

The release of NO_x stored over LNT catalysts: the first step of the reduction process

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Introduction

The reduction of NO_x stored on Lean NO_x Traps (LNT) has received a great attention in the last years. It is generally believed that the reduction of stored NO_x over NSR catalysts implies at first the release of NO_x from the catalyst surface in the gas-phase, followed by the fast reduction of the released NO_x to N₂ or other products. The mechanisms leading to the release of NO_x in the gas phase and their subsequent reduction is still under debate. Three main reasons can be individuated to cause the NO_x release: i) the heat generated by the exothermic reactions upon switching to the regenerating gases (thermal release) [1]; ii) the decrease in the equilibrium stability of the stored nitrates due to the decrease in the partial pressure of NO and /or oxygen (thermodynamic release) [2]; iii) the establishment of a net reducing environment (chemical release) [3]. Previous studies from our group pointed out that the last one is a Pt-catalyzed process involving surface species that are reduced prior their thermal desorption.

Investigations on the processes leading to the release of NO_x are rather scarce in the literature; besides, the NO_x release can be hardly separated from the subsequent reduction steps since in the presence of a reductant the released NO_x are readily reduced to N₂ and other species. Accordingly it is difficult to investigate the NO_x release process decoupled from the subsequent reduction step. This is the goal of this work, where ¹⁵NO isotopic labeling experiments have been carried out as a technique to study the NO_x release decoupled from the NO_x reduction. Accordingly NO_x have been stored on the catalyst surface starting from unlabelled NO and then exchanged with gas-phase labelled NO. The reactivity of different surface species (nitrites and nitrates) has been investigated, and the role of the noble metal (Pt) and of the presence of reductants have been addressed as well. The results obtained in these experiments have been compared with those collected during the thermal decomposition of the same species.

Materials and Methods

Nitrites and nitrates have been stored onto Pt-Ba/Al₂O₃ and Ba/Al₂O₃ catalyst samples starting from unlabelled NO/O₂ or NO₂ adsorption. After adsorption, the NO_x surface species have been contacted with ¹⁵NO and heated under temperature programming (Temperature Programmed Isotopic Exchange, TPIE). Similar experiments have been also carried out under inert atmosphere (TPD) and in the presence of reductants as well (Temperature Programmed Surface Reaction, TPSR) with H₂, CO, HC.

Results and Discussion

Temperature Programmed Isotopic Exchange (¹⁵NO-TPIE) of both unlabelled nitrites and nitrates (figure 1) showed that: i) both nitrites and nitrates are able to exchange with the gas phase; ii) the isotopic exchange reaction is already effective at a temperature well

below of the onset decomposition temperature measured by TPD (50°C vs. 130°C for nitrites; 260 °C vs. 330 °C for nitrates); iii) the onset of the isotopic exchange of nitrites is lower than that of nitrates, underlining a higher reactivity of nitrites with respect to nitrates; iv) Pt is necessary for the exchange between gaseous NO and stored NO_x species (the reaction is not observed in the case of a Pt-free sample), i.e. the isotopic exchange is a Pt-catalyzed reaction.

It can be argued that the presence of reduced Pt sites drives the decomposition of the NO_x stored species, leading to NO and PtO_x species. This reaction is reversible and involves gaseous ¹⁵NO, leading to the NO/¹⁵NO exchange of nitrites and nitrates. Notably, the isotopic exchange is an internal redox process during which the release and exchange between gas phase and surface take place leaving unchanged the PtO_x / Pt ratio, that is the isotopic exchange process does not involve a change in the oxidation state of Pt. The ¹⁵NO exchange is observed at much lower temperatures if compared to the thermal decomposition of the stored NO_x (TPD) ¹⁵NO because during TPD, upon decomposition of the adsorbed species, the Pt sites becomes oxidized and this blocks the process.

When a reductant is present, its role is to keep Pt sites in a reduced state and this leads to the low-temperature decomposition of the stored NO_x species. The evolved NO is then readily reduced to N₂ and other species by the reductant. Notably, in the case of poorly reactive reductants (e.g. CO, hydrocarbons) the released NO is not consumed and this leads to the NO “puff” which is observed at the beginning of the rich phase (and to N₂O formation as well).

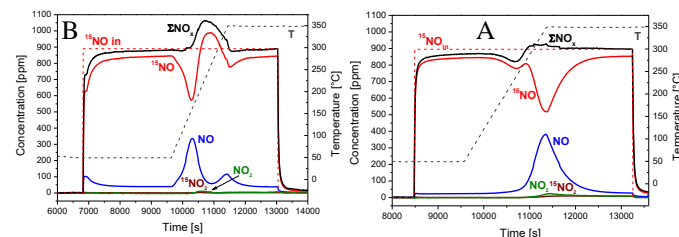


Figure 1. ¹⁵NO-TPIE in He from 50 to 350°C, 10°C/min, after ¹⁴NO_x adsorption at 350°C (A) and 150°C (B) of 1000 ppm NO + O₂ 3% v/v in He, over Pt-Ba/Al₂O₃ catalyst

Significance

The reactivity in the NO release (i.e. the first step in the reduction) of nitrites and nitrates adsorbed NO_x species is characterized by ¹⁵NO exchange experiments. Nitrites show higher reactivity than nitrates, in line with their higher reactivity during the reduction.

References

- [1] K.S. Kabin, R.L. Muncief, M.P. Harold, Catal. Today 96 (2004) 79
- [2] Z. Liu, J.A. Anderson, J. Catal. 224 (2004) 18
- [3] N.W. Cant, M.J. Patterson, Catal. Lett.85 (2003) 153

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Lean NO_x Traps (LNTs): pathways in the reduction of stored NO_x

• Mechanistic aspects of the reduction of stored NO_x are still under debate

Possible steps:

- I – release of stored NO_x from catalyst surface to gas-phase NO_x (surface diffusion / mobility of stored NO_x, spillover of reductant)
- II - reduction of released NO_x over Pt

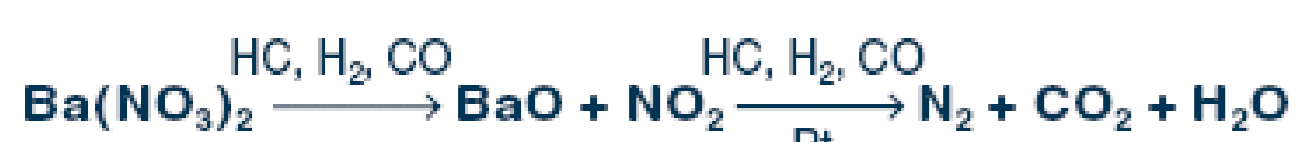
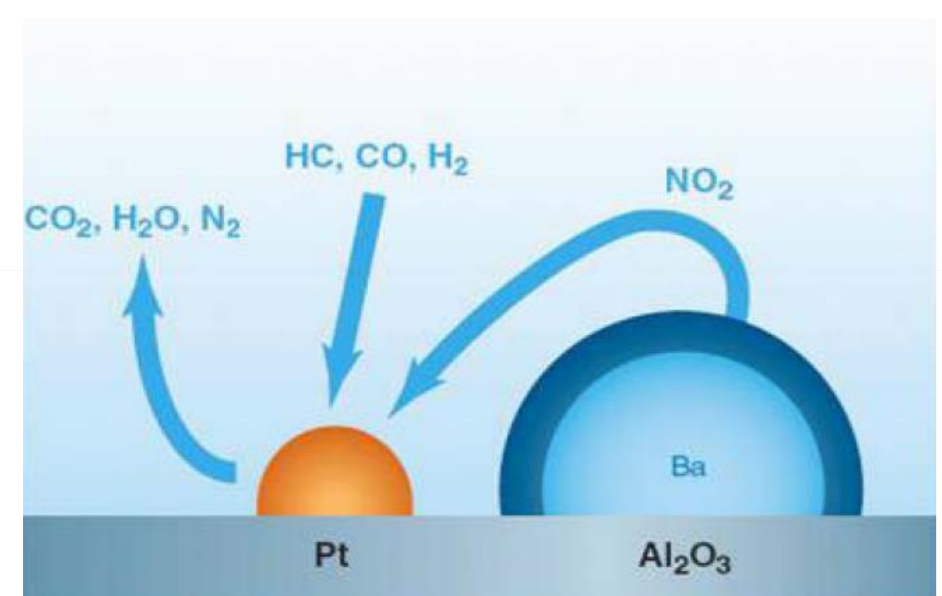
Possible driving force of NO_x release :

- heat of reductant combustion reactions (THERMAL RELEASE)
- decrease of equilibrium stability of NO_x due to decrease of P_{O₂} and P_{NO} (THERMODYNAMIC RELEASE)
- establishment of net reducing environment (CHEMICAL RELEASE)

• Open issues:

- Pathways of NO_x release not clarified yet since NO_x release and subsequent reduction can be hardly decoupled

➔ **¹⁵NO/NO Isotopic exchange technique has been used to investigate independently the two steps**

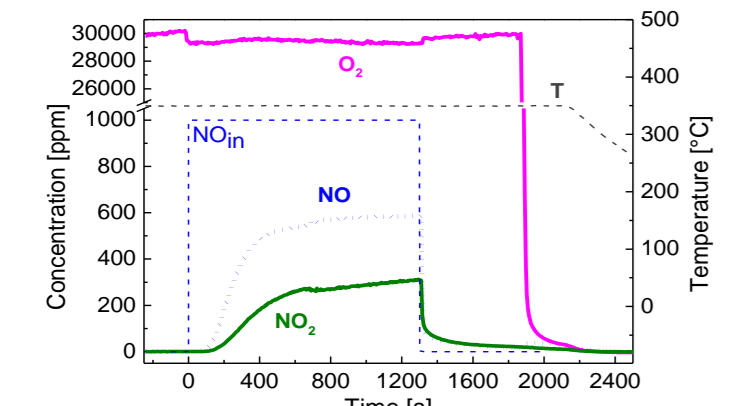


Methods

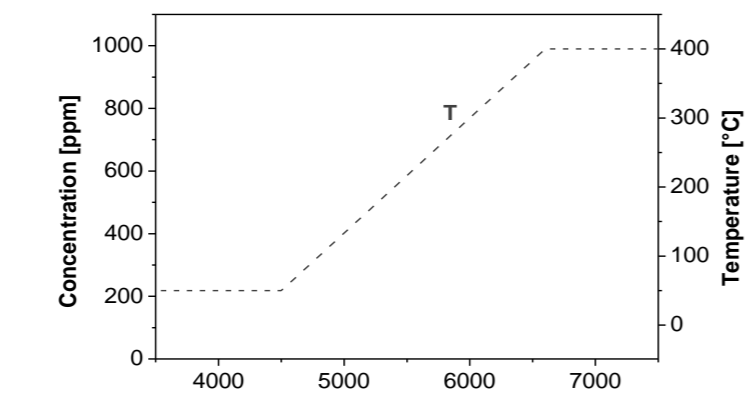
• Catalysts: Pt-Ba/Al₂O₃ (Pt=1% w/w; Ba=16% w/w) and Ba/Al₂O₃ (Ba=16% w/w) prepared by incipient wetness impregnation of commercial γ-Al₂O₃ calcined at 700°C

¹⁴NO_x storage

¹⁴NO/O₂ adsorption at 150°C (nitrites), at 350°C (nitrates) *



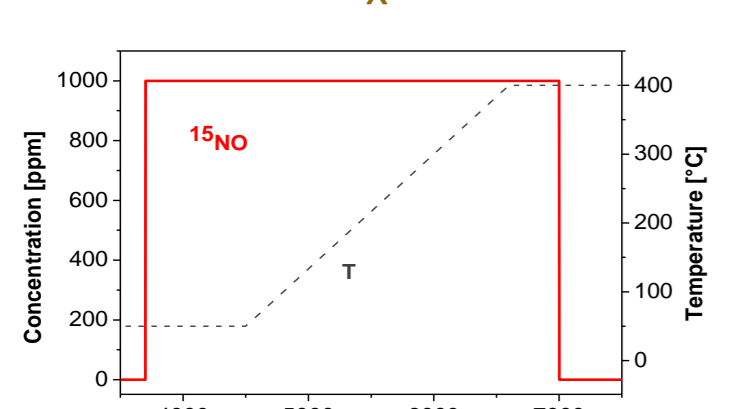
Temperature Programmed Desorption of stored NO_x (nitrites and nitrates)



Exposure to inert flow under T programming

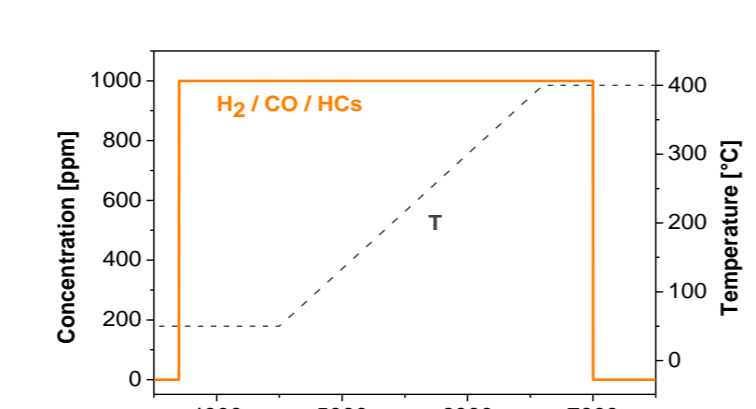
TPIE

Temperature Programmed ¹⁵NO/¹⁴NO Isotopic Exchange experiments with stored ¹⁴NO_x (nitrites and nitrates)



Exposure to ¹⁵NO under T programming

reactivity of reductant with adsorbed ¹⁴NO_x nitrates



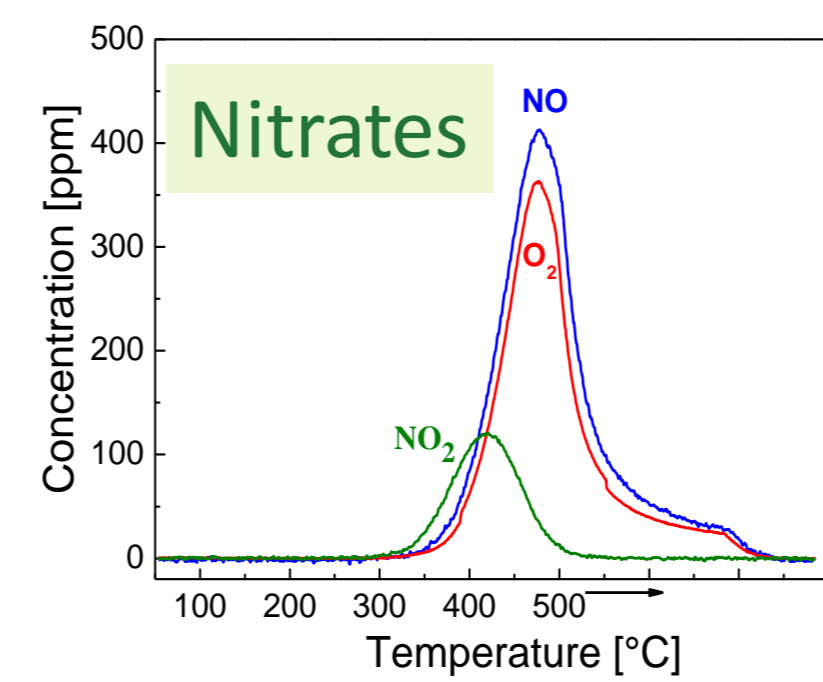
Exposure to reductant (H₂, CO, HCs) under T programming

* : In the case of Ba/Al₂O₃: ¹⁴NO₂ adsorption at 350°C

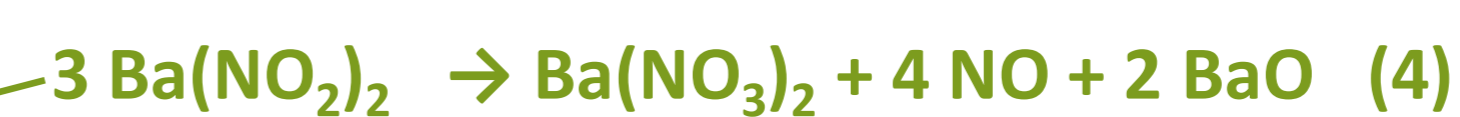
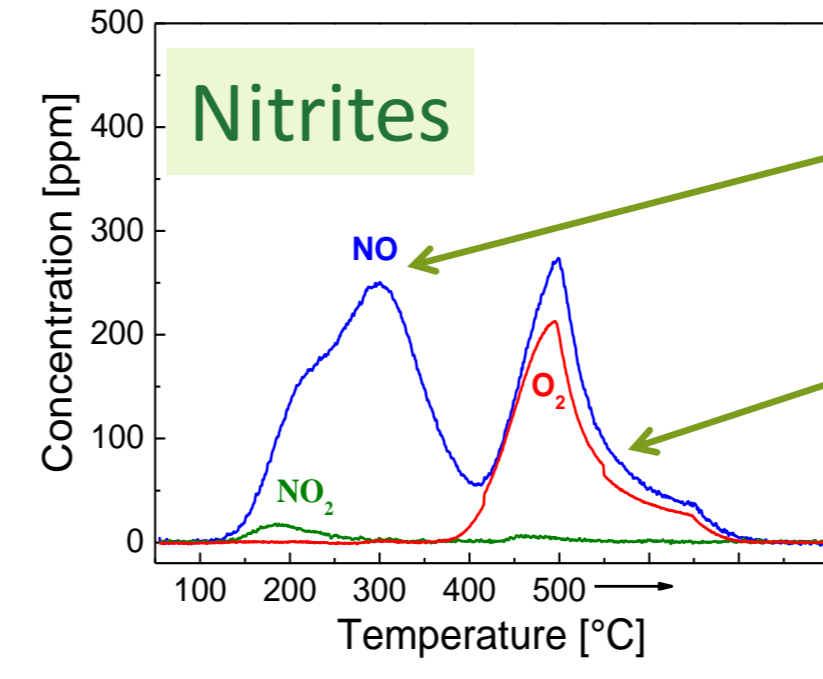
TPD: NO_x thermal release

PtBa/Al₂O₃

Heating from 50°C to 500°C in inert flow after NO/O₂ adsorption at 350°C and 150°C



• onset thermal decomposition (T_{DEC}) of nitrates ~ 320°C (near T_{ADS})



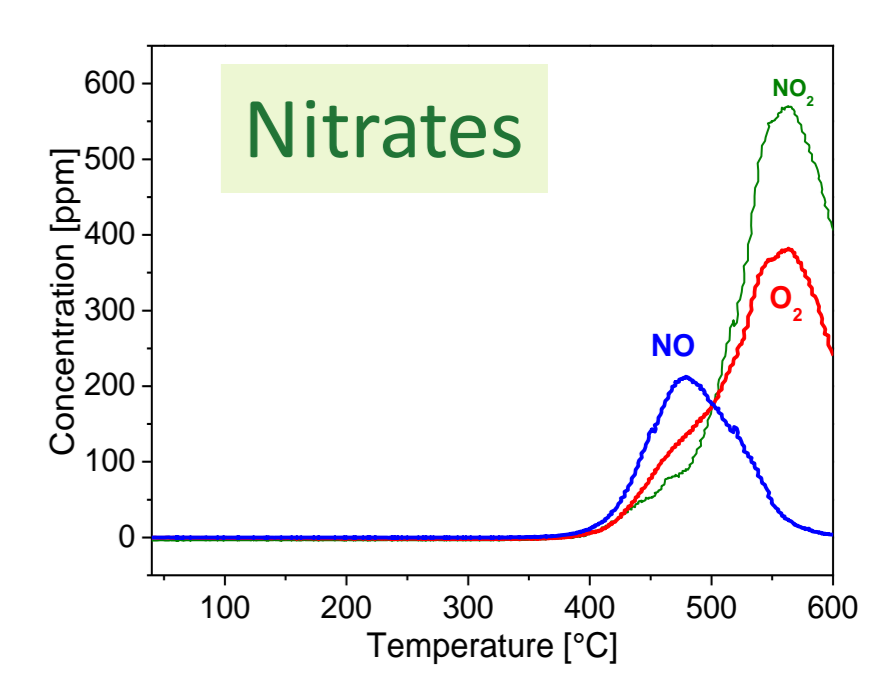
Reactions (1), (2), (3)

- nitrites T_{DEC} ~ 125°C (near T_{ADS})
- nitrites are converted into nitrates that decompose in the high T region

- T_{ADS} rules the onset T for the decomposition of stored NO_x; nitrites are less stable than nitrates
- thermal decomposition does not require Pt. Pt favors the nitrate decomposition

Ba/Al₂O₃

Heating from 50°C to 600°C over in inert flow after NO₂ adsorption at 350°C



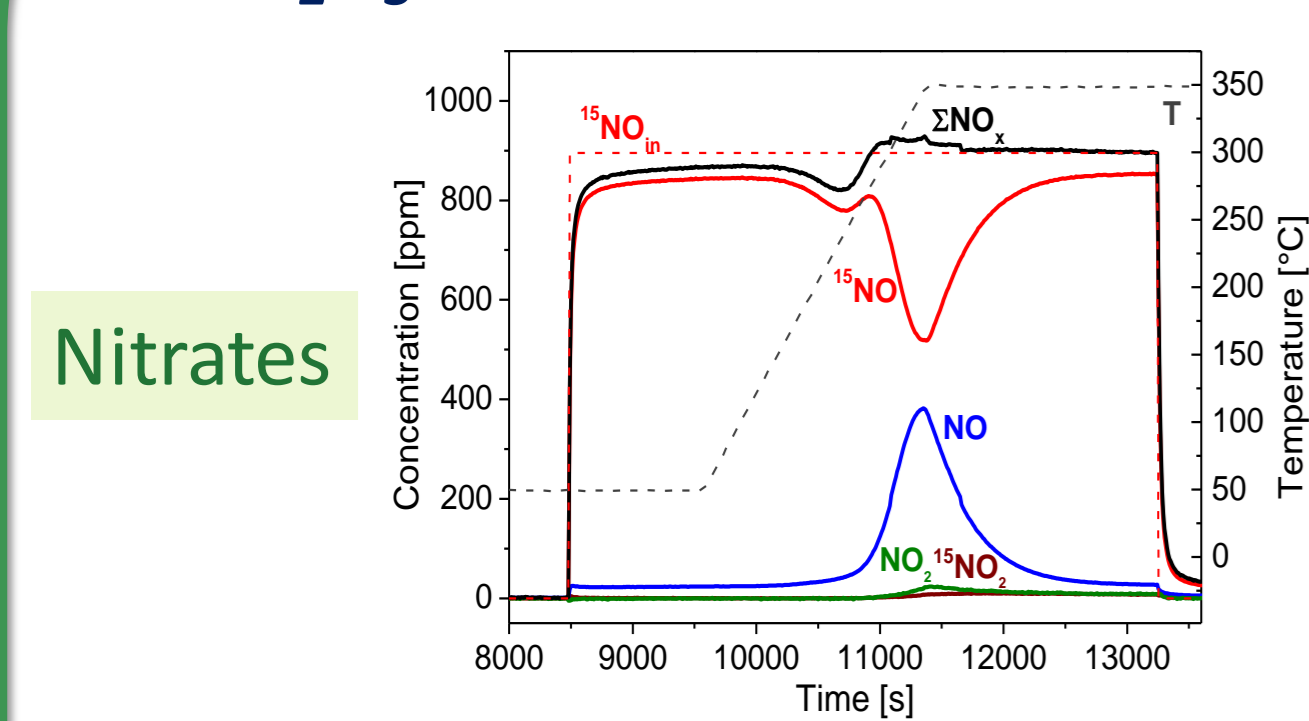
Without Pt:

- slightly higher T_{DEC}
- full decomposition attained after longer time at higher T (600°C vs 500°C)

Pt role

¹⁵NO/NO isotopic exchange

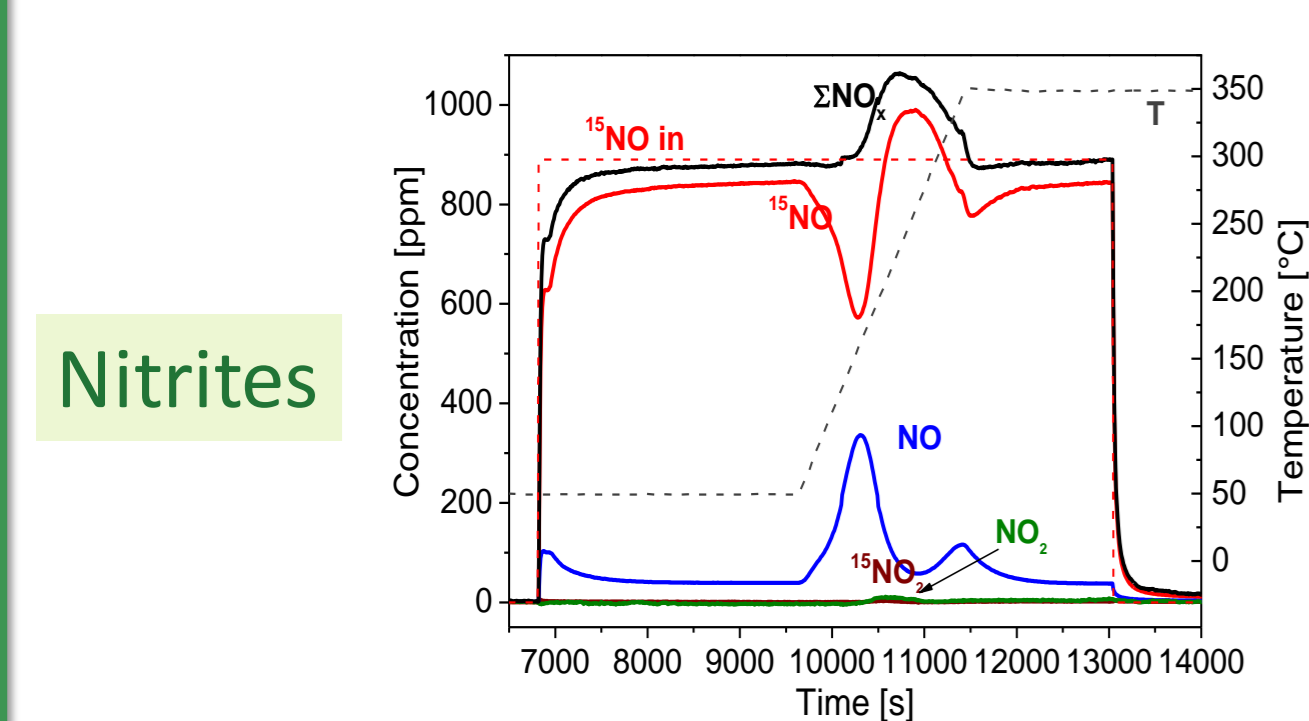
PtBa/Al₂O₃ Heating from 50°C in ¹⁵NO after NO/O₂ adsorption at 350°C



- ¹⁵NO/¹⁴NO exchange from 200-250 °C, i.e. below T_{ADS} & T_{DEC} (~350°C)



PtBa/Al₂O₃ Heating from 50°C in ¹⁵NO after NO/O₂ adsorption at 150°C



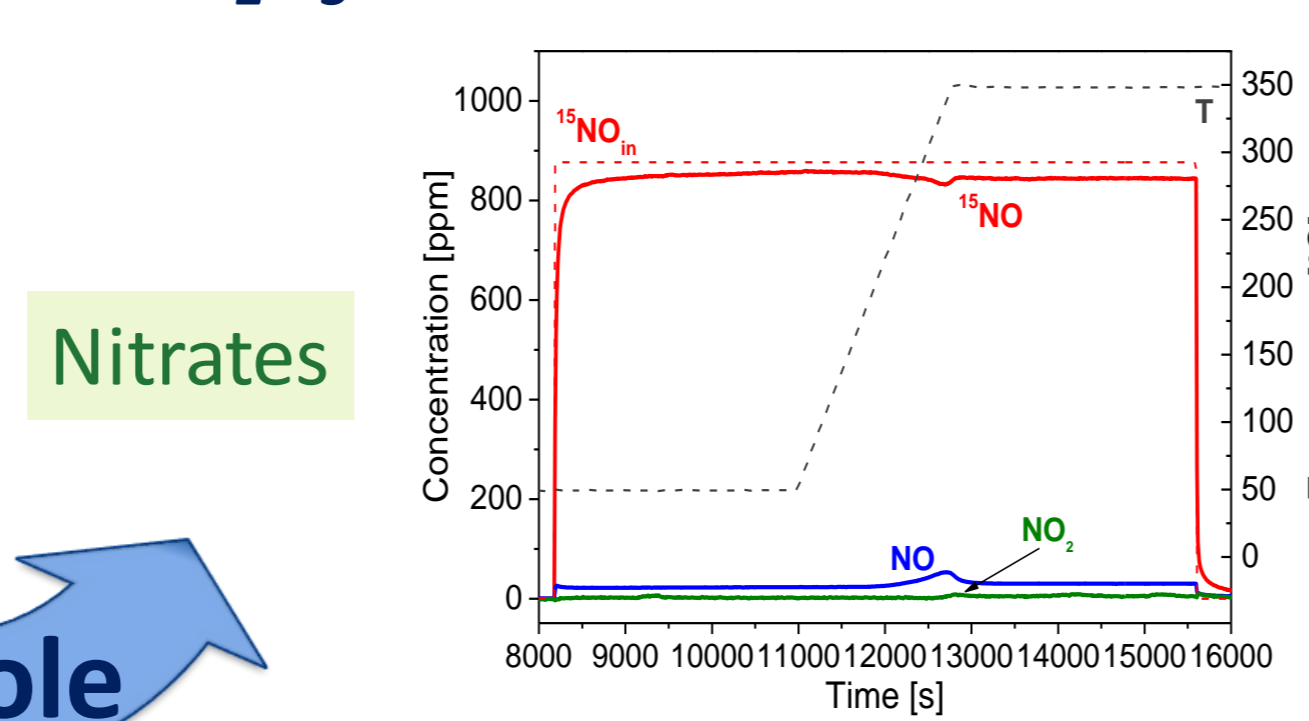
- ¹⁵NO/¹⁴NO exchange observed already at 50°C, well below T_{ADS} & T_{DEC} (~150°C)
- almost complete exchange reached at 250°C



- the ¹⁵NO/¹⁴NO exchange occurs at T < T_{ADS} & T_{DEC}; nitrites are more readily exchanged than nitrates

Pt role in isotopic exchange

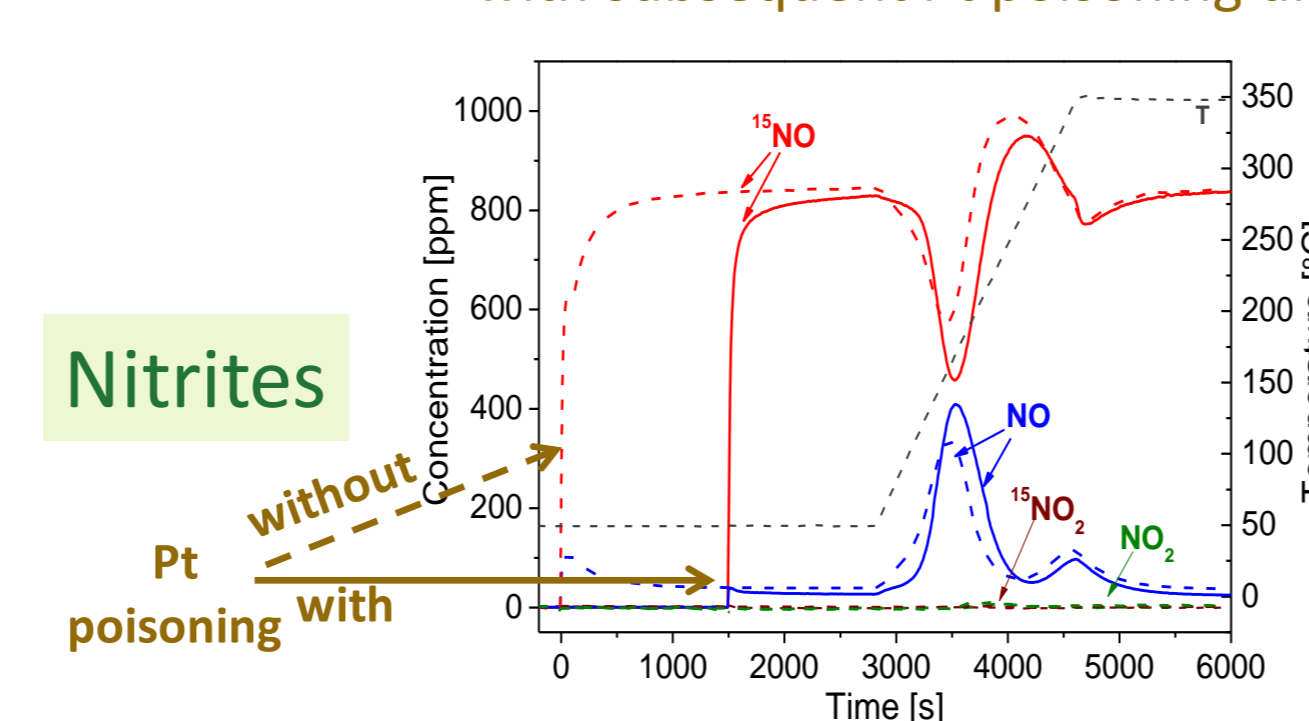
Ba/Al₂O₃ Heating from 50°C in ¹⁵NO after NO₂ adsorption at 350°C



- the ¹⁵NO/¹⁴NO exchange does not occur in the absence of Pt

Pt role

PtBa/Al₂O₃ Heating from 50°C in ¹⁵NO after NO/O₂ adsorption at 150°C with subsequent Pt poisoning under CO exposure at RT

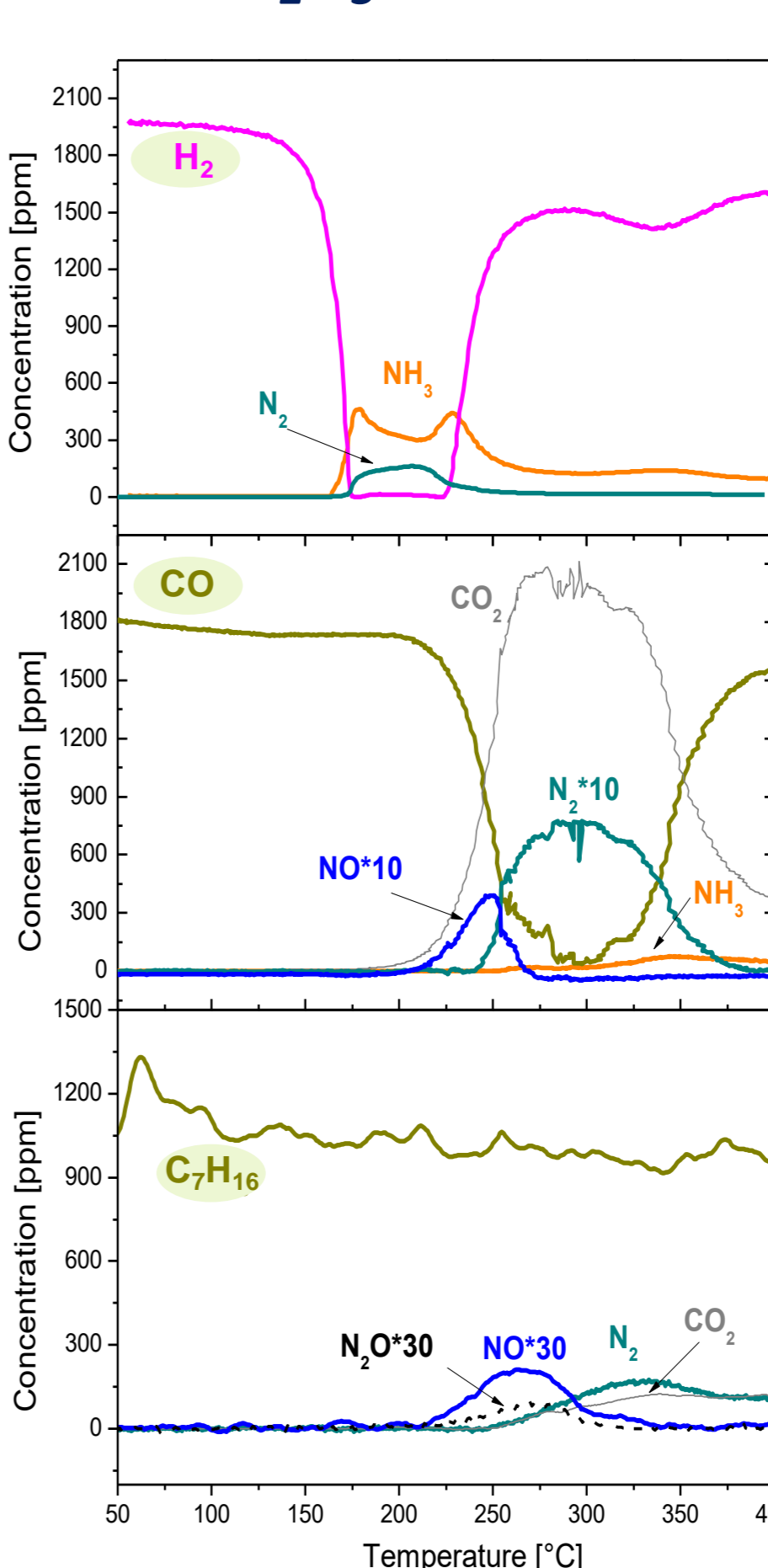


- After CO poisoning, ¹⁵NO/¹⁴NO exchange :
- at 50°C is almost negligible
- up to 160°C occurs at lower rate

- the ¹⁵NO/¹⁴NO exchange is a Pt catalyzed reaction

TPSR: NO_x chemical release

PtBa/Al₂O₃ Heating from 50°C in H₂/CO/n-C₇ after NO/O₂ adsorption at 350°C



By increasing the reducing power of the reagent (H₂ >> CO > n-C₇) the reduction onset T decreases (always well below T_{ADS} & T_{DEC} ~350°C)

- the reductant role is to keep Pt in a reduced state favoring NO_x release, thus ruling the reactivity of the reduction (and selectivity)

Conclusive remarks

- The reduction of stored NO_x is a two step process involving the release of NO_x and the subsequent reduction of the released NO_x
- The NO_x release is a Pt-catalyzed reaction, as pointed out by TPD and TPIE experiments. It involves the spillover of NO_x towards Pt with subsequent decomposition, whose rate limiting factor is the removal of O from Pt
- The reduction of stored NO_x is a Pt catalyzed reaction and the presence of reduced Pt sites is the driving force for the onset of the reduction process. According to one mechanism, stored NO_x are released at Pt sites, possibly with formation of NO or NO-related intermediates thus reduced to the reaction products (N₂, N₂O, NH₃)
- The role of the reductant is to keep Pt in a reduced state permitting the NO_x release and its ability to give and maintain reduced Pt sites rules the rate and the selectivity of the reduction

