

## Experimental investigation of the reduction of NO<sub>x</sub> species by CO over Pt-Ba/Al<sub>2</sub>O<sub>3</sub> Lean NO<sub>x</sub> Trap systems.

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### Introduction

Lean NO<sub>x</sub> Traps (LNTs) represent a viable solution for the abatement of NO<sub>x</sub> emissions from lean-burn engines [1]. Several studies were published on the mechanisms of both the NO<sub>x</sub> storage [1] and reduction [2], but a complete understanding of these processes has not yet been achieved.

We have previously shown that on Pt-Ba/Al<sub>2</sub>O<sub>3</sub> LNT systems the reduction of nitrates by H<sub>2</sub> involves a catalytic pathway involving Pt, and is not initiated by the thermal decomposition of the stored NO<sub>x</sub> ad-species [2]. We also showed that this process involves a 2-steps in series molecular pathway in which NH<sub>3</sub> is formed as intermediate [3]. In this study the reaction mechanism involved in the reduction of stored NO<sub>x</sub> when CO is used as reducing agent are analyzed, and the pathways originating the main reduction product (N<sub>2</sub>) are addressed.

### Materials and Methods

An homemade Pt-Ba/γ-Al<sub>2</sub>O<sub>3</sub> (1/20/100 w/w) sample was employed in this study. NO<sub>x</sub> were adsorbed at 350°C from NO (1000 ppm) in flowing He + O<sub>2</sub>; the so-formed surface nitrates were then reduced by CO in the absence and in the presence of water both under temperature programming (Temperature Programmed Surface Reaction, TPSR) or at constant temperature (Isothermal Step Concentration, ISC) at different temperatures. The reduction of the stored NO<sub>x</sub> species was also investigated in parallel by FT-IR *in situ* analyses.

### Results and Discussion

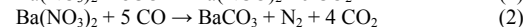
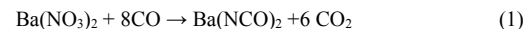
The temperature threshold for the reduction of the stored nitrates by gaseous CO was observed slightly above 180 °C during both temperature programming (TPSR) and FT-IR experiments. The onset temperature is well below that corresponding of the stored NO<sub>x</sub> thermal decomposition, observed near 350°C. N<sub>2</sub> and CO<sub>2</sub> were the main reaction products of nitrate reduction; even after heating at 400°C in the presence of CO only a part of the stored NO<sub>x</sub> have been removed.

The corresponding FTIR analysis pointed out, starting from 200°C, the formation of N=C=O species. These species are the product of the reduction of nitrates by CO, being N in the formal oxidation state -3. NCO are stable onto the catalyst surface under He up to 550°C.

During the ISC experiment, after NO/O<sub>2</sub> saturation at 350°C, 2000 ppm of CO were admitted to the reactor at the same temperature under dry conditions: about 150 ppm of nitrogen and 1550 of CO<sub>2</sub> were instantaneously produced. Then the N<sub>2</sub> concentration decreased due to depletion of the adsorbed NO<sub>x</sub> species, and evolution of very small amounts of NH<sub>3</sub> was observed. Like TPSR experiments, also in this case significant amounts of N-containing

species are left onto the catalyst surface at the end of the reduction.

FT-IR analysis (carried out upon CO admission at 350°C after NO<sub>x</sub> adsorption at the same temperature) pointed out that almost all the nitrate bands already disappeared after 1 min: in parallel, carbonates were formed, along with new bands @ 2222 and 2164 cm<sup>-1</sup>, related to formation of N=C=O (isocyanates) and/or N≡C-O<sup>-</sup> (cyanates). These species are still present on the catalyst surface at the end of the reduction phase. Accordingly ISC and FTIR data indicate that under dry conditions nitrates were reduced in part to N<sub>2</sub>, and in part to adsorbed cyanates/isocyanates. Accordingly the observed evolution of reactants and products under dry conditions can be described by the following overall stoichiometries:



Data suggest that Ba(NCO)<sub>2</sub> species are intermediate in reaction (2) as well: after reduction of part of the nitrates by CO to Ba(NCO)<sub>2</sub> (reaction 1), nitrogen formation occurs via oxidation of Ba(NCO)<sub>2</sub> by other nitrate species. It is indeed well known that NCO species are oxidized to N<sub>2</sub> and CO<sub>2</sub> by oxidants like O<sub>2</sub> and/or NO<sub>x</sub>; accordingly the oxidation of cyanates is likely accomplished in this case by surface NO<sub>x</sub> species, this step being rate determining in N<sub>2</sub> formation.

The same experiments were also performed in the presence of water in the feed flow. ISC data showed that water greatly enhances the reactivity of CO: indeed, at 350°C the NO<sub>x</sub> removal efficiency was almost complete. Besides, significant amounts of ammonia and hydrogen were found among the products, together with nitrogen and CO<sub>2</sub>. FTIR spectra confirmed the promoting effect of water on the NO<sub>x</sub> removal by CO; besides, in the presence of water NCO species were not observed. Under wet conditions it may be speculated that a pathway for nitrate reduction may involve CO as the actual reducing agent of nitrates, leading to the formation of cyanate intermediate species. These species are then readily and completely hydrolyzed to ammonia which is eventually involved in the reduction of residual nitrates to N<sub>2</sub>, as suggested in [3]. However a different pathway may also be suggested, in which the actual reductant of the stored nitrates is hydrogen formed via the Water Gas Shift Reaction. Additional pathways can be suggested, possibly involving other N-containing reduced intermediates: these aspects are currently under investigation in our labs.

### Significance

A reaction pathway involving N=C=O species in the formation of N<sub>2</sub> has been pointed out, either by direct reaction with nitrates or following hydrolysis leading to NH<sub>3</sub>. The knowledge of the catalytic pathways involved in the reduction of nitrates by CO is pivotal for the optimization of the catalytic performances.

### References

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