

Estimating the temperatures of the NO_x storage sites in a lean NO_x trap during oxidation reactions

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Abstract

The maximum temperatures of the potassium NO_x storage sites on a 0.64 cm long monolithic platinum/potassium/alumina lean NO_x trap (LNT) have been estimated during propylene (C₃H₆) oxidation under net lean conditions. This was accomplished by saturating the LNT with NO_x, injecting a high concentration of C₃H₆ for a specified period of time, estimating the amount of NO_x released from the LNT as a result of the C₃H₆ injection by calculating the amount of NO_x restored during a second saturation period after the injection, and comparing the amount of NO_x remaining on the LNT after the injection to a capacity versus temperature calibration curve. The LNT was evaluated behind a thermally aged Pd/Al₂O₃ three-way catalyst, which provided negligible NO_x storage capacity but oxidized most of the C₃H₆. The projected temperature increase of the NO_x storage sites on the LNT was in reasonable agreement with the temperature increase of the exhaust gas exiting the sample for different C₃H₆ concentrations, injection times, and base temperatures, which validated the technique. When the TWC was removed and 1800 ppm C₃H₆ was injected at a base temperature of 330 °C, the measured temperature of the exit gas and the inferred temperature of the NO_x storage sites increased by approximately 65 and 102 °C, respectively, under steady-state conditions. The elevated temperature of the NO_x storage sites relative to that of the exit gas was attributed to the very high temperatures generated on the neighboring precious metal sites of the LNT.

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1. Introduction

Lean-burn gasoline engines have the potential to provide improved fuel economy relative to engines operating at the stoichiometric A/F ratio due to improved combustion thermodynamics and reduced pumping losses. However, the exhaust from lean-burn engines contains a surplus of oxygen (O₂), and the three-way catalyst (TWC) used for emission control on current-production gasoline vehicles is not effective for reducing the oxides of nitrogen [i.e., nitrogen oxide (NO) and nitrogen dioxide (NO₂), collectively known as NO_x] in such a lean environment. A relatively new catalyst technology that

can be used to treat the NO_x emissions under lean conditions is the lean NO_x trap (LNT).

NO_x traps normally function by adsorbing and storing NO_x under lean conditions and then reducing the stored NO_x to nitrogen (N₂) during periodic rich purges [1]. NO_x traps are essentially three-way catalysts that contain precious metal [e.g., platinum (Pt) and rhodium (Rh)] as well as high concentrations of alkaline-earth metals [e.g., barium (Ba)] and/or alkali metals [e.g., potassium (K)], which serve as NO_x storage materials. During lean operation, the platinum in the LNT oxidizes the NO in the exhaust to NO₂. The NO₂ reacts with the NO_x storage materials and additional oxygen to form adsorbed NO_x species, such as nitrites [e.g., Ba(NO₂)₂] or nitrates [e.g., Ba(NO₃)₂]. As the NO_x storage sites begin to fill up, the storage efficiency will begin to drop. At that point, the LNT can be regenerated by operating the engine rich for 2 to 5 s. The reductants in the rich exhaust [hydrogen (H₂), carbon monoxide (CO), and hydrocarbons (HC)] react with the stored NO_x over the precious metal to form N₂. This purges the storage sites of the adsorbed NO_x.

Abbreviations: LNT, lean-NO_x trap; NS5, NO_x stored with final instantaneous storage efficiency of 5%; SCR, selective catalytic reduction; TWC, three-way catalyst

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species so that the LNT can store NO_x again during the next lean period.

The NO_x storage capacity of a LNT decreases with increasing temperature due to the decreasing stability of the adsorbed NO_x species. However, the amount of NO_x stored at low temperatures (e.g., below 350 °C) is limited by incomplete purging as well as by low rates of NO oxidation [2]. As a result, the measured or effective NO_x storage capacity of a LNT goes through a maximum at a temperature that varies with the formulation but is typically between 300 and 400 °C. For a model trap containing 5.7% K and 3.5 g/L Pt, it was shown that the amount of NO_x stored between 190 and 400 °C was significantly increased by increasing the temperature of the trap to 450 °C for the purges and by using NO_2 instead of NO during the storage periods. The resulting increase in low temperature NO_x capacity produced the expected result that the NO_x storage capacity continued to decrease with increasing temperature.

A novel approach for purging a LNT was presented recently that took advantage of this decrease in NO_x storage capacity with increasing temperature [2]. After storing NO_x on the LNT, propylene (C_3H_6) was oxidized on the trap under net lean conditions. The resulting exotherm caused some of the stored NO_x to be released from the LNT. Since the release occurred under lean conditions, the released NO_x was not reduced to N_2 by the LNT but was emitted primarily as NO. Therefore, the released NO was converted to N_2 by placing a selective catalytic reduction (SCR) catalyst downstream of the LNT and injecting NH_3 between the LNT and SCR catalysts during the C_3H_6 injections.

Relative to a SCR catalyst alone, this LNT + SCR system provided advantages at temperatures above 400 °C, where the NH_3 storage capacity of the SCR drops to low levels. Under these conditions, the NH_3 (or urea) has to be injected into the exhaust to precisely match the flux of NO_x from the engine. This can be a serious challenge for the urea injection control system during transient operation, where the NO_x flux can change rapidly. Therefore, the LNT in the LNT + SCR system was intended to simplify the control system for NH_3 (or urea) injection at these high temperatures by adsorbing the NO_x and then releasing some of it during a HC injection, thereby converting the highly transient NO_x concentration in the exhaust into a reproducible and predictable profile. At temperatures below 400 °C, where the NH_3 storage capacity of the SCR was significantly higher, the hydrocarbon injections would be disabled, and the SCR alone would be used to treat the NO_x emissions. Since the LNT in this system was intended to function at temperatures above 400 °C, a potassium-based LNT was optimized for this application.

Since the release of NO_x from the LNT was promoted by lean hydrocarbon oxidation, it was desired to estimate the temperatures of the platinum sites and NO_x storage sites on the LNT during oxidation reactions. Such information would be useful for modeling the operation of the LNT + SCR system described above. In a broader sense, this would provide a comparison of the temperatures of the precious metal sites and the catalyst washcoat during oxidation reactions, since the NO_x storage sites can be considered part of the washcoat.

Previous researchers have attempted to estimate the temperatures of the precious metals on a supported catalyst through mathematical models. Luss [3] developed a model assuming that the chemical reactions on a catalyst site occurred in a timeframe on the order of 10^{-13} s, which was several orders of magnitude shorter than the time between reactions events. The precious metal temperature increased by several hundred degrees Celsius but then cooled back to the original temperature during a relaxation time that was similar to the reaction time. Chan et al. [4] modified Luss' model to account for the finite rate of heat transfer and predicted significantly higher precious metal temperatures, but this model also predicted rapid cooling of the precious metals to the original temperature. Steinbruchel and Schmidt [5] modified Luss' model to account for thermal boundary resistance at the interface between the precious metal and the support. This model predicted similar temperature increases on the precious metal sites but slower cooling rates (i.e., 10^{-10} s). Due to the very short reaction times and cooling times, these models would predict that the time-averaged temperature of the precious metal sites would not change significantly under exothermic reaction conditions. Also, all of these models assumed that the temperature of the support remained constant during the reactions.

Boudart and co-workers [6] used macroscopic heat transfer equations to calculate the temperature gradient between a supported catalyst and its carrier under reaction conditions. In contrast to the models of Luss [3], Chan et al. [4], and Steinbruchel and Schmidt [5], Boudart's model estimated that the temperature difference between a catalyst site and its carrier would be under 0.03%.

Others have tried to determine the temperatures of the precious metals and the support through experimentation. Sharma et al. [7] experimented with a thin film of platinum supported on a non-porous quartz crystal during the oxidation of CO with O_2 . The temperature of the quartz support was estimated from its temperature-dependent vibrational frequencies, while the temperature of the platinum film was estimated from its resistivity. At a gas temperature of 200 °C, the steady-state temperatures of the support and the platinum were determined to be 210 and 235 °C, respectively. Thus, the steady-state temperature of the support and the precious metals exceeded the gas temperature by 10 and 35 °C, respectively.

Kember and Sheppard [8] recorded infrared emissions from pressed discs of a Pd/ SiO_2 catalyst during the oxidation of CO, where a thermocouple was placed in contact with the silica support to measure its temperature. The blackbody emission was higher than that which would be expected from the temperature indicated by the thermocouple. They suggested that this higher emission originated from the particles of palladium and estimated that their temperature exceeded the silica temperature by at least 190 °C. Kaul and Wolf [9] measured the surface temperatures on a 5% Pt/ SiO_2 wafer while studying self-sustaining temperature oscillations during CO oxidation. They measured fluctuations in the surface temperature of 150 °C and speculated that the metal crystal temperatures would be significantly higher.

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