

## Effect of CeO<sub>2</sub> on the Storage and Regeneration Behavior of Lean NO<sub>x</sub> Traps

Yaying Ji<sup>1</sup>, Todd J. Toops<sup>2</sup>, Jae-Soon Choi<sup>2</sup> and Mark Crocker<sup>\*</sup>

<sup>1</sup> Center for Applied Energy Research, University of Kentucky,  
2540 Research Park Drive, Lexington, KY 40511-8479

<sup>2</sup> Fuels, Engines, and Emissions Research Center, Oak Ridge National Laboratory,  
2360 Cherahala Blvd., Knoxville, TN 37932-1563

\*crocker@caer.uky.edu

### Introduction

Lean-burn engines provide more efficient fuel combustion and lower CO<sub>2</sub> emissions compared with traditional stoichiometric engines. However, the effective removal of NO<sub>x</sub> from lean exhaust represents a challenge to the automotive industry. In this context, Lean NO<sub>x</sub> Traps (LNTs) represent a promising technology. Although many studies have been conducted using model Pt/BaO/Al<sub>2</sub>O<sub>3</sub> type LNT catalysts, there have been few reports concerning the effect of ceria on LNT performance [1]. Ceria is an important component of LNTs formulated for lean burn gasoline applications, its role being principally to provide the necessary oxygen storage capacity when the engine is operating at the stoichiometric point (i.e., the catalyst is functioning as a conventional three-way catalyst) [2]. However, ceria also promotes H<sub>2</sub> formation under rich conditions via the water-gas shift (WGS) reaction [3], and can provide additional NO<sub>x</sub> storage capacity during lean operation. In this study, we focused on investigating the effect of CeO<sub>2</sub> on the functioning of both model and fully formulated LNTs.

### Materials and Methods

An in-situ Diffuse Reflectance Fourier Transform Infrared Spectroscopy (DRIFTS) reactor and a microreactor equipped with a mass spectrometer were employed to explore the storage and regeneration behavior of two model powder catalysts: 1 wt% Pt/20 wt% BaO/Al<sub>2</sub>O<sub>3</sub> (hereafter denoted as PBA) and a physical mixture of 1 wt% Pt/20 wt% BaO/Al<sub>2</sub>O<sub>3</sub> and 1 wt% Pt/CeO<sub>2</sub> in a 74:26 weight ratio (denoted as PBAC). In addition, LNTs were evaluated in washcoated monolith form (62 cells per cm<sup>2</sup>, 2.2 cm diameter, 7.62 cm length) on a bench flow reactor. The gas composition used for catalyst evaluation was 300 ppm NO, 10% O<sub>2</sub>, 5% CO<sub>2</sub>, 5% H<sub>2</sub>O, balance N<sub>2</sub> (lean), and 1.575% H<sub>2</sub>, 2.675% CO, 5% CO<sub>2</sub>, 5% H<sub>2</sub>O, balance N<sub>2</sub> (rich), with a gas space velocity of 3×10<sup>4</sup> h<sup>-1</sup>.

### Results and Discussion

NO<sub>x</sub> storage measurements were performed under both continuous lean flow and lean-rich cycling conditions after pretreatment of each catalyst in H<sub>2</sub>. Under a continuous flow of NO (300 ppm) in 8% O<sub>2</sub> (with 5% CO<sub>2</sub> and 5% H<sub>2</sub>O added) for 1 hour, both catalysts exhibited their highest NO<sub>x</sub> storage capacity at 300 °C. Compared to PBA, PBAC had higher NO<sub>x</sub> storage capacity (NSC) at 200 °C (0.24 versus 0.19 mmol/g), which clearly demonstrates the benefit of adding ceria with respect to low temperature NO<sub>x</sub> storage. Under lean-rich cycling conditions (6 min lean, 0.5 min rich), both catalysts attained their maximum NO<sub>x</sub> conversion at 300 °C (90% for PBAC versus 76% for PBA), while the beneficial effect of ceria addition on NO<sub>x</sub> conversion was evident over the entire range of 200 to 400 °C. Moreover, PBAC displayed a superior selectivity to N<sub>2</sub> over PBA for the entire range. At 300 °C, the measured selectivities to N<sub>2</sub> were 76% and 69% for PBAC and PBA, respectively. The results of microreactor cycling experiments are summarized in Table 1.

The regeneration behavior of PBA and PBAC was investigated using temperature programmed reduction (TPR) and desorption (TPD) techniques after NO<sub>x</sub> storage at 300 °C for 1 h. DRIFTS results indicated the presence of mainly monodentate nitrate on both catalysts after NO<sub>x</sub> storage at this temperature. Using H<sub>2</sub> as a reductant, both catalysts could be fully regenerated, as evidenced by the disappearance of the nitrate bands, at temperatures approaching 400 °C. An identical TPR experiment in a microreactor showed that N<sub>2</sub> production and H<sub>2</sub> consumption commenced simultaneously on PBA at 150 °C. However on PBAC, N<sub>2</sub> production began at a higher temperature (130 °C) than H<sub>2</sub> consumption (81 °C), with the initial H<sub>2</sub> consumption being ascribed to reduction of the ceria. Regeneration with CO resulted in more complicated DRIFT spectra. Additional species observed included isocyanate (~2160 cm<sup>-1</sup>), Pt-bound CO (2070 cm<sup>-1</sup>) and BaCO<sub>3</sub> (~1550 cm<sup>-1</sup>). CO was a less effective reductant than H<sub>2</sub>, such that upon heating to 450 °C both PBA and PBAC contained residual nitrate species. The addition of H<sub>2</sub>O improved the CO reduction efficiency for both catalysts, as significantly less nitrate remained on the surface. Mass spectra indicated that N<sub>2</sub> release commenced at higher temperatures during reduction with CO compared to reduction with H<sub>2</sub> and extended up to 500 °C for PBA and 431 °C for PBAC. The addition of H<sub>2</sub>O to the CO feed resulted in an initiation of N<sub>2</sub> release at a lower temperature for both catalysts, likely due to the water gas shift reaction, as evidenced by the detection of H<sub>2</sub>. PBAC exhibited much earlier N<sub>2</sub> release and higher H<sub>2</sub> formation than PBA.

Further tests were performed in a bench reactor using fully formulated monolithic LNT catalysts containing either no CeO<sub>2</sub> or 100 g/l La-stabilized CeO<sub>2</sub>. Under realistic cycling conditions (60 s lean/5 s rich), the ceria-containing catalysts exhibited higher NO<sub>x</sub> conversion than the ceria-free catalyst at all temperatures in the range 150-350 °C, with comparable activity at 450 °C. The presence of ceria also significantly improved the selectivity to N<sub>2</sub> at most temperatures, with markedly lower NH<sub>3</sub> release during the rich phase. Overall, these findings demonstrate that the incorporation of ceria in LNTs not only improves NO<sub>x</sub> storage efficiency but also positively impacts LNT regeneration behavior both in terms of conversion and selectivity, albeit at the expense of additional reductant consumed by the stored oxygen.

**Table 1. NO<sub>x</sub> conversion and N<sub>2</sub> selectivity under lean-rich cycling condition**

| Temperature (°C) | PBA                       |                         | PBAC                      |                         |
|------------------|---------------------------|-------------------------|---------------------------|-------------------------|
|                  | NO <sub>x</sub> conv. (%) | N <sub>2</sub> sel. (%) | NO <sub>x</sub> conv. (%) | N <sub>2</sub> sel. (%) |
| 200              | 46                        | 82                      | 67                        | 92                      |
| 300              | 76                        | 69                      | 90                        | 76                      |
| 400              | 74                        | 78                      | 82                        | 88                      |

### Significance

This work provides detailed information on the role of ceria in lean NO<sub>x</sub> trap chemistry, which could benefit the design and operation of commercial LNT catalysts.

### References

1. Theis, J., Ura, J., Goralski, C., Jen, H., Thanasiu, E., Graves, Y., Takami, A., Yamada, H., Miyoshi, S., SAE Paper no. 2003-01-1160.
2. Fornasiero, P., Balducci, G., Di Monte, R., Kaspar, J., Sergo, V., Gubitosa, G., Ferrero, A., Graziani, M.J., J. Catal., 164, 173 (1996).
3. Jacobs, G., Williams, L., Graham, U., Sparks, D.E., Davis, B.H., Appl. Catal. A 252, 107 (2003).