

## Regeneration of Pt/BaO/Al<sub>2</sub>O<sub>3</sub> NO<sub>x</sub> Traps with H<sub>2</sub>: Role of Ammonia

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### Introduction

The NO<sub>x</sub> storage/reduction (NSR) process is one of the technologies in development to abate the NO<sub>x</sub> (NO+NO<sub>2</sub>) emitted from combustion engines. This system works by the Pt catalyst transforming the NO in the exhaust to NO<sub>2</sub>, which then reacts with a barium or potassium component to form a stable compound, which is periodically reduced to release most of the nitrogen as N<sub>2</sub> [1]. This cycle of oxidation, trapping, release and reduction is performed, for example, with a sixty second capture or lean phase (oxidation and trapping) followed by a four second regeneration or rich phase (release and reduction). On a commercial system, the efficiency in transforming the emitted NO<sub>x</sub> to N<sub>2</sub> is over 95%. The objective of this contribution is to gain insight into the mechanism governing the reduction of stored NO<sub>x</sub> species and provide a model of how the reduction process occurs, including why it is so selective to N<sub>2</sub>. We will show that the reduction process can be explained by the release of NO or NO<sub>2</sub> which is then optimally reduced to N<sub>2</sub> or over-reduced to NH<sub>3</sub> on the Pt clusters. If N<sub>2</sub>O is formed, most of it continues to react with hydrogen on the Pt surface to form N<sub>2</sub> or NH<sub>3</sub>. Additionally, we will show that the NH<sub>3</sub> formed is as effective as H<sub>2</sub> in the reduction/regeneration process and is eventually transformed to N<sub>2</sub>.

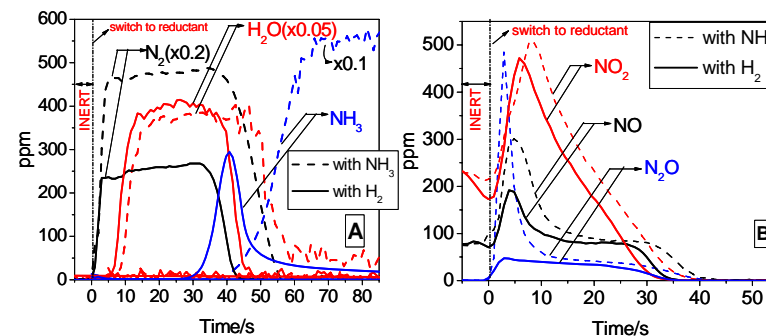
### Materials and Methods

The Pt/BaO/Al<sub>2</sub>O<sub>3</sub> catalyst used in this study was supplied by EmeraChem, LLC in monolithic form. The monolith had a cell density of 200 channels per in<sup>2</sup>, a Pt loading of ca. 50 g ft<sup>-3</sup> and Ba loading of 20 wt%. The total gas flow rate over the sample was 7.0 standard L min<sup>-1</sup> (GHSV = 30,000 h<sup>-1</sup>). The Pt metal dispersion, as measured by H<sub>2</sub>-O<sub>2</sub> titration, was 60%. The experimental apparatus used for this study is described in detail elsewhere [2]. All the experiments reported here were run at 300°C, except where specified. The NO, NO<sub>2</sub>, N<sub>2</sub>O, NH<sub>3</sub> and H<sub>2</sub>O concentrations in the outlet gas stream were detected with an FTIR gas analyzer (MKS MultiGas<sup>TM</sup> Analyzer, Model 2030), while the N<sub>2</sub> concentration was detected with a quadrupole mass spectrometer (SRS RGA 200). Argon was used as the carrier gas to allow for the measurement of the released N<sub>2</sub>. The gas flows were controlled by mass flow controllers and calibrated needle valves. The system was automated to switch 3-way valves between lean-rich cycles. Thermocouples were placed 6 mm before and after the catalyst sample to verify inlet and outlet gas temperatures.

### Results and Discussion

Figure 1 shows a comparison of the evolution of the outlet gas concentrations from a Pt/BaO/Al<sub>2</sub>O<sub>3</sub> catalyst after the switch to regeneration gases containing either 0.75% H<sub>2</sub>/Ar or 0.53% NH<sub>3</sub>/Ar (the number of H atoms per unit of time flowing over the sample kept nearly identical). This rich phase (3 minutes long) was preceded by a 7 minute long lean phase, that contained 350 ppm NO, 10% O<sub>2</sub>, balance Ar, and a 5 second purge with Ar. The nitrogen

balance between capture and regeneration phases was found to close within experimental error. As seen in Fig. 1-A, the N<sub>2</sub> and H<sub>2</sub>O traces for both regenerating mixtures have a rectangular wave shape indicating a “plug flow” type of mechanism, implying a complete reaction between the reductant and the NO<sub>x</sub> to produce N<sub>2</sub> and H<sub>2</sub>O. The reductant was found to be the limiting reagent as evidenced by the evolution of the H<sub>2</sub> or NH<sub>3</sub> traces only towards the end of the cycle, and also by the fact that the time required for regeneration was inversely proportional to the H<sub>2</sub> amount fed per unit time, as we verified experimentally. Lowering the temperature for the tests from 300°C to 242°C made no difference on the reduction profiles, suggesting that the regeneration is limited by transport of reactants and not by kinetics. From Fig. 1 it is also clear that either NH<sub>3</sub> or H<sub>2</sub> is capable of regenerating the trap in a similar way. In the case of regeneration by H<sub>2</sub>, the NH<sub>3</sub> evolution curve is the result of the competition between its generation by NO<sub>x</sub>-H<sub>2</sub> reaction and its subsequent oxidation by NO<sub>x</sub>. The NO<sub>x</sub> (NO+NO<sub>2</sub>) released from the trapping sites reacts with H<sub>2</sub> over Pt to form NH<sub>3</sub>, N<sub>2</sub> and N<sub>2</sub>O, the selectivity depending on the local NO<sub>x</sub>/H<sub>2</sub> ratio, as verified by experiments on a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst [3]. When H<sub>2</sub>/NO<sub>x</sub> > 1, the reaction will form mostly NH<sub>3</sub>. The NH<sub>3</sub> thus formed moves along the catalyst bed in a plug flow manner and is completely consumed in reducing the NO<sub>x</sub> to N<sub>2</sub>, thereby regenerating the catalyst. When this NH<sub>3</sub> front reaches the end of the catalyst bed, it begins to break through due to the absence of NO<sub>x</sub> to oxidize the NH<sub>3</sub> to N<sub>2</sub> and H<sub>2</sub>O, giving rise to the NH<sub>3</sub> trace seen at the end of the cycle. Thus, NH<sub>3</sub> serves as a hydrogen carrier while regenerating the trap with H<sub>2</sub> and eventually gets oxidized by the stored NO<sub>x</sub> to N<sub>2</sub>, thereby maintaining the high selectivity of the process towards N<sub>2</sub>.



**Figure 1.** Evolution of the species after the switch to the rich phase containing 0.75% H<sub>2</sub>/Ar (solid lines) or 0.53% NH<sub>3</sub>/Ar (dashed lines) at 300°C. (A) N<sub>2</sub>, H<sub>2</sub>O and NH<sub>3</sub> traces, (B) NO<sub>2</sub>, NO and N<sub>2</sub>O traces

### References

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