CLEERS

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Mechanistic Detailed Kinetic Modeling of the NH_3-NO/NO_2 SCR Reactions over a Cu-Zeolite Catalyst

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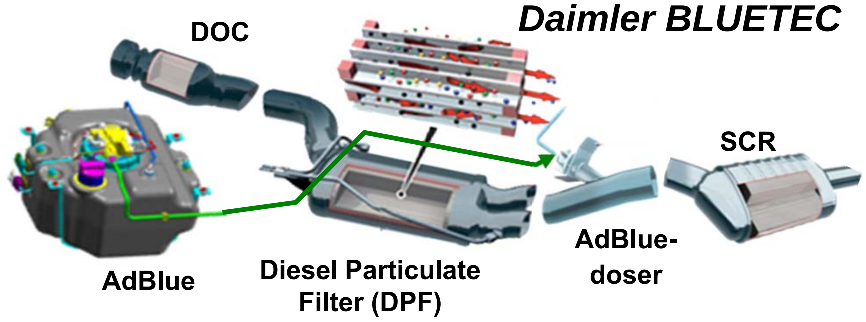
OUTLINE

1. ***SCR technology***
2. ***Methods***
3. ***NO_2 related SCR chemistry***
4. ***Detailed micro-kinetic model***
5. ***Results and discussion***
6. ***Conclusions & future work***

SCR technology

The context: ***NH_3/urea SCR well established in the exhaust aftertreatment system for DeNOx under lean conditions***



$NH_3^* + NO + \frac{1}{4} O_2 \rightarrow N_2 + 3/2\ H_2O$ **Standard SCR**

$2\ NH_3^* + NO + NO_2 \rightarrow 2\ N_2 + 3\ H_2O$ **Fast SCR**

$NH_3^* + \frac{3}{4} NO_2 \rightarrow 7/8\ N_2 + 3/2\ H_2O$ **NO_2 SCR**

The needs: ***simulation of complex exhaust gas aftertreatment systems more and more important in the automobile development process with***

increasing focus @ Cold-start behavior

→ increasing importance of understanding reaction mechanism & storage phenomena

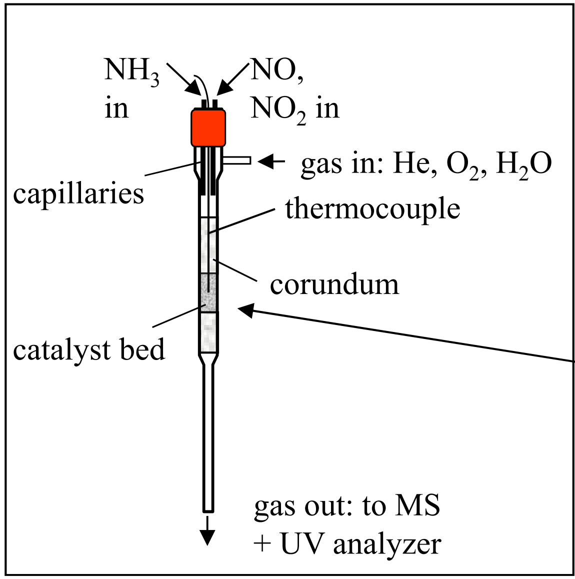
The task: ***study of chemistry, mechanism, kinetics of the SCR reactions over commercial Cu-zeolite catalysts***

Dynamic methods are applied to analyze the steps of the $NO\text{-}NO_2/NH_3$ SCR mechanism

Commercial Cu-zeolite washcoted monolith catalyst

crushed monolith

Microreactor



Catalyst bed
D_{in} =7 mm
h=10 mm
W_{cat} = 60 mg

Dynamic runs
(e.g. adsorption runs, TPD, TPR, TPSR runs)
Analyzed reaction systems
(**WITHOUT O_2** in He + 3% v/v H_2O):

- NH_3
- NO_2
- NO_2 + NO
- NO_2 + NH_3
- NO_2 + NH_3 + NO

Lab-scale tests in microreactor afford:
- chemical regime
- isothermal operation
- N-balances
- fast transients

NITRITES

S - ONO

+

NITRATES

S - NO_3

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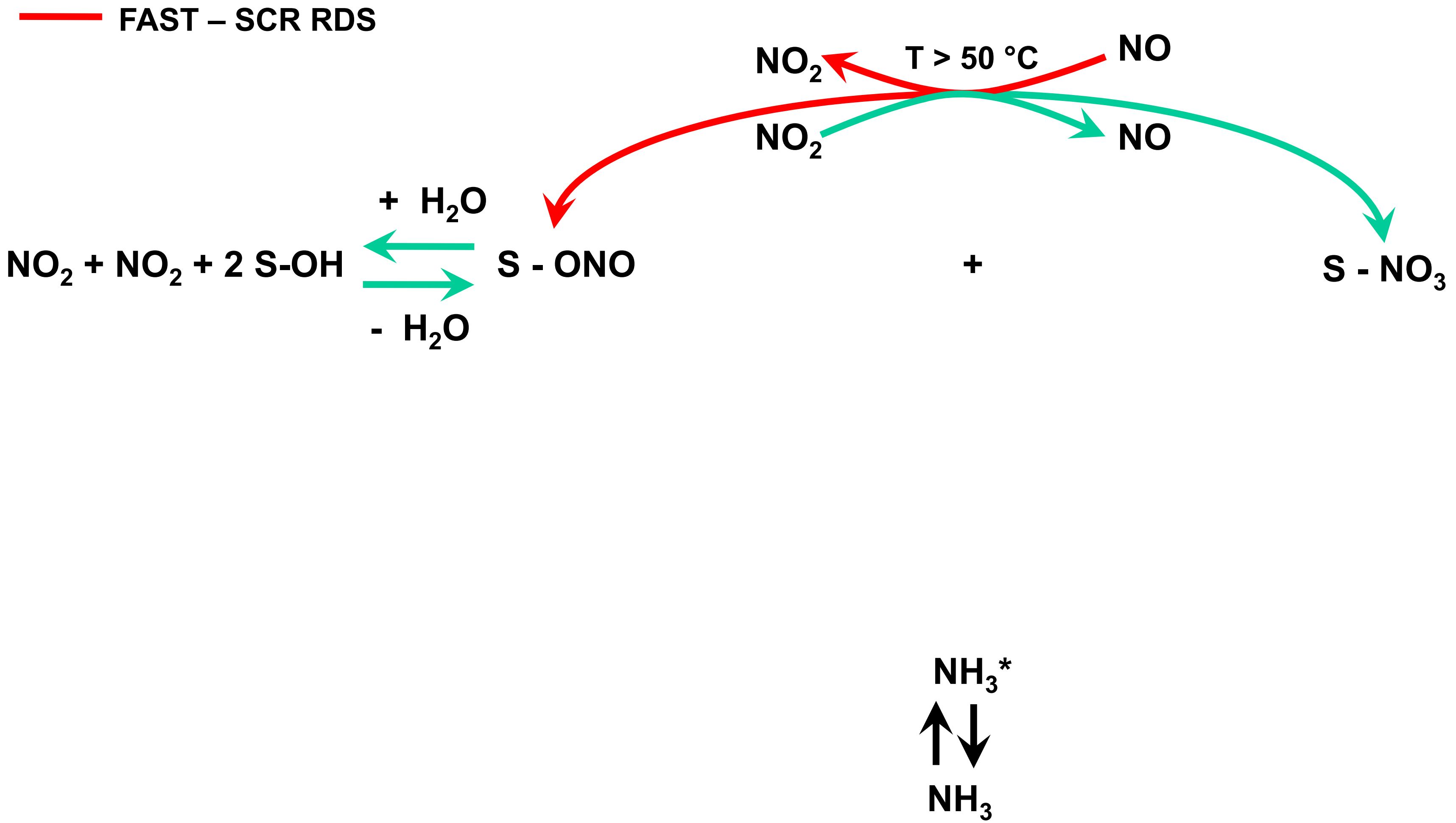
Key role of
surface nitrites/nitrates

NO_2 related SCR chemistry



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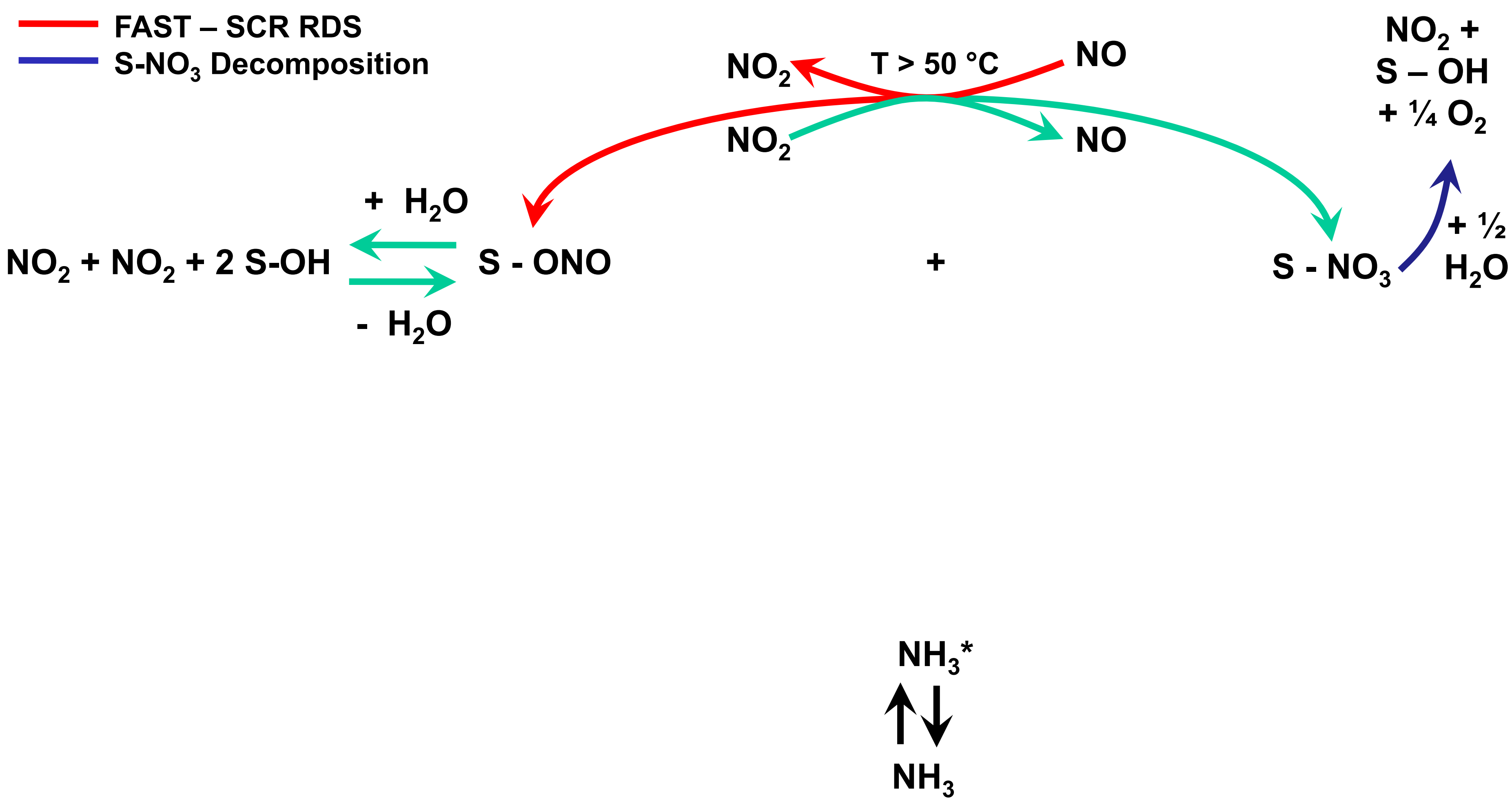
NO_2 related SCR chemistry



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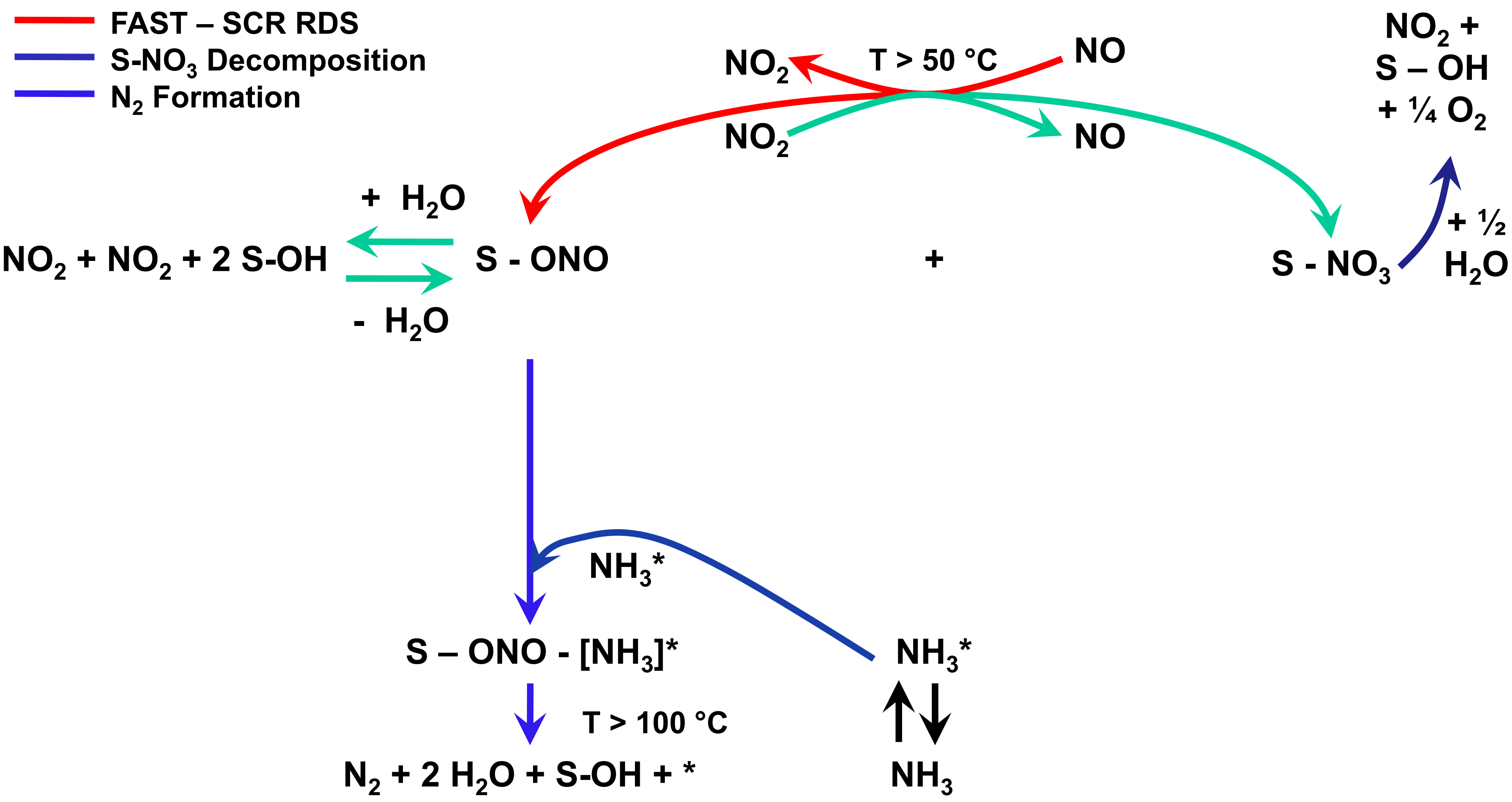
NO_2 related SCR chemistry



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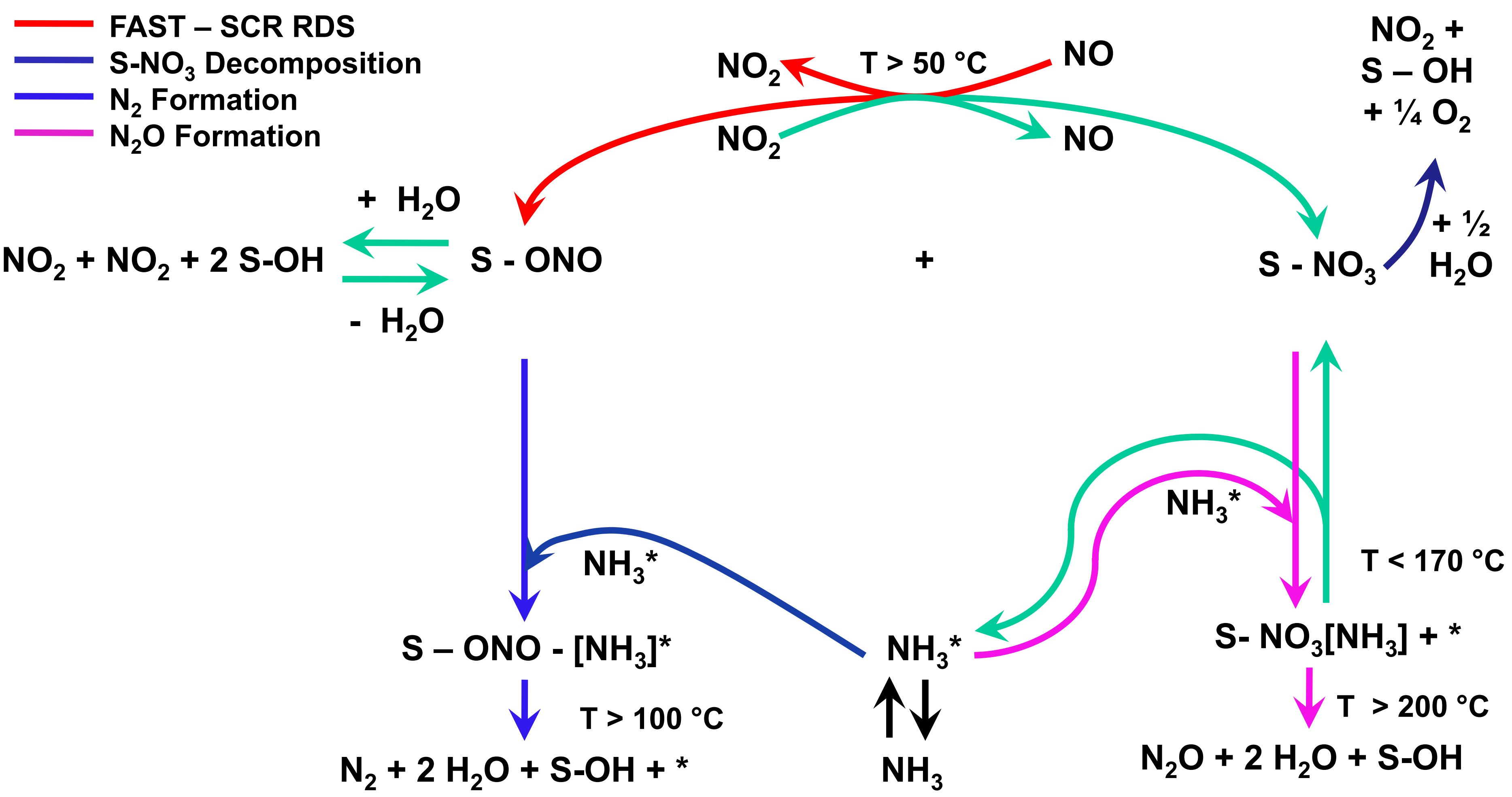
NO_2 related SCR chemistry



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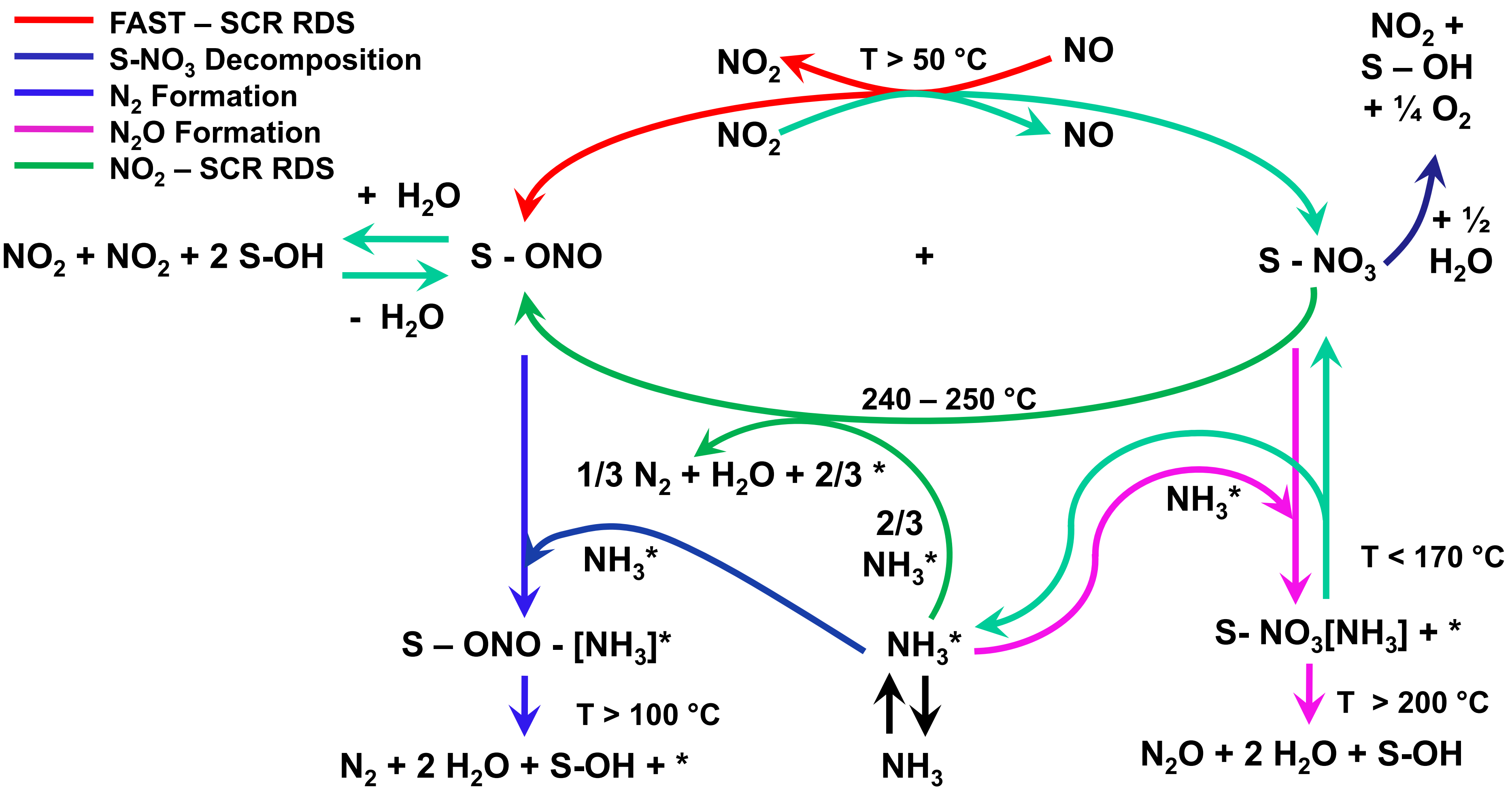
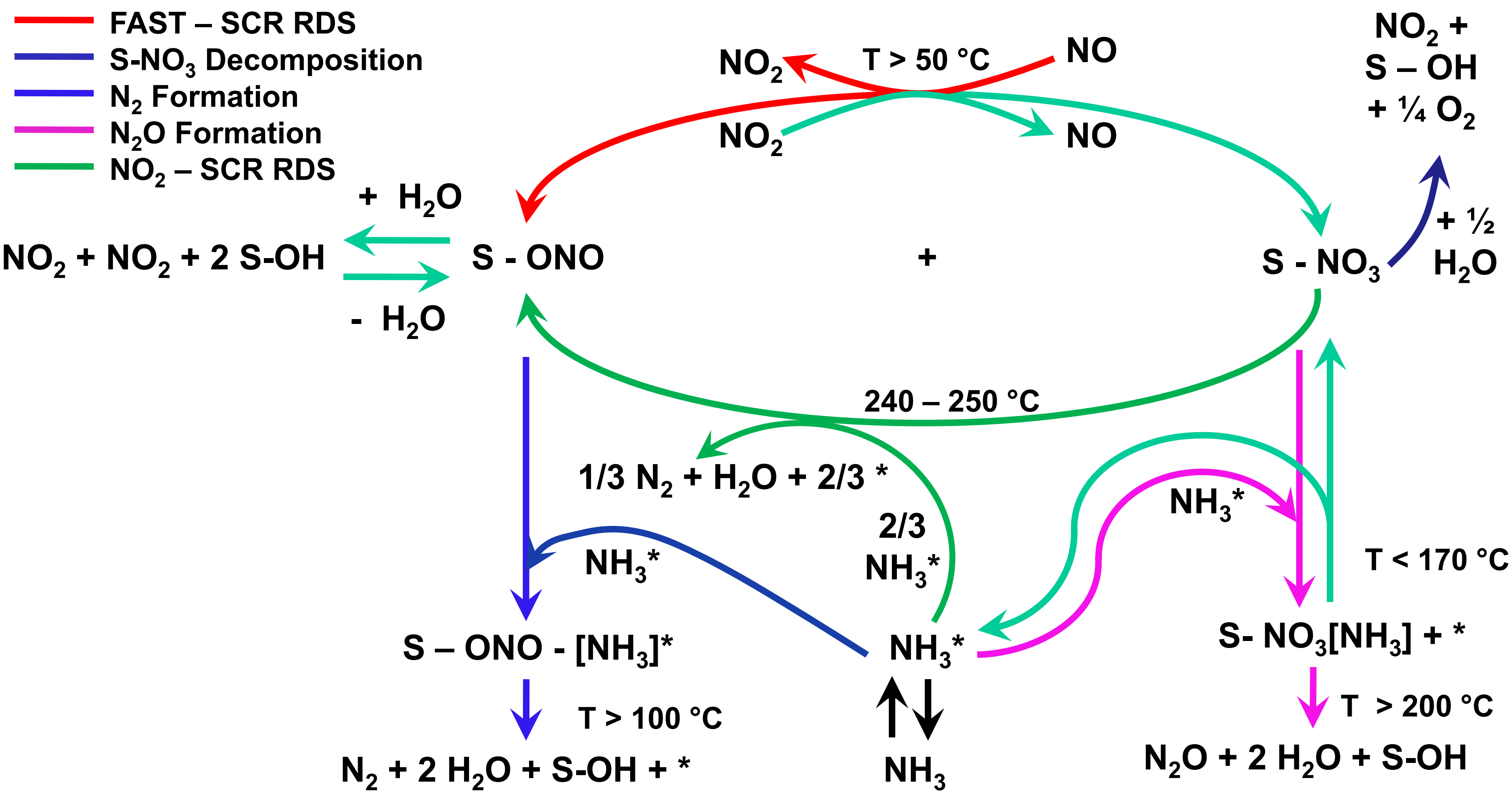
NO_2 related SCR chemistry



NO_2 related SCR chemistry



Fast-SCR (T > 170 – 180 °C) NO_2/NO_x = 0.5 :

$$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O$$

NO_2-SCR (T > 220-230 °C) NO_2/NO_x > 0.5 :

$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$$

Reactions and rate equations

- **Balance of S-sites :** $1 = \sigma_{free} + \sigma_{ONO} + \sigma_{NO3} + \sigma_{NO3[NH3]}$
- **Balance of *-sites :** $1 = \vartheta_{free} + \vartheta_{NH3} + \vartheta_{NH4NO3}$
- **Rate equations assume elementary steps: e.g.**

$2\ NO_2 + 2\ S\text{-}OH \leftrightarrow S\text{-}ONO + S\text{-}NO_3 + H_2O$: ***$R1 = k1\ (CNO_2\ s_{free})^2 - k1inv\ sNO_3^*\ sNO_2^*$***

$NO_2 + S\text{-}ONO \leftrightarrow NO + S\text{-}NO_3$: ***$R2 = k2\ CNO_2\ sONO - k2inv\ CNO\ sNO_3^*$***

Kinetic parameters: $k_i = \exp\left[\beta_i - \gamma_i \cdot \left(\frac{1000}{T} - \frac{1000}{T_{REF}}\right)\right]$ $T[K]$ $T_{REF} = 473K$

Detailed micro-kinetic model

1) NH_3 adsorption/desorption

$$NH_3 \leftrightarrow NH_3^*$$

$$r_1 = k_{1_{ADS}} \cdot C_{NH_3} \cdot \vartheta_{free} - k_{1_{DES}} \cdot \vartheta_{NH_3}$$

Where : $$k_{1_{DES}} = \exp\left\{\beta_{1_{DES}} - \gamma_{1_{DES}} \cdot \left[\frac{1000 \cdot \left(1-\alpha \cdot (\vartheta_{NH_3} + \vartheta_{NH_4NO3}\right)}{T} - \frac{1000}{T_{REF}}\right]\right\}$$

2) Reversible NO_2 disproportionation

$$2NO_2 + 2S-OH \leftrightarrow S-ONO + S-NO_3 + H_2O$$

$$r_2 = k_{2_{DIR}} \cdot \left(C_{NO_2} \cdot \sigma_{free}\right)^2 - k_{2_{INV}} \cdot \sigma_{ONO} \cdot \sigma_{NO_3}$$

3) Reversible nitrites oxidation by NO_2

$$NO_2 + S-ONO \leftrightarrow S-NO_3 + NO$$

$$r_3 = k_{3_{DIR}} \cdot C_{NO_2} \cdot \sigma_{ONO} - k_{3_{INV}} \cdot C_{NO} \cdot \sigma_{NO_3}$$

4) Nitrates thermal decomposition

$$S-NO_3 + 1/2\, H_2O \rightarrow NO_2 + 1/4 O_2 + S-OH$$

$$r_4 = k_4 \cdot \sigma_{NO_3}$$

5) Ammonium nitrite thermal decomposition to N_2

$$S-ONO + NH_3^* \rightarrow N_2 + H_2O + S-OH$$

$$r_5 = k_5 \cdot \vartheta_{NH_3} \cdot \sigma_{ONO}$$

6) Direct nitrates reduction by NH_3

$$S-NO_3 + 2/3\, NH_3^* \rightarrow 1/3\, N_2 + H_2O + S-ONO$$

$$r_6 = k_6 \cdot \sigma_{NO_3} \cdot \vartheta_{NH3}$$

Global reaction

7) Ammonia-nitrates complex formation

$$S-NO_3 + NH_3^* \leftrightarrow S-NO_3[NH_3]$$

$$r_7 = k_{7_{DIR}} \cdot \vartheta_{NH_3} \cdot \sigma_{NO_3} - k_{7_{INV}} \cdot \sigma_{NO_3[NH_3]}$$

8) N_2O formation from ammonia-nitrates complex decomposition

$$S-NO_3[NH_3] \leftrightarrow N_2O + H_2O + S-OH$$

$$r_8 = k_8 \cdot \sigma_{NO_3[NH_3]}$$

Detailed micro-kinetic model – Additional global reactions

9) Reversible NO oxidation

$$NO + 1/2O_2 \leftrightarrow NO_2$$

$$r_9 = \left\{ k_9 \cdot \left[C_{NO} \cdot \left(P_{O_2}\right)^{0.5} - \frac{C_{NO_2}}{K_{eq_{NO}}} \right] \right\} \cdot \left(\frac{P_{H_2O}}{0.03} \right)^{\theta}$$

10) SLOW - SCR

$$3/2\,NO + NH_3^{*} \rightarrow 5/4N_2 + 3/2H_2O$$

$$r_{10} = k_{10} \cdot C_{NO} \cdot \vartheta_{NH_3}$$

11) Ammonium nitrate formation on ammonia adsorption sites

$$2NO_2 + 2NH_3^{*} \rightarrow N_2 + [NH_4]^{*} NO_3 + H_2O$$

$$r_{11} = \frac{k_{11} \cdot \vartheta_{NH_3} \cdot \left(C_{NO_2}\right)^2}{1 + K_{AMM} \cdot \vartheta_{NH_4NO_3}}$$

Where : $K_{amm} =$ ammonium nitrate self inhibition

12) Ammonium nitrate sublimation

$$[NH_4]^{*} NO_3 \rightarrow [NH_4]NO_{3(g)}$$

$$r_{12} = k_{12} \cdot \vartheta_{NH_4NO_3}$$

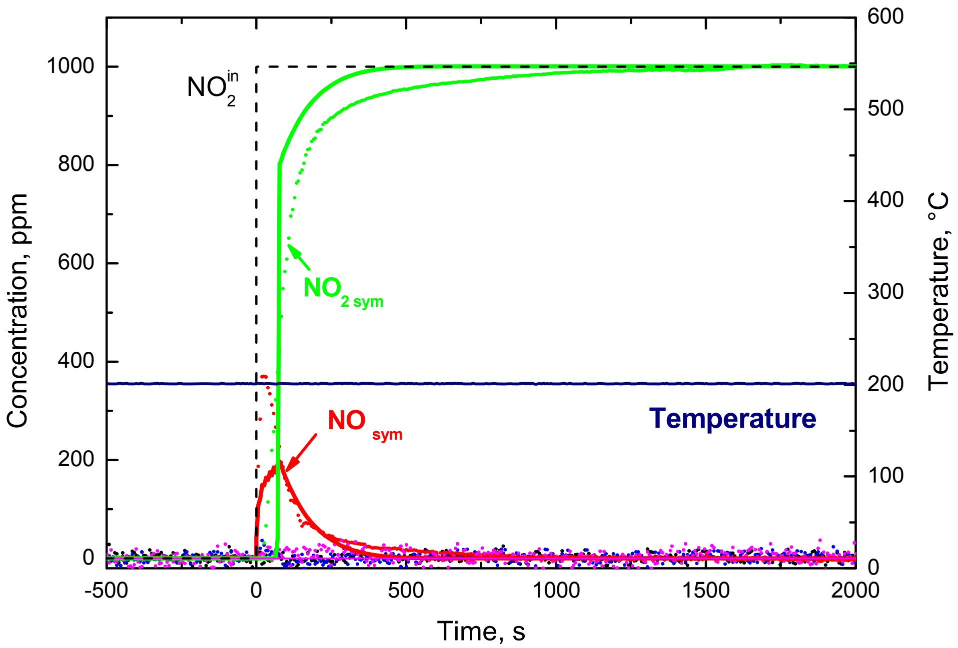
13) Ammonium nitrate thermal decomposition to N_2O

$$[NH_4]^{*} NO_3 \rightarrow N_2O + 2H_2O$$

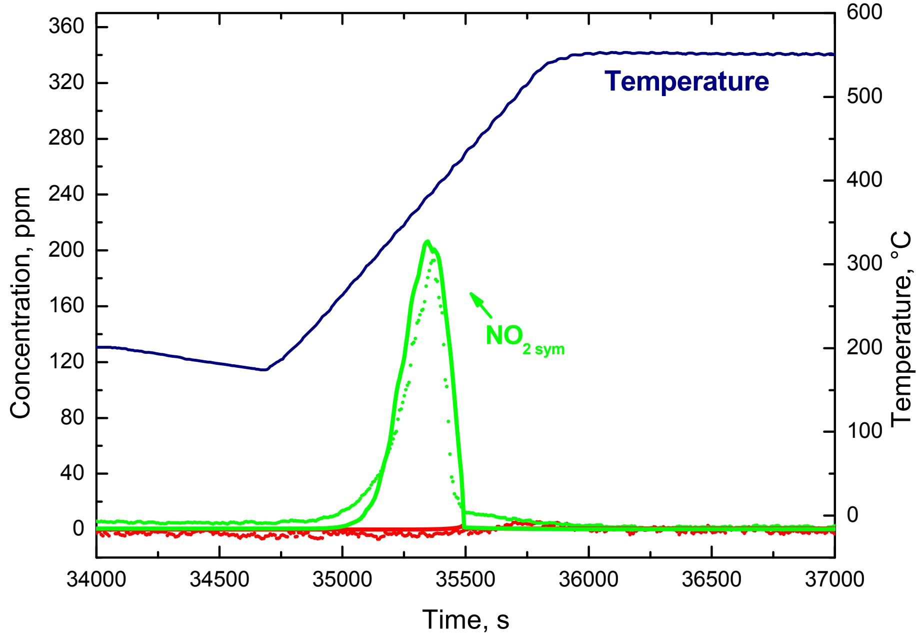
$$r_{13} = k_{13} \cdot \vartheta_{NH_4NO_3}$$

NO_2 storage

Nitrates formation



Nitrates decomposition



$2\ NO_2 + O^{2-} \rightarrow NO_3^- + NO_2^-$

$NO_2 + NO_2^- \rightarrow NO_3^- + NO$

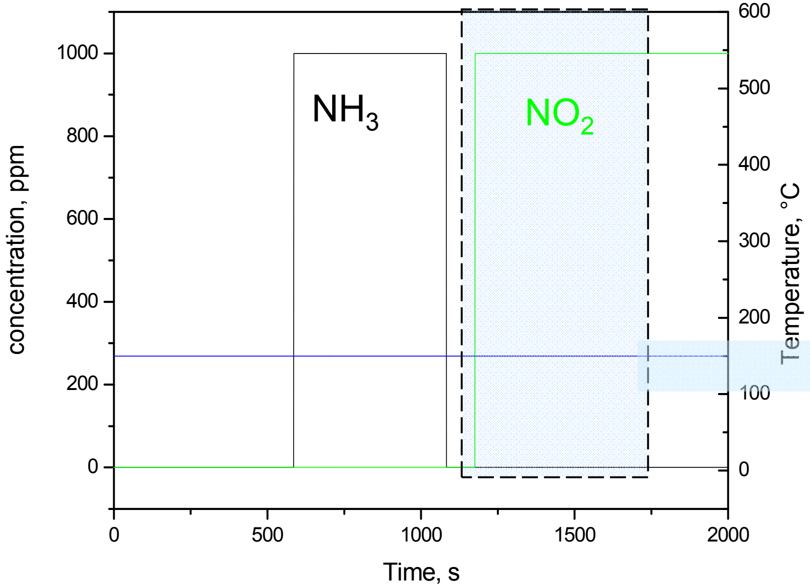
$3\ NO_2 + O^{2-} \rightarrow 2NO_3^- + NO$

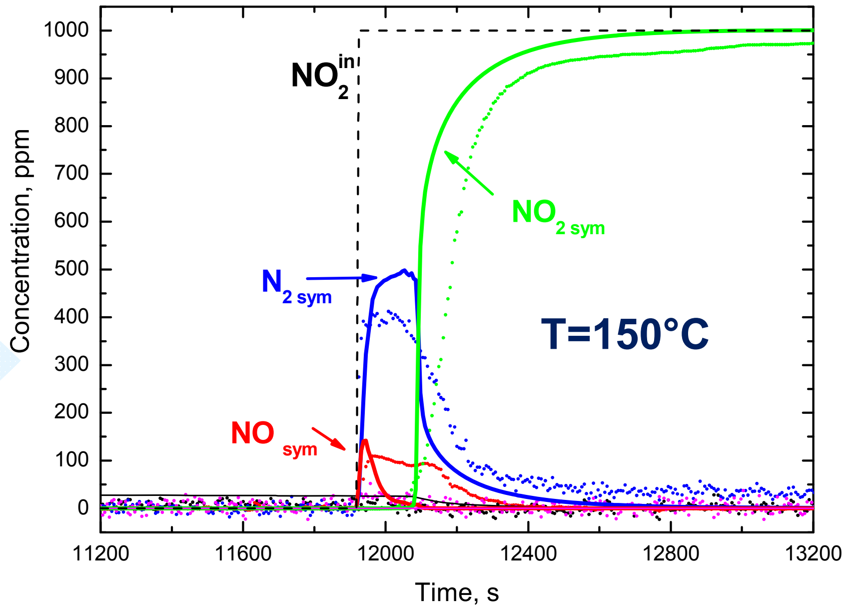
⇒ $NO/\Delta\ NO_2 = 1/3$

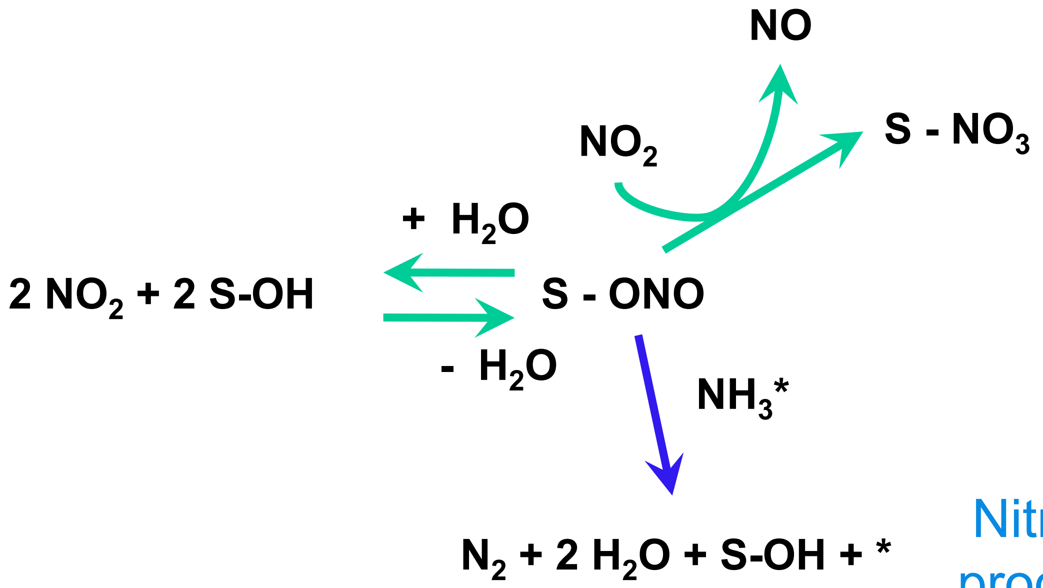
$2NO_3^- \rightarrow 2NO_2 + ½\ O_2 + O^{2-}$

Formation of nitrite & nitrate ad-species according to the disproportionation reaction

NO_2 storage in presence of adsorbed NH_3





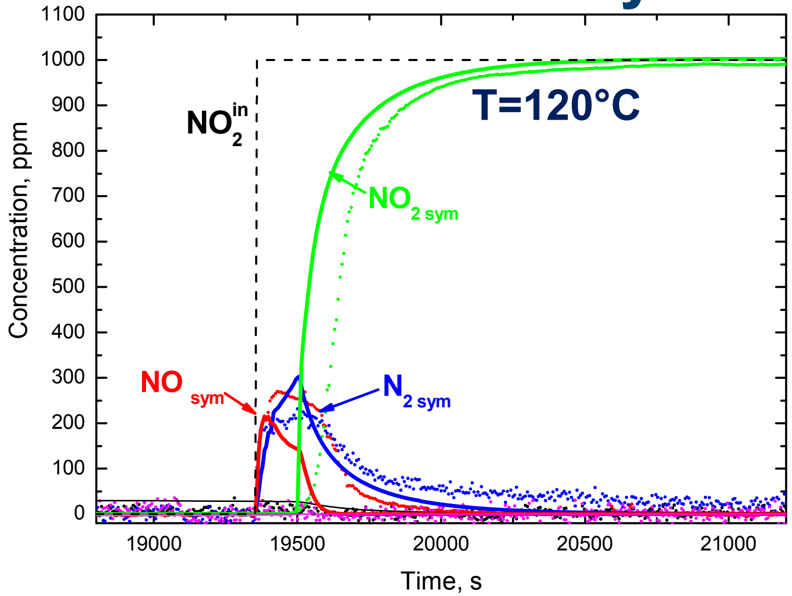


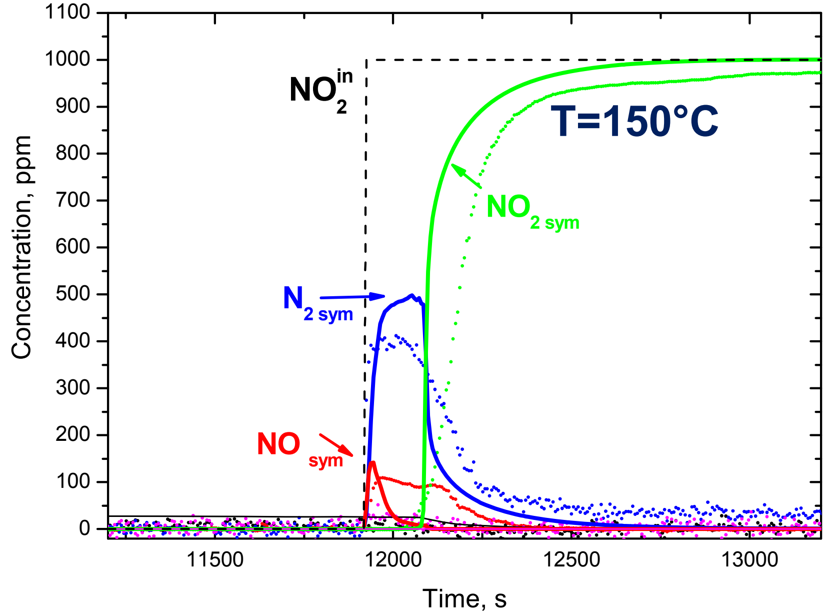
Nitrites are oxidized by NO_2 to form nitrites

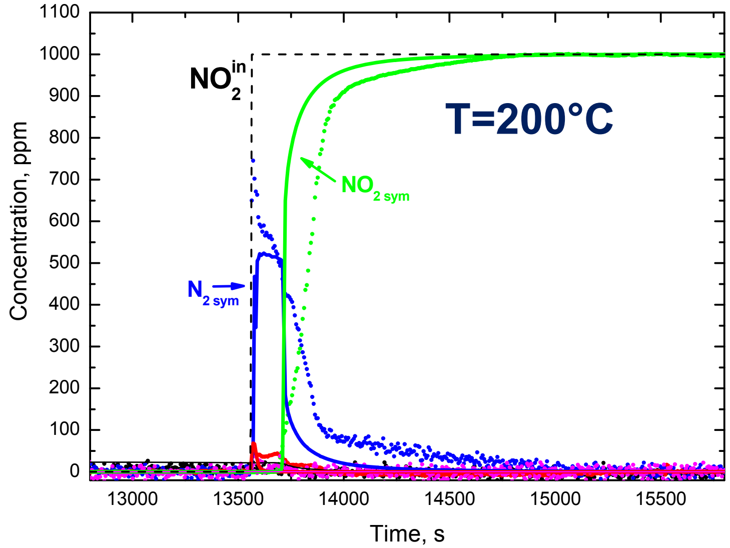
Competition for nitrites between NO_2 and NH_3

Nitrites are reduced by ammonia to produce N_2

NO_2 storage in presence of adsorbed NH_3: T-effect on selectivity



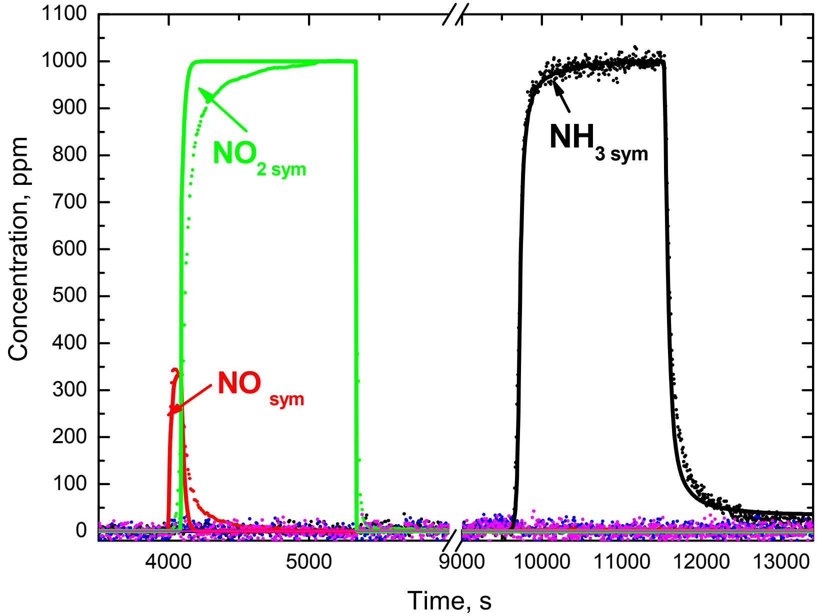




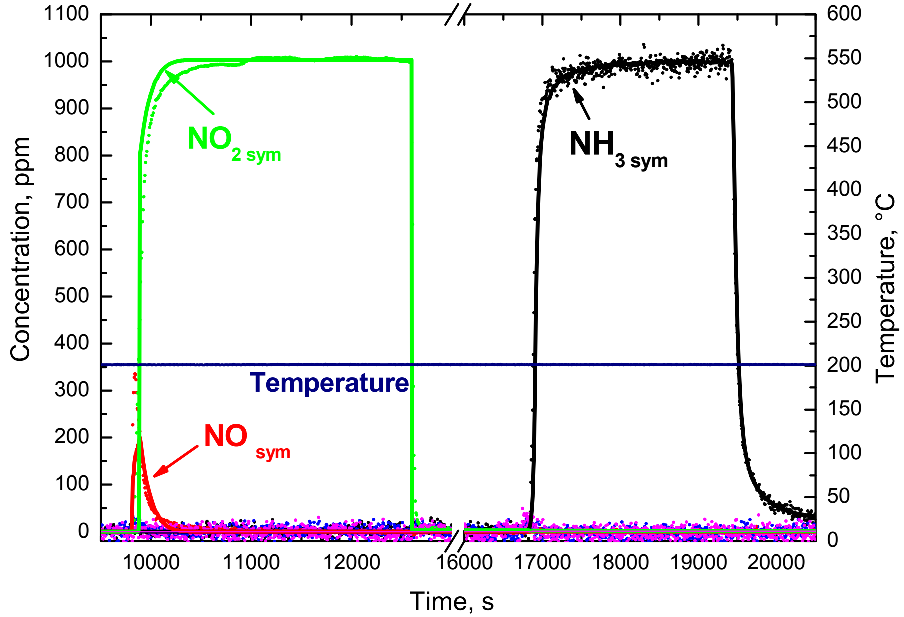
Increasing temperature favors nitrite reduction by NH_3

NH_3 adsorption in presence of nitrates

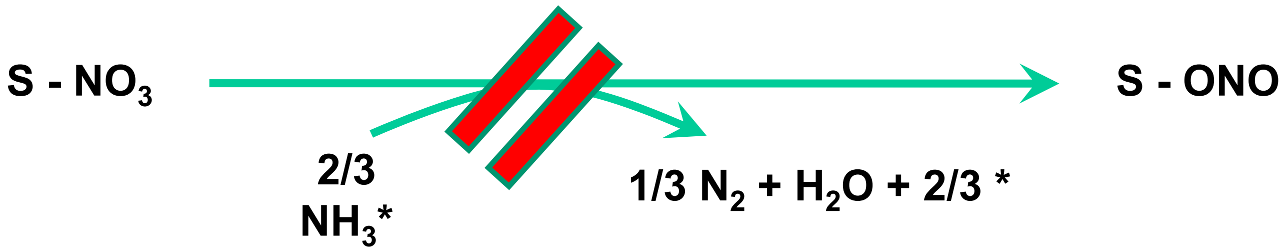
T=120°C



T=200°C

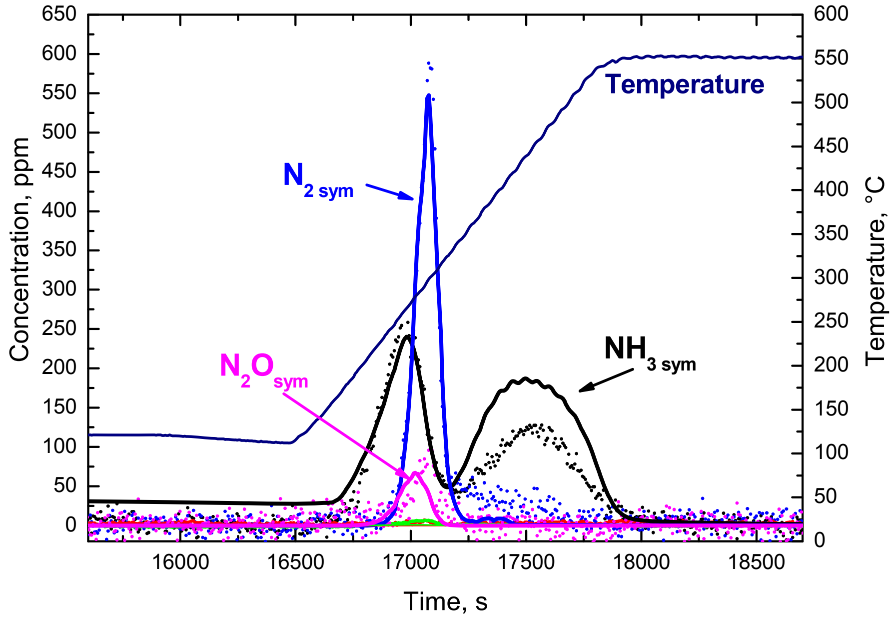


NH_3 is NOT able to reduce stored nitrates at T ≤ 200°C

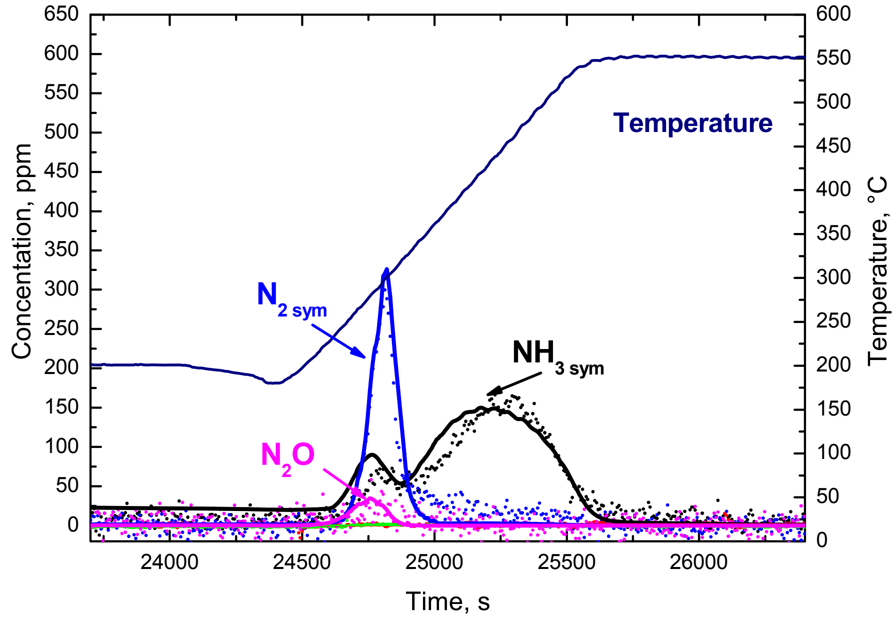


TPR of Nitrates + adsorbed NH_3

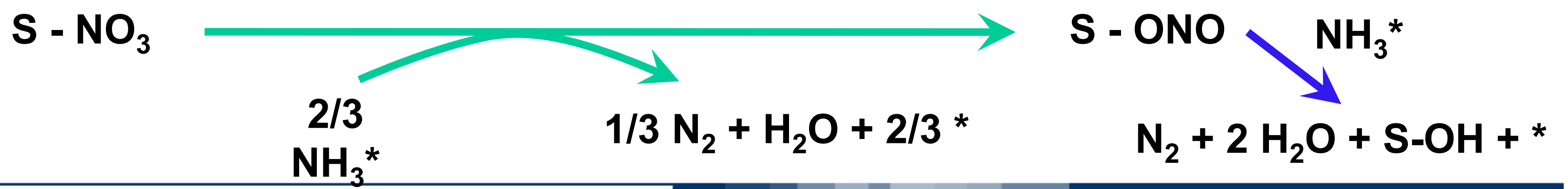
T-ads=120°C



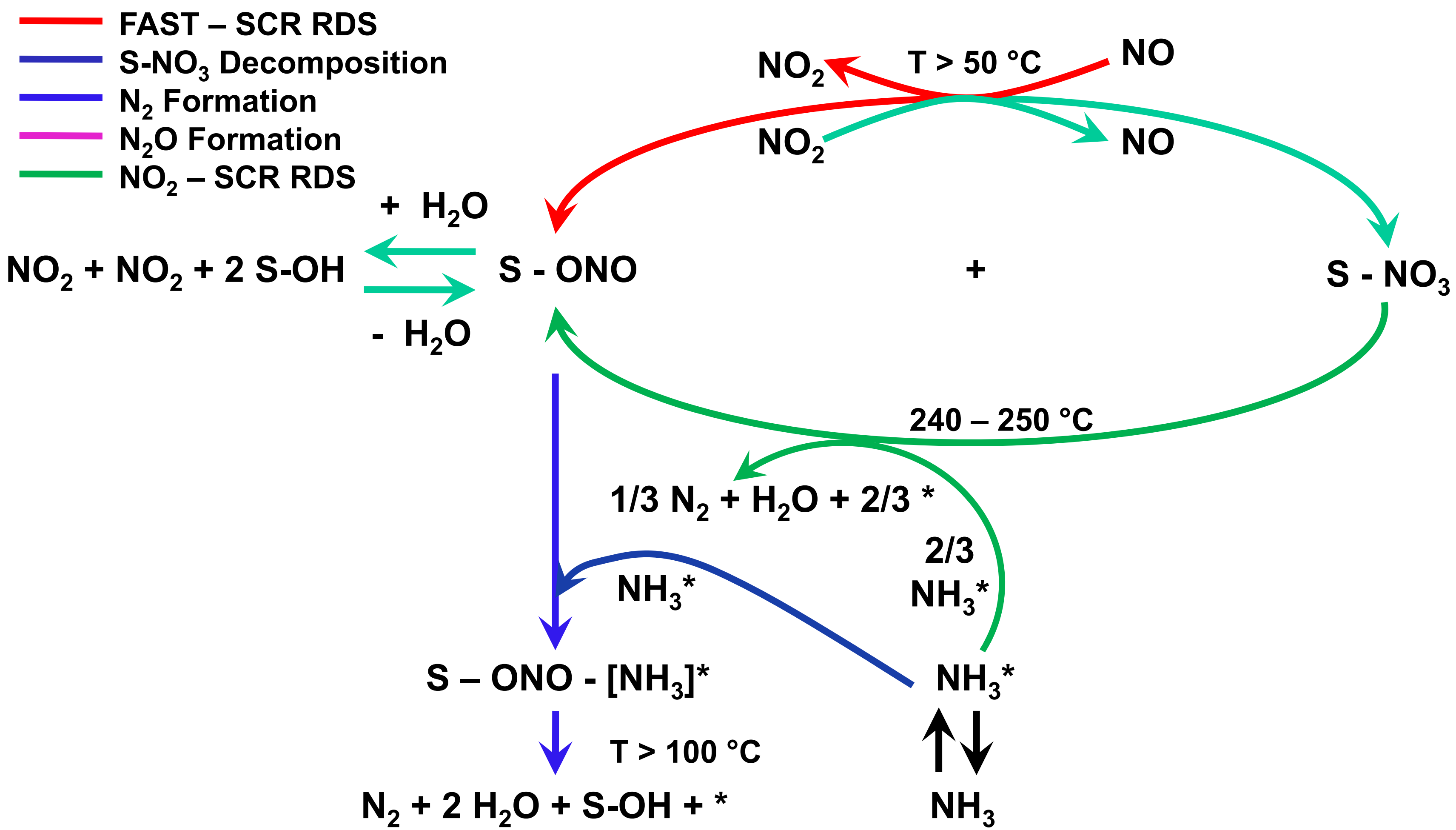
T-ads=200°C



- **NH_3 reduces nitrates at T ≥ 240°C, mainly to N_2**
- **Production of N_2 limited by nitrates stored amount → desorption of unreacted NH_3**



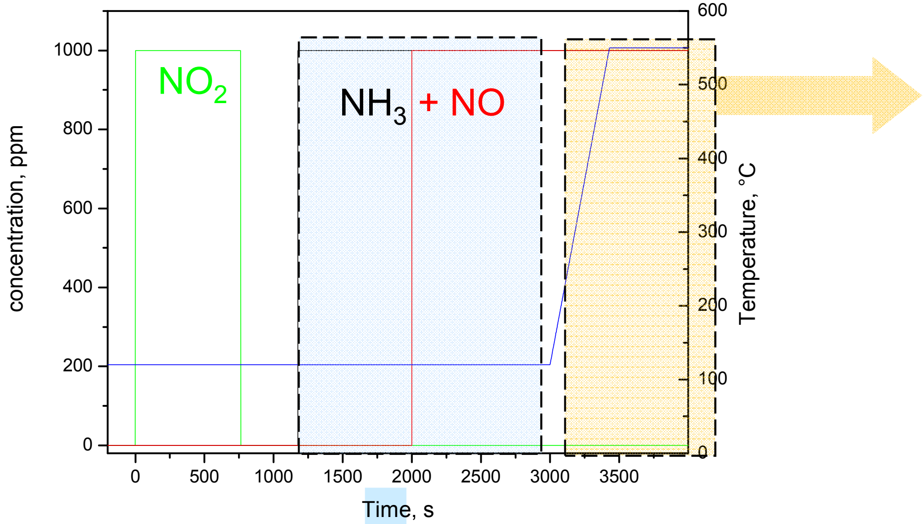
NO_2 related SCR chemistry

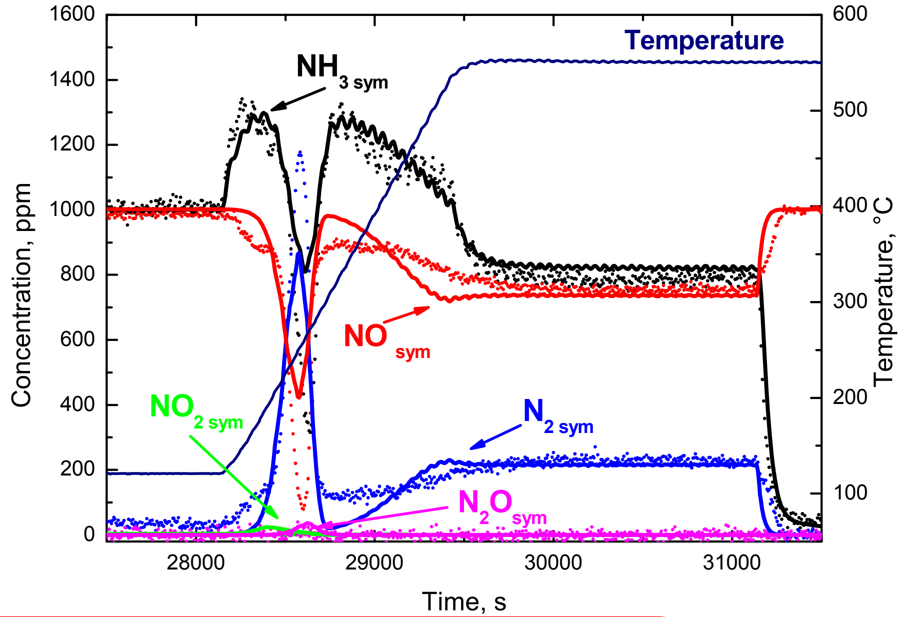


Fast-SCR (T > 170 – 180 °C) NO_2/NO_x = 0.5 :

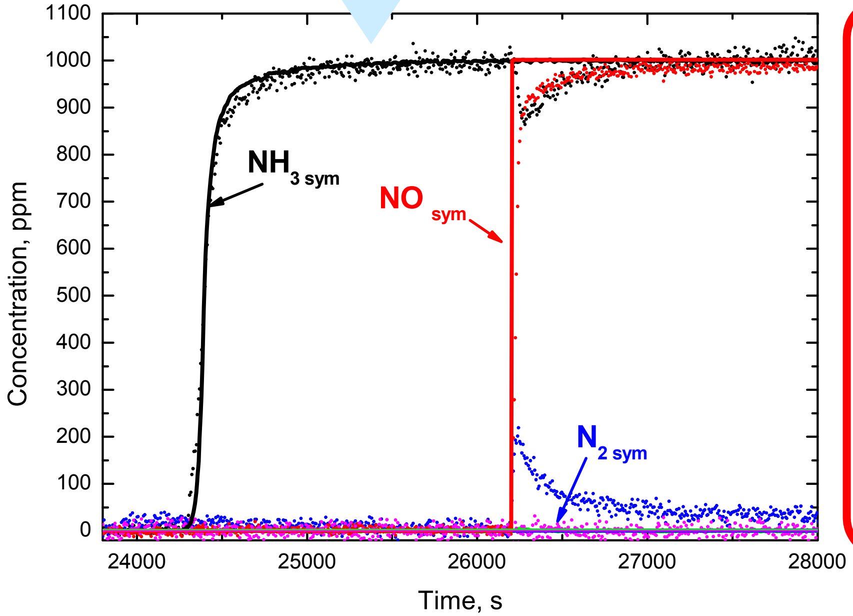
$$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O$$

TPSR of NH_3 + NO on nitrates

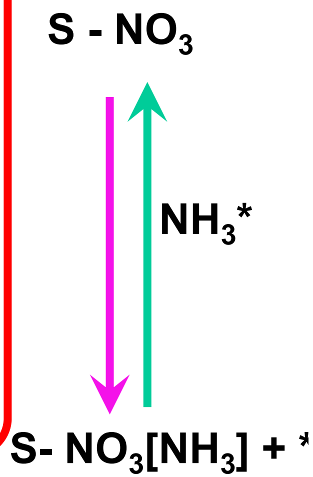




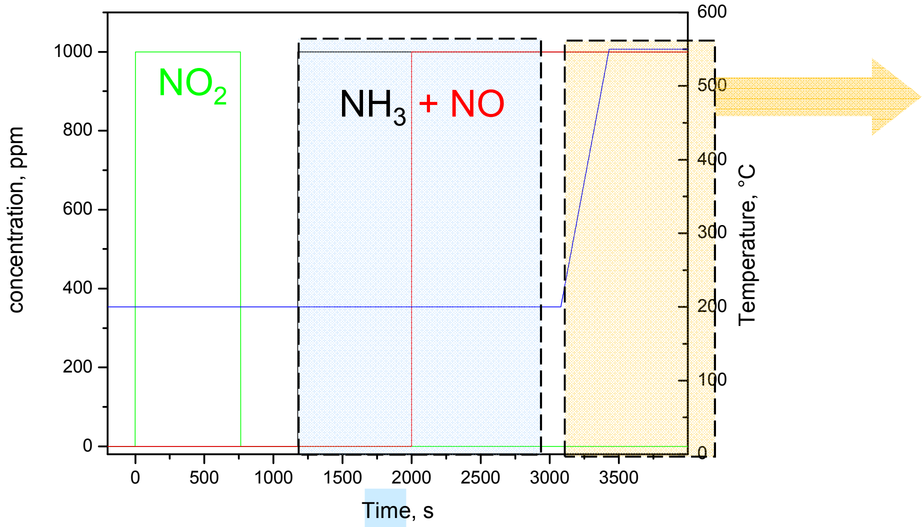
T=120°C

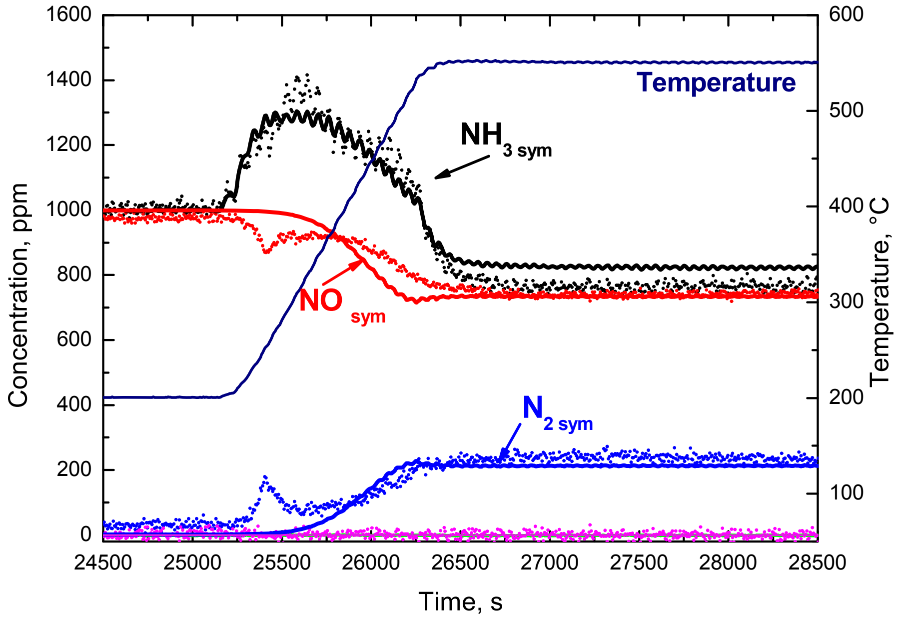


- NH_3 blocks nitrates reduction by NO at T≤ 120-150°C
- The blocking effect disappears on increasing temperature → complete consumption of nitrates
- High T (>400°C) reactivity related to Slow SCR

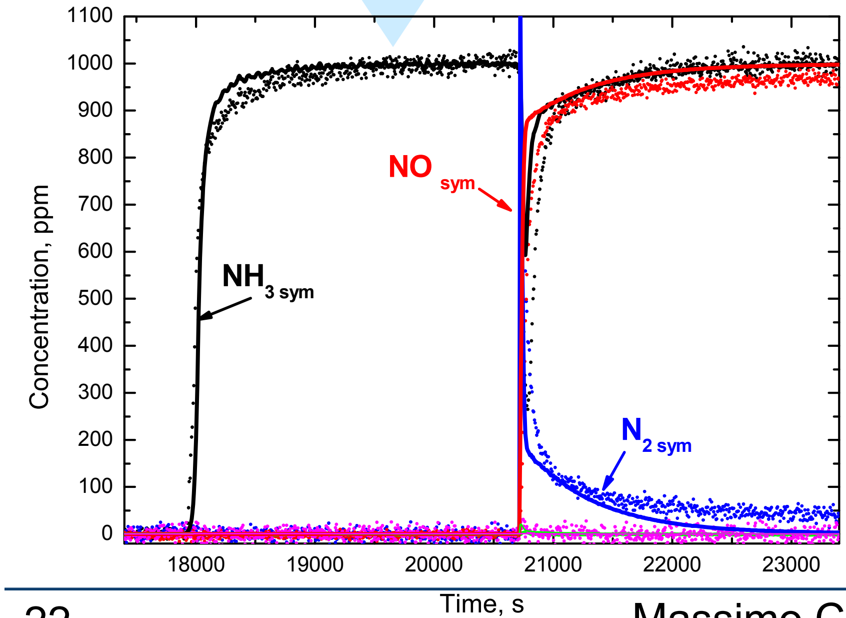


TPSR of NH_3 + NO on nitrates





T=200°C



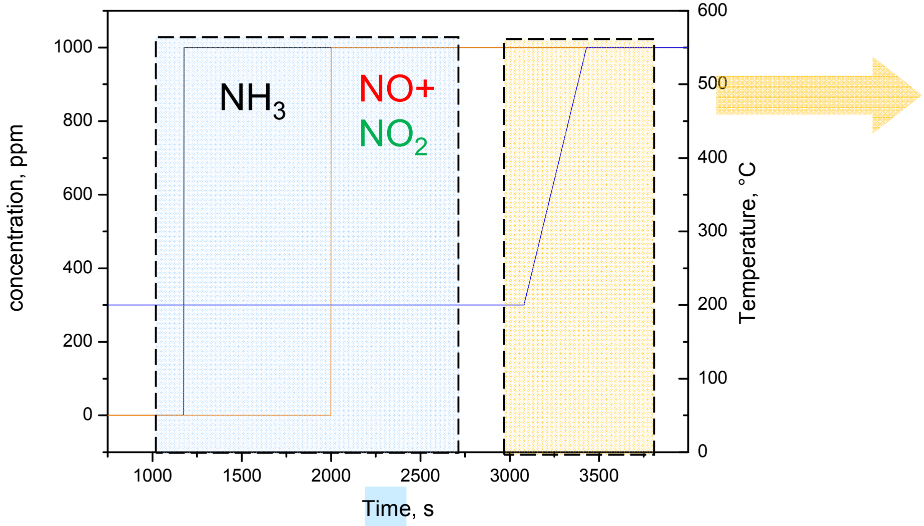
- NH_3 blocking effect absent at 200°C
- Nitrates completely consumed during isothermal phase

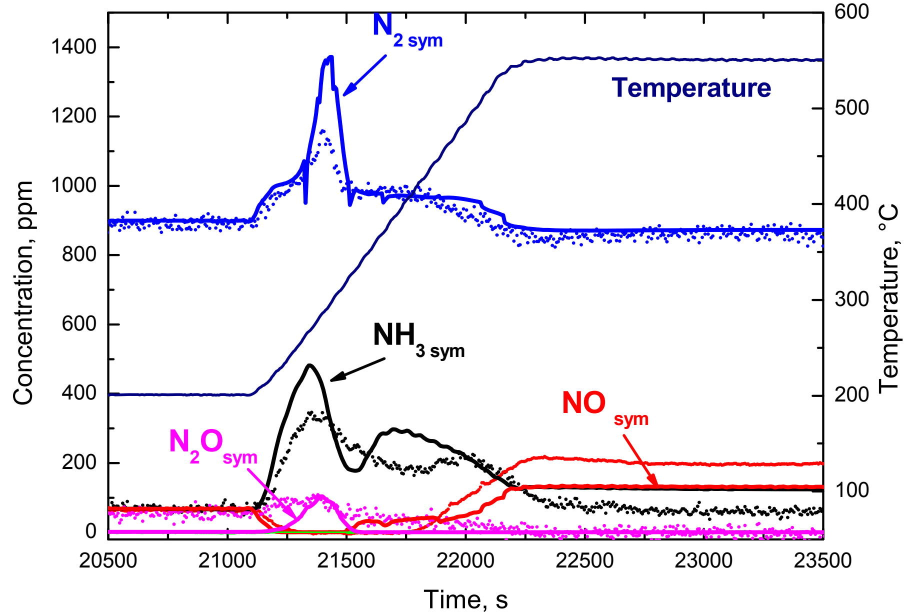
S - NO_3

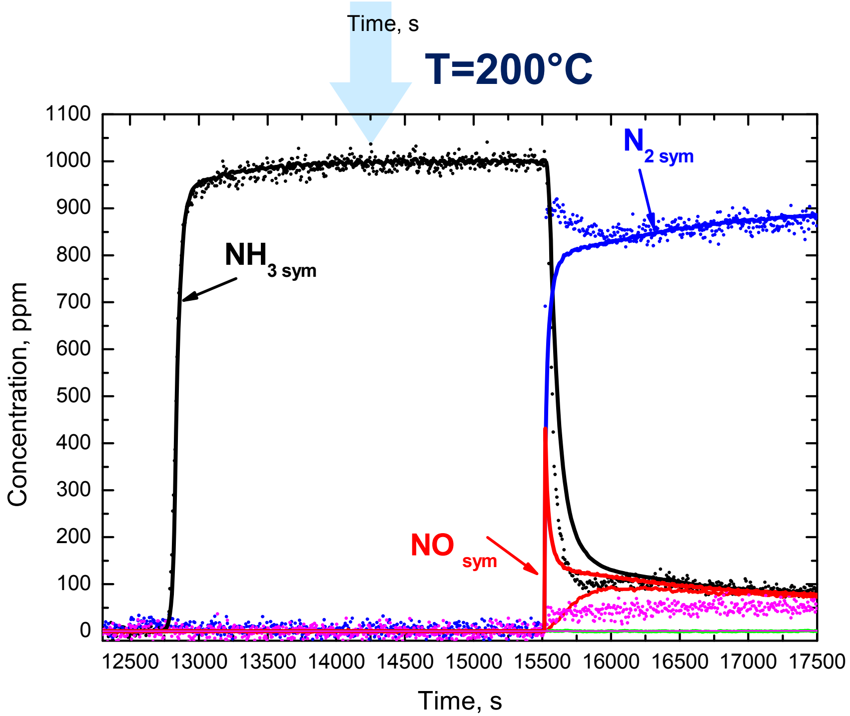
NH_3*

S- $NO_3[NH_3]$ + *

TPR NH_3+NO+NO_2: predictive simulation







- Strong formation of ammonium nitrate at low temperature
- FAST-SCR activity quantitatively described by **predictive simulation!!**

CONCLUSIONS

- ✓ Developed model accounts for ammonia and nitrates storage/reactivity in close agreement with surface chemistry
- ✓ Nitrite/nitrates storage/reactivity key to transient kinetic modeling of NH_3-SCR at low-T over Cu-zeolites
- ✓ Good quantitative agreement between kinetic fit & experiments over a wide range of experimental conditions
- ✓ Successful validation against TPR data
- ✓ Further developments: extension to other SCR catalysts (Fe-zeolite, $V_2O_5/WO_3/TiO_2$)

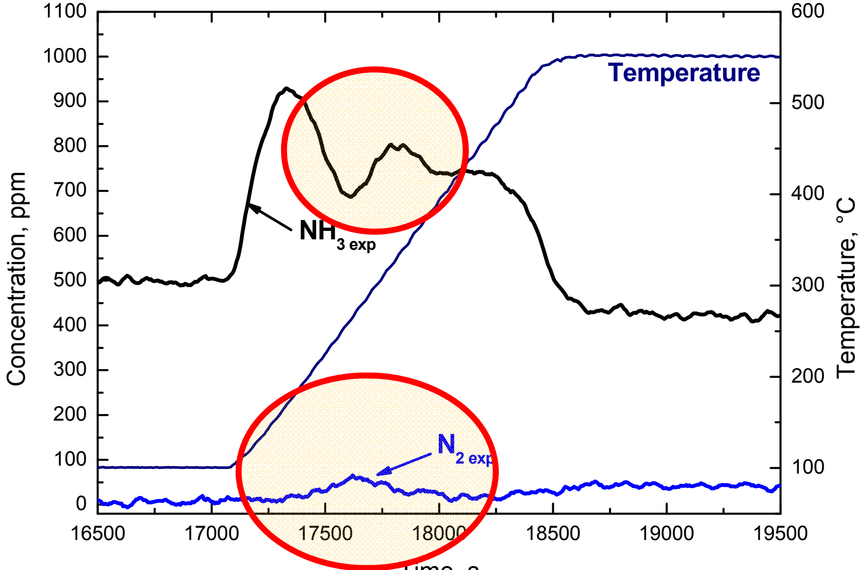
Model limits & future developments

Changes of the catalyst Red-Ox state are NOT considered yet:

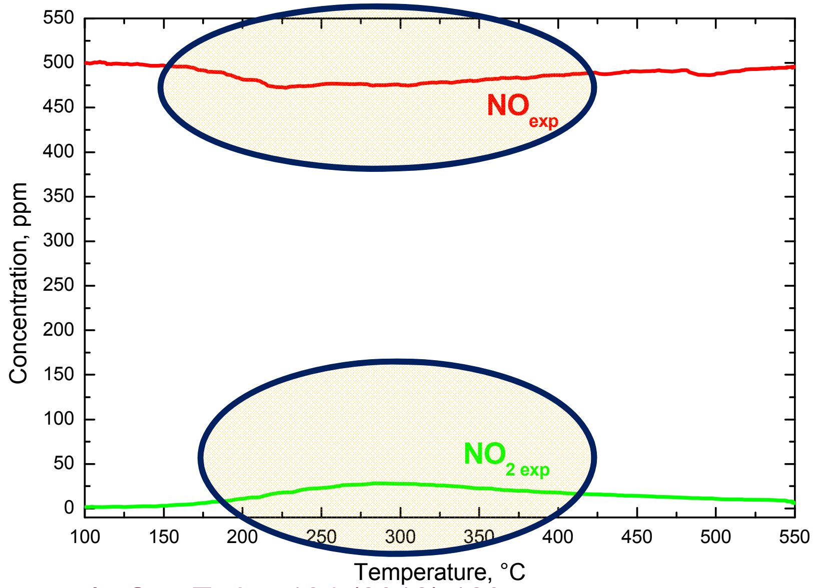
- In presence of NO_2/nitrates the catalyst is mostly in its oxidized state[1,2] → description of catalyst red-ox features not mandatory

- In absence of NO_2/nitrates key role of catalyst red-ox features → e.g. Standard-SCR chemistry, NH_3 oxidation

Catalyst reduction by NH_3



Catalyst reduction by NO



[1] Colombo et al., App.Cat.B: Environmental. 111 (2012) 433; [2] Ribeiro et al., Cat. Today 184 (2012) 129

Acknowledgements

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Thank you for your attention!

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