Study of Pt-Ba/Al_2O_3 LNT catalysts for the simultaneous removal of NO_x and soot: new insights on the role of stored NO_x in the soot combustion

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Abstract

Soot or particulate matter (PM) and NO_X are the main pollutants in diesel engine emissions and represent health and environmental problems. Therefore the automotive industry is currently facing serious challenges to meet the specific requirements of future regulations concerning both NO_x and particulate emissions. Recently the potential use of lean NO_x Traps (LNT) in the simultaneous removal of soot and NO_x has been proposed [1-3]. These systems accomplish the reduction of soot and NO_x under cyclic conditions by switching between fuel-lean and fuel-rich conditions.

The aim of the present study is to analyze the effects of the presence of soot on the behaviour of LNT catalysts. Besides, we want to provide new insights on the role in the soot combustion of NO_x stored onto the catalytic surface.

A homemade Pt-Ba/Al_2O_3 (1/20/100 w/w) catalyst was prepared by impregnation of γ-alumina with Pt and Ba soluble salts. The effect of the presence of soot on the NO_x storage and reduction activity was studied by performing lean-rich cycles over both the pure catalyst sample and soot/catalyst mixture. For this purpose rectangular step feeds of NO (1000 ppm) in He + 3% v/v O_2 and of H_2 (4000 ppm) in He were alternatively fed to the reactor in the presence of CO_2 and H_2O in the feed stream at different temperatures. The interaction between soot and the stored NO_x species has been investigated also by TPD and TPO experiments (heating rate 10 °C/min in He or in O_2 (3%) from 250°C up to 500°C), in the presence and in the absence of soot.

The results obtained during the lean NO_x adsorption over the Pt-Ba/Al_2O_3-soot mixture showed that the presence of soot decreased the NO_x storage capacity of the catalyst; in particular the presence of roughly 10% w/w of soot decreased by nearly 30% the amounts of stored NO_x with respect to the soot-free catalyst. The decrease of the NO_x adsorption capability is possibly related to the decrease of the NO_2 concentration, due to its reaction with soot. However the presence of soot does not appreciably affect the behavior of the PtBa/Al_2O_3 catalyst in the reduction by H_2 of the stored nitrates, being in all cases N_2 the major reaction product.

TPD results pointed out that the thermal stability of the adsorbed nitrates is also decreased in the presence of soot. This indicates an interplay between adsorbed NO_x species and soot: soot affects the NO_x storage but the adsorbed nitrates favor the oxidation of soot. These species actively oxidize soot by direct interaction due to their mobility on the surface and/or participate in the soot oxidation upon release of NO_2 and O_2 during decomposition. The participation of the adsorbed NO_x species in the soot oxidation has also been clearly pointed out by TPO experiments showing that the oxidation of soot is greatly enhanced by the presence of adsorbed NO_x species. Indeed larger amounts of CO_2 are produced upon soot oxidation when the reaction is carried out in the presence of stored NO_x.

1. N. Koichiro, S. Hirota, S. Takeshima, K. Itoh, T. Tanaka, K. Dohmae, SAE paper (2002) N. 01-0957
2. L.Castoldi. R.Matarrese, L.Lietti, P.Forzatti Appl.Catal.B: 64 (2006) 25
3. R.Matarrese, L.Castoldi,L.Lietti, P.Forzatti, Top. Catal. 42-43 (2007) 293

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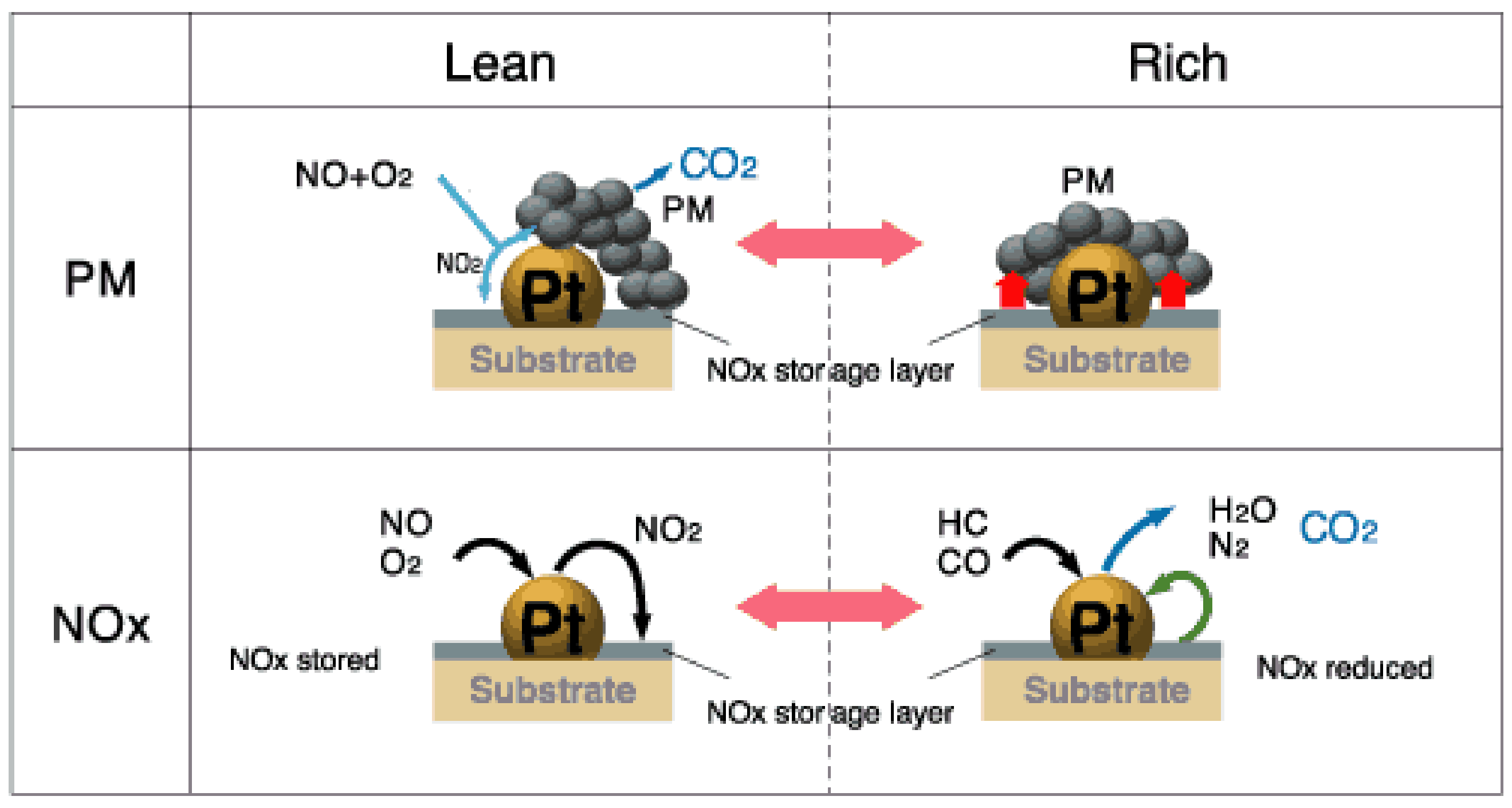
Diesel Particulate NO_x Reduction (DPNR) system

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.



In spite of the fact that many studies are available in the literature concerning the behavior of NSR systems in NOx removal, investigation on the combined soot-NO_x removal according to the DPNR concept are very limited.

Aim of the work

- ➢ analyze the effects of soot on the behaviour of the catalyst
- ➢ provide new insights on the role of NO_x stored onto the catalytic surface in the soot combustion

Materials and Techniques

Catalyst Pt-Ba/γAl_2O_3 (1 % w/w Pt, 16 % Ba w/w),
Preparation technique: incipient wetness impregnation

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

•Micro-flow reactor studies
Catalyst weight: 60 mg - flow 100 Ncc/min

Transient Response Method (TRM)
NOx storage @ 350°C: 1000 ppm NO in 3%O_2 + 1% H_2O + 0,1% CO_2;
Regeneration @ 350°C: 4000 ppm H_2 in 1% H_2O + 0,1% CO_2

Temperature Programmed Desorption (TPD)
Heating from 250 to 500°C (10°C/min) with 1% H_2O and 0.1% CO_2 in Helium

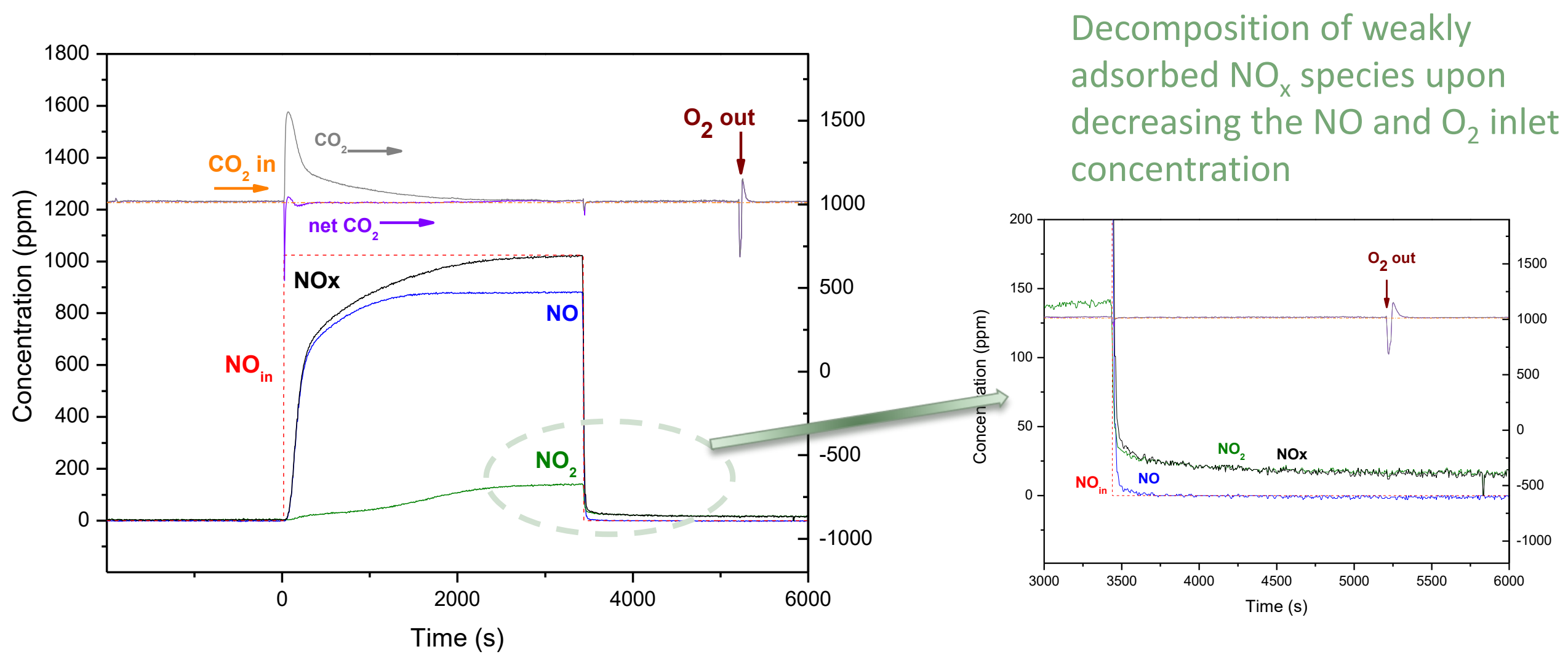
TRM - Adsorption phase @ 350°C

NO 1000 ppm in He - O_2 3% v/v - CO_2 0.1% v/v - H_2O 1% v/v

Without soot

- initial NO_x storage
- NO oxidation to NO_2
- CO_2 release upon NO_x storage due to Ba carbonate decomposition

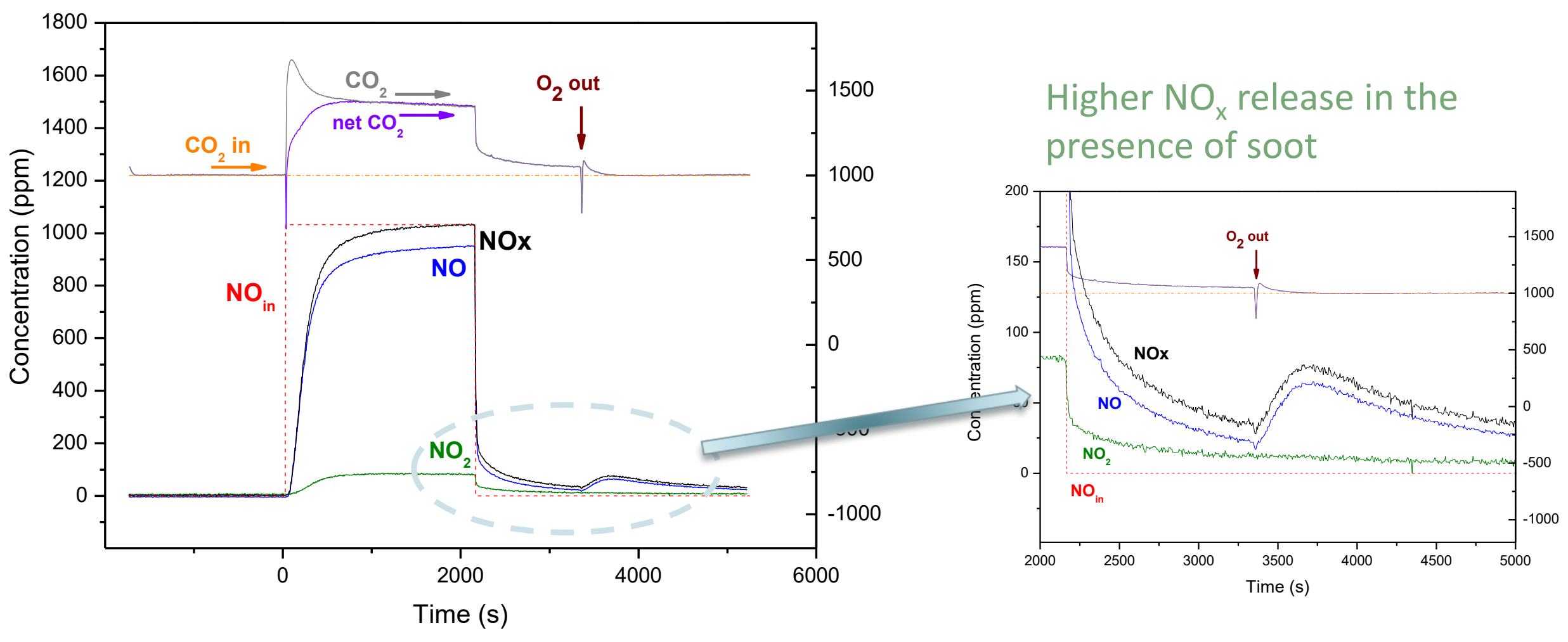
$$Ba\,CO_3 + 2\,NO + 3/2\,O_2 \rightarrow Ba(NO_3)_2 + CO_2$$



Decomposition of weakly adsorbed NO_x species upon decreasing the NO and O_2 inlet concentration

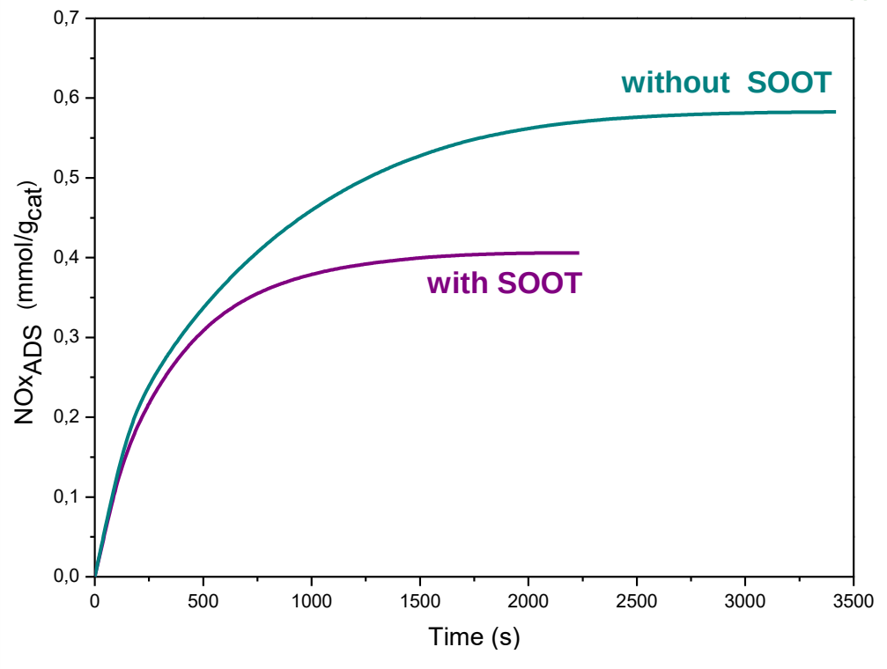
With soot

- Soot oxidation upon NO admission (net CO_2 production)
- Lower NO_2 production
- Higher NO/NO_2 ratio in presence of soot



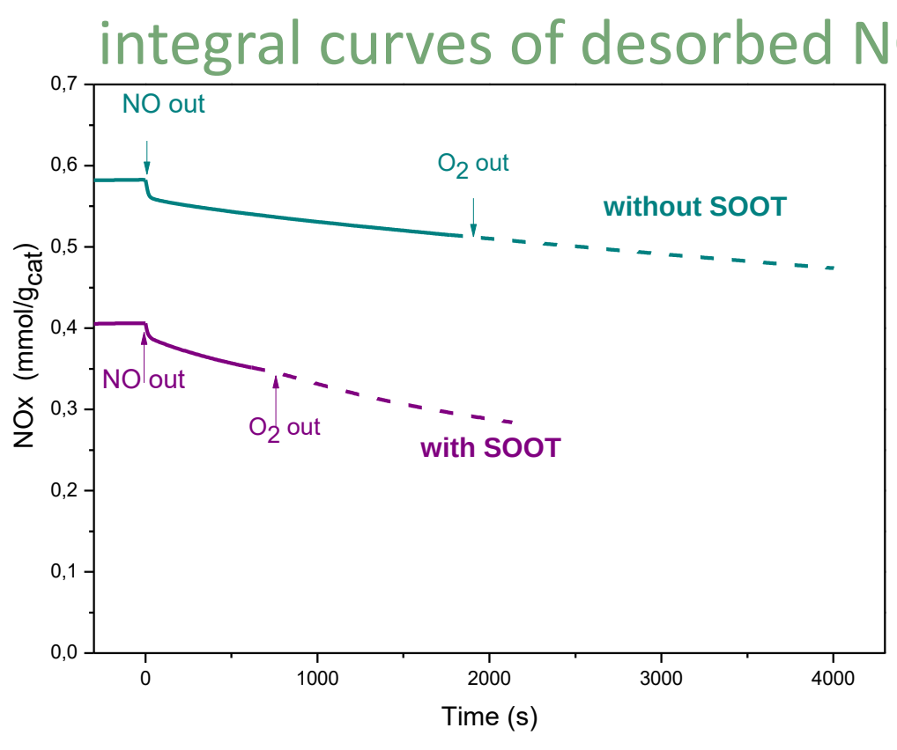
Higher NO_x release in the presence of soot

integral curves of stored NO_x

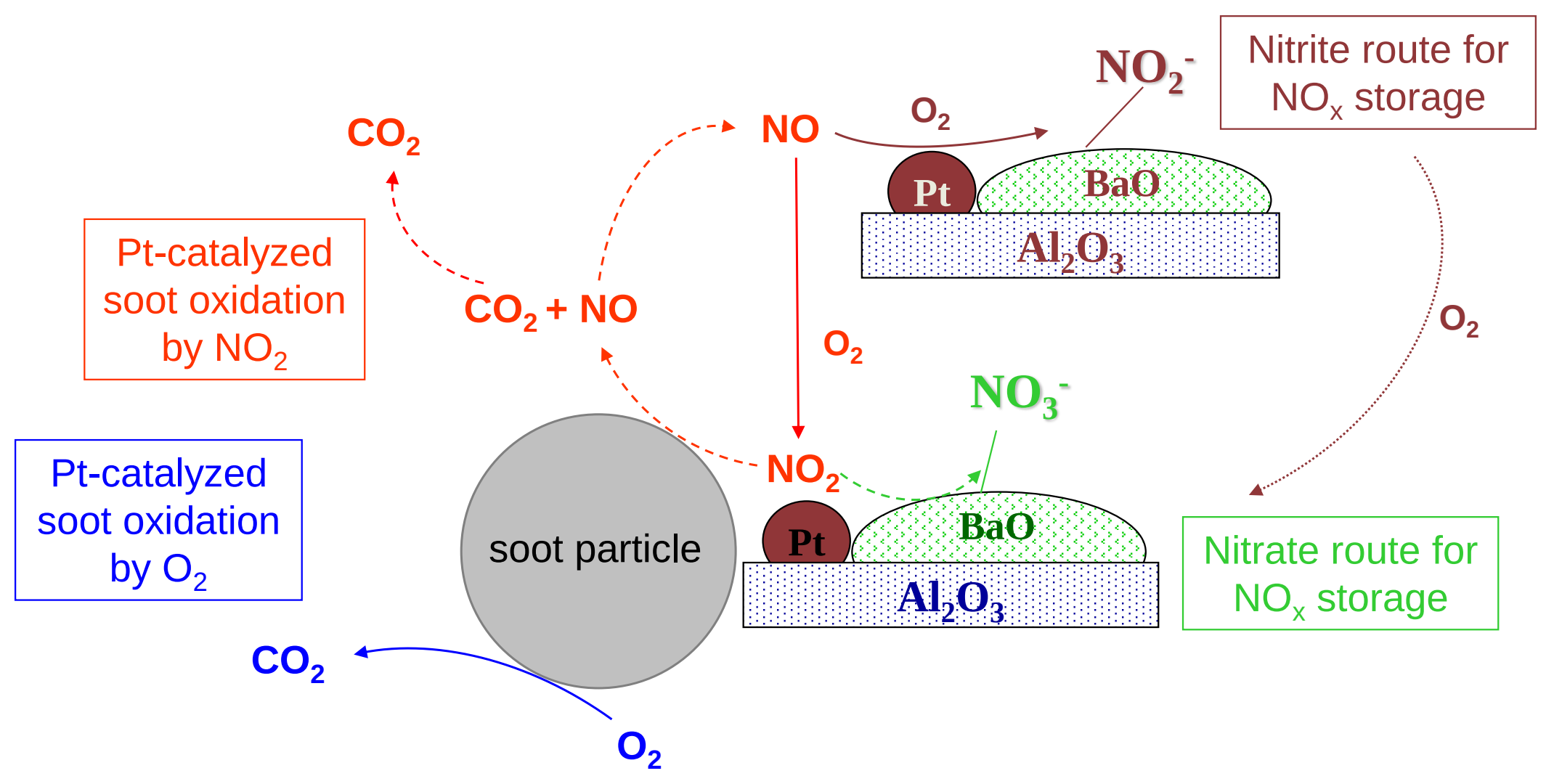


- Stored NO_x
  Without soot 0.58 mmol/g_{cat}
  With soot 0.41 mmol/g_{cat}

integral curves of desorbed NO_x



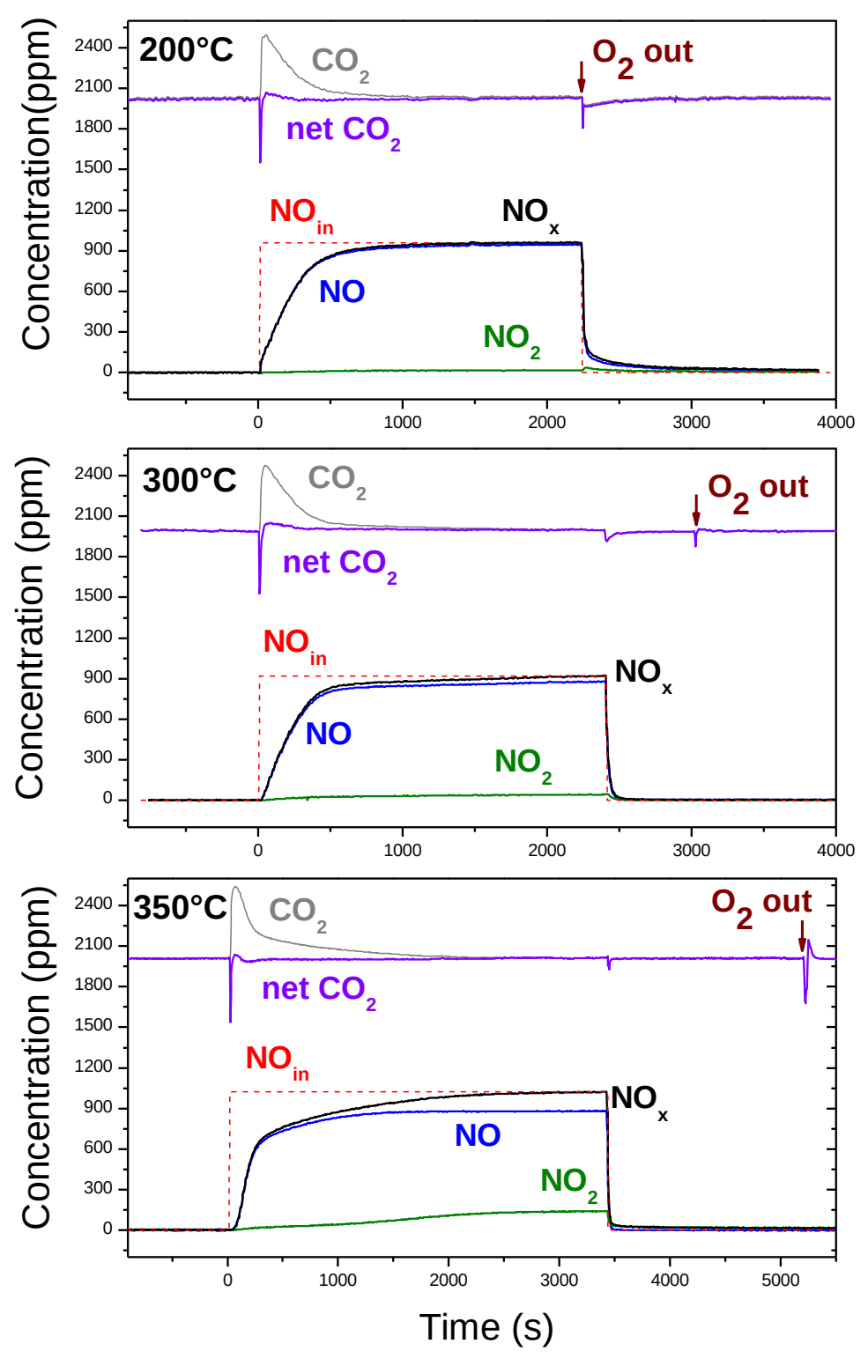
- Desorbed NO_x (at 2000s)
  Without soot 0.07 mmol/g_{cat} (12.4% of ads NO_x)
  With soot 0.12 mmol/g_{cat} (29% of ads NO_x)



⇒ Ba sites and soot compete for reaction with NO_2
⇒ NO_2 concentration is lower in presence of soot and higher NO/NO_2 ratios are measured.
This could justify the lower storage rate and the lower amount of stored NO_x

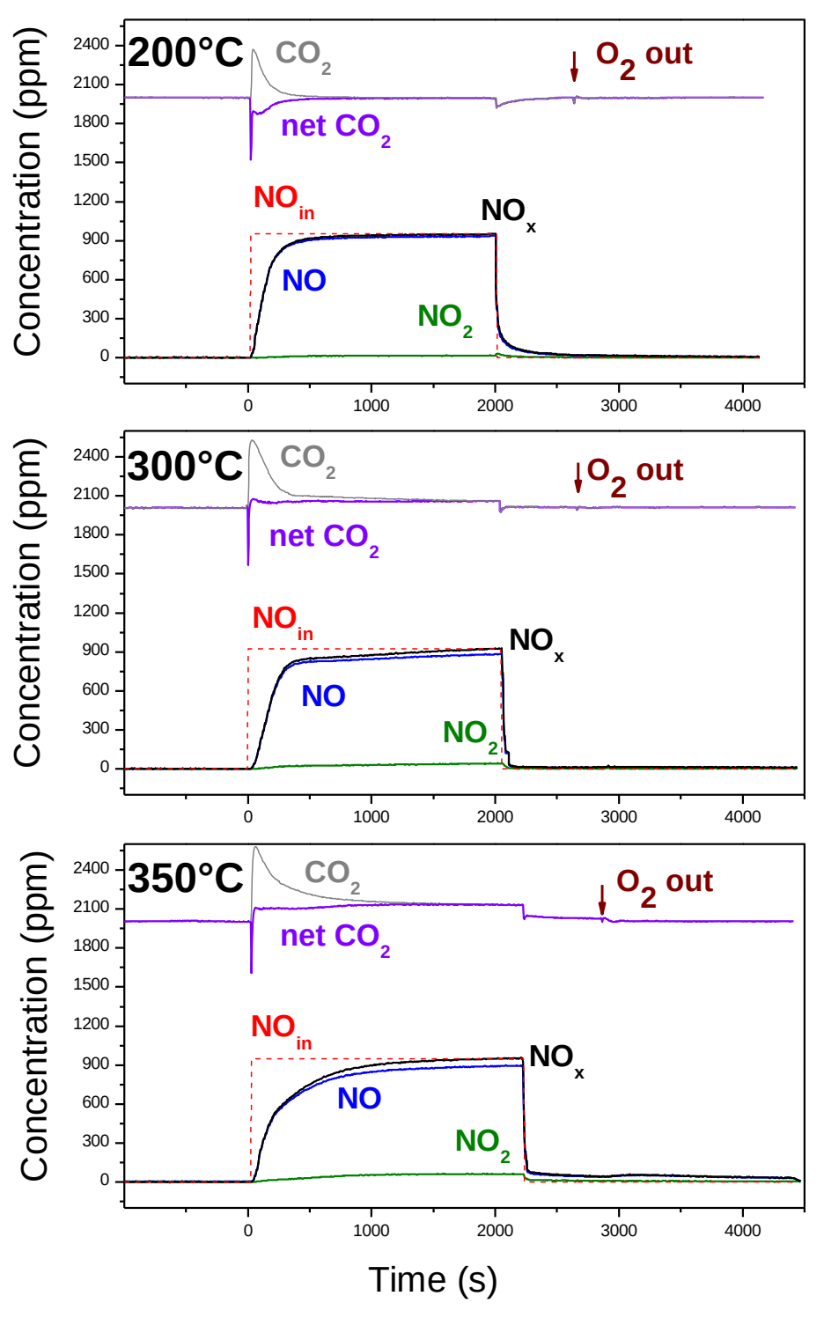
TRM - Adsorption phase @ different temperature

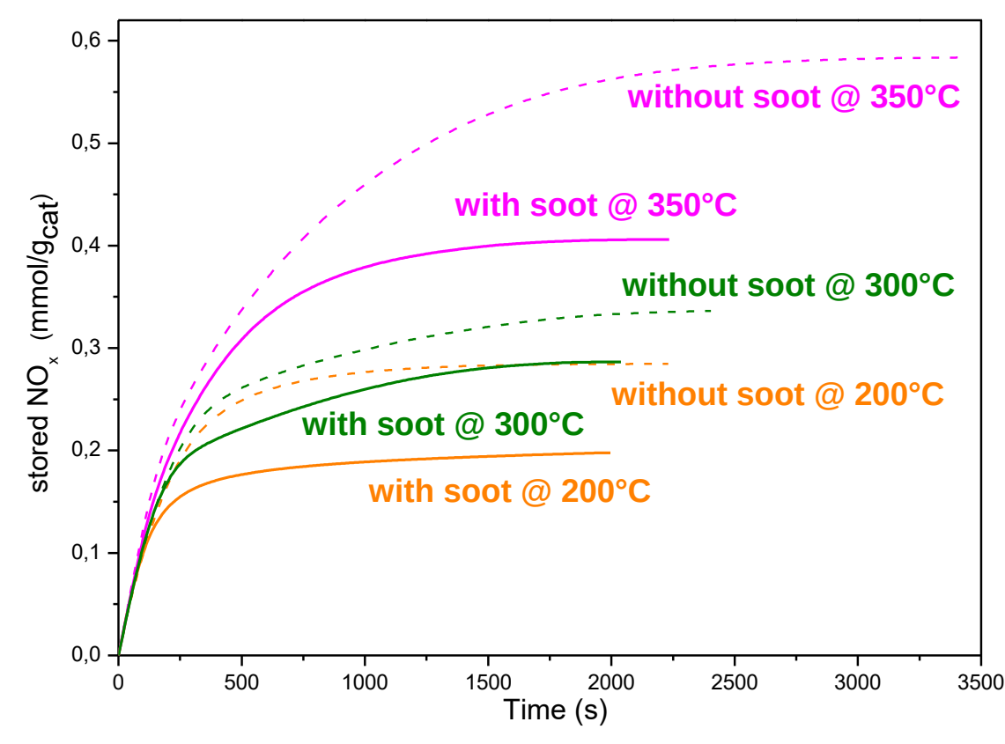
Without Soot



- ✓ Initial storage of NO_x
- ✓ NO oxidation to NO_2
- ✓ CO_2 release upon NO_x storage due to barium carbonate decomposition and/or soot oxidation

With Soot

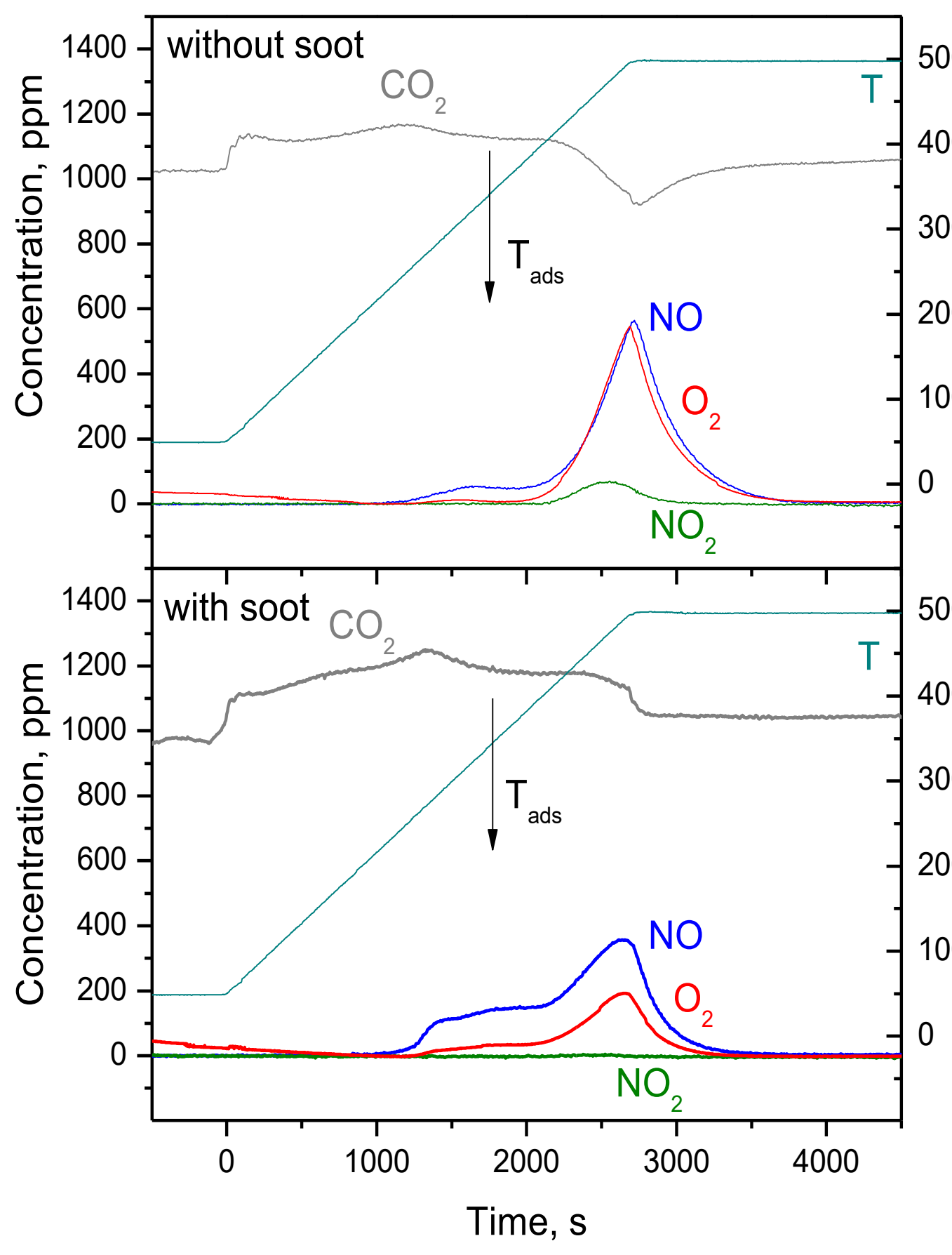




At any temperature the presence of soot decreases the amounts of stored NO_x and affects the stability of the surface nitrates

TPD of nitrates

T rt-500°C @ 10°C/min in He –CO_2 0.1% v/v - H_2O 1% v/v (after NO_x adsorption @ 350°C)



- ✓ Most decomposition of nitrates above adsorption temperature (350°C)
- ✓ Decomposition of nitrates not complete at 500°C
- ✓ Re-adsorption of CO_2 due to formation of $BaCO_3$
- ✓ Evolved NO, O_2 and NO_2 are well in line with the stoichiometry of nitrates decomposition:

$$Ba(NO_3)_2 + CO_2 \rightarrow BaCO_3 + 2\,NO + 3/2\,O_2$$

$$Ba(NO_3)_2 + CO_2 \rightarrow BaCO_3 + 2\,NO_2 + ½\,O_2$$

- ✓ Significant release of NO and O_2 below 350°C
- ✓ Nitrates decomposition concludes at lower T without NO_2 formation
- ✓ Below 350°C the concentration of the evolved products obeys the stoichiometry of nitrate reduction by soot:

$C + Ba(NO_3)_2 \rightarrow BaCO_3 + 2\,NO + ½\,O_2$

Direct reaction between stored nitrates and soot !