining nitrates from previous runs.

Table 1. NO_x cycling experiment conditions

Lean/Rich Cycle Time (sec)	Temp. (°C)	H ₂ in Rich Phase (%)
100/5	200	2, 4, 6, 8
100/5	300	2, 4, 6, 8
150/5	300	2, 4, 6, 8
100/10	300	2, 8

PROPYLENE OXIDATION EXPERIMENTS

Propylene oxidation was used to isolate the effect of thermal degradation on the oxidation ability of the NSR catalyst

precious metal components. Two temperatures were used in these tests, 200°C and 300°C. The concentration of propylene for the experiments was 2000 ppm with 10% O₂ and balance N₂.

RESULTS AND DISCUSSION

The catalyst solid temperature was measured every 0.5 in. along its length using the IR camera, with a representation of the sample and points where data were extracted depicted in [Figure 1](#). The thermography technique generates data comparable to using a thermocouple at each of these positions.

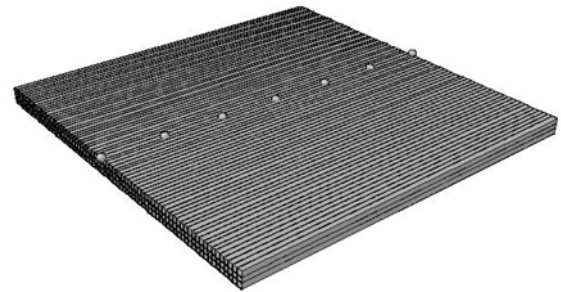


Figure 1. Catalyst temperature data collection locations.

In analyzing the IRT data, significant temperature changes were only observed at the onset of the rich phase through a few seconds after the lean phase began. During the rest of the lean phase, no significant exothermic or endothermic reactions occur, leading to flat temperature profiles. To compare changes more easily, the temperature rise for each point was calculated by subtracting the average temperature measured well into the lean phase. Such temperature changes provide an estimate of when and where exo- or endothermic chemical reactions occur on the catalyst surface. [Figure 2](#) shows the temperature rise as a function of time at a point 0.5 in. from the inlet face of the catalyst for runs with NO and without NO in the lean-phase gas composition. Both runs show two distinct peaks; the first peak at 100 sec. corresponds to the switch from the lean to the rich phase, and the second one at 105 sec. corresponds to the switch from the rich back to the lean phase. With NO in the lean phase, the first peak corresponds to the heat released by two reactions - trapped NO_x is reduced and hydrogen reacts with stored oxygen. Without NO in the lean phase, the first peak corresponds to the hydrogen reaction with stored oxygen only. Therefore, the difference in the temperature rise profile between these first peaks is the temperature increase attributed to surface nitrate reduction.