

# Al<sub>2</sub>O<sub>3</sub>-based passive NO<sub>x</sub> adsorbers for low temperature applications

Yaying Ji, Mark Crocker\*

Center for Applied Energy Research, University of Kentucky, KY 40511, USA

\*corresponding author: mark.crocker@uky.edu

## Introduction

The control of NO<sub>x</sub> emissions from lean-burn engines represents an on-going challenge to the automotive industry, particularly at the low exhaust temperatures associated with modern, fuel-efficient engines. The ability to deploy urea-SCR at low operating temperatures is limited due to the slow rate of urea decomposition. Consequently, a system is required which combines low temperature NO<sub>x</sub> storage with subsequent NO<sub>x</sub> reduction. An attractive option which to date has been little explored is the use of a passive NO<sub>x</sub> adsorber (PNA) device in combination with a urea SCR catalyst. In this system, the PNA adsorbs NO<sub>x</sub> emitted from the engine during cold starts, and then releases the NO<sub>x</sub> at higher temperatures, e.g., above 200 °C. At this point the SCR catalyst is sufficiently warm to function efficiently. The first reference to such a concept appears to be a U.S. Patent granted to Ford in 2001 [1], in which  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was claimed as the NO<sub>x</sub> adsorber, promoted with a platinum group metal. A recent presentation [2] made by Cummins showed that a PNA/urea SCR system was able to achieve lower emissions on a light duty (V8) truck than the corresponding urea SCR-only system. To acquire the basic knowledge required for the development of effective PNA materials, we performed an initial study using a simple Al<sub>2</sub>O<sub>3</sub>-based PNA.

## Materials and Methods

Two PNA materials were prepared and applied in this study: 1 wt% Pt/Al<sub>2</sub>O<sub>3</sub> and 1 wt% Pt/La-Al<sub>2</sub>O<sub>3</sub> (hereafter denoted as Pt-Al and Pt-La-Al, respectively). The La-modified Al<sub>2</sub>O<sub>3</sub> (1 wt% La) was obtained by impregnating  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Sasol, BET surface area of 201 m<sup>2</sup>/g) with aqueous La(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O followed by calcination at 500 °C for 3 h. Pt was loaded onto the supports by incipient wetness impregnation [3]. The NO<sub>x</sub> storage capacity of the PNAs was investigated at three temperatures (80 °C, 120 °C and 160 °C) under lean conditions (300 ppm NO, 5% O<sub>2</sub>, 5% CO<sub>2</sub>, 3.5% H<sub>2</sub>O, He bal.). Temperature-programmed desorption (TPD) of NO<sub>x</sub> was performed under the same lean conditions but without NO in the feed gas; TPD was performed after NO<sub>x</sub> adsorption at the desired temperature. NO<sub>x</sub> storage-regeneration cycling studies were carried out by storing NO<sub>x</sub> at 120 °C for 10 min and then ramping the sample (10 °C/min) under lean conditions (without added NO) to 250 °C to induce NO<sub>x</sub> desorption. Five such storage-regeneration cycles were performed.

## Results and Discussion

The cumulative amount of NO<sub>x</sub> stored as a function of time for Pt-Al and Pt-La-Al is displayed in Fig.1. Both samples show significantly increased NO<sub>x</sub> storage capacity (NSC) with increase of the adsorption temperature from 80 to 120 °C. However, further increase of the temperature to 160 °C negatively impacts NSC. Compared to Pt-Al, the La-modified sample shows higher NSC at all of the tested temperatures. Indeed, Pt-La-Al exhibits over two-fold higher NSC compared to Pt-Al during the first 5 min of NO<sub>x</sub> storage. Similarly, Pt-La-Al shows much higher NO<sub>x</sub> storage efficiency (i.e., percentage of NO<sub>x</sub> fed that is actually stored) than the Pt-Al analog, as demonstrated by the fact that the NO<sub>x</sub> storage efficiency (NSE) of Pt-

La-Al for the first 1 min is over 90%, whereas the NSE of Pt-Al is less than 50%. Evidently, La addition to Pt-Al significantly improves NO<sub>x</sub> storage properties at short storage times.

For PNA applications, NO<sub>x</sub> thermal release behavior is also critical. This was studied by means of TPD after NO<sub>x</sub> storage at 120 °C for periods of 5 and 10 min. In general, two NO<sub>x</sub> desorption events (occurring at <250 °C and 250-500 °C) are observed during TPD measurements. Pt-Al shows higher NO<sub>x</sub> desorption efficiency (i.e., percentage of stored NO<sub>x</sub> that is released) below 250 °C than Pt-La-Al (37.9% vs. 18%). With increasing storage time, both samples display increased desorption efficiency below 250 °C, consistent with the occurrence of NO<sub>x</sub> adsorption on progressively weaker adsorption sites with increased storage time.

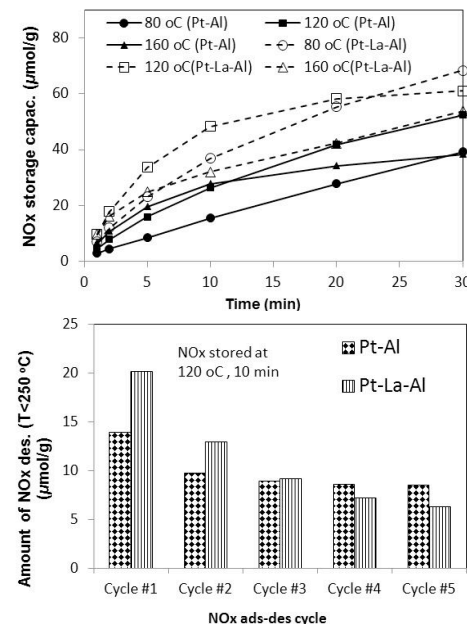


Fig. 2. Amount of NO<sub>x</sub> desorbed during cycling.

NO<sub>x</sub> storage-regeneration cycling studies show that Pt-Al reached steady state after three cycles, as evidenced by the attainment of a constant value for the amount of NO<sub>x</sub> desorbed (see Fig. 2) and the NSE (not shown). However, Pt-La-Al exhibits a trend of decreasing NO<sub>x</sub> desorption (and NSE), even after five cycles (Fig. 2). Notably, although Pt-La-Al shows a higher amount of NO<sub>x</sub> desorbed for the first two cycles, this value is lower than that for Pt-Al after the third cycle. From this it follows that balancing NO<sub>x</sub> storage capacity and desorption efficiency is of prime importance in the development of improved PNA materials.

## Significance

Development of NO<sub>x</sub> reduction systems possessing satisfactory low temperature performance has a high priority in order to facilitate the implementation of more energy efficient engines.

## References

1. M. Jarvis, K.M. Adams, U.S. patent 6,182,443, to Ford Global Technologies (2001).
2. C. Henry, D. Langenderfer, A. Yezerets, M. Ruth, H.-Y. Chen, H. Hess, M. Naseri, Presented at the 2011 DEER Conference, Detroit, MI.
3. Y. Ji, T.J. Toops, U.M. Graham, G. Jacobs and M. Crocker, *Catal. Lett.* **110** (2006) 29.