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EXPERIMENTAL AND MODELLING STUDY OF THE EFFECT OF DIFFUSIONAL LIMITATIONS ON THE NH_3 SCR ACTIVITY

Maria Pia Ruggeri, **Isabella Nova**, Enrico Tronconi

POLITECNICO DI MILANO

Laboratory of Catalysis and Catalytic Processes LCCP

Outline

Introduction

- mass transfer phenomena in SCR honeycomb monolith catalysts

Kinetic data collected over powdered catalyst

- diffusion-free analysis

Validation runs over monolith catalyst

- assessment of mass transfer resistances from powdered vs. monolith data

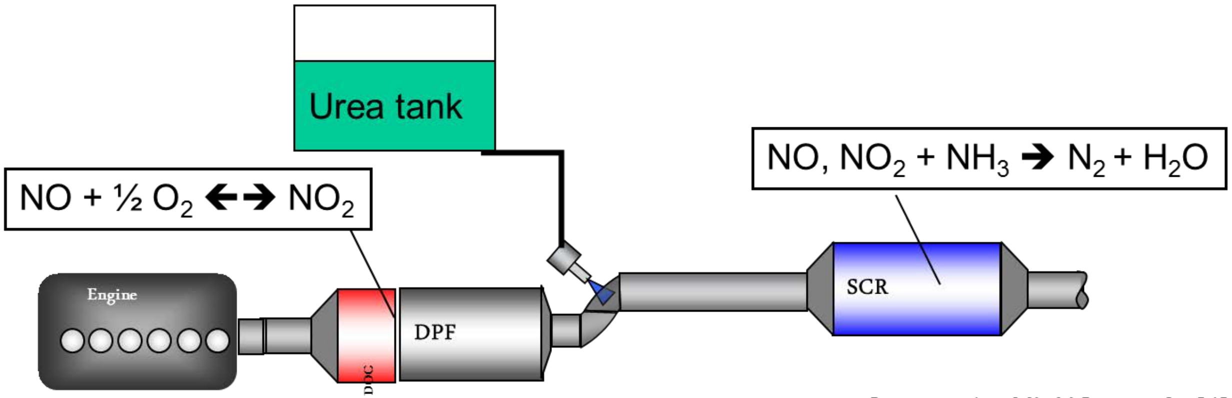
Model simulations

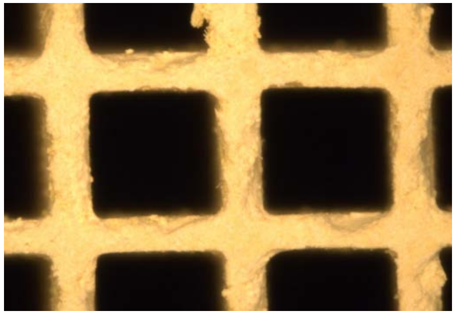
- analysis of internal and external diffusional limitations

Conclusions

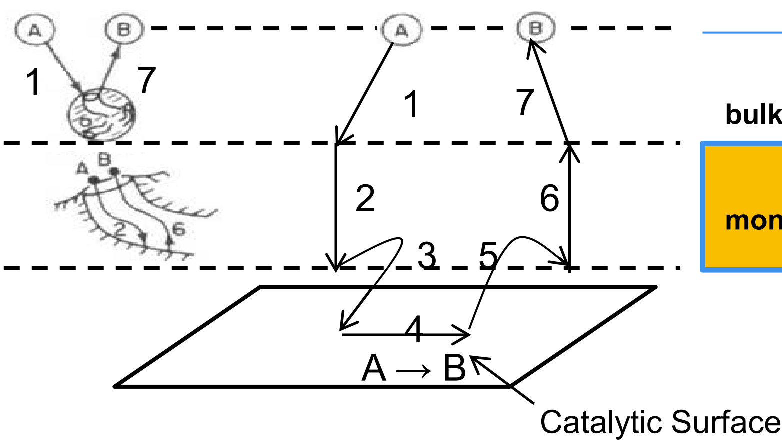
Introduction

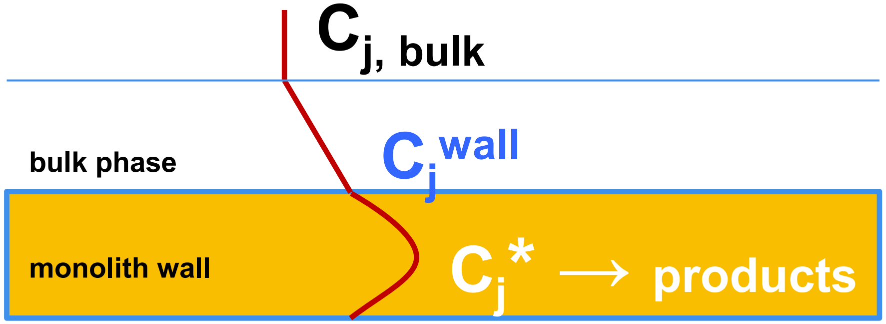
Development of chemically consistent mathematical models of SCR monolithic converters equipped with V-based extruded or Fe- and Cu-promoted washcoated monoliths for Diesel vehicles.





Source: 1st MinNOx conf., 2/2007

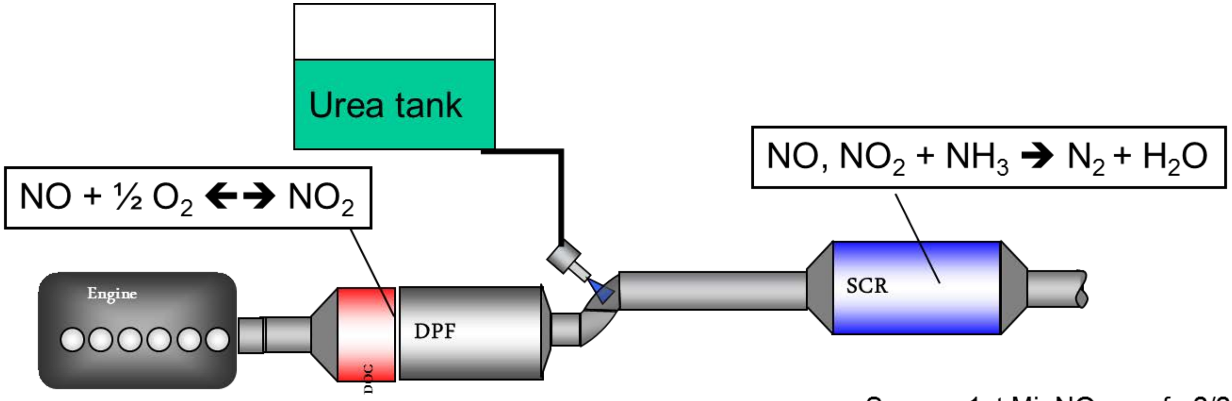




Metkar et al., Chem. Eng. Sci. 66 (2011) 5192
Nova et al., Ind. Eng. Chem. Res. 50 (2011) 299

Introduction

Development of chemically consistent mathematical models of SCR monolithic converters equipped with V-based extruded or Fe- and Cu-promoted washcoated monoliths for Diesel vehicles.



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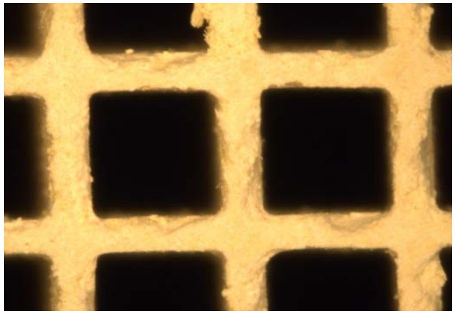


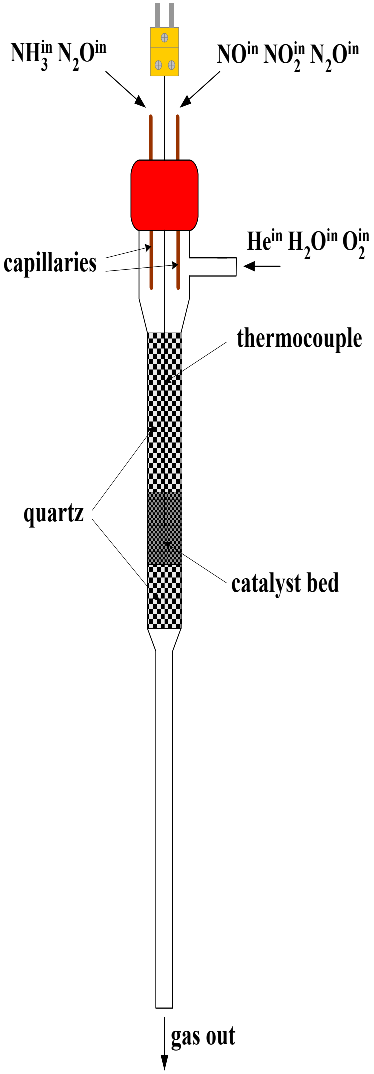
Aim of the work:

quantification of the intra- and interphase diffusional limitations in V-based extruded monolith SCR catalysts

Kinetic data collected over powdered catalyst

… diffusion-free analysis

Micro-reactor experiments



average particle size = 90 μm

80 mg of catalyst diluted with cordierite up to 160 mg

catalyst bed height = 1 cm

Experimental conditions:

GHSV = 30’000-70’000 h^{-1}
H_2O = 8 %; O_2 = 2-8 %
NH_3 = 500-1000 ppm
NO = 0-500 ppm
NO_2 = 0-500 ppm
NO/NO_2 = 0-1
T = 150-550°C

Micro-reactor model

Hypothesis:

1D heterogeneous plug flow dynamic model

isothermal, isobaric

Gaseous phase: $$\varepsilon \frac{\partial C_i}{\partial t} = -v \frac{\partial C_i}{\partial z} - (1-\varepsilon) R_i$$

$i = \{NH_3, NO, NO_2, N_2O\}$

Adsorbed phase: $$\Omega_j \frac{\partial \theta_j}{\partial t} = -R_j$$

$j = NH_3^*$

$$R_{i-j} = \left[mol / \left(m^3_{cat} \cdot s \right) \right]$$

V-based catalyst: SCR kinetics

Ammonia adsorption/desorption

$NH_3 \Leftrightarrow NH_3^*$

$$r_{ads} = k_{ads}\, C_{NH3}\, (1 - \theta_{NH3} - \theta_{HNO3})$$

$$r_{des} = \exp[k_{des} - \frac{E_{des}}{RT}(1 - \alpha\Theta_{NH3})]\Theta_{NH3}$$

Ammonia oxidation

$NH_3^* + 3/4\ O_2 \rightarrow 1/2\ N_2 + 3/2\ H_2O$

$$r_{ox} = \exp\left(k_{ox} - \frac{E_{ox}}{RT}\right)\theta_{NH3}(\frac{p_{O2}}{0.02})^{0.275}$$

Standard-SCR

$NH_3^* + NO + 1/4\ O_2 \rightarrow N_2 + 3/2\ H_2O$

$$r_{NO} = \frac{\exp(k'_{NO} - \frac{E_{NO}}{RT})C_{NO}\theta_{NH3}}{\left(1 + K_{NH3}\frac{\theta_{NH3}}{1 - \theta_{NH3}}\right)\left(1 + k_{O2}\frac{C_{NO}\,\theta_{NH3}}{p_{O2}^{1/4}}\right)}$$

Fast-SCR

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

$$r_{fst} = \exp\left(k_{fst} - \frac{E_{fst}}{RT}\right)\theta_{NH3}\theta_{HNO3}C_{NO}$$

Nitrates formation

$2\ NO_2 + NH_3^* \rightarrow N_2 + H_2O + HNO_3^*$

$$r_{amm} = \frac{k_{amm}C_{NO2}^2\theta_{NH3}(1 - \theta_{NH3} - \theta_{HNO3})}{\theta_{HNO3}}$$

Nitrates adsorption/desorption

$HNO_3^* \Leftrightarrow HNO_3$

$$r_{nit} = \beta\,\theta_{HNO3} - k_{nit}\,C_{HNO3}(1 - \theta_{NH3} - \theta_{HNO3})$$

NO_2-SCR

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

$$r_{NO2} = \exp\left(k_{NO2} - \frac{E_{NO2}}{RT}\right)\theta_{NH3}C_{NO2}$$

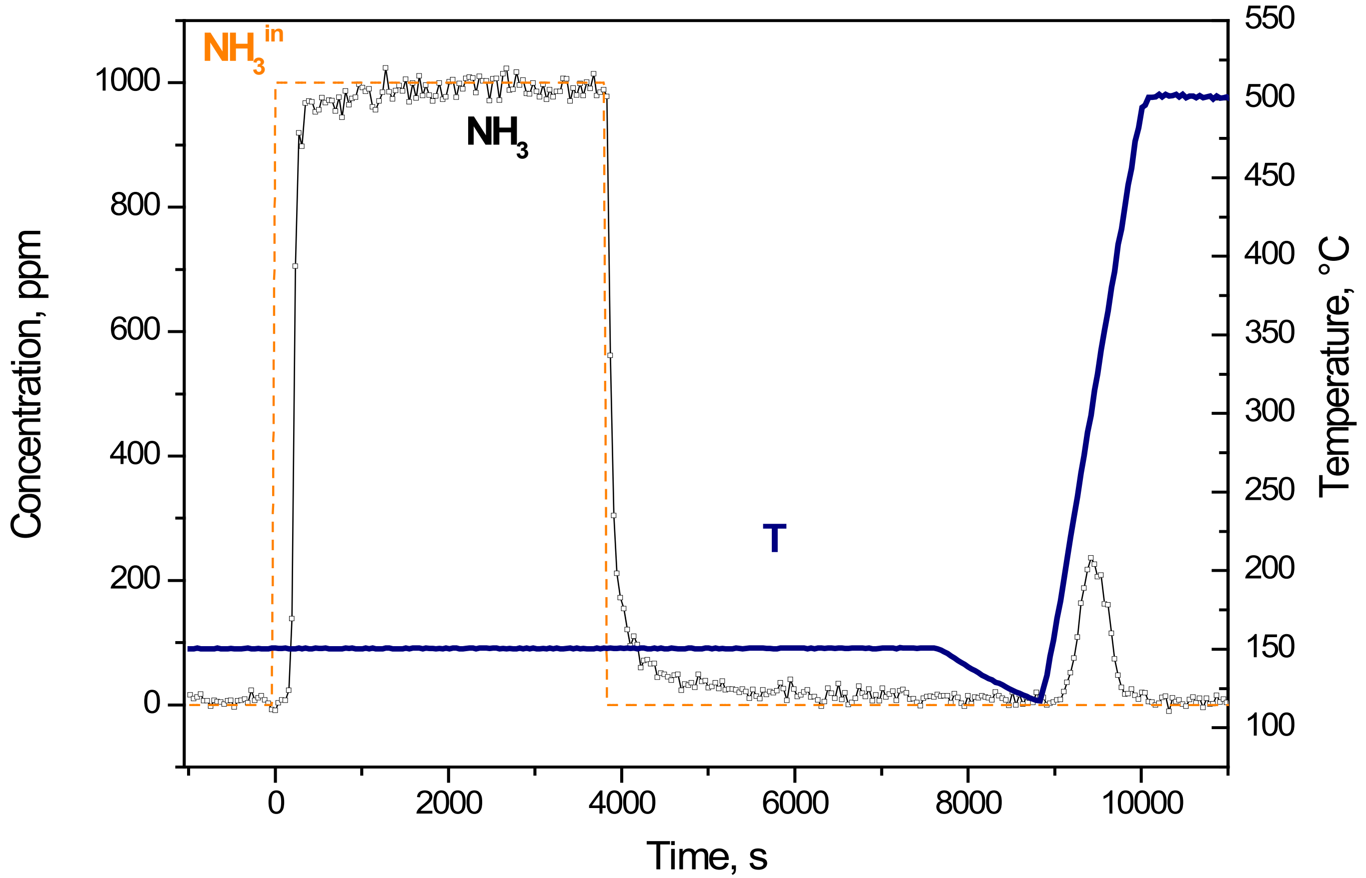
N_2O formation

$NH_3^* + HNO_3^* \rightarrow 2N_2O + 2H_2O$

$$r_{N2O} = \exp\left(k_{N2O} - \frac{E_{N2O}}{RT}\right)\theta_{NH3}\theta_{HNO3}$$

Podwered catalyst: NH_3 adsorption/desorption

Symbols = experimental



Experimental conditions:

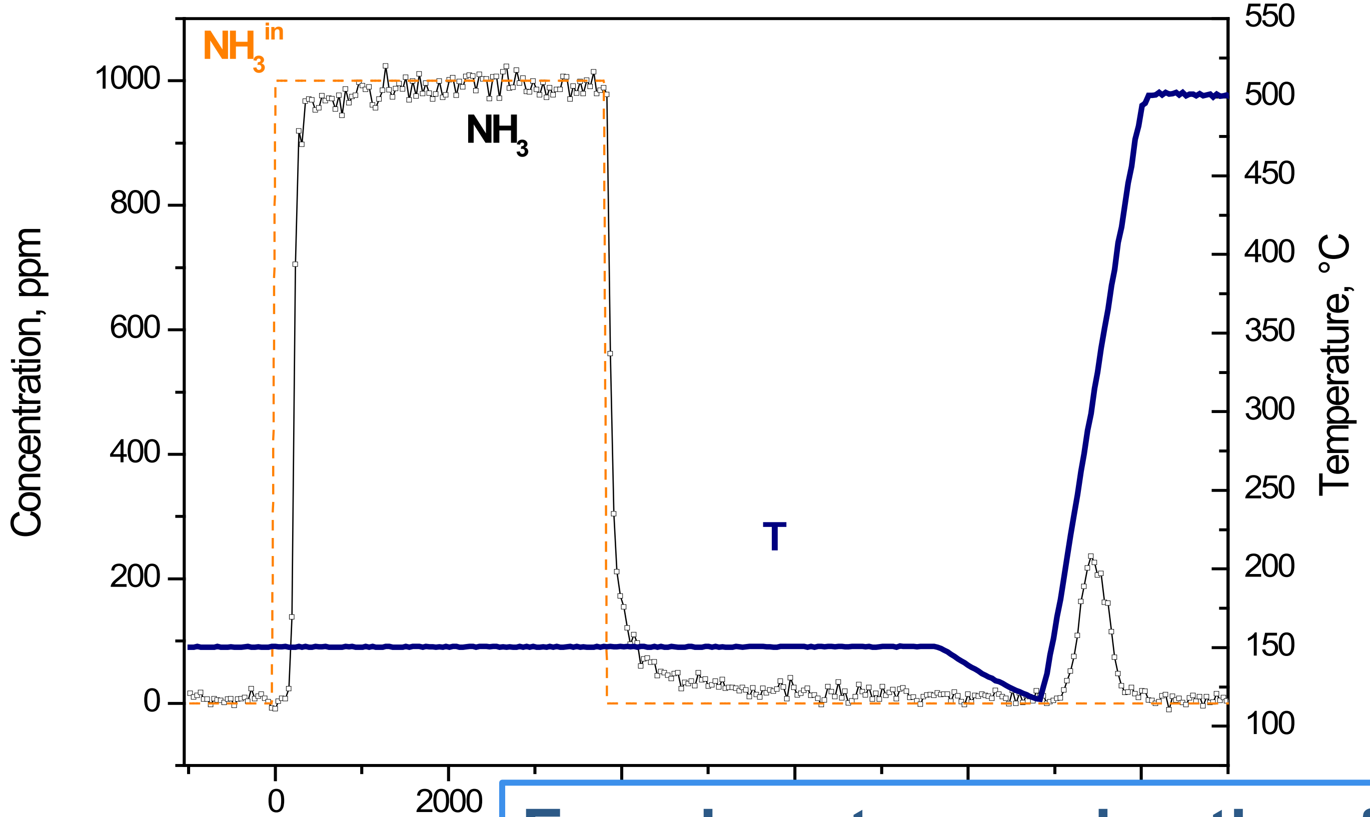
NH_3 = 1000 ppm

$H_2O = O_2$= 0%; T_{ads} = 150°C, heating rate = 15°C/min

GHSV = 30’000 h^{-1}

Podwered catalyst: NH_3 adsorption/desorption

Symbols = experimental



Experiments covering the effects of:

- ammonia concentration
- adsorption temperature
- TPD heating rate

Experimental conditions:

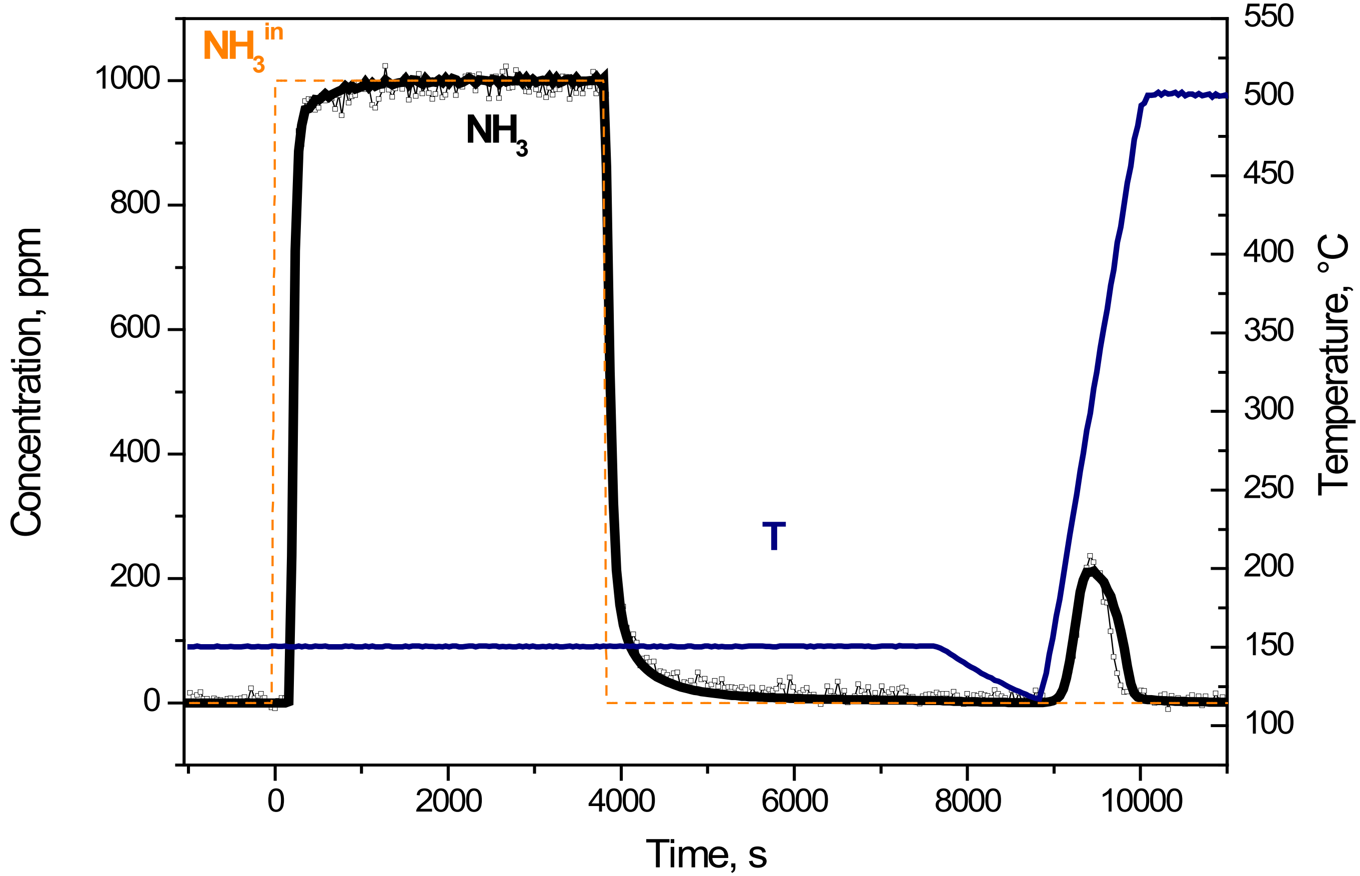
NH_3 = 1000 ppm

H_2O = O_2= 0%; T_{ads} = 150°C, heating rate = 15°C/mi

GHSV = 30’000 h^{-1}

Podwered catalyst: NH_3 adsorption/desorption

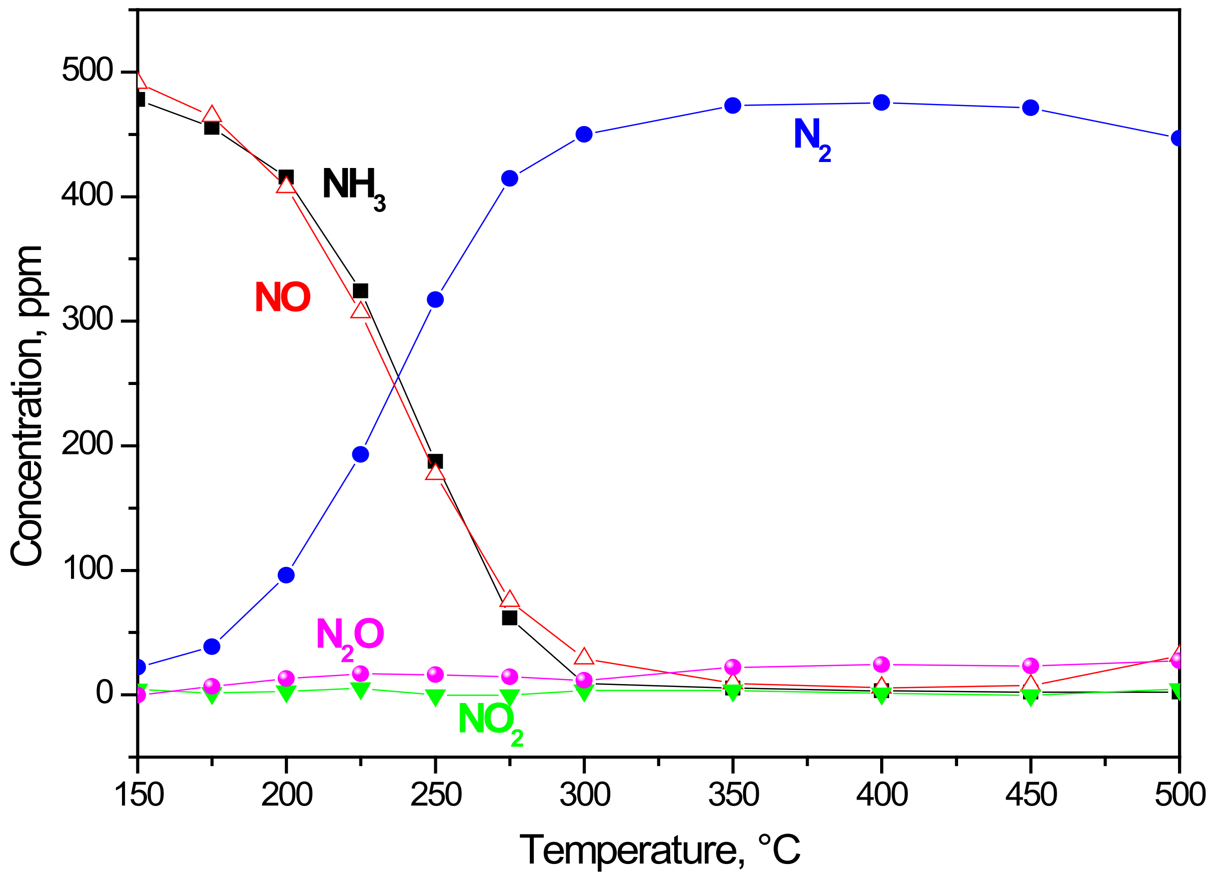
Symbols = experimental
Thick lines = kinetic fit



Experimental conditions:
NH_3 = 1000 ppm
H_2O = O_2= 0%; T_{ads} = 150°C, heating rate = 15°C/min
GHSV = 30'000 h^{-1}

Podwered catalyst: $NH_3/NO/O_2$

Symbols = experimental



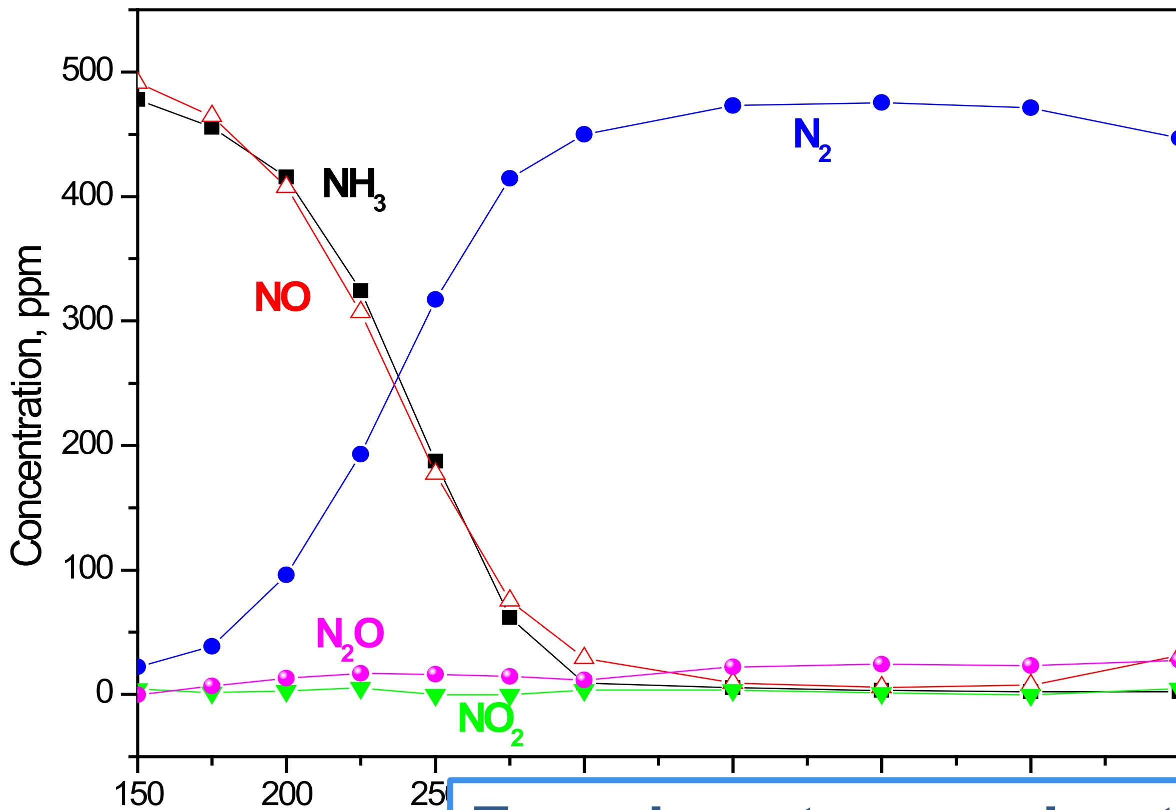
Experimental conditions:
NH_3 = 500 ppm; NO = 500 ppm
H_2O = 8%; O_2 = 8%
GHSV = 70'000 h^{-1}

Standard SCR

$$NH_3 + NO + 1/4\,O_2 \rightarrow N_2 + 3/2\,H_2O$$

Podwered catalyst: $NH_3/NO/O_2$

Symbols = experimental



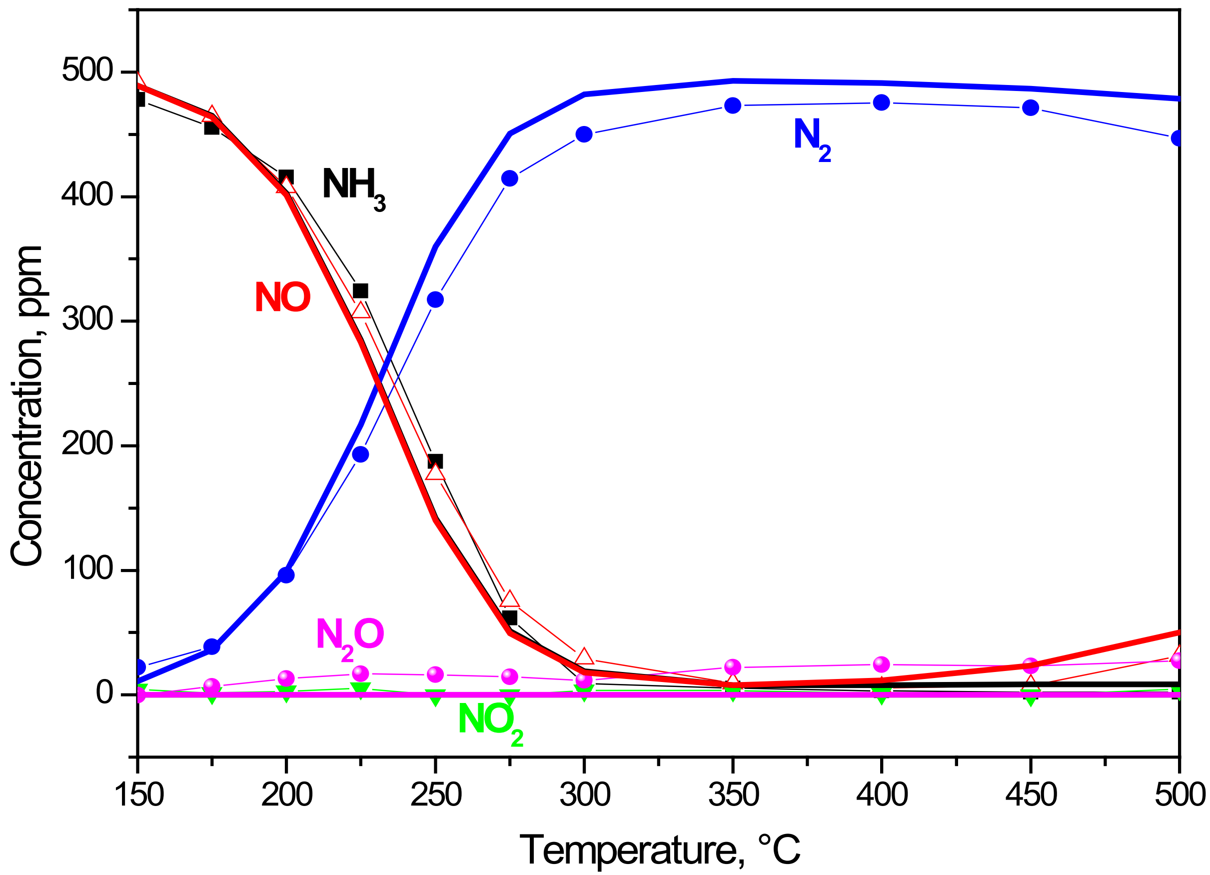
Experimental conditions:
NH_3 = 500 ppm; NO = 500 ppm
H_2O = 8%; O_2 = 8%
GHSV = 70’000 h^{-1}

Experiments covering the effects of:

- Flow rates
- O_2 concentration
- Transient behavior

Podwered catalyst: $NH_3/NO/O_2$

Symbols = experimental
Thick lines = kinetic fit



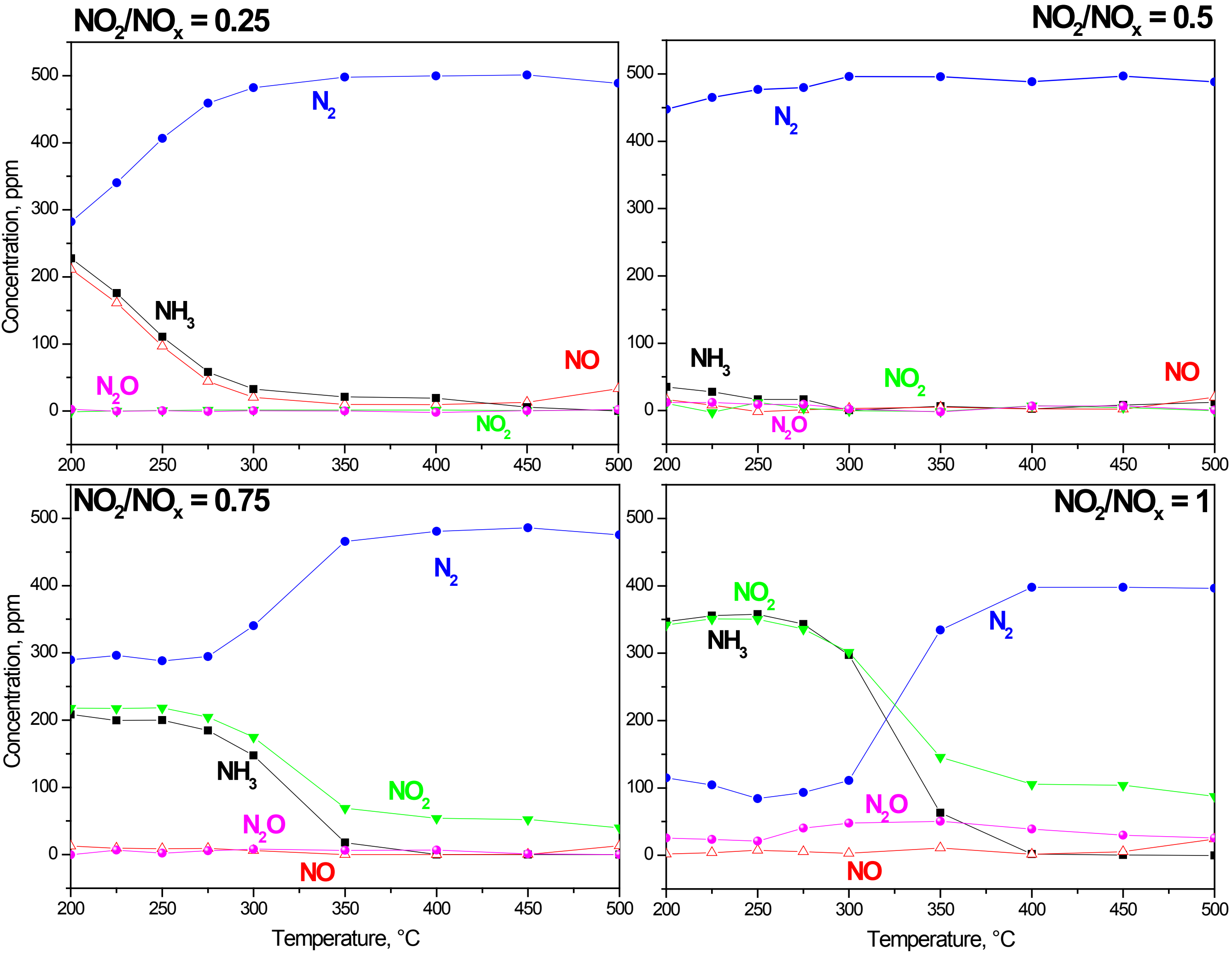
Experimental conditions:
NH_3 = 500 ppm; NO = 500 ppm
H_2O = 8%; O_2 = 8%
GHSV = 70'000 h^{-1}

Standard SCR

$$NH_3 + NO + 1/4\,O_2 \rightarrow N_2 + 3/2\,H_2O$$

Podwered catalyst: $NH_3/NO_x/O_2$

Symbols = experimental



Fast SCR

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

Formation of NH_4NO_3

$$2NH_3 + 2NO_2 \rightarrow NH_4NO_3 + N_2 + H_2O$$

Formation of N_2O

$$2NH_3 + 2NO_2 \rightarrow N_2 + N_2O + 3H_2O$$

NO_2 SCR

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

Experimental conditions:

NH_3 = 500 ppm; NO $_x$= 500 ppm

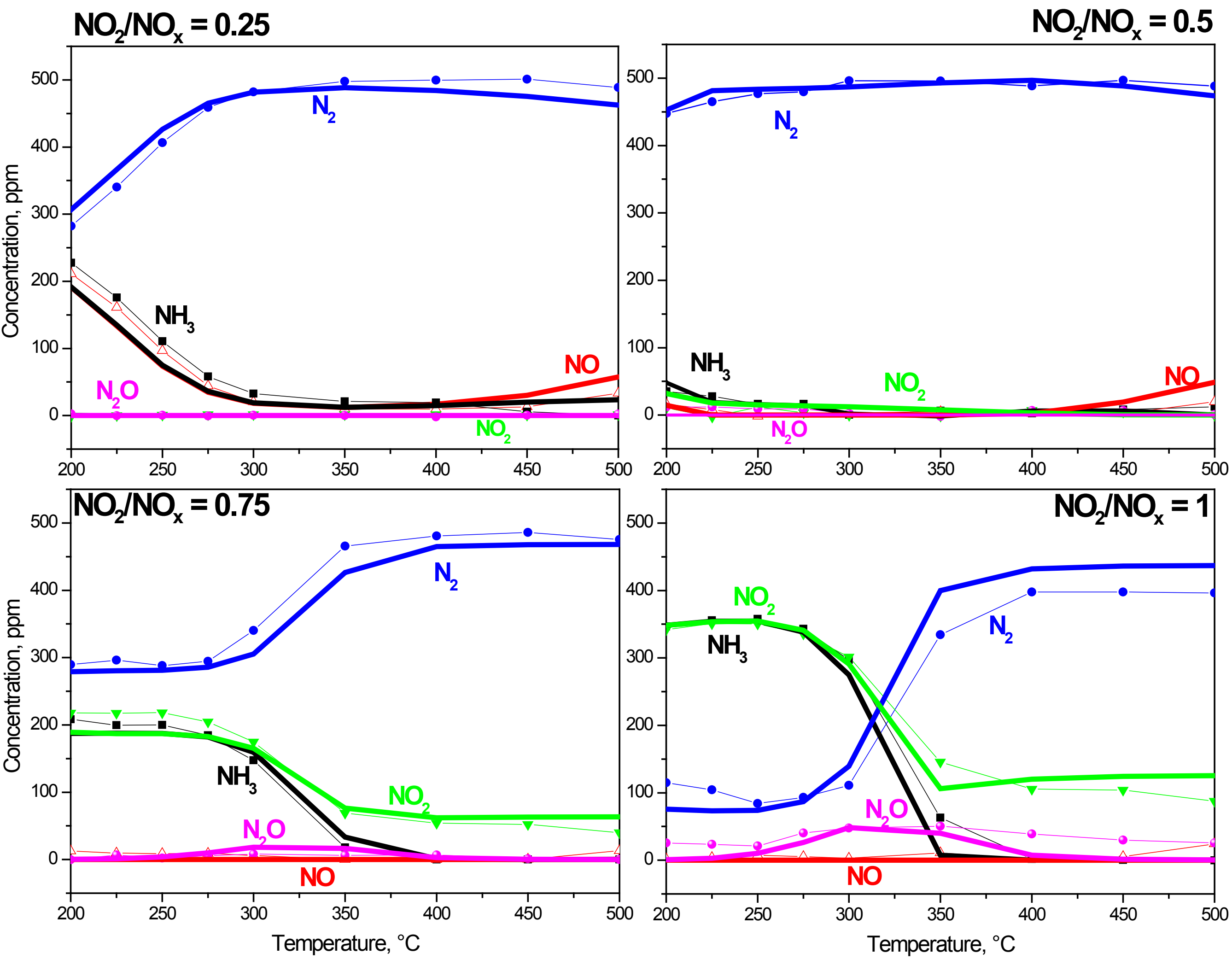
H_2O = 8%; O_2 = 2%

GHSV = 70’000 h^{-1}

Podwered catalyst: $NH_3/NO_x/O_2$

Symbols = experimental

Thick lines = kinetic fit



Fast SCR

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

Formation of NH_4NO_3

$$2NH_3 + 2NO_2 \rightarrow NH_4NO_3 + N_2 + H_2O$$

Formation of N_2O

$$2NH_3 + 2NO_2 \rightarrow N_2 + N_2O + 3H_2O$$

NO_2 SCR

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

Experimental conditions:

NH_3 = 500 ppm; NO_x= 500 ppm

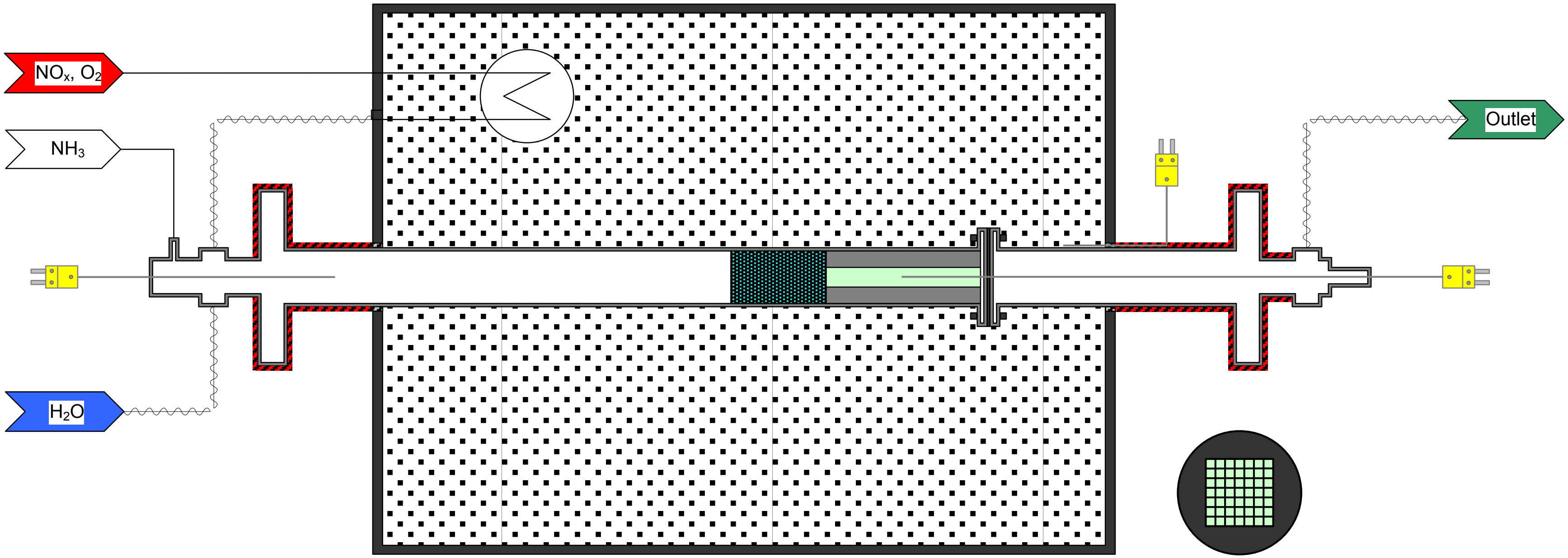
H_2O = 8%; O_2 = 2%

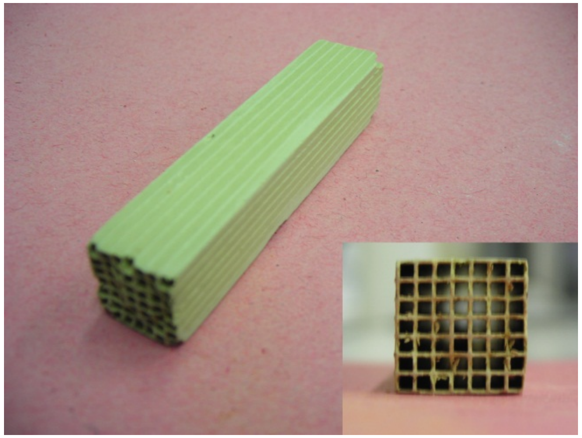
GHSV = 70’000 h^{-1}

Validation runs over monolith catalyst

… assessment of mass transfer from powdered vs. monolith data

Monolith reactor experiments





Sample:

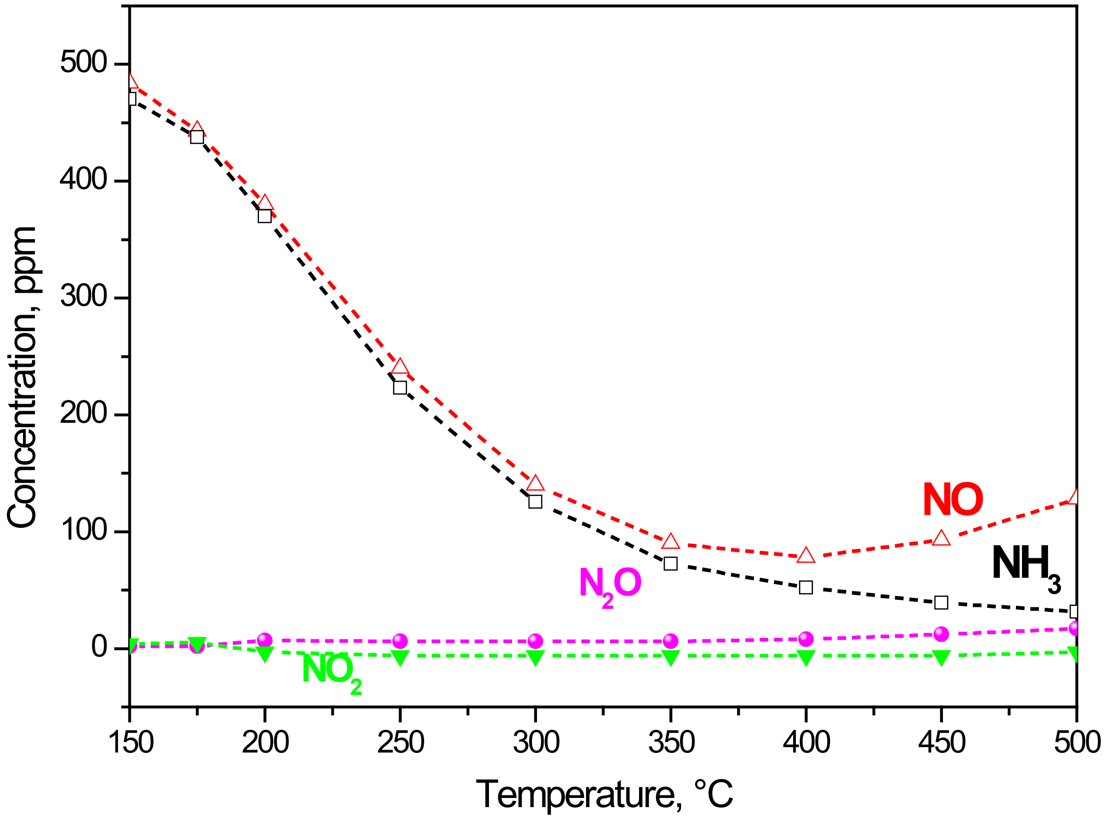
CPSI= 300
Wall thickness = 0.32 mm
V = 5 cm^3
Lenght = 5.2 cm
Channels = 49

Experimental conditions:

GHSV = 30'000-70'000 h^{-1}
H_2O = 8 %; O_2 = 2-8 %
NH_3 = 500-1000 ppm
NO = 0-500 ppm
NO_2 = 0-500 ppm
NO/NO_2 = 0-1
T = 150-550°C

Monolith data: $NH_3/NO/O_2$

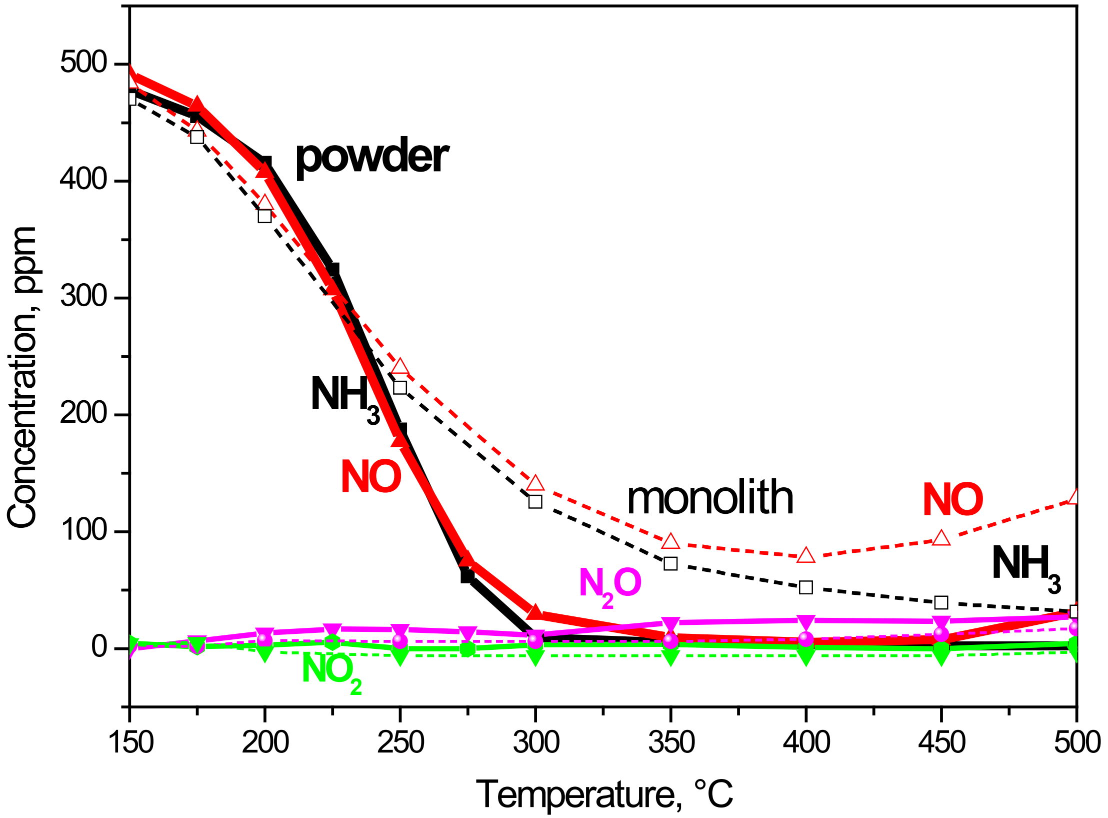
Dashed lines = monolith data



Experimental conditions:
NH_3 = 500 ppm; NO = 500 ppm
H_2O = 8%; O_2 = 8%
GHSV = 70’000 h^{-1}

Monolith vs. powdered data: $NH_3/NO/O_2$

Dashed lines = monolith data
Thick lines = podwer data

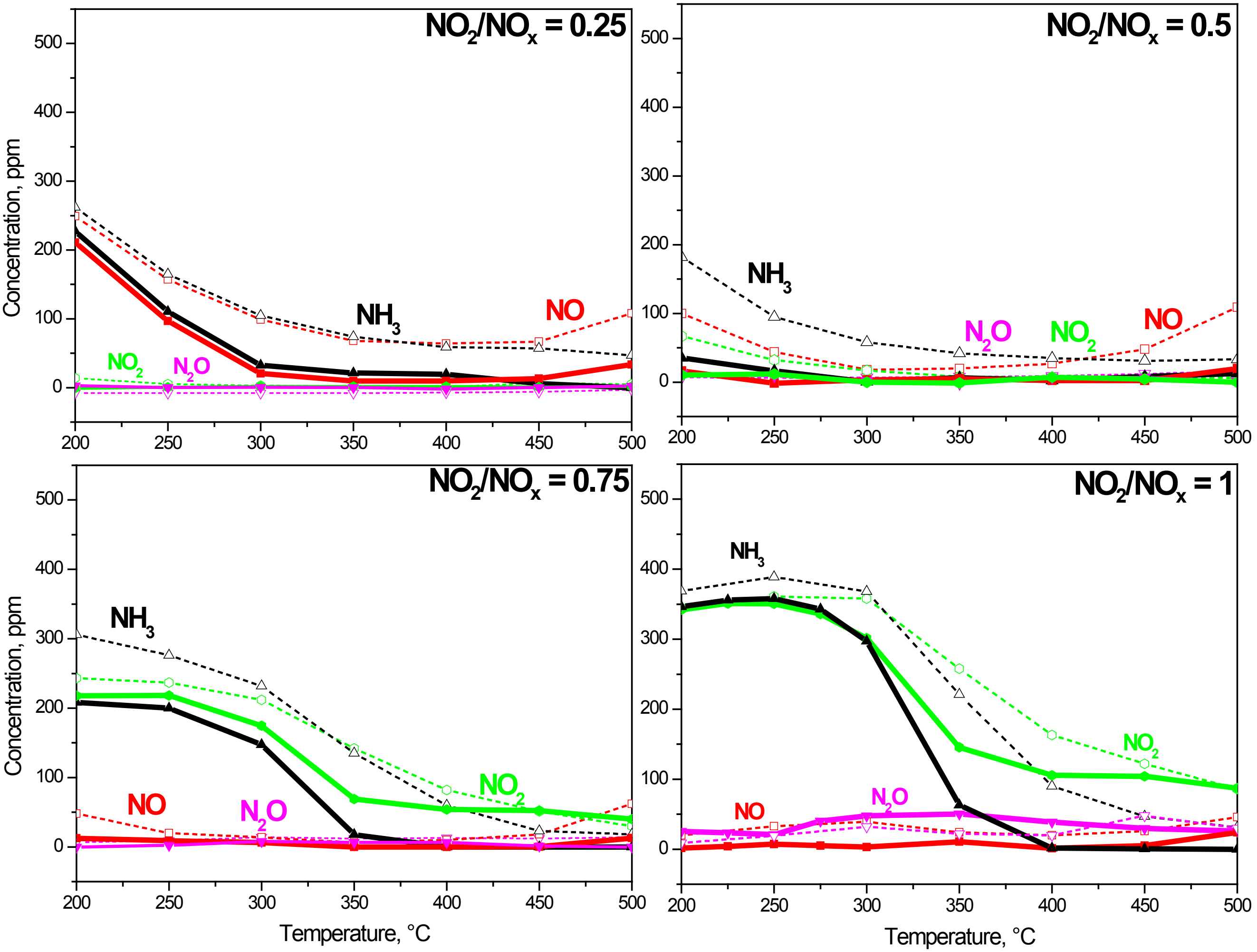


The monolith shows lower conversions at T > 250°C

onset of diffusional limitations

Experimental conditions:
NH_3 = 500 ppm; NO = 500 ppm
H_2O = 8%; O_2 = 8%
GHSV = 70'000 h^{-1}

Monolith vs. powdered data: $NH_3/NO_x/O_2$



Dashed lines = monolith data
Thick lines = podwer data

Consistent deviations in the range 200 <T < 500°C in the presence of NO_2

Experimental conditions:
NH_3 = 500 ppm; NO_x= 500 ppm
H_2O = 8%; O_2 = 2%
GHSV = 70’000 h^{-1}

Model simulations

… analysis of internal and external diffusional limitations

1D + 1D model for monolith converters

Hypothesis: identical conditions within each channel, negligible axial dispersion and pressure drop

1D: heat and mass transfer along the monolith channel

gas phase

$$\frac{\delta C_j}{\delta t} = -\frac{v}{L}\frac{\delta C_j}{\delta z} - \frac{4}{d_h} k_{mt,j}(C_j - C_j^W)$$

solid phase

$$0 = k_{mt,j}(C_j - C_j^W) + R_{eff,j}$$

$j = NH_3, NO, NO_2$

External limitations:
mass tansfer coefficient

$$k_{mt,i} = \frac{Sh}{d_h}(D_{m,i})$$

$$Sh = Sh_\infty + 8.827 \cdot \left(1000 \cdot \frac{L}{d_h Sc \operatorname{Re}}\right)^{-0.545} \exp\left(-48.2 \cdot \frac{L}{d_h Sc \operatorname{Re}}\right)$$

$$Sh_\infty = 2.976$$

1D: reaction and diffusion within the porous structure of the catalyst

flat plate assumption

$$0 = D_{eff,j}\frac{\delta^2 C_j^*}{\delta x^2} + S_W^2 R_j$$

$$R_{eff,j} = -\frac{D_{eff,j}}{S_W}\left.\frac{\delta C_j^*}{\delta x}\right|_W$$

Internal limitations:
effective diffusivity

$$D_{eff_i} = \varepsilon_M^2 \cdot D_{M,i} + \frac{\varepsilon_\mu^2 \cdot (1 + 3 \cdot \varepsilon_M)}{1 - \varepsilon_M} \cdot D_{\mu_i}$$

ε_i and D_i from morphological data

$$D_{eff_i} = \sim 3\text{-}4 \cdot 10^{-6}\ m^2/s\ @200°C$$

Chatterjee et al. SAE 2006-01-0468
Tronconi and Forzatti, AIChE J. 38 (1992) 201
Shah and London, in Advances in Heat Transfer, Ac.Press (1978)
Beekman, Ind. Eng. Chem. Res., 30 (1991) 428

1D + 1D model for monolith converters

Intrinsic kinetics, estimated from powder data

geometrical and morphological properties of the catalyst ($k_{mt,j}$, $D_{eff,j}$)

→ **1D + 1D monolith model**

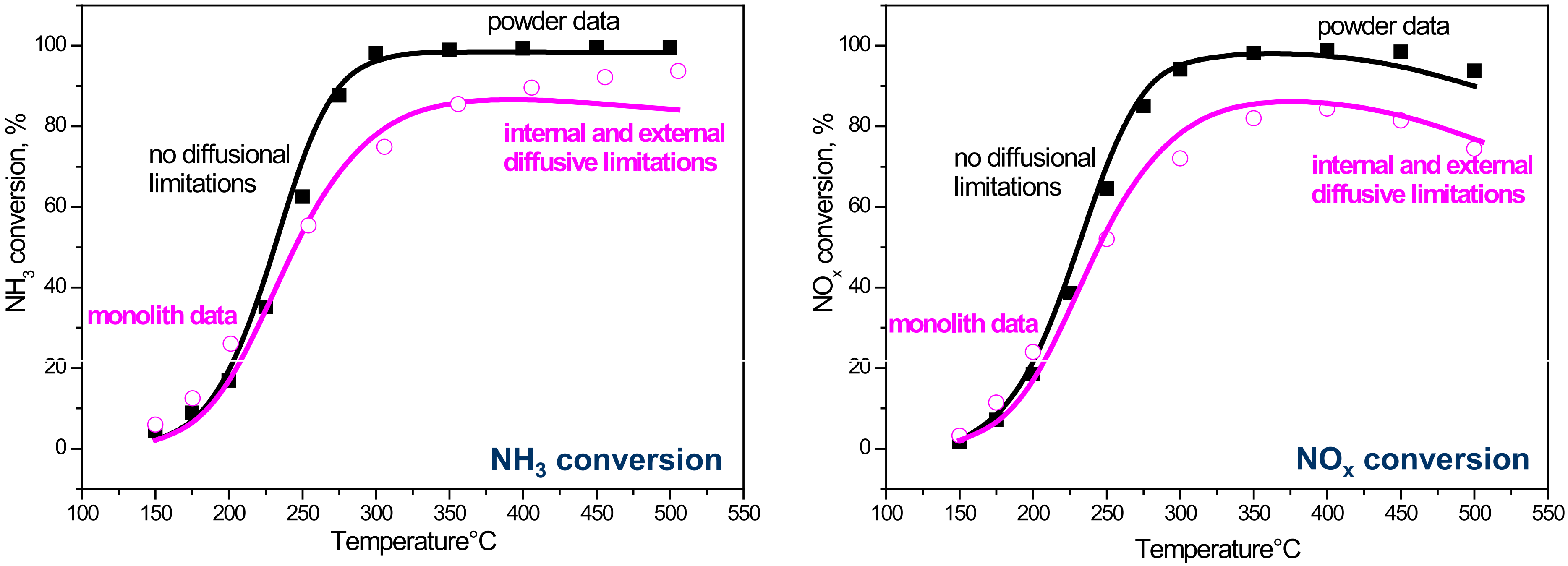
accounting for **external** and **internal** diffusional limitations

Decoupling of the contributions of internal and external mass transfer resistances:

- Simulations for internal diffusional limitation only: $k_{mt,j}$ set to 300 $k_{mt,j}$
- Simulations for external diffusional limitation only: $D_{eff,j}$ set to 30 $D_{eff,j}$

Tronconi and Forzatti, AIChE J. 38 (1992) 201
Shah and London, in Advances in Heat Transfer, Ac.Press (1978)

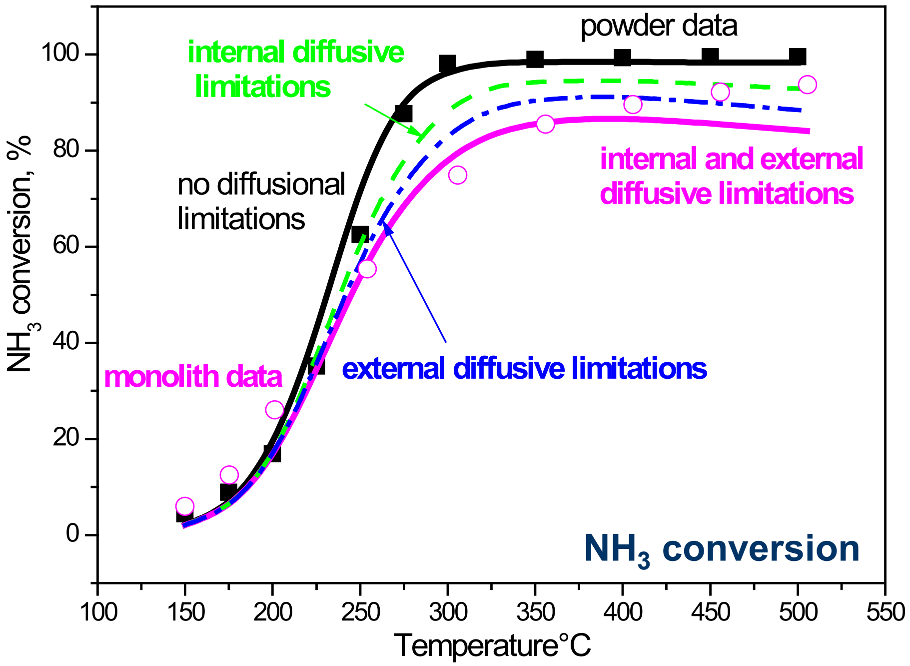
Model simulations: $NH_3/NO/O_2$

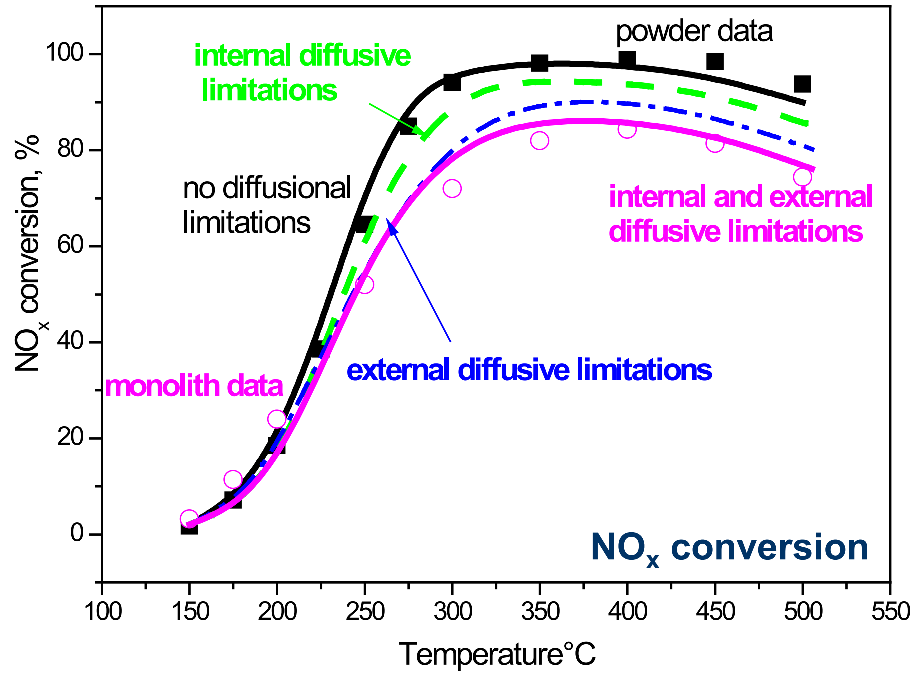


Model simulations in good agreement with monolith data.

Experimental conditions:
NH_3 = 500 ppm; NO = 500 ppm
H_2O = 8%; O_2= 8%
GHSV = 70'000 h^{-1}

Model simulations: $NH_3/NO/O_2$





Model simulations in good agreement with monolith data.

Modest intra-phase limitations already at 200°C, increasing with T

External diffusional limitations starting from 225°C and dominant at higher temperatures

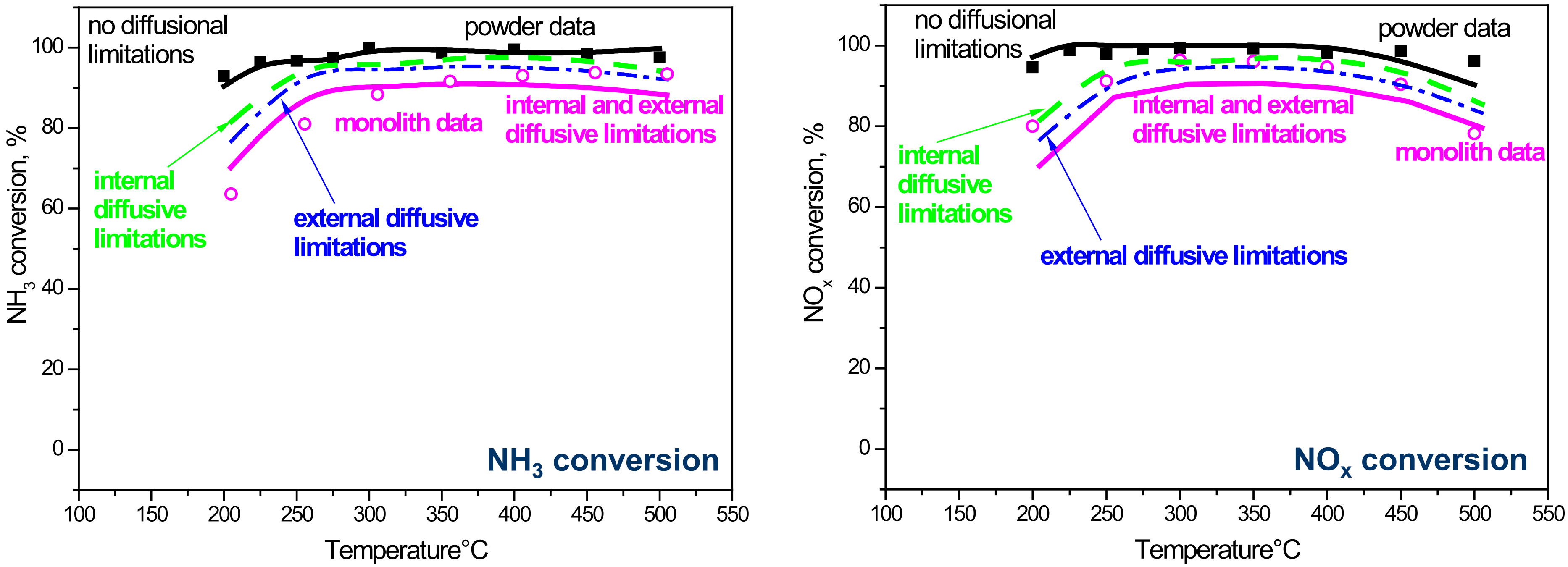
Experimental conditions:

NH_3 = 500 ppm; NO = 500 ppm

H_2O = 8%; O_2= 8%

GHSV = 70’000 h^{-1}

Model simulations: $NH_3/NO/NO_2/O_2$



Both intra and interphase diffusional limitations play a significant role already at 200°C.

External mass transfer phenomena are dominant at T>250°C.

Experimental conditions:
NH_3 = 500 ppm; NO =NO_2= 500 ppm
H_2O = 8%; O_2= 8%
GHSV = 70'000 h^{-1}

Conclusions

- Important role of mass transfer resistances in reducing NH_3-SCR performance pointed out by direct comparison between powder and monolith catalyst data
- Negative deviations observed at 250°C for the Standard SCR and at lower temperature when NO_2 was present
- Predictive 1D+1D model simulations show good agreement with data collected at the monolith scale
- Model analysis allowed discrimination between contributions of internal and external diffusional limitations

Acknowledgements

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B.Bandl-Konrad

DAIMLER

Thank you for your attention!

Laboratory of Catalysis and Catalytic Processes LCCP

Raffaello, The school of Athens, 1509,
Apostolic Palace, Roma

Politecnico di Milano