

## Interaction between soot and stored NO<sub>x</sub> during operation of LNT catalysts

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### Introduction

Diesel-equipped vehicles are considered as one of the primary sources of NO<sub>x</sub> and particulate (soot) emissions in industrialized countries. Accordingly, in the transport sector remarkable research efforts are being made to find viable solutions to limit their emission.

Recently the potential use of LNT catalyst in the simultaneous removal of soot and NO<sub>x</sub> has been proposed according to the DPNR (Diesel Particulate-NO<sub>x</sub> Reduction) concept [1].

In previous works of our group the potentiality of both Ba- and K-based LNT catalysts in the simultaneous removal of soot and NO<sub>x</sub> has been investigated. It has been shown that during the lean phase soot oxidation occurs by NO<sub>2</sub> (formed upon NO oxidation), while NO<sub>x</sub> are being stored on the catalyst surface [2,3]. More recently it has also been shown that NO<sub>x</sub> species stored onto the trapping component of the catalyst may participate in the combustion of soot via the release of NO<sub>x</sub> upon nitrate decomposition and/or by directly reacting with soot according to a surface reaction [4].

Aim of this work is to provide new insights on the interplay existing between soot combustion and NO<sub>x</sub> storage, and in particular on the interactions between soot and the stored NO<sub>x</sub>. The investigation has been carried out over PtBa/Al<sub>2</sub>O<sub>3</sub> and PtK/Al<sub>2</sub>O<sub>3</sub> catalysts and over the corresponding Pt-free binary samples to evaluate the role of Pt in the reaction.

### Materials and Methods

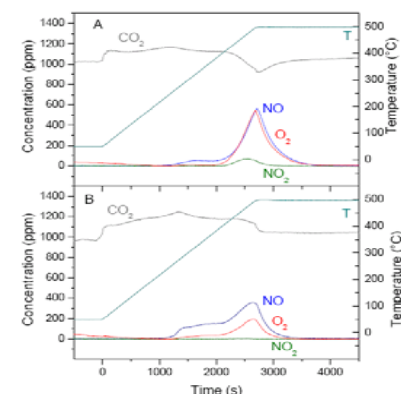
Home made Ba/Al<sub>2</sub>O<sub>3</sub> (20/100 w/w), K/Al<sub>2</sub>O<sub>3</sub> (5.4/100 w/w), PtBa/Al<sub>2</sub>O<sub>3</sub> (1/20/100 w/w) and PtK/Al<sub>2</sub>O<sub>3</sub> (1/5.4/100 w/w) catalysts have been prepared by impregnation of  $\gamma$ -alumina. The interaction between soot and the stored NO<sub>x</sub> species has been investigated by temperature programmed methods under inert flow (TPD) or in the presence of oxygen (TPO) starting from soot/catalyst mixtures on which NO<sub>x</sub> have been preadsorbed at 350°C.

### Results and Discussion

The results of the TPD runs carried out over PtBa/Al<sub>2</sub>O<sub>3</sub> catalyst are shown in Figure 1A (absence of soot) and 1B (presence of soot). In the case of the soot-free catalyst (Figure 1A), it clearly appears that most of the nitrate decomposition is observed above 350°C (the adsorption temperature) and the process is not complete at temperatures as high as 500°C, corresponding to the maximum heating temperature. In correspondence of NO<sub>x</sub> and oxygen evolution an uptake of CO<sub>2</sub> is observed due to the formation of barium carbonates.

Worth to note that the overall amounts of evolved NO, O<sub>2</sub> and NO<sub>2</sub>, estimated by integration of the TPD peaks, are well in line with the stoichiometry of the nitrates decomposition reactions:  
 $\text{Ba}(\text{NO}_3)_2 + \text{CO}_2 \rightarrow \text{BaCO}_3 + 2 \text{NO} + 3/2 \text{O}_2$   
 $\text{Ba}(\text{NO}_3)_2 + \text{CO}_2 \rightarrow \text{BaCO}_3 + 2 \text{NO}_2 + 1/2 \text{O}_2$

A completely different situation is apparent in the presence of soot (Figure 1B). In this case the decomposition of nitrates is observed at lower temperature indicating that the presence of soot lowers the stability of stored nitrates. No detectable amounts of NO<sub>2</sub> are observed, a lower amount of O<sub>2</sub> are observed. This suggests that in the presence of soot NO<sub>2</sub> and O<sub>2</sub> produced from the nitrates decomposition are readily consumed in the soot combustion. As matter of fact, in line with the occurrence of soot oxidation, no significant CO<sub>2</sub> uptake is observed.



**Figure 1.** TPD run after NO<sub>x</sub> adsorption at 350°C over (A) Pt-Ba/Al<sub>2</sub>O<sub>3</sub> catalyst; (B) Pt-Ba/Al<sub>2</sub>O<sub>3</sub>-soot mixture

nitrate reduction during lean/rich operation of LNT catalysts [5]. Notably, the presence of Pt does not affect the soot-nitrate interaction, as pointed out by dedicated experiments carried out over Pt-free catalyst samples.

### Significance

New insights on the interaction between soot and adsorbed nitrates is given. Adsorbed nitrates are able to oxidize soot below the temperature of their thermal decomposition, which implies the direct reaction of the nitrates ad-species with soot. This pathway parallels the oxidation of soot by NO<sub>2</sub> that occurs in the presence of gas-phase NO<sub>2</sub>, i.e. upon the NO<sub>x</sub> storage during lean/rich operation of the LNT catalyst.

### References

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