

# Effect of Ceria on the Desulfation Characteristics of Model Lean NO<sub>x</sub> Trap Catalysts

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## Introduction

Lean NO<sub>x</sub> traps (LNTs) represent a promising technology for the abatement of NO<sub>x</sub> under lean conditions. Although LNTs are starting to find commercial application, the issue of catalyst durability remains problematic. For diesel applications, LNT susceptibility to sulfur poisoning is the single most important factor determining effective catalyst lifetime. The NO<sub>x</sub> storage element of the catalyst has a greater affinity for SO<sub>3</sub> than it does for NO<sub>2</sub>, and the resulting sulfate is more stable than the stored nitrate. Although this sulfate can be removed from the catalyst by means of high temperature treatment under rich conditions, the required conditions result in catalyst degradation. It is well known that ceria is able to store sulfur (as sulfate); hence, for ceria-containing LNTs, the ceria may help to protect the main NO<sub>x</sub> storage component from sulfur poisoning. To better understand the role of ceria in LNT catalysis, we have studied the impact of ceria addition on the sulfation and desulfation behavior of model Ba-based LNTs. Furthermore, the importance of maintaining the Pt and Ba phases in close proximity for efficient LNT desulfation has been investigated.

## Materials and Methods

Studies were conducted using two types of model LNT catalyst samples: powder catalysts and fully formulated monolithic catalysts. Powder samples were prepared by incipient wetness impregnation and consisted of i) 1 wt% Pt/Al<sub>2</sub>O<sub>3</sub>; ii) 1 wt% Pt/CeO<sub>2</sub>; iii) 1 wt% Pt/20 wt% BaO/Al<sub>2</sub>O<sub>3</sub> (denoted hereafter as "PBA"); iv) 1 wt% Pt/20 wt% BaO/Al<sub>2</sub>O<sub>3</sub> (74 wt%) + 1 wt% Pt/CeO<sub>2</sub> (26 wt%), physical mixture (denoted as "PBAC"); and (v) a physical mixture of equal parts of 1 wt% Pt/Al<sub>2</sub>O<sub>3</sub> and 20 wt% BaO/Al<sub>2</sub>O<sub>3</sub>. The samples were sulfated at 350 °C by exposure to feed gas containing 100 ppm SO<sub>2</sub> and 8% O<sub>2</sub>, with Ar as the balance. Temperature programmed reduction (TPR) experiments were performed using a feed of 2% H<sub>2</sub>, 5% H<sub>2</sub>O and 5% CO<sub>2</sub> in Ar, the temperature being increased by 5 °C/min from 350 to 800 °C. The product stream was analyzed using an Airsense chemical-ionization mass spectrometer. The preparation of the model monolith catalysts has been described elsewhere [1].

## Results and Discussion

In order to study their desulfation behavior, temperature-programmed reduction (TPR) experiments were performed on sulfated samples of Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/CeO<sub>2</sub>, in addition to catalysts PBA and PBAC (Figure 1). During H<sub>2</sub>-TPR, sulfur was released from both catalysts mainly as H<sub>2</sub>S; release of H<sub>2</sub>S occurred at ~725°C from PBA (containing no ceria), whereas PBAC showed two discrete H<sub>2</sub>S release events at ~460°C and ~725°C. From this it follows that the H<sub>2</sub>S release at ~460°C corresponds to desulfation of the ceria phase (confirmed by the reference experiment with Pt/CeO<sub>2</sub>), with Ba desulfation occurring at the higher temperature. Significantly, PBAC displayed relatively lower H<sub>2</sub>S evolution from the Ba phase than PBA, confirming that the presence of ceria in PBAC lessened the degree of sulfur accumulation on the Ba phase.

These findings are supported by results obtained with model Ba-based monolith catalysts containing varying ceria loadings (physically mixed with Pt/BaO/Al<sub>2</sub>O<sub>3</sub>). In general, the effectiveness of desulfation at a given temperature is found to increase with the ceria loading of the catalyst. In effect, this results in a lowering of the temperature required for catalyst desulfation.

TPR experiments were also performed with the aim of ascertaining the effect of Pt location on the sulfation and desulfation behavior of Ba-based LNT formulations. For this purpose, a physical mixture of 1 wt% Pt/Al<sub>2</sub>O<sub>3</sub> and 20 wt% BaO/Al<sub>2</sub>O<sub>3</sub> was used. As shown in Figure 1, two main desorption events are observed. The first corresponds to sulfur release from the alumina phase (380°C, confirmed by the reference experiment using Pt/Al<sub>2</sub>O<sub>3</sub>), while the second maximum extends up to 800°C. Comparing these results with those obtained for PBA at the same sulfur loading, it is apparent that physical separation of the Pt and Ba phases results in increased sulfur storage on the alumina, presumably as a consequence of SO<sub>3</sub> spillover from Pt to the alumina support during sulfation. Additionally, the desulfation maximum of the BaSO<sub>4</sub> is shifted by ~65°C towards higher temperature, i.e., towards the position characteristic of bulk BaSO<sub>4</sub> [2]. This is in keeping with the idea that decomposition of surface BaSO<sub>4</sub> is facilitated by H ad-atoms which spill over from the Pt sites onto the sulfated Ba phase, a process which can be viewed as being analogous to LNT regeneration (denitrification) during rich phase purging [3].

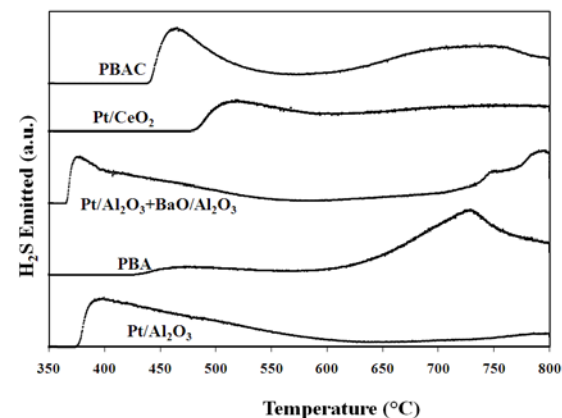


Figure 1. H<sub>2</sub>S emitted from sulfated powder samples during TPR

## Significance

These results show that the incorporation of ceria is beneficial with respect to the desulfation characteristics of LNT catalysts. Further, the importance of maintaining the Pt and Ba phases in close contact for efficient desulfation has been demonstrated.

## References

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