

# Labelled $^{15}\text{NO}$ experiments for the study of $\text{NO}_x$ reduction over Pt-Ba/Al $_2$ O $_3$ LNT catalyst

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## Introduction

Lean  $\text{NO}_x$  Traps (LNT) are considered to be one of the most promising solutions for  $\text{NO}_x$  removal from lean burn engine exhausts [1]. Recently, the reduction by  $\text{H}_2$  of  $\text{NO}_x$  stored onto a Pt-Ba/Al $_2$ O $_3$  LNT model catalyst has been studied in our labs and a reduction pathway has been proposed [2]. The reduction proceeds through a 2-steps in series molecular pathway, in which the first step (fast) is the reduction of stored  $\text{NO}_x$  with  $\text{H}_2$  giving the formation of  $\text{NH}_3$ . In the second step (slow) the so formed ammonia reacts with residual stored  $\text{NO}_x$  to give  $\text{N}_2$ . The present study aims to better elucidate the pathways involved in the reduction of the stored  $\text{NO}_x$ , and in particular the second step of the proposed mechanism for  $\text{N}_2$  formation involving stored  $\text{NO}_x$  and ammonia. For this purpose experiments have been carried out using isotopically labelled molecules and different reductants, including  $\text{H}_2$  and  $\text{NH}_3$ .

## Experimental

A homemade Pt-Ba/Al $_2$ O $_3$  model catalyst has been prepared by impregnation of  $\gamma$ -alumina with Pt(NH $_3$ ) $_2$ (NO $_2$ ) $_2$  and subsequently with (CH $_3$ COO) $_2$ Ba.

$\text{NO}_x$  have been stored on Pt-Ba/Al $_2$ O $_3$  catalyst at different temperatures, feeding either  $\text{NO}$  (1000ppm) or isotopically labelled  $^{15}\text{NO}$  (1000ppm) in O $_2$  (3%) + He. The reactivity of the reductants with adsorbed  $\text{NO}_x$  (i.e. nitrite and nitrate) species has been investigated. These species are obtained upon  $\text{NO}_x$  adsorption at low and high temperature, respectively; notably, nitrites has been claimed as intermediate in the reduction of the stored nitrates.

The reduction of stored  $\text{NO}_x$  has been investigated using  $\text{NH}_3$  (1000 ppm) and  $\text{H}_2$  (2000 ppm) as reductants under both isothermal conditions and temperature programming (Temperature Programming Surface Reaction, TPSR). The reduction products were monitored with an UV-Vis analyzer (LIMAS H11, ABB) and a mass-spectrometer (Thermostar, Pfeiffer Vacuum) in order to quantify all the isotopic species present at the reactor outlet.

## Results/Discussion

Fig. 1 shows the results of the TPSR run using  $^{14}\text{NH}_3$  as reductant after  $^{15}\text{NO}$  adsorption at 150°C in the presence of oxygen. In this case, stored species are mainly nitrites. Accordingly the following overall stoichiometry of reduction is the expected:



i.e.  $\text{N}_2$  formation involves equimolecular amounts of nitrites and  $\text{NH}_3$ .

As apparent from the Figure, the  $\text{NH}_3$  concentration initially increases due to its desorption and then decrease being consumed in the reaction with stored  $\text{NO}_x$ . The temperature threshold for the reaction can be set near 150°C. Only nitrogen has been observed, with different isotopic composition. In particular,  $^{15}\text{N}^{14}\text{N}$  ( $m/z = 29$ ) represents the main product, along with minor amounts of  $^{14}\text{N}_2$  ( $m/z = 28$ ) and  $^{15}\text{N}_2$  ( $m/z = 30$ ). Based on this distribution, the preferential route for the formation of  $\text{N}_2$  is the coupling of one N atom coming from the nitrite ( $^{15}\text{NO}_2$ ) and the other from  $^{14}\text{NH}_3$ . This pathway may have same analogies with  $\text{N}_2$  formation in the  $\text{NH}_3$ -SCR reaction [3], even if the presence of non negligible amounts of other  $\text{N}_2$  products (i.e.  $^{14}\text{N}^{14}\text{N}$  and  $^{15}\text{N}^{15}\text{N}$ ) indicates that  $\text{N}_2$  is also formed upon coupling of two N atoms coming from the stored nitrites ( $^{15}\text{N}^{15}\text{N}$ ) and from ammonia ( $^{14}\text{N}^{14}\text{N}$ ). Accordingly other reduction route should be considered. Further experiments are under way to investigate these preliminary findings and to clarify the pathways involved in the reduction of the stored  $\text{NO}_x$ .

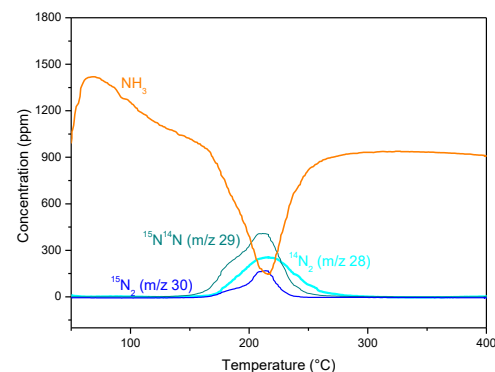


Figure 1. TPSR experiment in  $\text{NH}_3$  after  $^{15}\text{NO}/\text{O}_2$  storage at 150°C over Pt-Ba/Al $_2$ O $_3$  catalyst.

## References.

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2. L. Lietti, I. Nova, P. Forzatti, *J. Catal.*, **257**, 270 (2008)
3. G. Busca, L. Lietti, G. Ramis, F. Berti, *Appl. Catal. B: Environmental* **1** (18) 1988