EFFECT OF THERMAL AGING ON CATALYST MORPHOLOGY AND PERFORMANCE OF LEAN NO_X TRAPS

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Introduction

Lean-burn technology is being slowly introduced into the automobile market in order to increase fuel efficiency and reduce emissions. A major challenge with lean-burn technology is the abatement of nitrogen oxides (NO_x), since unlike unburned hydrocarbons and CO, which are reacted in an oxidizing environment, NO_x is most-efficiently reduced in a fuel-rich environment. Of the common de-NO_x technologies, the lean NO_x trap (LNT) is one of the leading candidates. Significant progress in improving LNT performance has been recently achieved, but sulfur tolerance and its high temperature removal currently limit LNT commercialization. As improvements are made to LNTs with respect to durability, a consistent rapid-aging protocol that can be used to evaluate new formulations is necessary. This presentation discusses the development of a system of high temperature cycles that expose the LNT to both lean and rich conditions at elevated temperatures and can be implemented in either small-engine research facilities [1-2] or bench-core reactors [3]. This protocol also includes a set of characterization techniques that enable modeling of both the deactivation mechanisms and their impact on performance.

Materials and Methods

A small single-cylinder diesel engine is used to thermally age model (Pt+Rh/Ba/γ-Al_2O_3) Lean NO_x Traps (LNTs) under lean/rich cycling at target temperatures of 600, 700, and 800°C with a space velocity of 60,000 h^{-1}. During an aging cycle, fuel is injected into the exhaust to achieve reproducible exotherms under lean and rich conditions with the average temperature approximating the target temperature. NO_x reduction performance is measured throughout the aging sequence to monitor deactivation. More controlled thermal aging is also performed in a bench-core reactor to simulate the engine behavior, and to produce a wide range of deactivated LNTs for future modeling efforts. In addition to performance evaluation, characterization of the aged LNTs is performed with X-ray diffraction, transmission electron microscopy, and various chemisorption/physisorption techniques are employed to measure total surface area, NO_x storage capacity, and Pt surface area.

Results and Discussion

Aging is performed on the engine-based system until the NO_x conversion is approximately constant. The NO_x reduction measured with the engine diagnostic system decreases by 42% after 60 cycles at 600°C, 36% after 76 cycles at 700°C and 57% after 46 cycles at 800°C. The catalyst samples are removed and characterized by XRD and using a microreactor that allows controlled measurements of surface area, precious metal size, NO_x storage, and reaction rates. Three aging mechanisms responsible for the deactivation of LNTs have been identified: (i) loss of dispersion of the precious metals, (ii) phase transitions in the washcoat materials, and (iii) loss of surface area of the storage component and support. These three mechanisms are accelerated when the aging temperature exceeds 850°C—the γ to δ transition temperature of Al_2O_3. Normalization of rates of NO reacted at 400°C to surface area demonstrates the biggest impact on performance stems from surface area losses rather than from precious metal sintering as demonstrated in Figure 1.

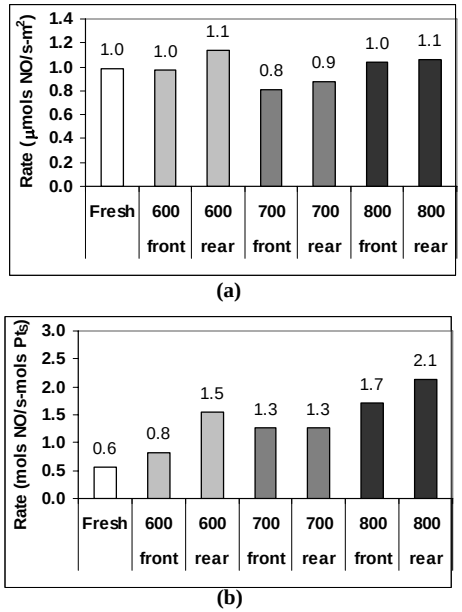

Figure 1. NO reduction rates at 400°C for LNTs thermally-aged at 600°C, 700°C, and 800°C in engine-based system. Rates are normalized with respect to (a) total surface area and (b) Pt surface sites.

Significance

The technique outlined in this protocol can be implemented in any research facility that is interested in evaluating LNTs for thermal durability using either engine-based research or bench-core simulated exhaust conditions. The current results demonstrate that the loss of total surface area is at least as important as the loss of precious metal sites.

References

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