

# Reduction of NO<sub>x</sub> by H<sub>2</sub> over Pt-K/Al<sub>2</sub>O<sub>3</sub> Lean NO<sub>x</sub> Trap catalysts

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## Introduction

Lean NO<sub>x</sub> Trap (LNT) catalysts are viable catalysts for the abatement of NO<sub>x</sub> emissions from lean-burn engines [1]. These systems work under periodic cyclic conditions, alternating lean (NO<sub>x</sub> storage) and rich conditions during which the stored NO<sub>x</sub> are reduced by a reductant. Although PtBa/Al<sub>2</sub>O<sub>3</sub> is a typical model catalyst for this application, systems containing K have also been proposed.

In previous studies the reduction with hydrogen of nitrates stored on a model PtBa/Al<sub>2</sub>O<sub>3</sub> catalyst has been investigated [2]. It has been shown that the formation of N<sub>2</sub> occurs via a 2-steps in series molecular pathway involving at first the formation of ammonia upon reaction of nitrates with H<sub>2</sub> (step 1), followed by the reaction of NH<sub>3</sub> with residual nitrates to give N<sub>2</sub> (step 2). Step 1 (i.e. the reduction of stored nitrates to NH<sub>3</sub>) is faster than step 2, the subsequent reaction of NH<sub>3</sub> with nitrates. Hence this step is rate determining in the formation of N<sub>2</sub>, and high NH<sub>3</sub> formation is observed at low temperatures where the reactivity of NH<sub>3</sub> towards nitrates is low. Besides, due to the high reactivity of H<sub>2</sub> towards nitrates, and due to the integral nature of the reactor, an H<sub>2</sub> front develops so that NH<sub>3</sub> which is formed at the front reacts with nitrates stored downstream the H<sub>2</sub> front, if the temperature is high enough. This explains the typical product sequence observed upon regeneration of LNT catalysts, with NH<sub>3</sub> evolution following that of N<sub>2</sub> [2].

Objective of this work is to investigate mechanistic aspects of the reduction process when a Pt-K/Al<sub>2</sub>O<sub>3</sub> system is employed, i.e. to analyze the effect of the storage component on the reduction of the stored NO<sub>x</sub>.

## Materials and Methods

NO<sub>x</sub> have been adsorbed on a model Pt-K/Al<sub>2</sub>O<sub>3</sub> catalyst at constant temperatures (350°C), feeding NO (1000ppm) in O<sub>2</sub> (3%) + He. NO<sub>x</sub> are stored primarily in the form of nitrates at this temperature [2]. The reduction of the stored NO<sub>x</sub> has been investigated in the presence of water (1% v/v) using H<sub>2</sub> or NH<sub>3</sub> as reductants. Temperature Programmed Surface Reaction experiments (H<sub>2</sub>-TPSR and NH<sub>3</sub>-TPSR) and Isothermal Step Concentration experiments at constant temperature (H<sub>2</sub>-ISC and NH<sub>3</sub>-ISC) have been carried out.

## Results and Discussion

The results obtained upon reduction of the stored NO<sub>x</sub> with H<sub>2</sub> at constant temperature (200°C, ISC experiments) show that nitrate species are readily reduced by H<sub>2</sub>; the reaction is very fast and is limited by the concentration of H<sub>2</sub>. N<sub>2</sub> represents the major reaction product; small amounts of ammonia have also been observed at the reactor outlet, after N<sub>2</sub> evolution. These results are very similar to those obtained in the case of the Pt-Ba/Al<sub>2</sub>O<sub>3</sub> catalyst sample [3], but in the case of the K-containing catalyst significantly lower amounts of

NH<sub>3</sub> have been formed. Accordingly the N<sub>2</sub> selectivity obtained upon reduction of stored nitrates in the case of the Pt-K/Al<sub>2</sub>O<sub>3</sub> catalyst sample is much higher than that measured over Pt-Ba/Al<sub>2</sub>O<sub>3</sub>.

The reduction of stored nitrates has also been investigated by TPSR experiments as well. In the case of H<sub>2</sub>-TPSR, H<sub>2</sub> consumption is observed starting from 80°C. Ammonia at first and N<sub>2</sub> later on are detected as reaction products. NH<sub>3</sub> formation precedes that of N<sub>2</sub>; then the NH<sub>3</sub> concentration decreases and N<sub>2</sub> evolution is observed, when the H<sub>2</sub> concentration approaches zero. A second NH<sub>3</sub> peak is seen at high temperatures. Notably, the temperature onset for H<sub>2</sub> consumption (80°C) is higher than that observed in the case of Pt-Ba/Al<sub>2</sub>O<sub>3</sub> (near 50-60°C).

TPSR have also been performed with NH<sub>3</sub>. Ammonia itself exhibits a significant activity in the reduction of the stored nitrates, with an onset temperature (near 120°C) which is slightly higher to that of H<sub>2</sub>. Complete selectivity to nitrogen is observed in this case. Accordingly these data are in line with the reduction mechanism already proposed in the case of PtBa/Al<sub>2</sub>O<sub>3</sub> [2], and supporting the occurrence of a 2-steps in series molecular pathway for the formation of N<sub>2</sub>. However, at variance with that observed in the case of the Pt-Ba/Al<sub>2</sub>O<sub>3</sub> sample, over the PtK/Al<sub>2</sub>O<sub>3</sub> catalyst the temperature onset for H<sub>2</sub> consumption to give NH<sub>3</sub> (step 1) is higher than that of Pt-Ba/Al<sub>2</sub>O<sub>3</sub> (80°C vs. 50-60°C) and is very close to the temperature threshold for the NH<sub>3</sub> + nitrate reaction to give N<sub>2</sub> (step 2) (80 vs 120°C). Therefore over PtK/Al<sub>2</sub>O<sub>3</sub> NH<sub>3</sub> is readily consumed once formed, and this might explain the higher selectivity to N<sub>2</sub> if compared to PtBa/Al<sub>2</sub>O<sub>3</sub>.

TPSR experiments have also been carried out by co-feeding H<sub>2</sub>+NH<sub>3</sub>. H<sub>2</sub> is consumed starting from 80°C with formation of ammonia. At temperatures slightly above 150°C, H<sub>2</sub> is abruptly consumed: a correspondent NH<sub>3</sub> consumption and N<sub>2</sub> production is observed. Notably, during N<sub>2</sub> production the H<sub>2</sub> concentration is nihil. The onset temperature for NH<sub>3</sub> consumption is higher than that recorded in the NH<sub>3</sub>-TPSR (150°C vs 120°C), suggesting that the presence of H<sub>2</sub> inhibits the reactivity of NH<sub>3</sub> towards nitrates. This has also been confirmed by other data, and points out a competition of H<sub>2</sub> and NH<sub>3</sub> for the activation at the noble metal sites. As a matter of fact, only when the H<sub>2</sub> concentration is nihil ammonia reacts with nitrates and N<sub>2</sub> formation is apparent. This indicates that in the two-steps in series molecular process for N<sub>2</sub> formation, the reaction of NH<sub>3</sub> with nitrates (step 2) is inhibited by the presence of H<sub>2</sub>. We note that the H<sub>2</sub> inhibition of the N<sub>2</sub> formation via step 2 does not imply a low N<sub>2</sub> selectivity during the isothermal reduction of nitrates since NH<sub>3</sub> reacts with NO<sub>x</sub> stored downstream the H<sub>2</sub> front, where the H<sub>2</sub> concentration is nihil. This further confirms the occurrence of the two steps process for N<sub>2</sub> formation; details on these aspects are currently under investigation in our labs.

## Significance

A molecular pathway is suggested for the removal of NO<sub>x</sub> stored on Pt-K/Al<sub>2</sub>O<sub>3</sub> catalysts, in which NH<sub>3</sub> is intermediate in N<sub>2</sub> formation. This pathway is in line with previous findings obtained in the case of Ba-based catalysts; besides, a specific inhibition of H<sub>2</sub> on the reactivity of NH<sub>3</sub> has also been pointed out.

## References

1. H. Shinjoh et al., *Appl.Catal. B:Environmental* 1998, 15, 189-201
2. L. Lietti, I. Nova, P. Forzatti, *J. Catal.*, 257 (2008) 270