

Interaction between soot and stored NO_x during operation of LNT Pt-K/Al₂O₃ catalysts

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Introduction

The reduction of both soot and NO_x emissions from diesel vehicles is nowadays mandatory to cope with the next coming emission standards. The potential use of LNT catalyst in the simultaneous removal of soot and NO_x has been proposed according to the DPNR concept. The aim of the present study is to analyse the effects of the presence of soot on the behaviour of the PtK/Al₂O₃ LNT catalysts and in particular to provide new insights on the interaction between soot and the stored NO_x during the De-soot and De-NO_x activity of the catalyst.

Experimental

Home made PtK/Al₂O₃ catalyst was prepared by impregnation of γ -alumina. De-NO_x and De-soot activity has been investigated by performing lean-rich cycles at constant temperature (rectangular step feeds of 1000 ppm of NO, in He and O₂ alternated with 4000 ppm of H₂ in He, in the presence of CO₂ and water), in the range 250-350°C. The interaction between soot and the stored NO_x species has been investigated by temperature programmed methods under inert flow (TPD) or in O₂ (TPO). These experiments have been also carried out over a platinum-free catalyst (e.g. K/Al₂O₃) in order to assess the role of Pt.

Main results

Lean NO_x adsorption performed at 350°C over Pt-K/Al₂O₃ in the absence and presence of soot, is shown in Fig. 1A and 1B, respectively. In both cases NO_x dead time is observed, showing that the catalytic system is able to store NO_x even in the presence of soot. However the amounts of NO_x stored up to steady-state in the presence of soot are lower than those measured in the absence (0.38 vs 0.58 mmol/gcat) pointing out the negative impact of soot on De-NO_x activity. The evolution of CO₂ in the absence of soot is uniquely due to the decomposition of surface carbonates upon NO_x uptake. Besides the huge evolution of CO₂ measured in the presence of soot reflects both the carbonates decomposition and the soot oxidation capability of the samples. Accordingly, the NO₂ concentration measured at the

reactor outlet is significantly lower in the presence of soot because of to the participation of NO_2 in soot oxidation. Notably, upon NO and O_2 shutoff, a release of NO_x takes place due to the desorption/decomposition of the NO_x species previously

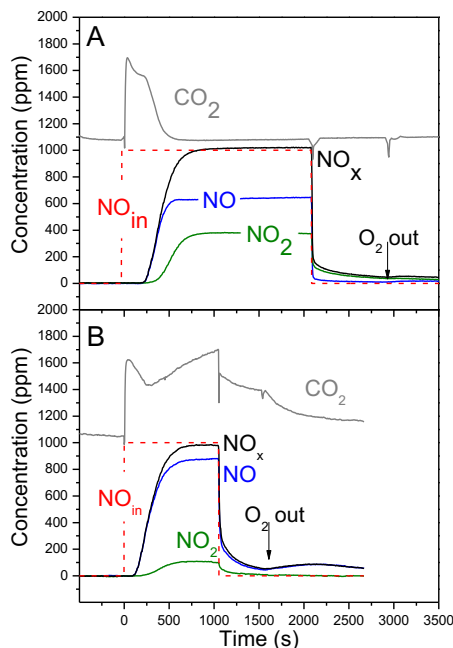


Figure 1- Results of NO (1000ppm)/O₂(3%) adsorption over Pt-K/Al₂O₃ (A) and Pt-K/Al₂O₃/soot (B), in presence @ 350°C

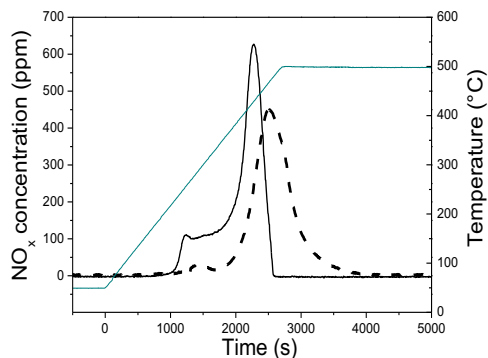


Figure 2 - TPD after NO_x adsorption at 350°C over PtKAl/Al₂O₃ in the absence (dashed lines) and in the presence of soot (solid lines)

stored. In the presence of soot both desorption contributions appear more remarkable thus indicating a destabilizing effect of soot on the NO_x species adsorbed onto the catalytic surface.

TPD/TPO experiments of the stored nitrates in the presence and in the absence of soot have been carried out to gain further insight into the effect of soot on the adsorbed NO_x species and in particular on their stability/reactivity. The results of the TPD runs carried out in the absence and in the presence of soot (dashed and solid lines, respectively) over pre-nitrated Pt-K/Al₂O₃ are shown in Fig. 2, in terms

of NO_x concentrations. In the absence of soot the NO_x decomposition is observed mainly above 350 °C (i.e. the NO_x adsorption temperature). Notably, in presence of soot the decomposition of nitrates is shifted at lower temperatures, e.g. near 250°C. The concomitant CO_2 production (not shown) indicates the occurrence of soot oxidation.

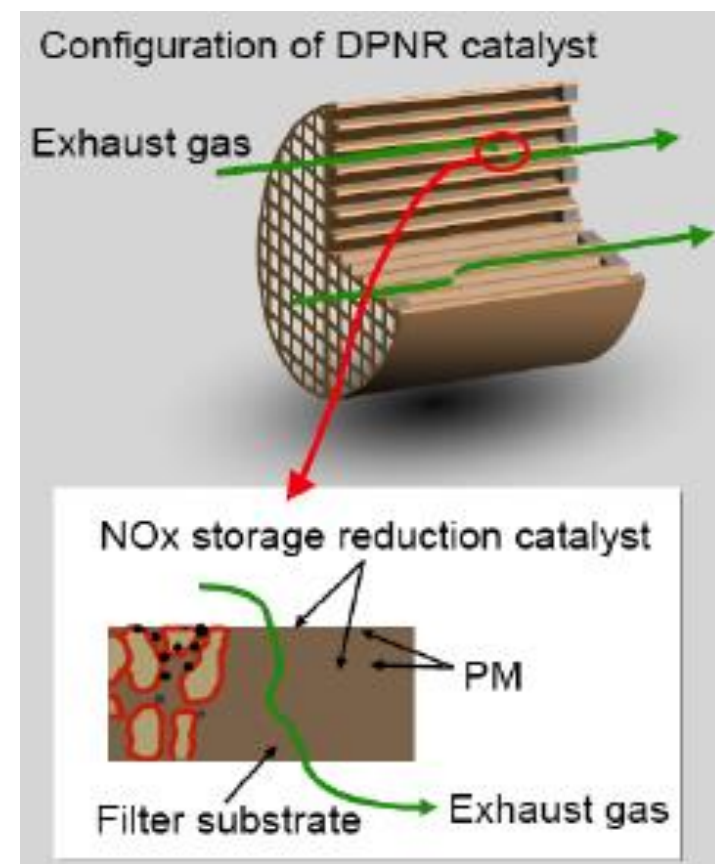
The same experiments performed over K/Al₂O₃ indicate that even in the absence of the noble metal, soot reacts with the NO_x ad-species that, in fact, decompose at lower temperatures if compared to the soot-free sample. Hence, clear indication on the occurrence of a surface reaction involving soot and the stored nitrates has been pointed out by TPD experiments, leading to soot oxidation (and nitrates reduction). This reaction possibly involves the surface mobility of the stored nitrates, soot particles being the driving force for the process and acting as reduced centres. Finally, this pathway parallels the oxidation of soot by NO_2 that occurs in the presence of gas-phase NO_2 , i.e. upon the NO_x storage during lean/rich operation of the LNT catalyst.

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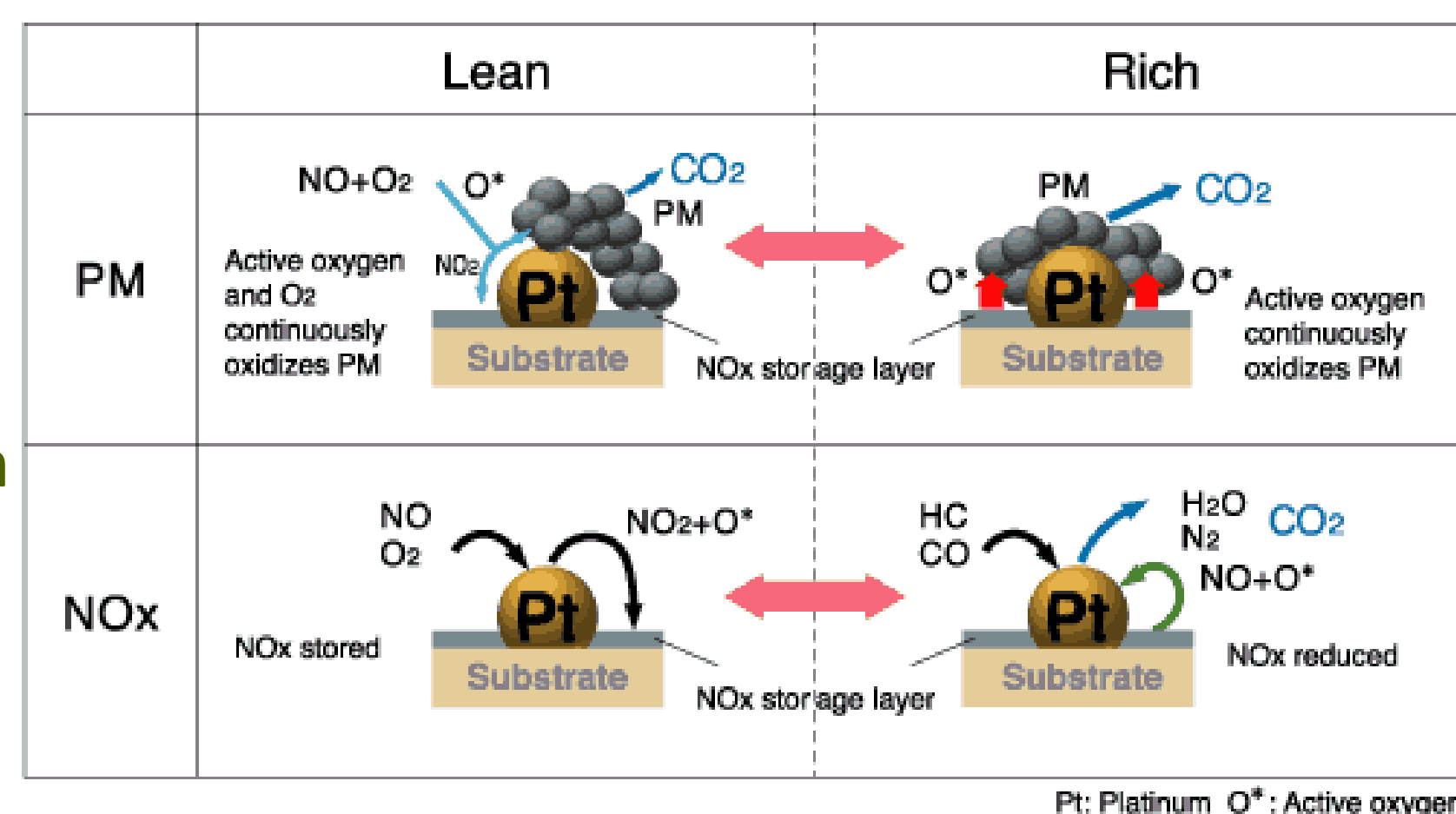
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Diesel Particulate-NO_x Reduction (DPNR) system



DPNR system is a novel after-treatment technology for the simultaneous removal of NO_x and diesel soot that consists in a catalytic wall-through filter coated with a NSR (NO_x Storage-Reduction) catalyst

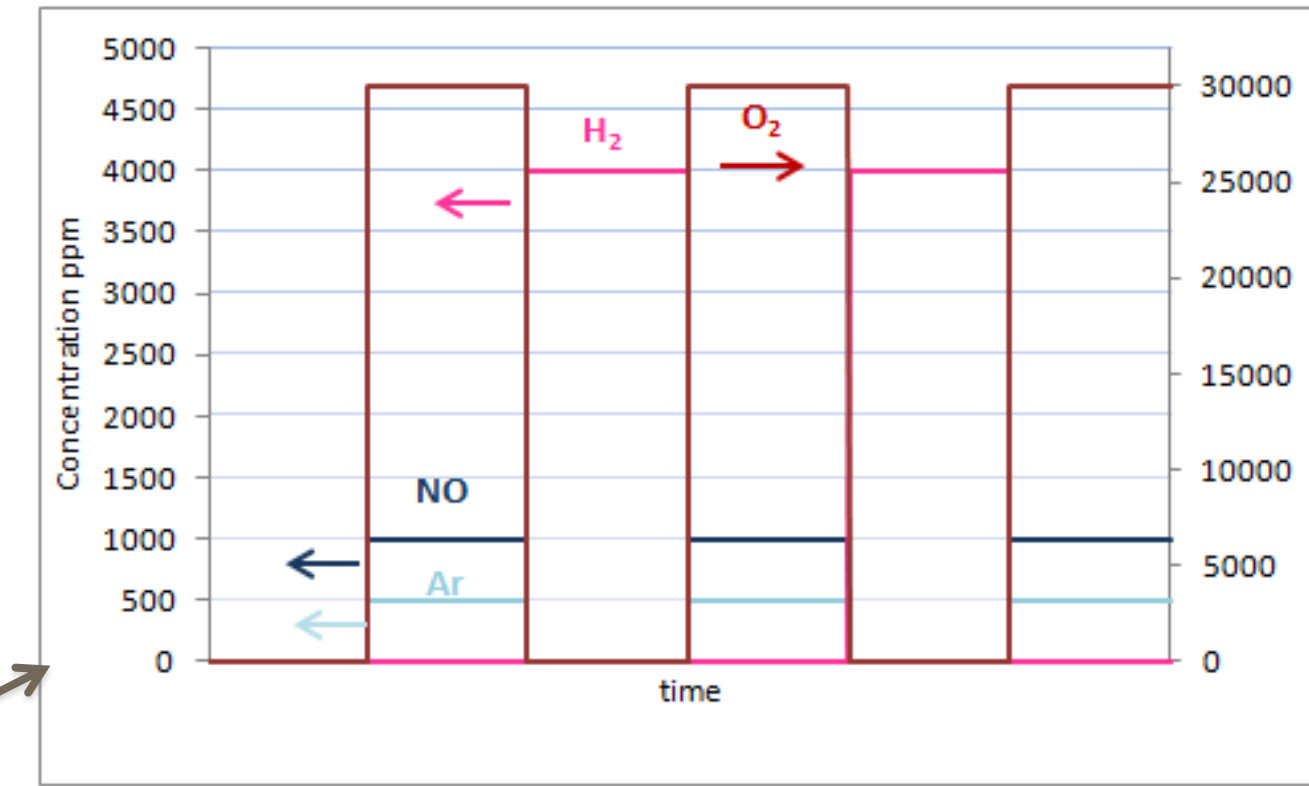


Materials and Techniques

Catalyst Pt-K/γAl₂O₃ (1 % Pt, 5.4 % K, w/w, γ-Al₂O₃)

Preparation technique: incipient wetness impregnation

Soot Printex U (Degussa) mixed with catalyst catalyst/soot ratio: 9/1w/w (loose contact)



•Micro-flow reactor studies

Transient Response Method (TRM)

NO_x storage @ 350° C: 1000 ppm NO in 3%O₂ + 1% H₂O + 0,1% CO₂;

Regeneration @ 350° C: 4000 ppm H₂ in 1% H₂O + 0,1% CO₂

Temperature Programmed Desorption (TPD)

Heating from 50 to 500° C (10° C/min) with 1% H₂O and 0,1% CO₂ in Helium

Temperature Programmed Oxidation (TPO)

Heating from 50 to 400° C (10° C/min) with 1% H₂O and 0,1% CO₂ with 3% O₂ in Helium

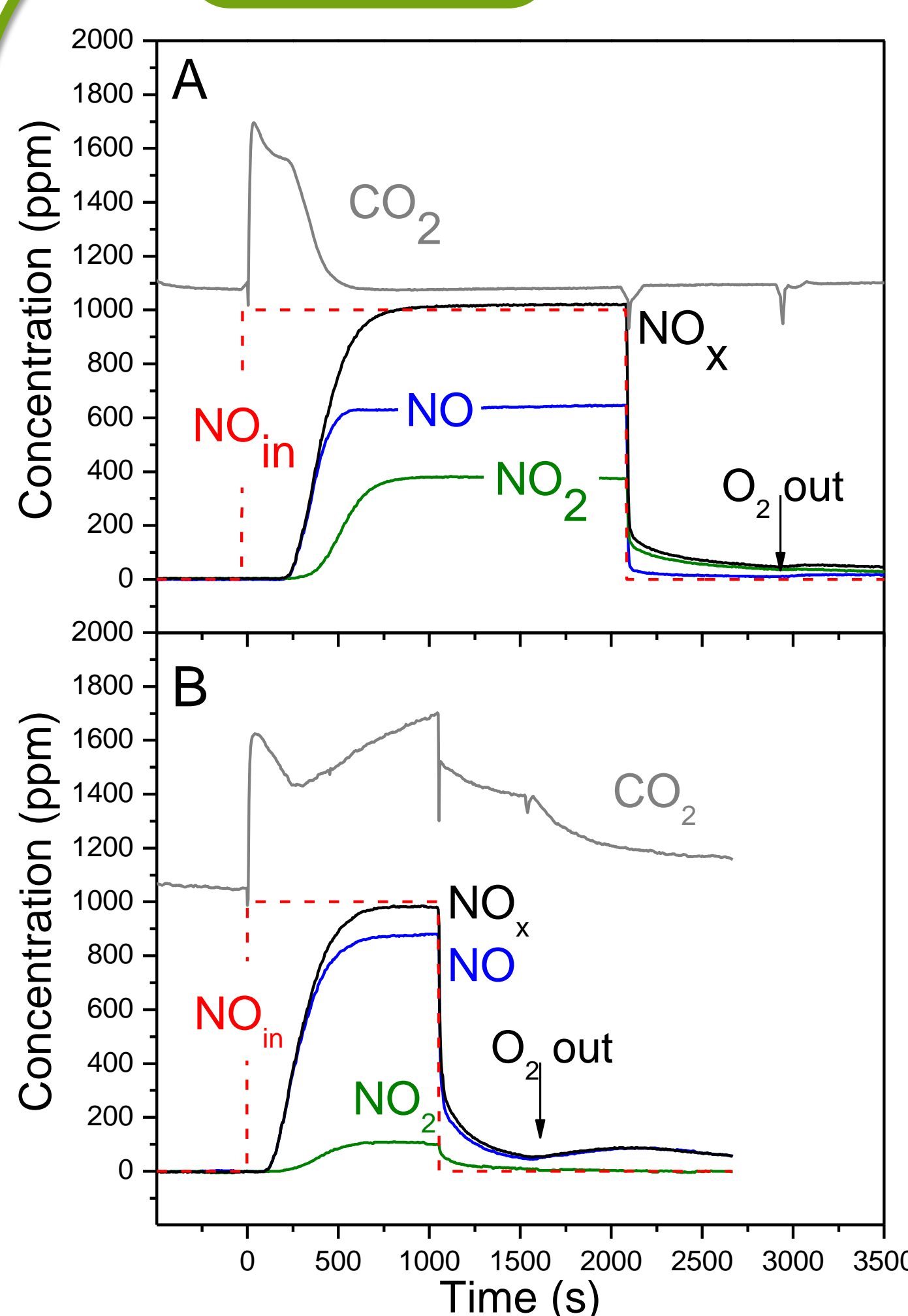
Temperature Programmed Surface Reaction (TPSR)

Heating from 50 to 400° C (10° C/min) with 1% H₂O and 0,1% CO₂ with 4000ppm H₂ or 660ppm NH₃

- Analysis of catalytic performance of the system Pt-K/γ-Al₂O₃ in presence of soot in the typical operative conditions
- new insights on the interplay existing between soot and NO_x removal (DeNO_x/Desoot)

TRM

Adsorption phase @ 350° C



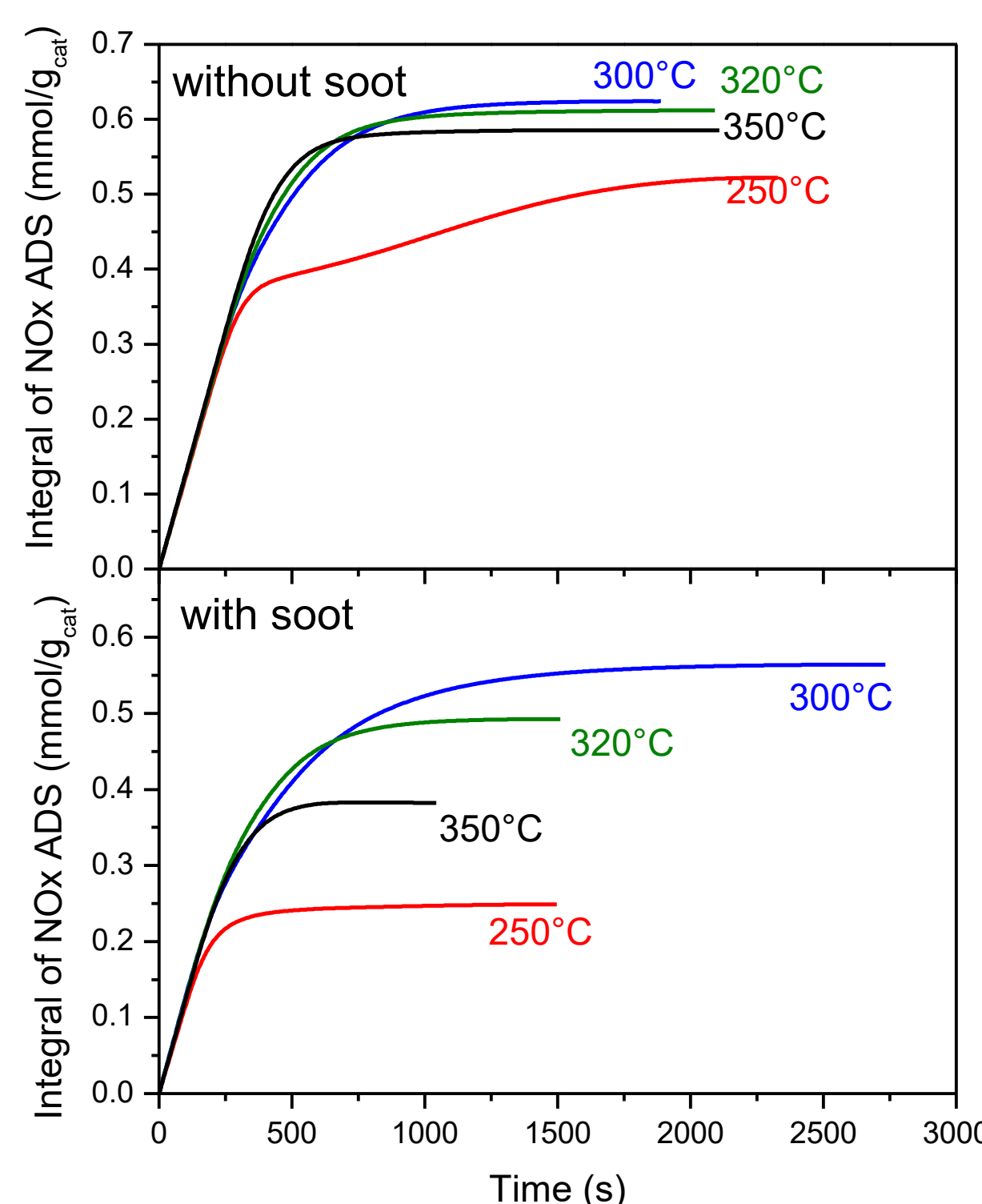
A_ WITHOUT SOOT

- Initial complete NO_x uptake
- NO oxidation to NO₂
- CO₂ release upon NO_x storage due to Ba carbonate decomposition:
 $K_2CO_3 + 2 NO + 3/2 O_2 \rightarrow 2 KNO_3 + CO_2$

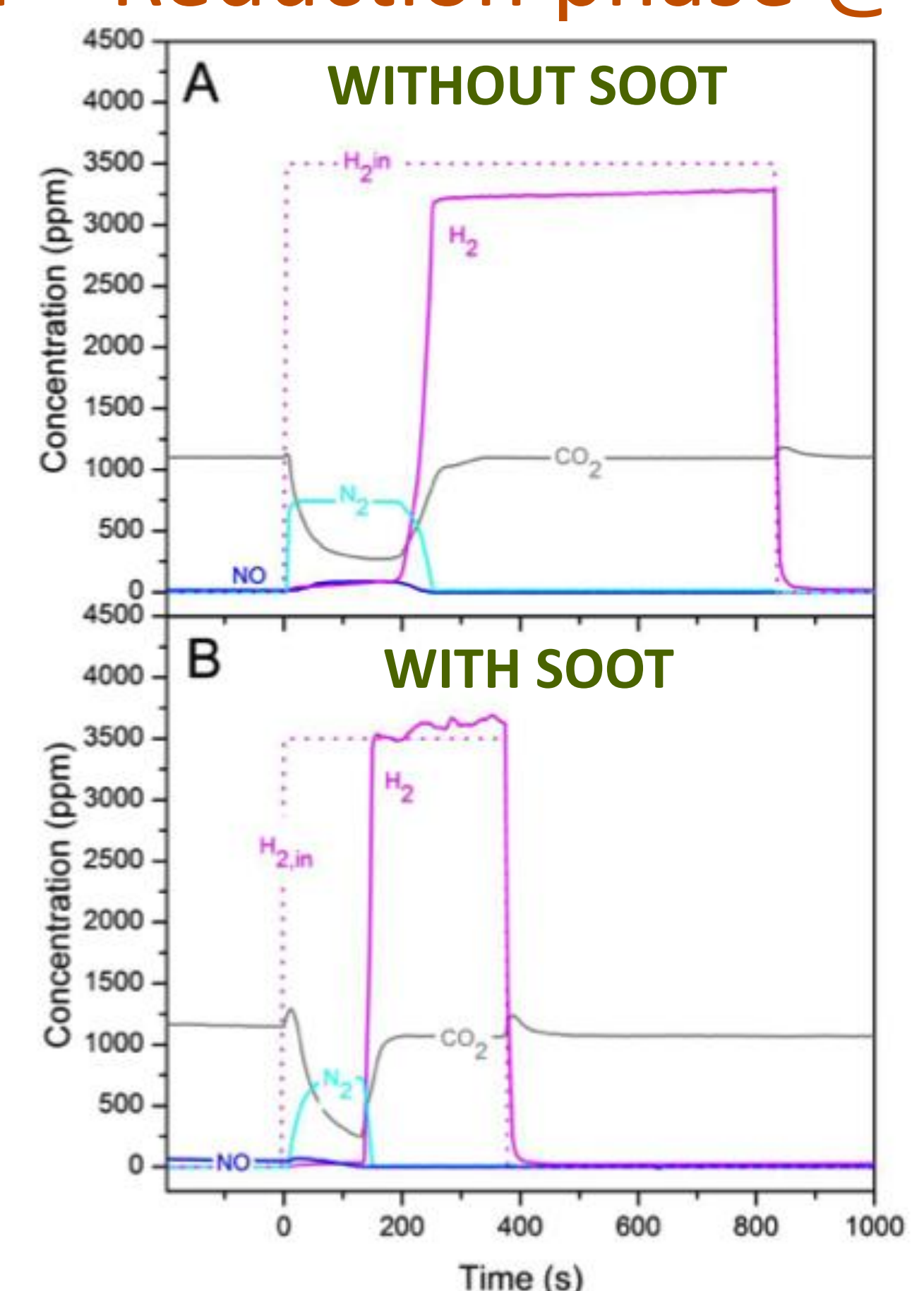
B_ WITH SOOT

- Soot oxidation upon NO admission (net CO₂ production)
- Lower NO₂ production
- Decrease of NO_x storage
- Higher NO_x release in the presence of soot (upon decreasing the NO inlet concentration)

EFFECT OF TEMPERATURE



TRM – Reduction phase @ 350° C

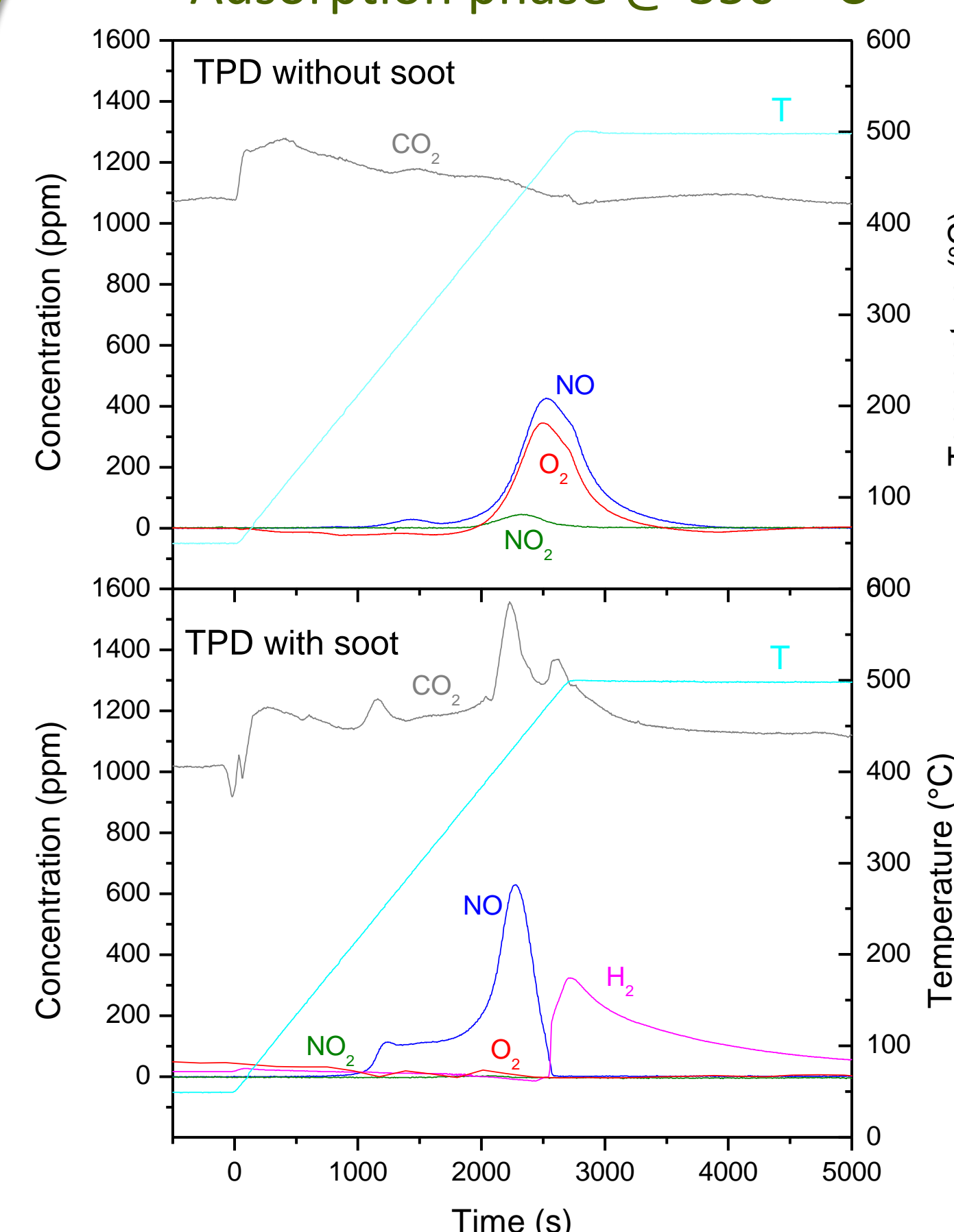


- CO₂ uptake due to K₂CO₃ formation
 $2 KNO_3 + 8 H_2 + CO_2 \rightarrow 2 NH_3 + K_2CO_3 + 5 H_2O$
 $6 KNO_3 + 10 NH_3 + 3 CO_2 \rightarrow 8 N_2 + 3 K_2CO_3 + 15 H_2O$

- The presence of soot decreases the **storage capacity** of the catalytic system measured at different T
- Reduction of nitrates: no significant differences in the presence of soot

TPD

Adsorption phase @ 350° C



A_ WITHOUT SOOT

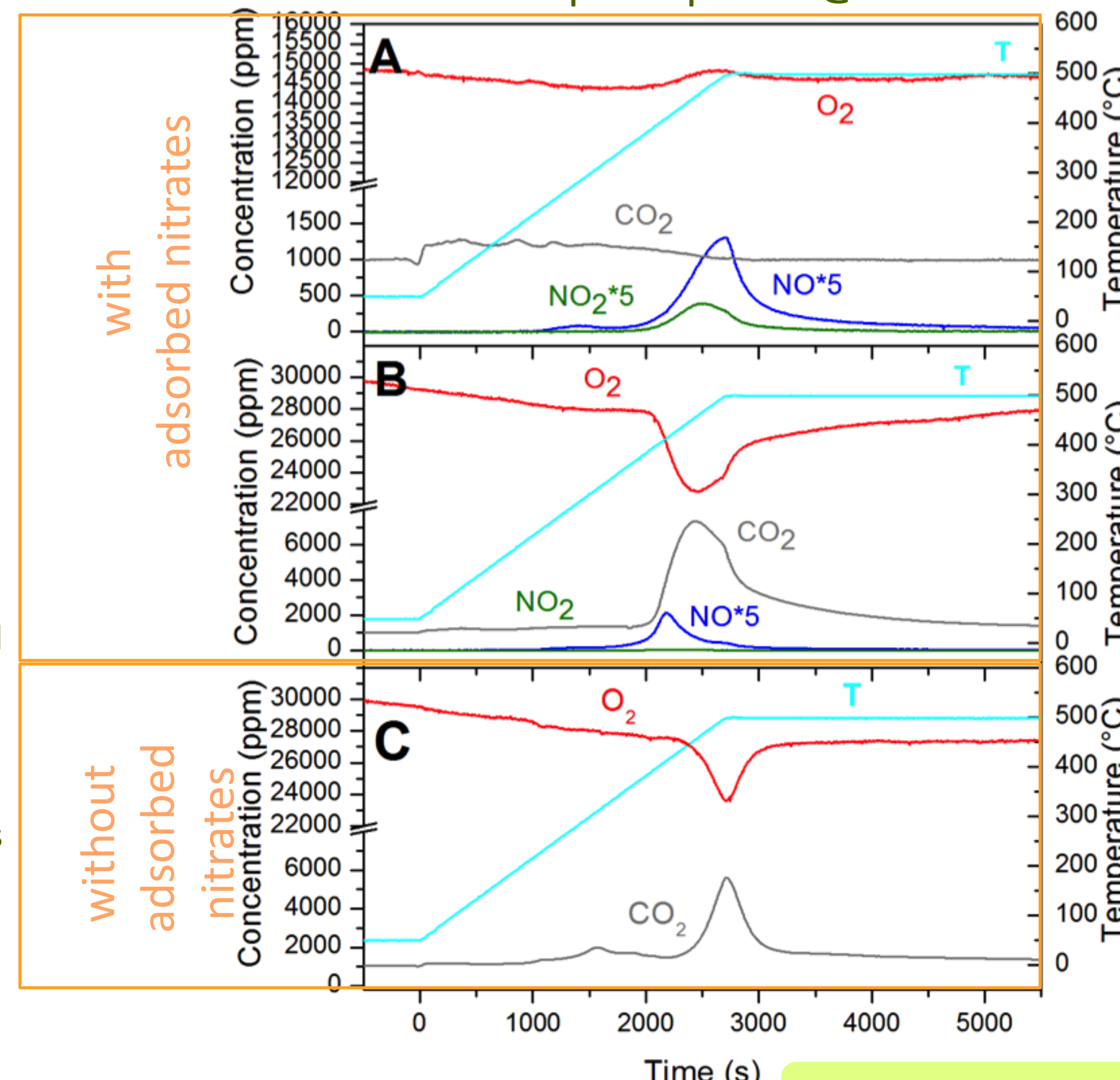
- Decomposition of nitrates mainly above the adsorption temperature (350° C)
- Re-adsorption of CO₂ due to formation of K₂CO₃
- Evolved NO, O₂ and NO₂ are well in line with the stoichiometry of nitrates decomposition:
 $2 KNO_3 + CO_2 \rightarrow K_2CO_3 + 2 NO + 3/2 O_2$
 $2 KNO_3 + CO_2 \rightarrow K_2CO_3 + 2 NO_2 + 1/2 O_2$

B_ WITH SOOT

- Nitrates decomposition observed at lower T
- **The presence of soot lowers the stability of stored nitrates**
- No significant CO₂ uptake is observed
- **CO₂ production upon soot oxidation by nitrates**
- Below 350° C the concentration of the products obeys the stoichiometry of nitrates reduction by soot:
 $C + 2 NO_2 \rightarrow CO_2 + 2 NO + 1/2 O_2$
- **Direct reaction between stored nitrates and soot**

TPO

Adsorption phase @ 350° C



A_ WITHOUT SOOT

- Similar product distribution observed IN TPD experiments
- Re-adsorption of CO₂ forming K carbonates

B, C_ WITH SOOT

- Decomposition of nitrates at lower temperature
➢ **lower thermal stability of NO_x adsorbed species**

• NO₂ involvement in soot oxidation

2 oxidation routes:

- Oxidation with NO₂ upon nitrate decomposition
- Oxidation with O₂

The presence of soot decreases **stability** of the surface nitrates

the presence of surface NO_x favors soot oxidation