POLITECNICO DI MILANO
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Milano, Italy

Catalytic Mechanism, Detailed Kinetics and Converter Model for NH_3-SCR of NOx Emissions from Vehicles

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in cooperation with

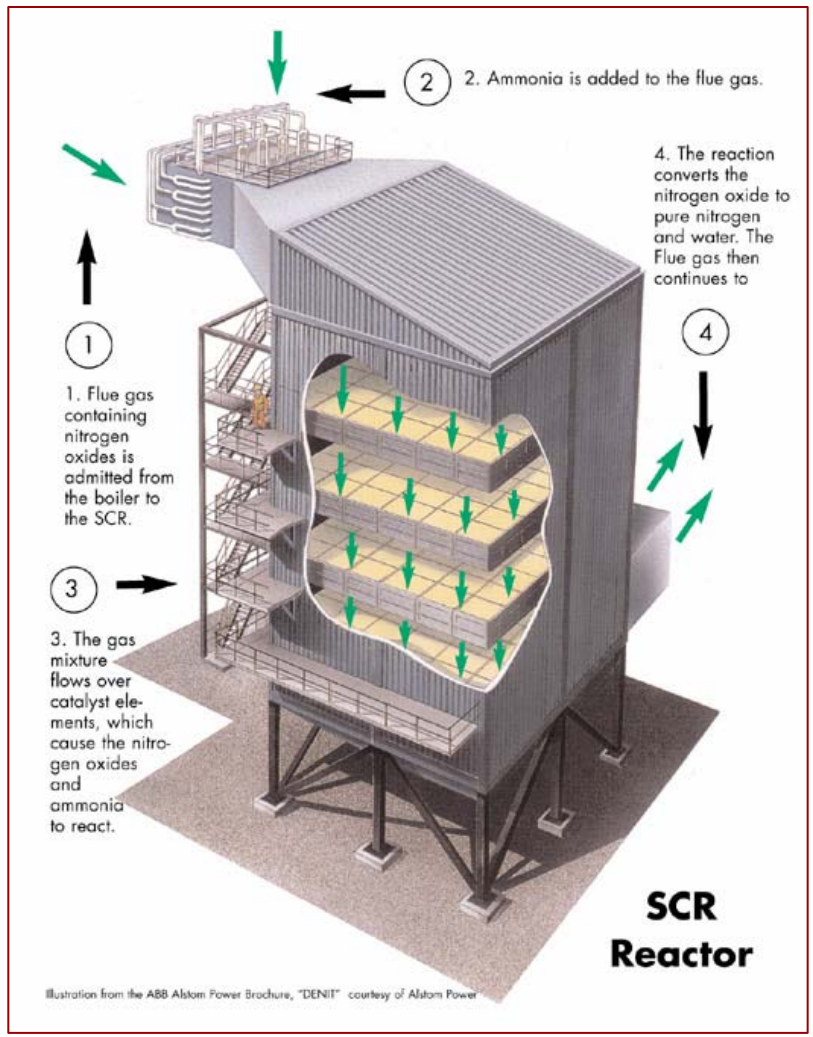
DAIMLERCHRYSLER

Outline

- ***Introduction and previous experience***
- ***Approach and methods***
- ***NH_3 SCR over a V_2O_5-WO_3/TiO_2 catalyst:***
  - NH_3/O_2 system
  - NO/O_2 and NO_2/O_2 systems
  - $NH_3/NO/O_2$ system ("Standard" SCR)
  - Chemistry & Mechanism of "Fast" SCR: role of NO_2
  - Kinetic study of the $NH_3/NO/NO_2/O_2$ system
  - Modeling & scale-up
- ***NH_3 SCR over a Fe-Zeolite catalyst:***
  - Comparison with V-based catalyst: reactivity, chemistry & scale-up to monoliths
- ***Conclusions***

NH_3-SCR process for stationary sources

NH_3-SCR is a well established NO_x abatement technology for stationary sources:



$2NH_3 + 2NO + ½\ O_2 \rightarrow 2N_2 + 3H_2O$

"*Standard*" SCR reaction

Commercial catalysts:
V_2O_5–WO_3/TiO_2 extruded honeycomb monoliths

Operating temperatures:
300 – 400 °C

Investigated at PoliMI
in cooperation with ENEL during the '90s

Motivation and aim of the work

Development of a chemically consistent mathematical model of SCR monolithic converters for vehicles

study of chemistry, mechanism, kinetics of the SCR reactions **over commercial V-based and zeolite catalysts** with focus on characteristics of mobile applications: NO/NO_2–NH_3 reacting system, transient operating conditions…

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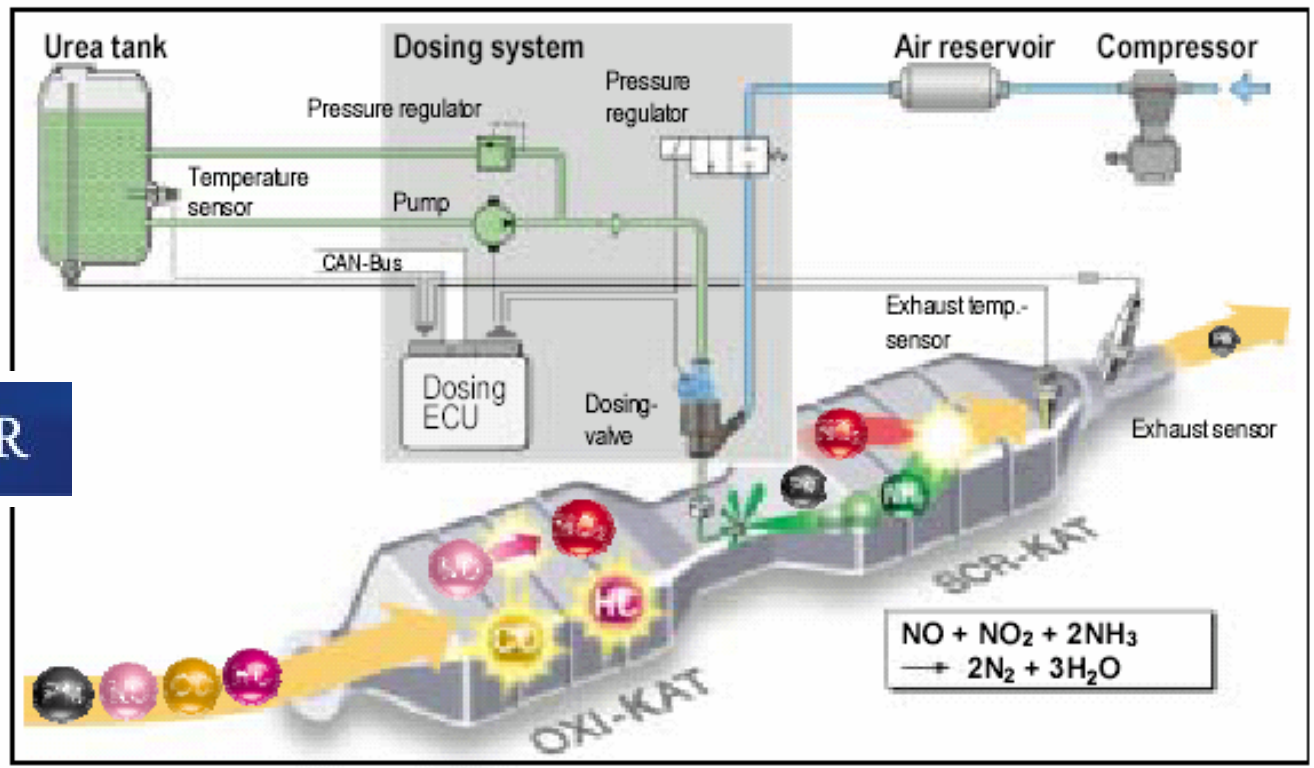


Methods

- **Transient Response reactive experiments**
- **Multiscale experimental approach:**

Powdered catalyst (at **PoliMI**) dp~90 μm
Scale: 80 - 160 mg

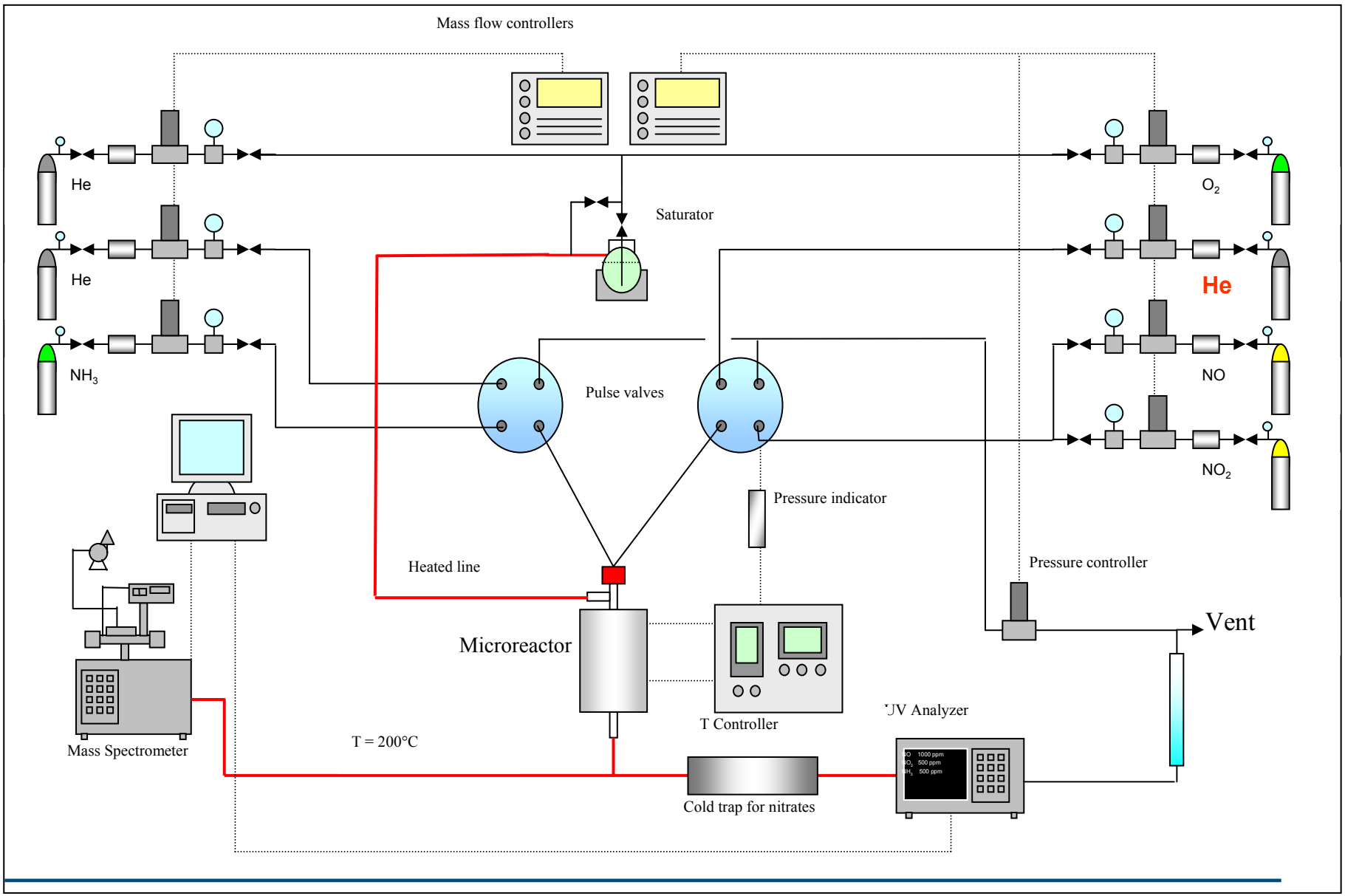
} Fit of intrinsic kinetics

Lab scale monolith catalyst (at **PoliMI + DC**)
Scale: 3 -10 cm^3

Full scale monolith catalyst (at **DC**)
Test bench runs with real exhaust gases from Diesel engines.
Scale: up to 18 - 43 liters

} Model validation

Experimental: microreactor rig



Microreactor model & kinetic analysis

Dynamic, isothermal, isobaric,heterogeneous 1D PFR model

Mass balances

adsorbed phase:

$$\Omega_j \frac{\partial \theta_j}{\partial t} = R_j$$

j = NH_3* , NH_4NO_3*

gas phase:

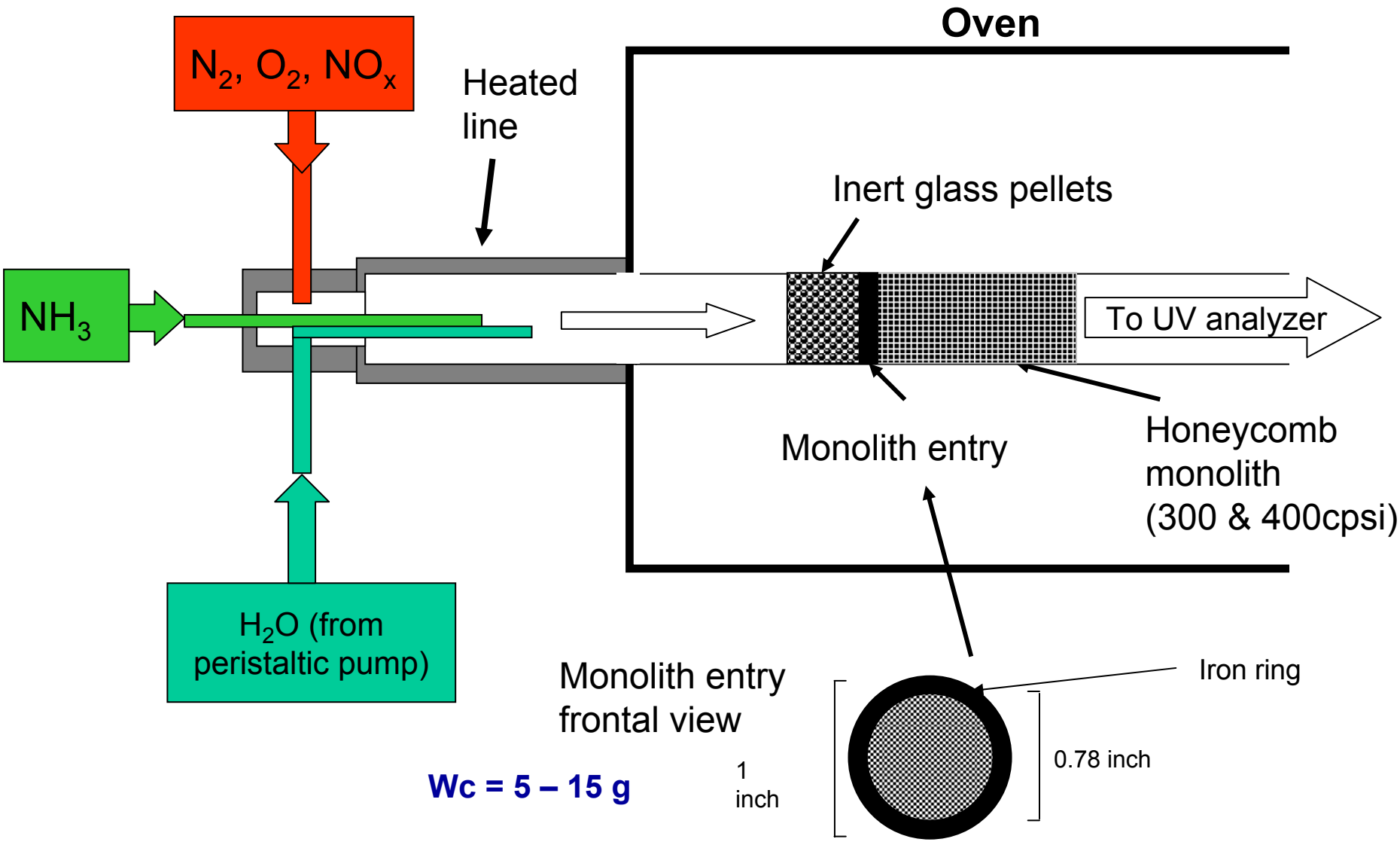
$$\varepsilon \frac{\partial C_i}{\partial t} = -v \frac{\partial C_i}{\partial z} + (1-\varepsilon) R_i$$

i = NH_3, N_2 , NO, NO_2 , N_2O, HNO_3

- Fitted by multiresponse nonlinear regression to transient kinetic runs
- Up to 5 exp. responses (C_{NH3},C_{NO},C_{NO2},**C_{N2},C_{N2O}**)
- Up to 24 fitting parameters
- Sequential fitting strategy to minimize correlation among parameter estimates
- Up to over 50 transient kinetic runs fitted simultaneously

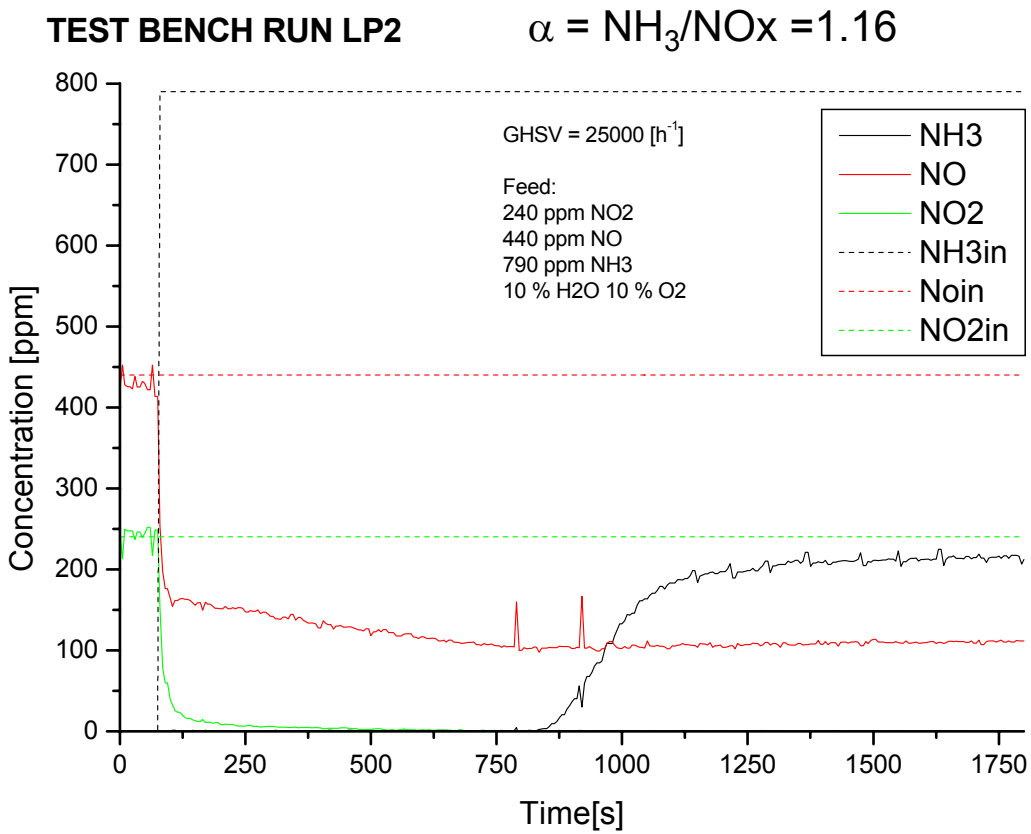
Experimental: monolith reactor rig

Integral reactor rig for validation experiments over honeycomb catalysts



V-based catalyst: NH_3/O_2 System

SCR dynamics and NH_3 storage



- Step feed of NH_3 on honeycomb catalyst leads to steady-state after > 20 minutes!
- No NH_3 slip observed for over 13 minutes
- Transient duration controlled by:
  - ammonia storage capacity
  - kinetics of ammonia adsorption/desorption/reaction
- NH_3 dosage strategy critical to prevent ammonia slip

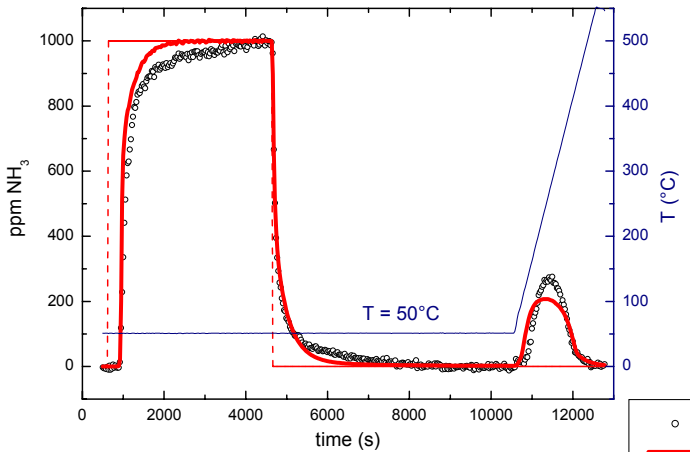
NH_3 adsorption – desorption

Rate equations:

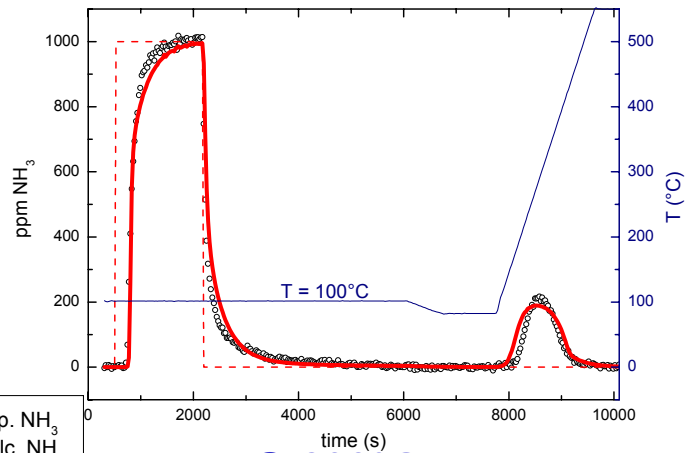
$$\begin{cases} r_{ads} = k_{ads} C_{NH_3} (1-\theta) \\ r_{des} = k_{des}^{o} \exp\left[-\dfrac{E_{des}^{\circ}}{RT} (1-\alpha\theta) \right] \cdot \theta \end{cases}$$

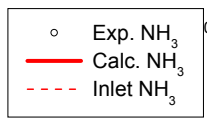
L. Lietti, I. Nova, S. Camurri, E. Tronconi, P. Forzatti, AIChE J. 43 (1997) 2559.

TRM @ 50°C + TPD

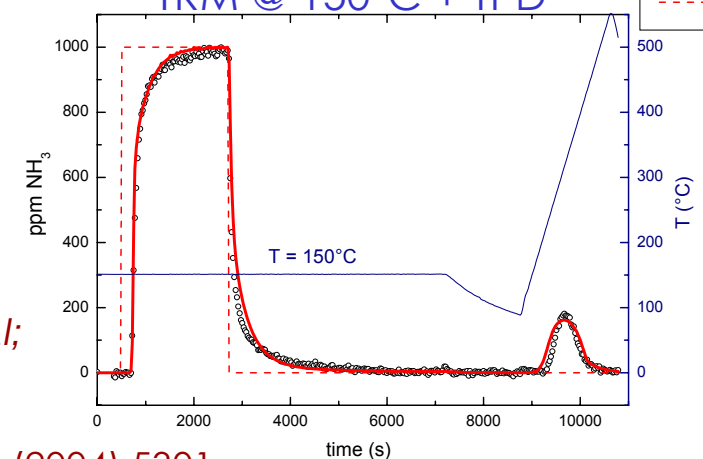


TRM @ 100°C + TPD

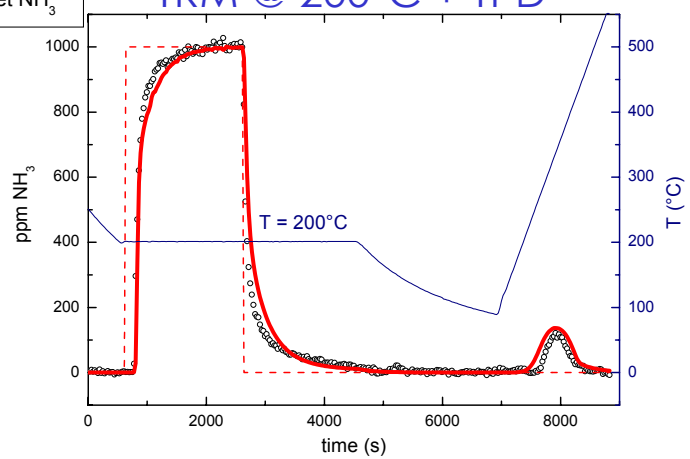




TRM @ 150°C + TPD



TRM @ 200°C + TPD

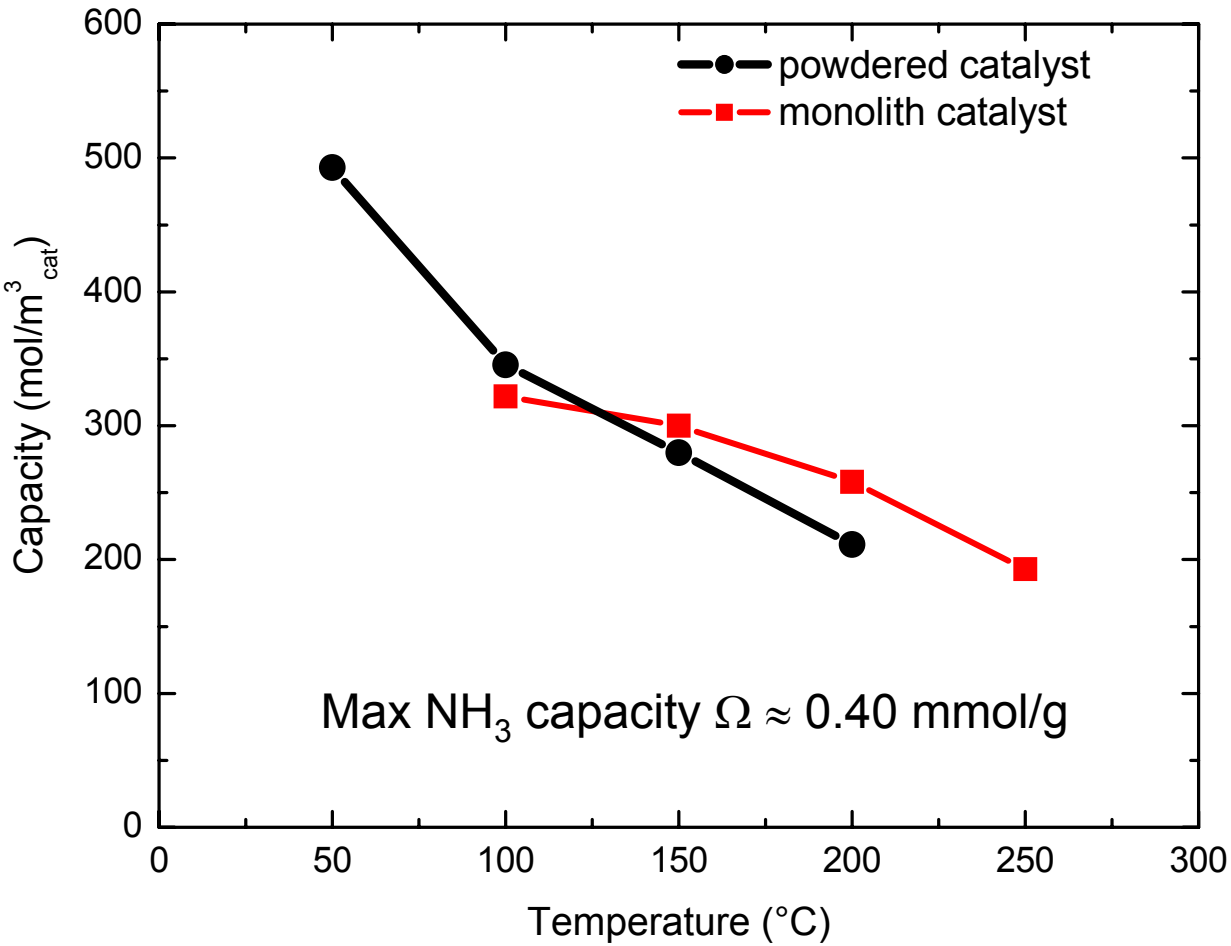


symbols: experimental;
solid lines: model fit

Ciardelli et al., CES 59 (2004) 5301

NH_3 storage capacity

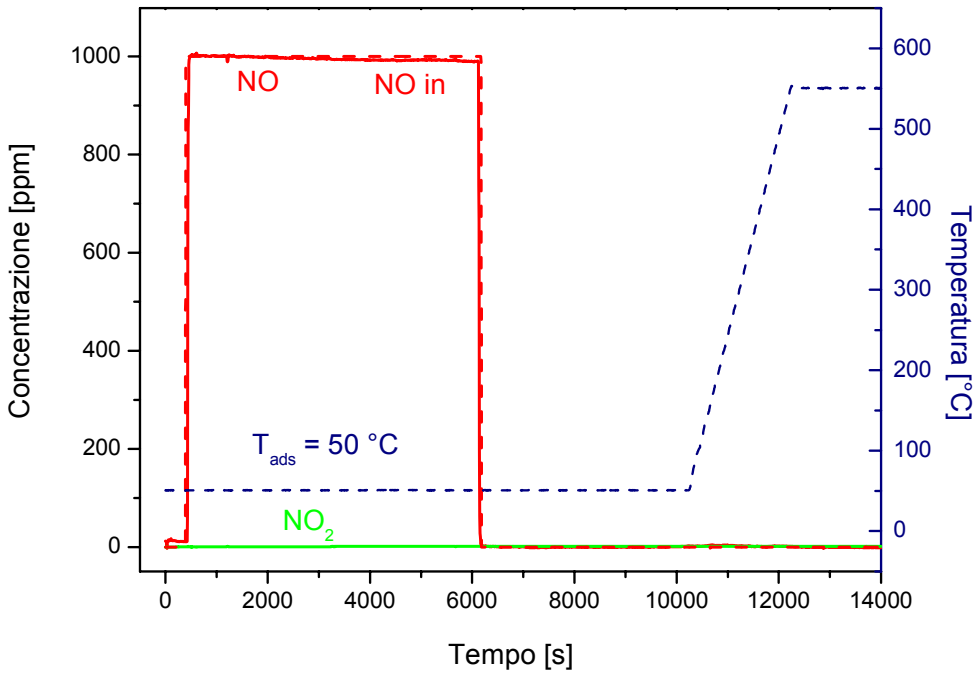
Equilibrium adsorption capacity vs. temperature for:
a) powdered catalyst (POLIMI microreactor runs)
b) monolith catalyst (DC runs in test rig)



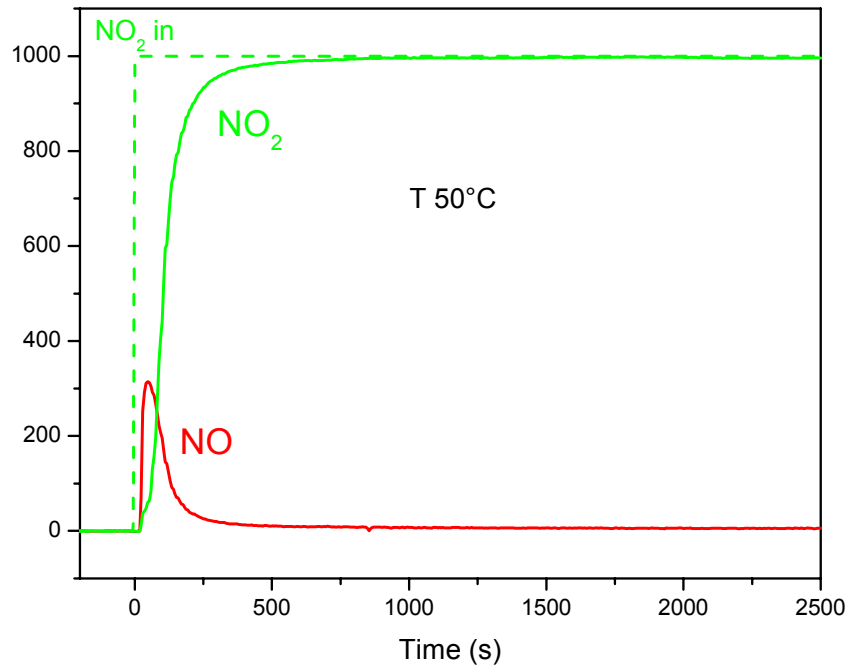
V-based catalyst: NO/O_2 & NO_2/O_2 Systems

NO & NO_2 adsorption

NO adsorption



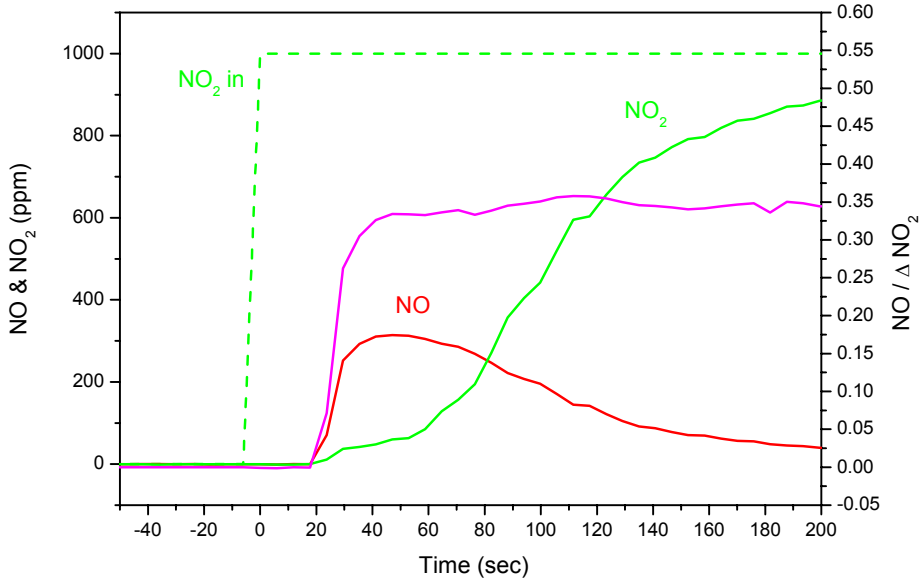
NO_2 adsorption



Experimental conditions:
Flow rate 280 Ncc/min
Temperature 50°C
Catalyst load 100 mg
NO_2 1000 ppm
O_2 2% H_2O 1%

NO_2 disproportionation route

Nitrate formation



Max NO_3^- storage capacity = 0.20 mmol/g

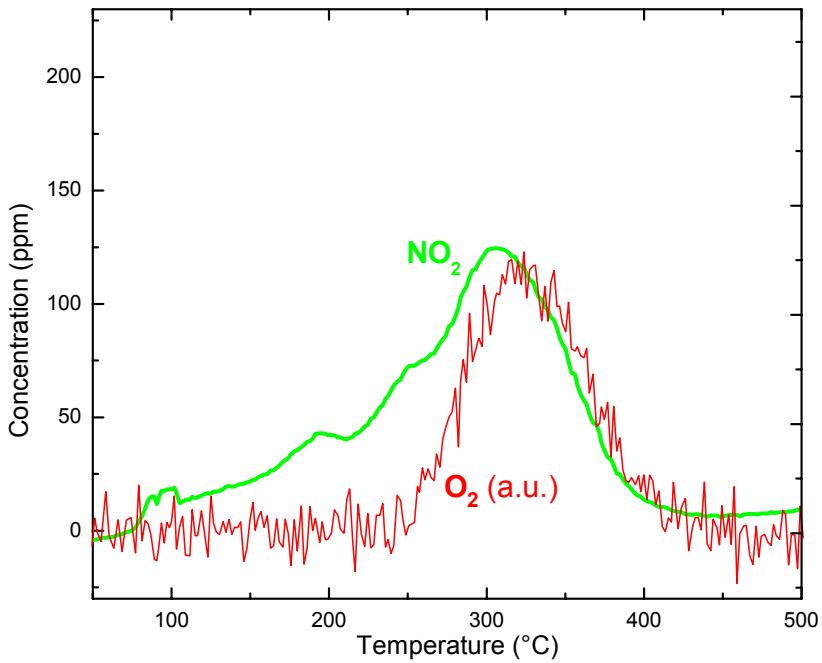
$$2\ NO_2 + O^{2-} \rightarrow NO_3^- + NO_2^-$$
$$NO_2 + NO_2^- \rightarrow NO_3^- + NO$$
$$3\ NO_2 + O^{2-} \rightarrow 2\ NO_3^- + NO$$

$NO/\Delta\ NO_2 = 1/3$

NO_2 storage mechanism similar to LNTs!

Nitrate decomposition (TPD)

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



On TiO_2 : Despres et al., Appl. Catal. B 43 (2002) 389

On Al_2O_3: Apostolescu et al., Appl. Catal. B 51 (2004) 43

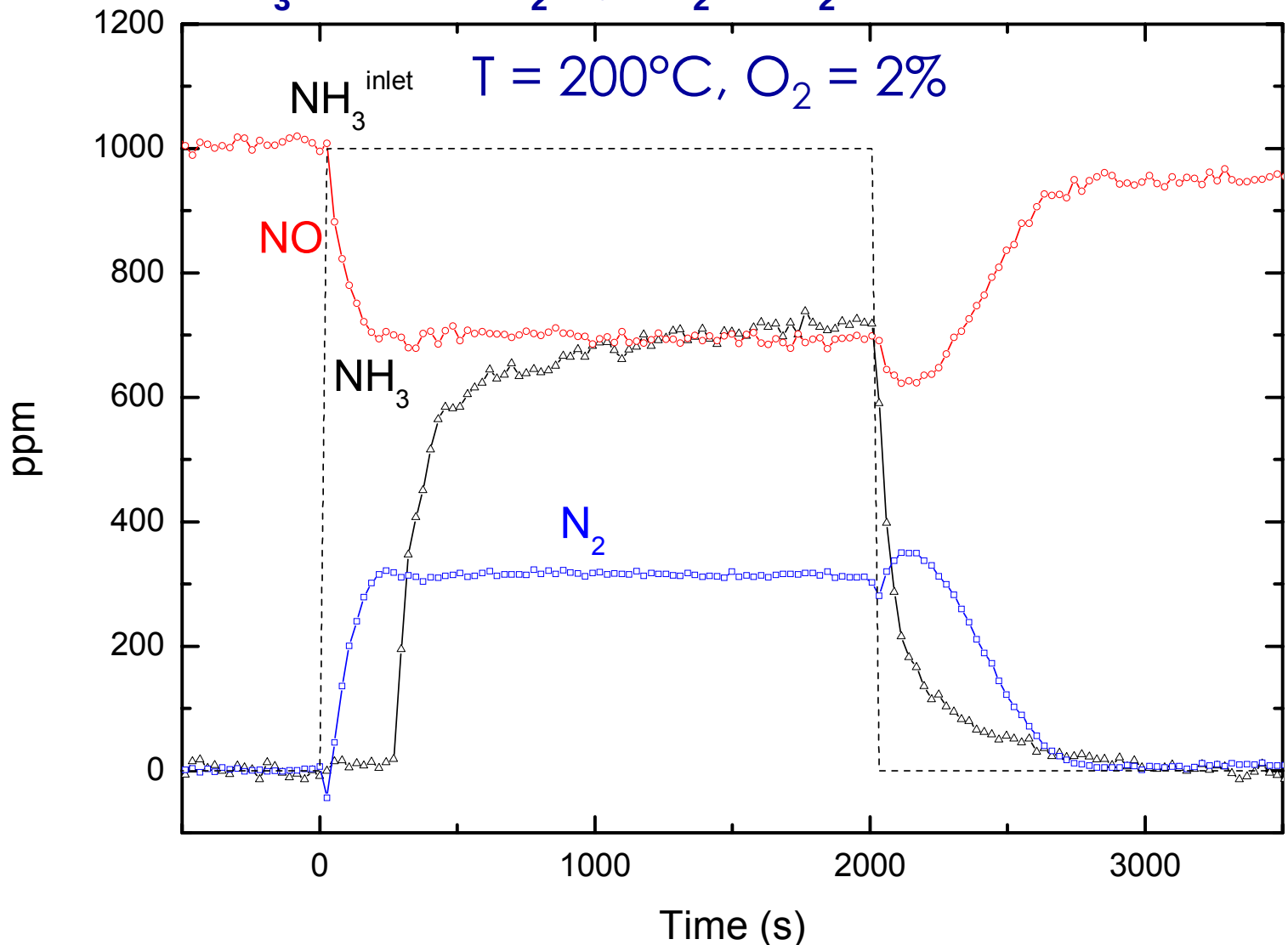
V-based catalyst: $NH_3 + NO/O_2$ System

Transient response experiments

Experimental conditions:

GHSV = 90000-230000 h^{-1}; C_{NO}=C_{NH3}= 0-1000 ppm; C_{H2O}=1-10%; C_{O2} = 2-10% T = 50-550°C

$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$ "*Standard*" SCR



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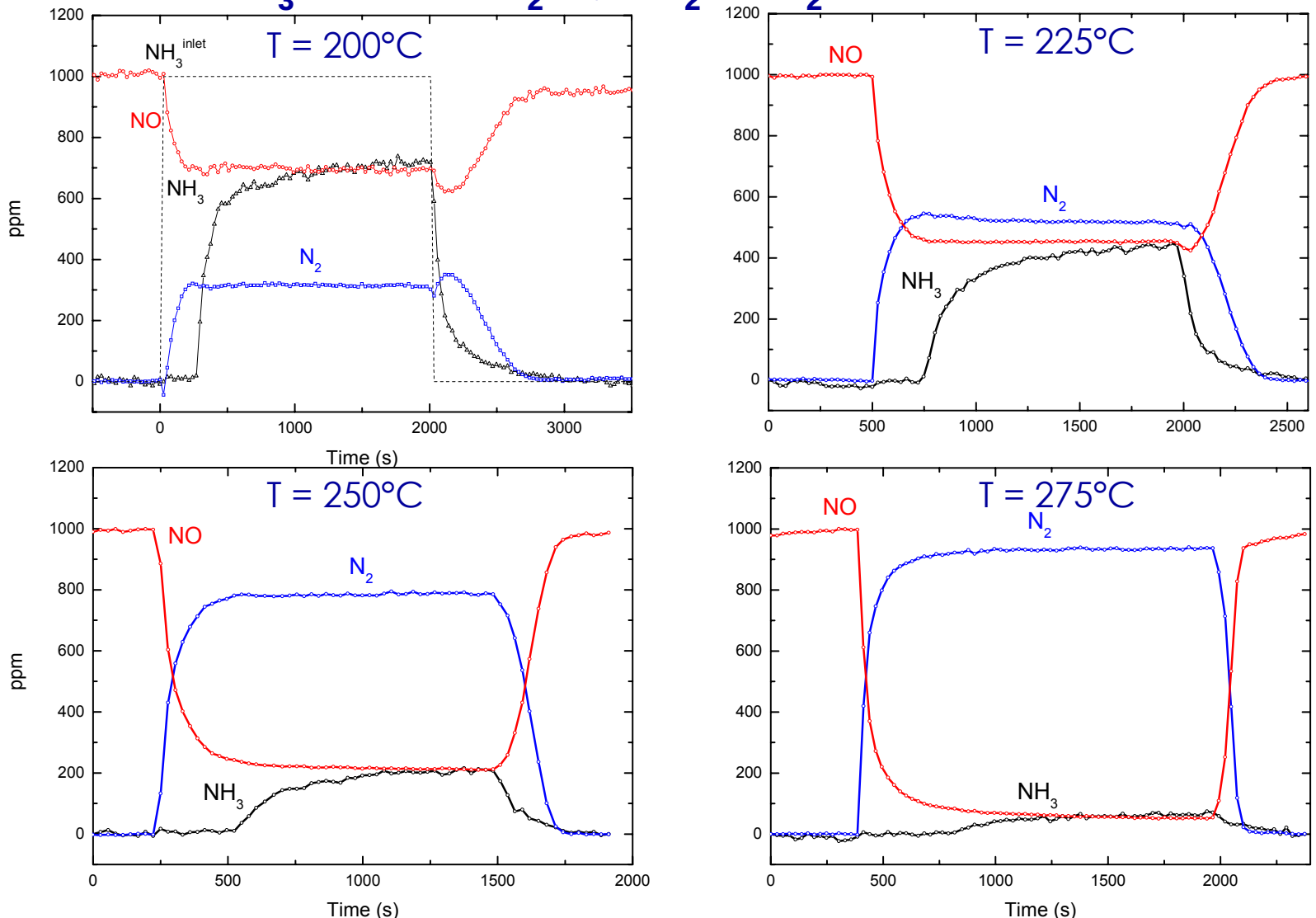


Std. SCR: Rate expressions

1. Eley-Rideal Kinetics (ER)

$$r_{NO} = k^{o}_{NO} \exp[-\frac{E^{\circ}_{NO}}{RT}] \cdot C_{NO} \cdot \theta$$

(*) C. Ciardelli, I. Nova, E. Tronconi, B. Konrad, D. Chatterjee, K. Ecke, M. Weibel, Chem. Eng. Sci. 59 (2004) 5301.

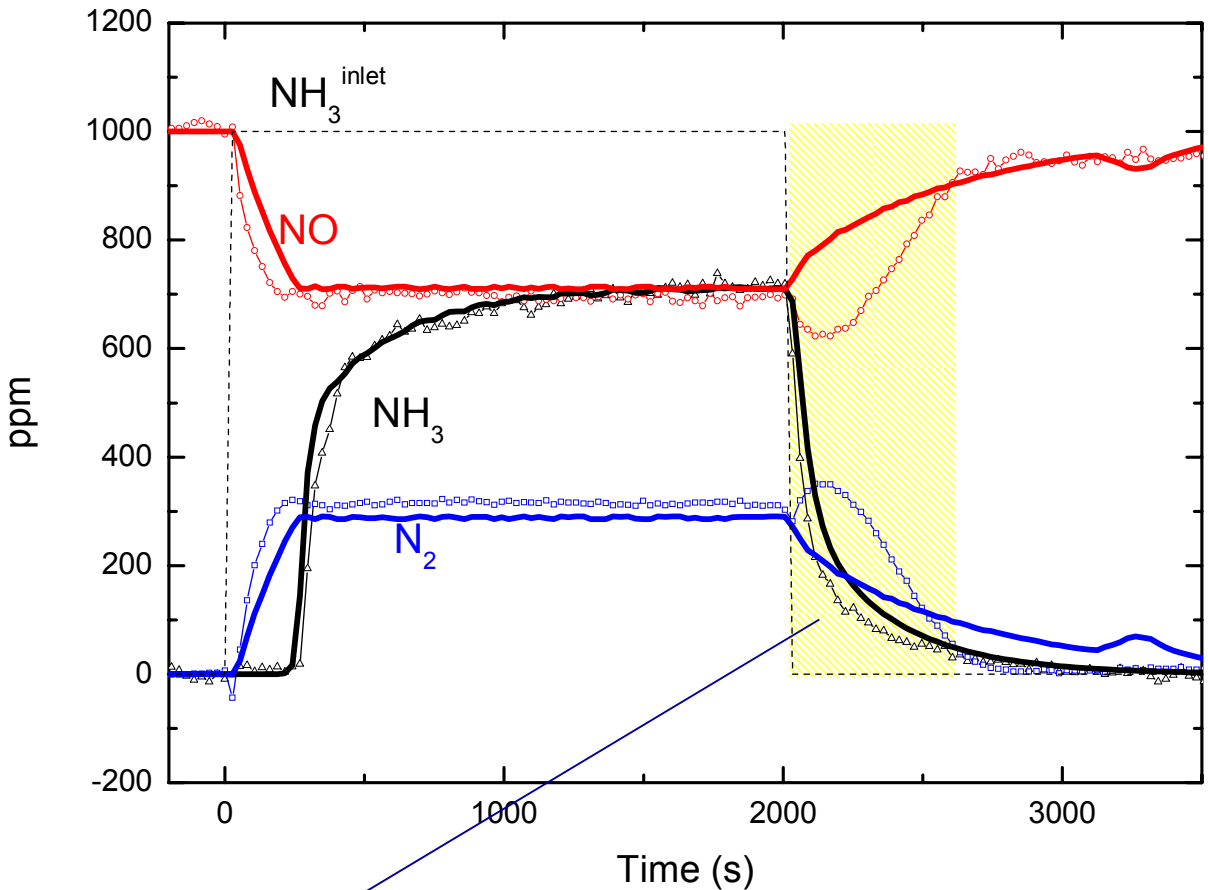
GHSV = 90000 h^{-1};

$C_{NO} = C_{NH3}$ = 1000 ppm;

C_{H2O} = 1%;

C_{O2} = 2%;

T = 200°C



Unable to reproduce the NH_3 inhibition effect at low T

Std. SCR: Rate expressions

2. Derivation of a Dual-site Redox rate law

S_1 = redox sites (associated with V)
S_2 = acidic sites (possibly associated with W/Ti)

(a) $S_1{=}O + NO \Leftrightarrow S_1{=}O[NO]$

(b) $S_2 + NH_3 \Leftrightarrow S_2[NH_3]$

(c) $S_1{=}O[NO] + S_2[NH_3] \rightarrow N_2 + H_2O + S_1\text{-}OH + S_2$

(d) $S_1\text{-}OH + ¼\ O_2 \rightarrow S_1{=}O + ½\ H_2O$

(e) $S_1 + S_2[NH_3] \Leftrightarrow S_1[NH_3] + S_2$ ← NH_3 inhibition

$r_{NO} = k_{NO}\ \sigma_{NO}\ \theta_{NH3}$

$r_{reox} = k_{reox}\ C_{O2}^{1/4}\ \sigma_{OH}$

Overall balances of S_1- and S_2-sites:

$1 = \sigma_O + \sigma_{NO} + \sigma_{NH3} + \sigma_{OH}$; $1 = \theta_{free} + \theta_{NH3}$

On imposing that $r_{NO} = r_{reox}$, assuming quasi-equilibrium for steps (a) and (e) and assuming negligible surface concentration of adsorbed NO,

$$r_{NO} = \frac{k_{NO}^{o} \cdot e^{-E^{\circ}_{NO}/RT} C_{NO} \theta_{NH3}}{\left(1 + K_{NH3} \frac{\theta_{NH3}}{1-\theta_{NH3}}\right)\left(1 + k_{O2} \frac{C_{NO}\theta_{NH3}}{C_{O2}^{1/4}}\right)}$$

"Modified Redox" rate law

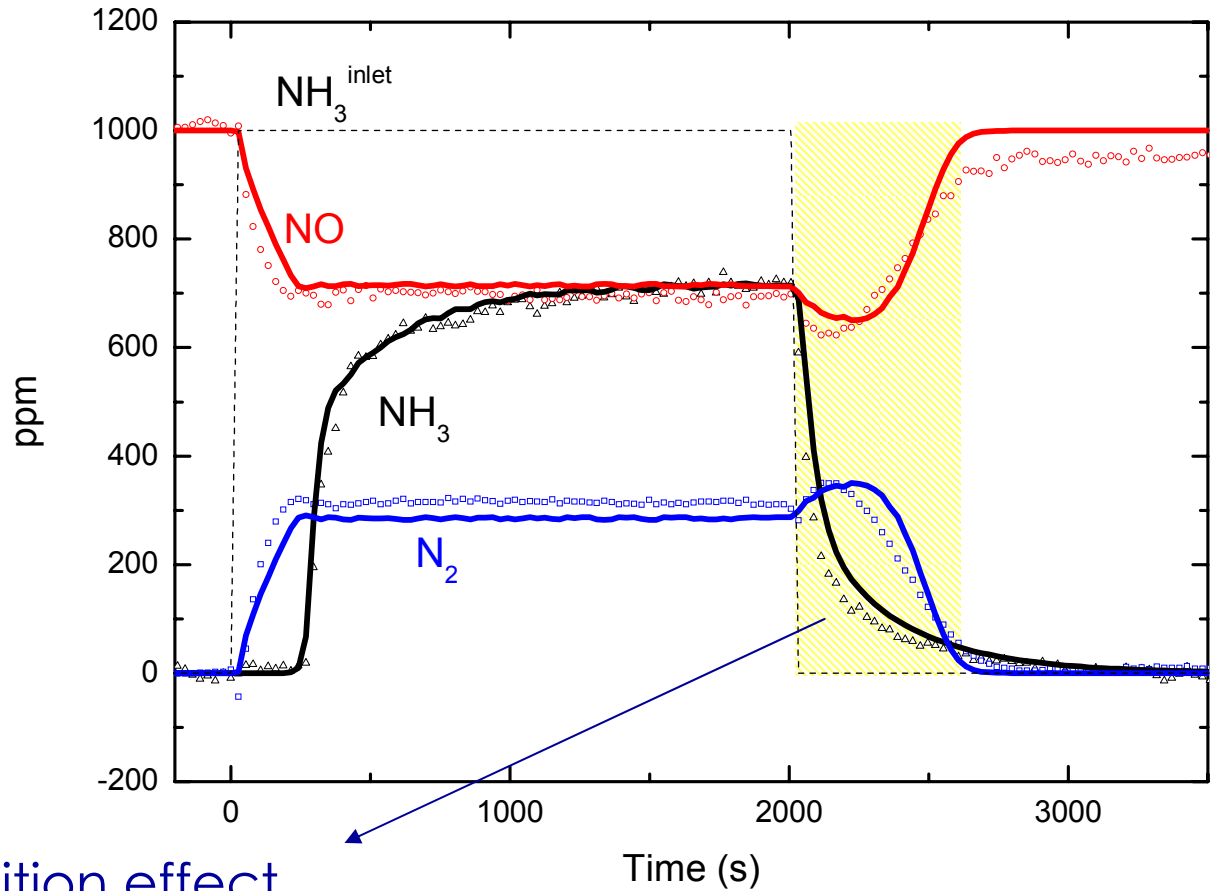
Std. SCR: Rate expressions

2. Modified Redox kinetics (MR)

$$r_{NO} = \frac{k^{o}_{NO} \cdot e^{-E^{\circ}_{NO}/RT} C_{NO} \theta_{NH3}}{(1 + K_{NH3} \frac{\theta_{NH3}}{1-\theta_{NH3}})(1 + k_{O2} \frac{C_{NO}\theta_{NH3}}{C^{1/4}_{O2}})}$$

E. Tronconi et al. Cat. Tod. 105 (2005) 529
E. Tronconi et al. AIChE J 52 (2006) 3222

GHSV = 90000 h^{-1};
$C_{NO} = C_{NH3}$ = 1000 ppm;
C_{H2O} = 1%;
C_{O2} = 2%;
T = 200°C

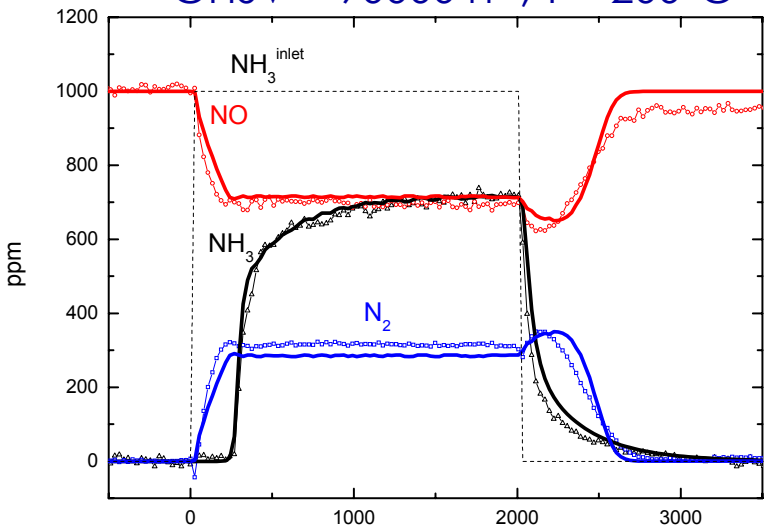


reproduces the NH_3 inhibition effect

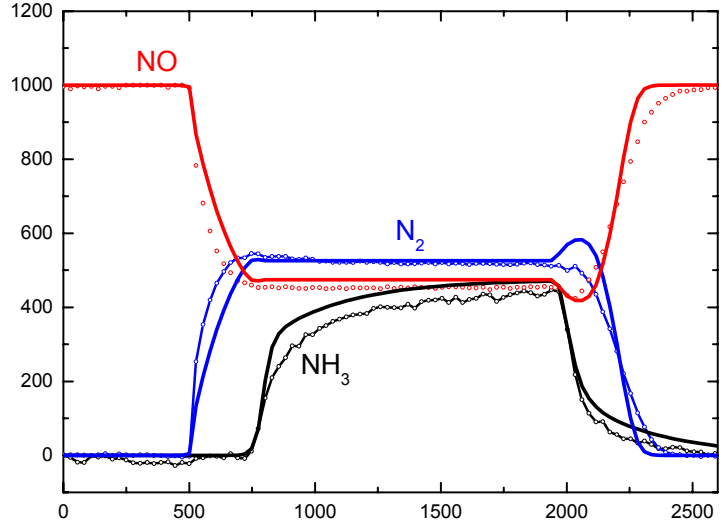
Fit results – MR kinetics (C_{O2}= 2%)

$C_{NO} = C_{NH3}$ = 1000 ppm; C_{H2O} = 1%;

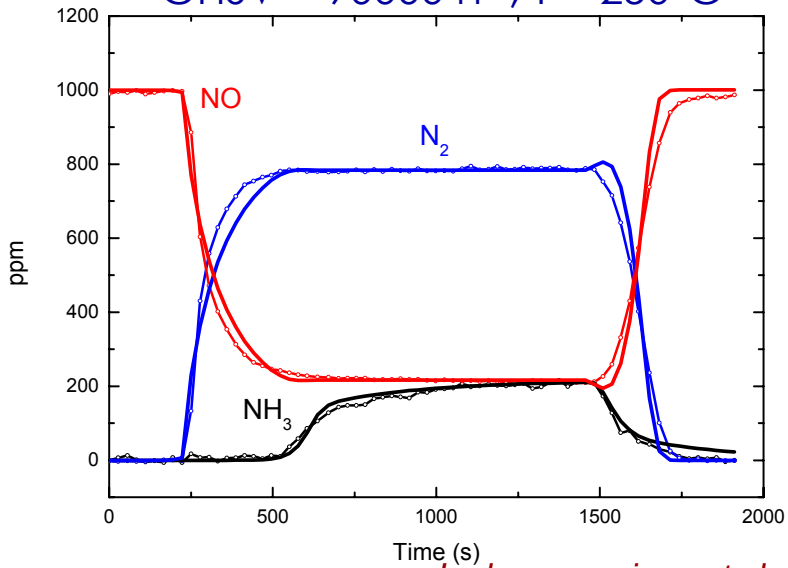
GHSV = 90000 h^{-1}; T = 200°C



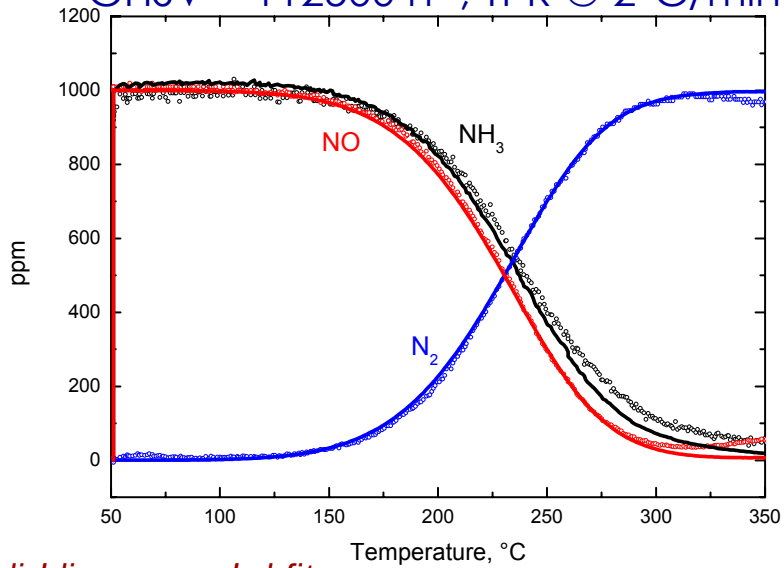
GHSV = 90000 h^{-1}; T = 225°C



GHSV = 90000 h^{-1}; T = 250°C



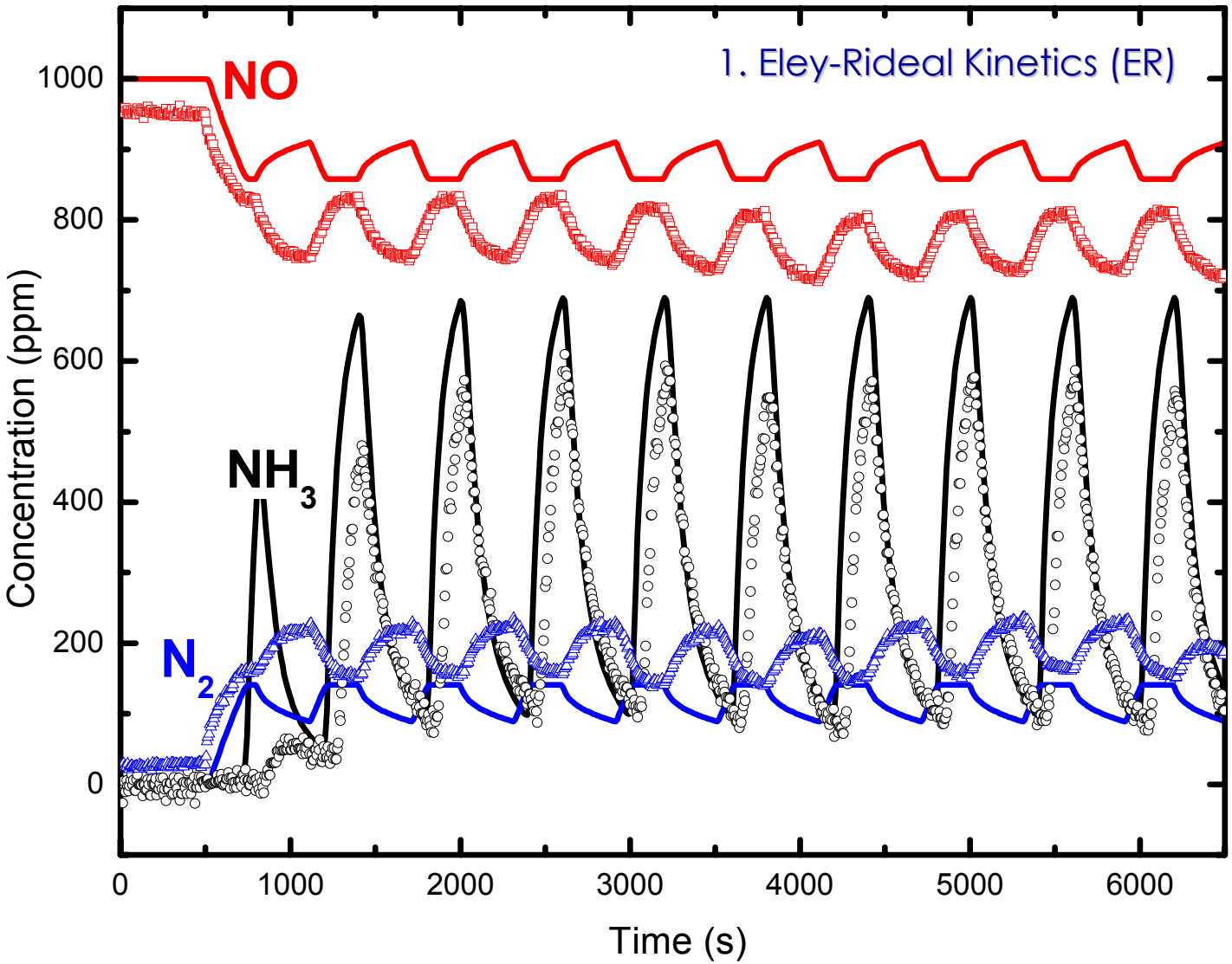
GHSV = 112500 h^{-1}; TPR @ 2°C/min



symbols: experimental; solid lines: model fit

Eley-Rideal vs. Redox SCR Kinetics

*Simulation of **NH_3+NO/O_2** fast transients over powdered catalyst*



T = 180°C

GHSV = 90000 h^{-1}

NO = 1000 ppm

NH_3 = 0-1000 ppm

300 s on/300 s off

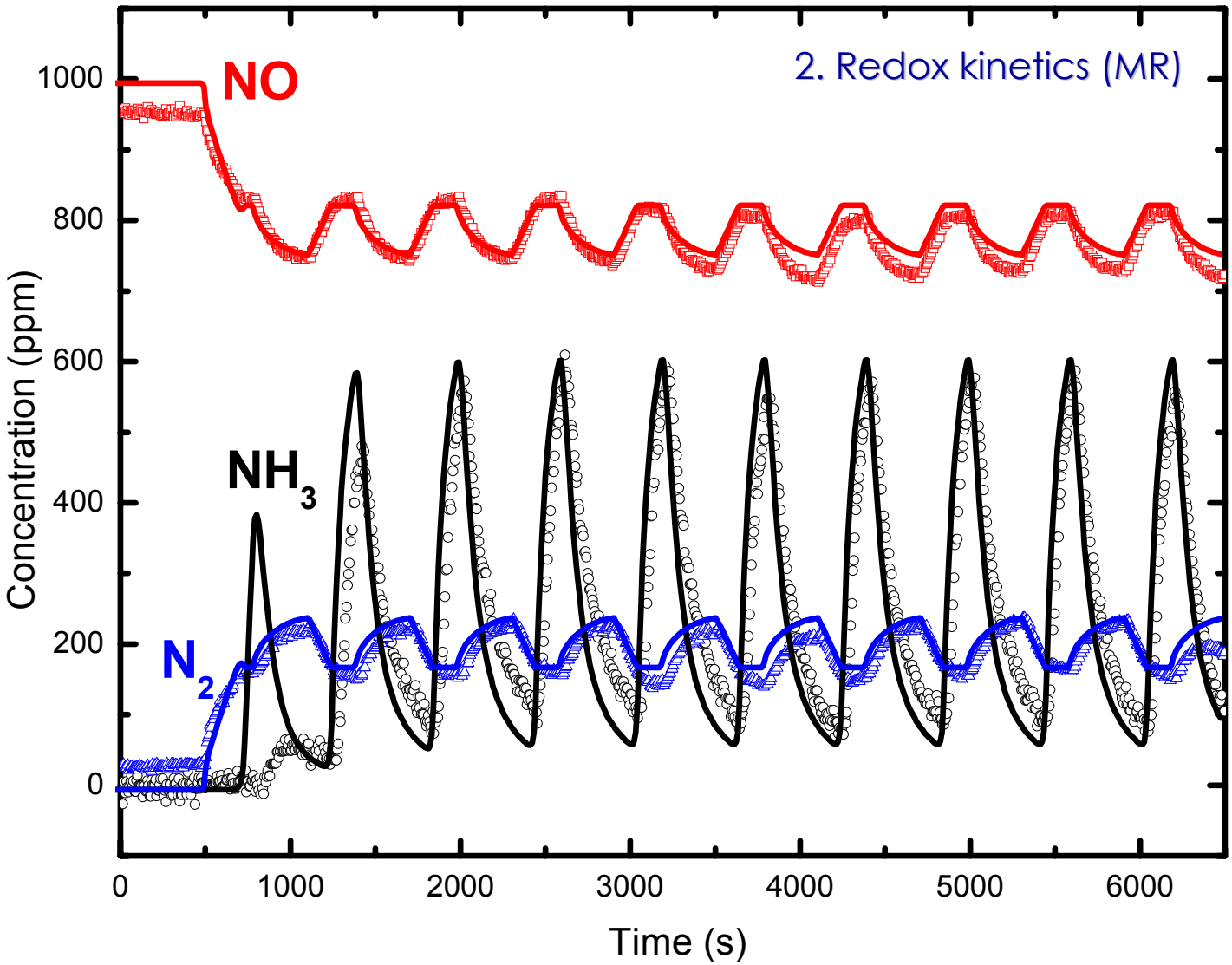
H_2O = 1%;

O_2 = 2%

E. Tronconi et al.
Cat. Tod. 105 (2005) 529

Eley-Rideal vs. Redox SCR Kinetics

*Simulation of **NH_3+NO/O_2** fast transients over powdered catalyst*



T = 180°C

GHSV = 90000 h^{-1}

NO = 1000 ppm

NH_3 = 0-1000 ppm

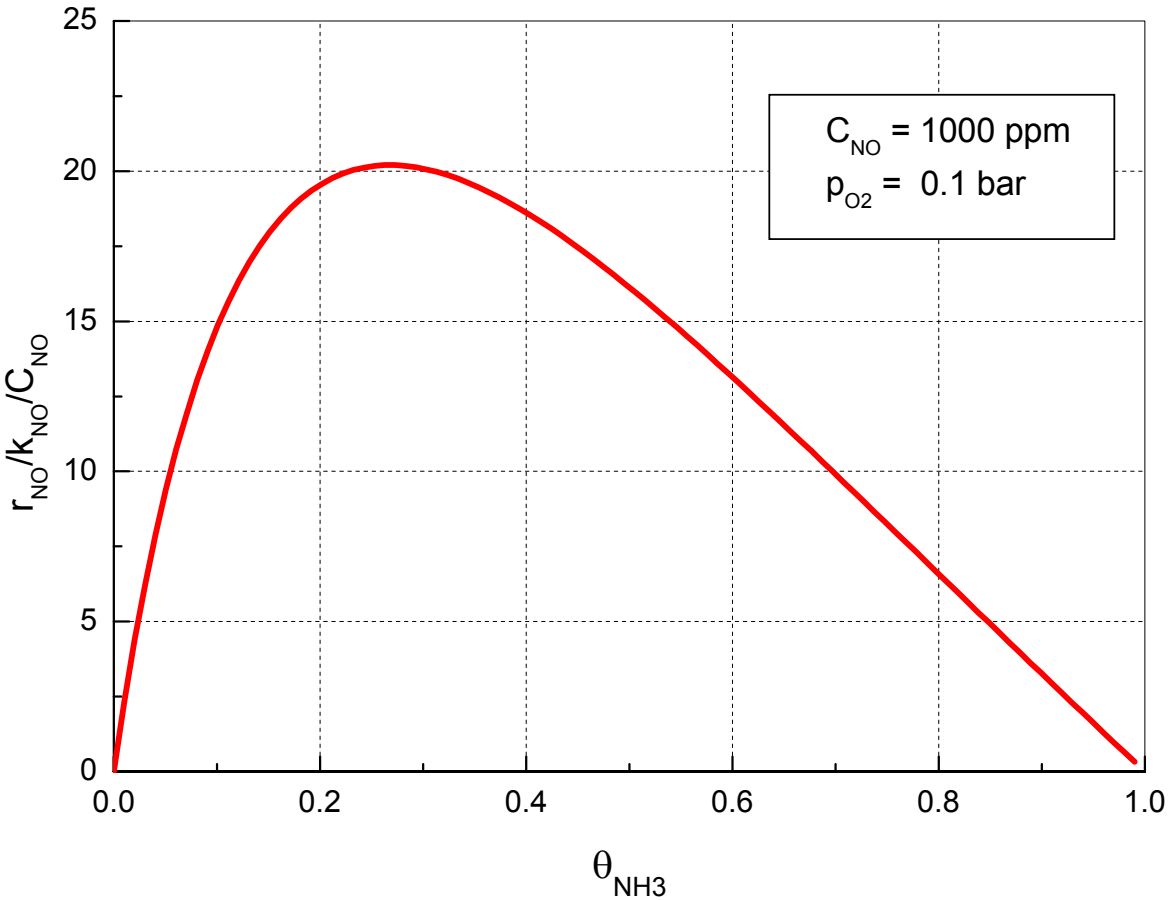
300 s on/300 s off

H_2O = 1%;

O_2 = 2%

E. Tronconi et al.
Cat. Tod. 105 (2005) 529

Redox kinetics: optimal NH_3 coverage



E. Tronconi et al.
AIChE J 52 (2006) 3222

V-based catalyst: $NH_3 + NO/NO_2/O_2$ System

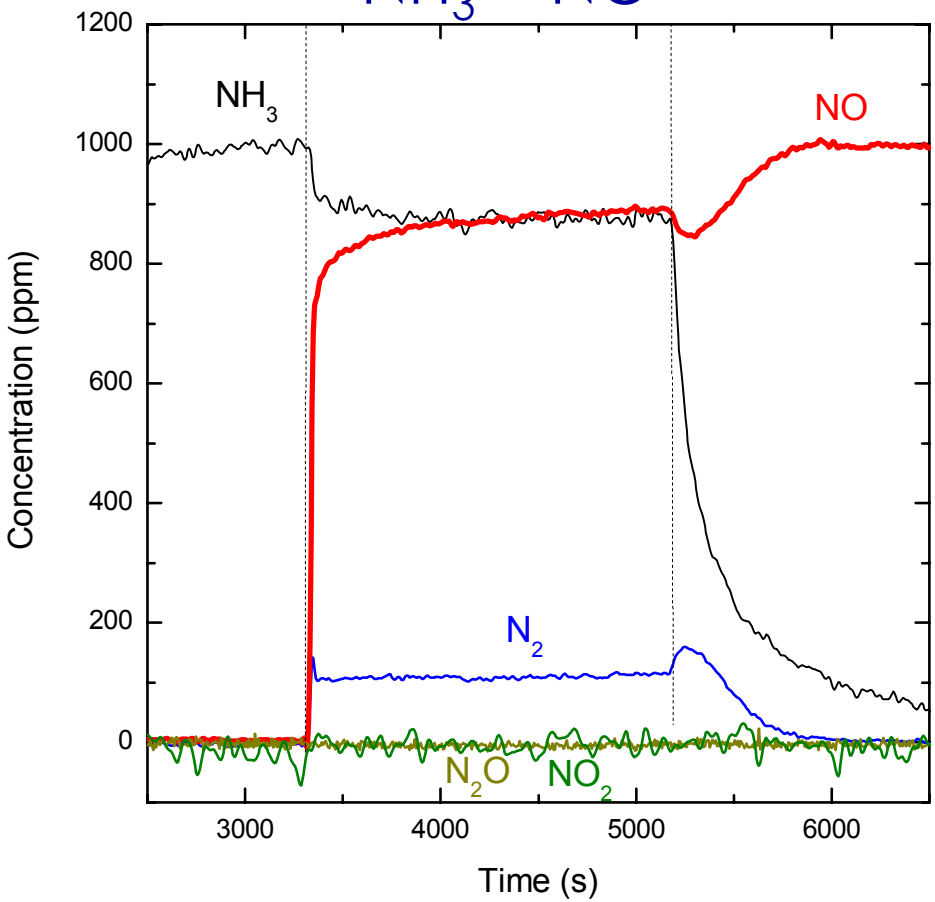
Chemistry & Mechanism

NO_2 promoting effect

Experimental conditions:

GHSV= 210000 h^{-1}; T= 200 °C; C_{O2}= 2 %; C_{H2O}= 1%; C_{NH3}= C_{NOx}= 1000 ppm

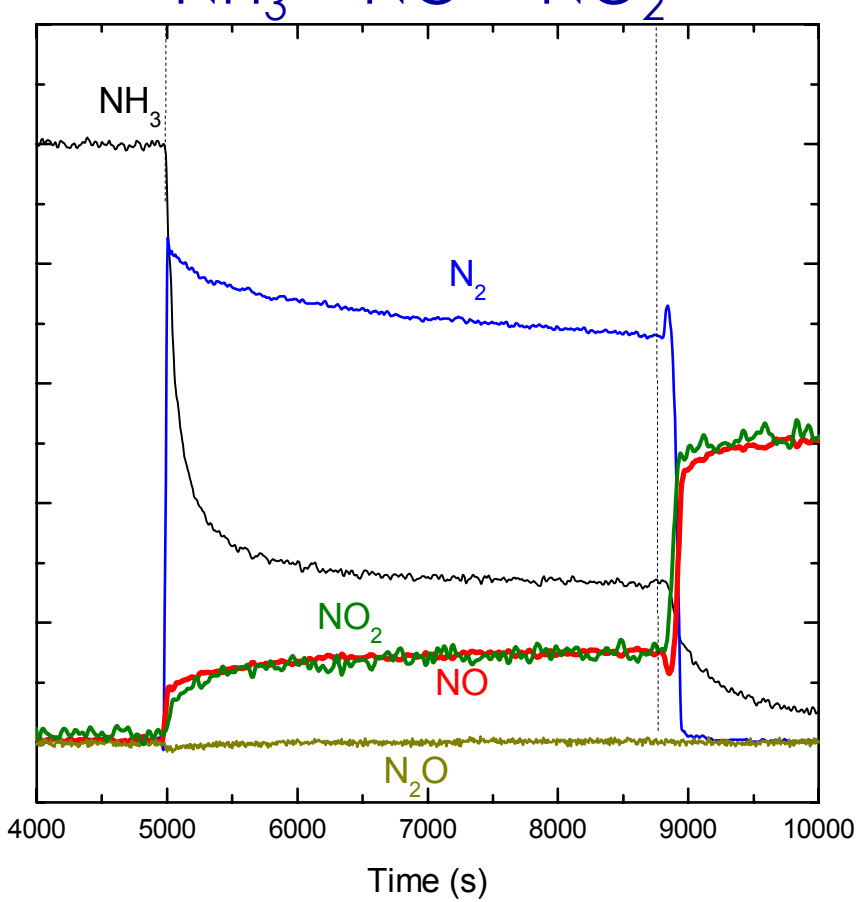
NH_3 + NO



$2NH_3 + 2NO + ½\ O_2 \rightarrow 2N_2 + 3H_2O$

DeNOx=11%

NH_3 + NO + NO_2



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

DeNOx=70%

Chemistry according to the literature

$NH_3 \Leftrightarrow NH_3^*$ (NH_3 ads./des.)

$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$ (NH3 oxidation)

$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$ (standard SCR)

$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O$ (fast SCR)

$2NH_3 + 2NO_2 \rightarrow N_2 + NH_4NO_3 + H_2O$ (Nitrate formation)

$2\ NH_4NO_3 + NO \rightarrow 3\ NO_2 + 2\ NH_3 + H_2O$

$NH_4NO_3 \rightarrow N_2O + 2\ H_2O$

(Nitrate decomp.)

$4NH_3 + 3NO_2 \rightarrow 3.5N_2 + 6H_2O$ (NO_2-SCR)

All regarded as parallel reactions

Koebel et al., IEC Res. 40 (2001) 52

TRM experiments

Experimental conditions:

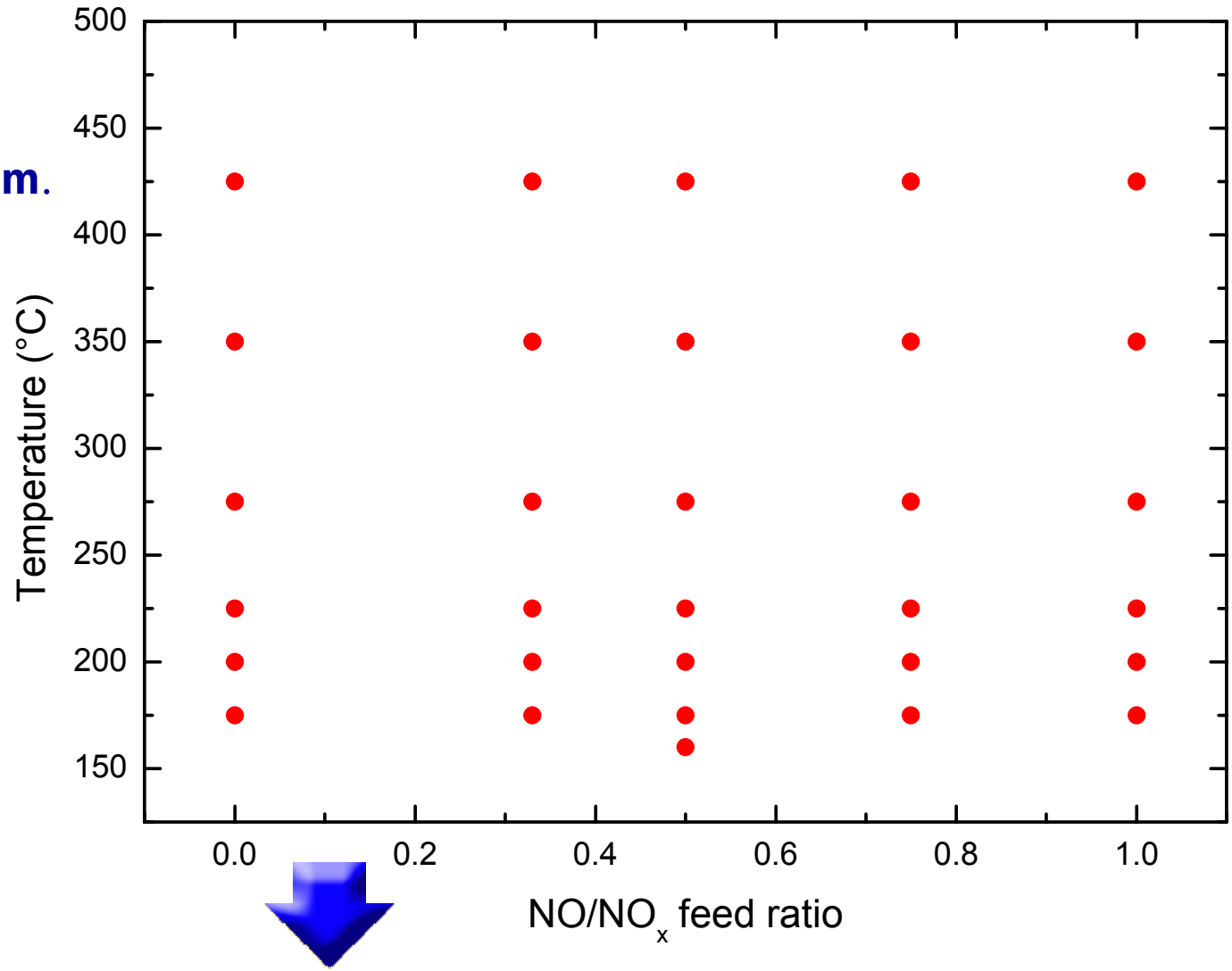
GHSV = 210000 h^{-1};

T = **160-425 °C**;

C_{O2} = 2 %; C_{H2O} = 1%;

C_{NH3} = C_{NOx} = 1000 ppm.

R = NO/NO_x = 0 → 1



Wide range of T and NO/NO_x feed ratios investigated

Reactions involved

NO_2 – SCR

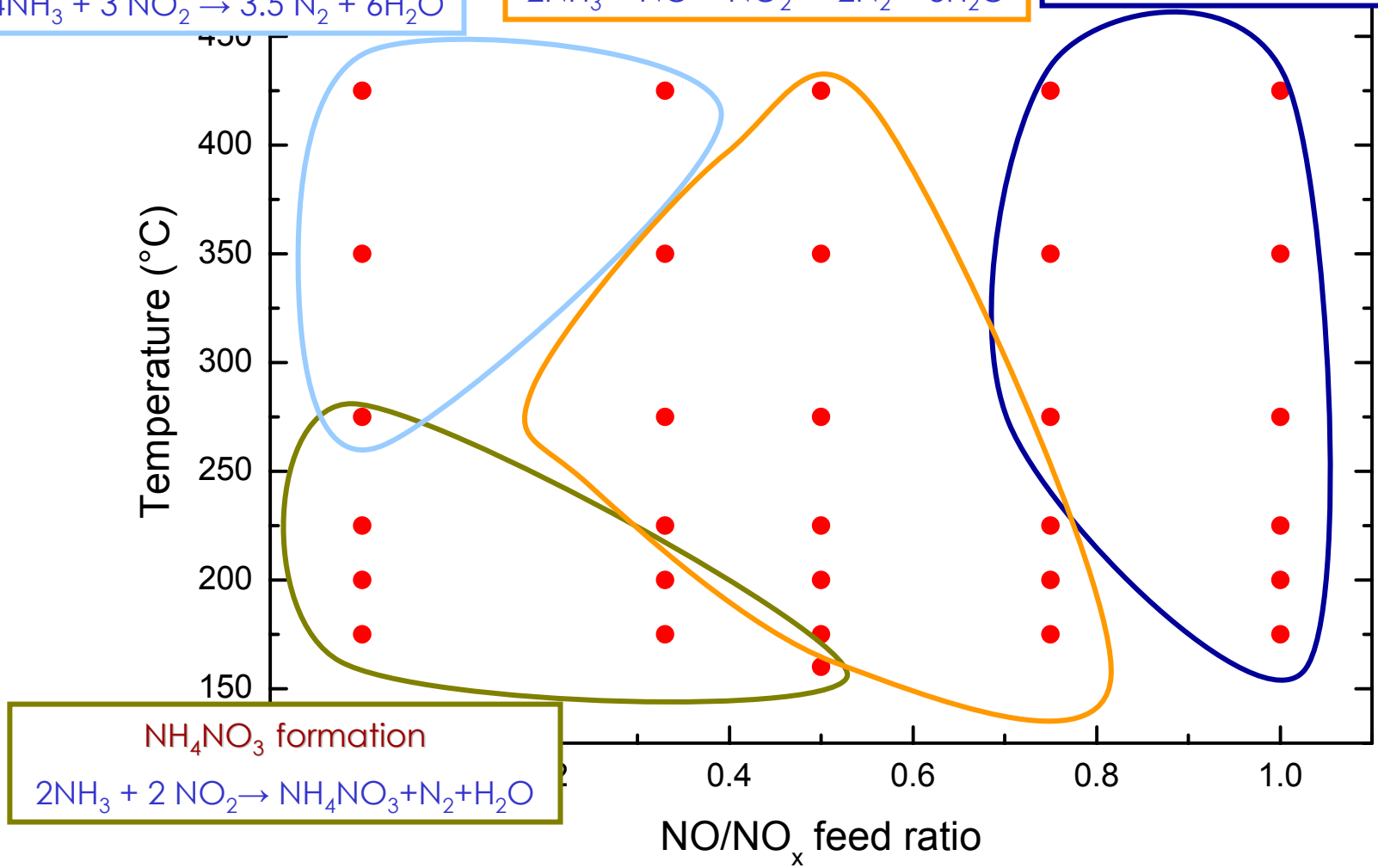
$4NH_3 + 3\,NO_2 \rightarrow 3.5\,N_2 + 6H_2O$

Fast SCR

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

Standard SCR

$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$



NH_4NO_3 formation

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

C. Ciardelli et al. Appl. Catal. B: Environm. 70 (2007) 80

Influence of NO_2 feed content

TRM experiments:

GHSV = 210,000 h^{-1}

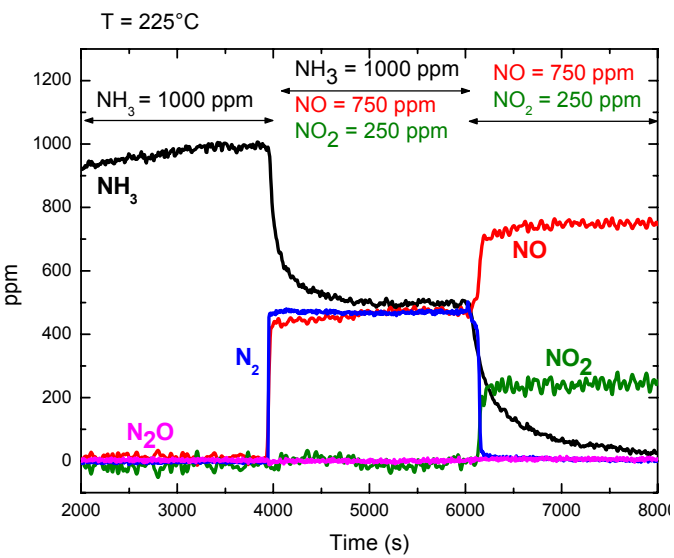
$C_{NH3} = C_{NOx}$ = 1000 ppm

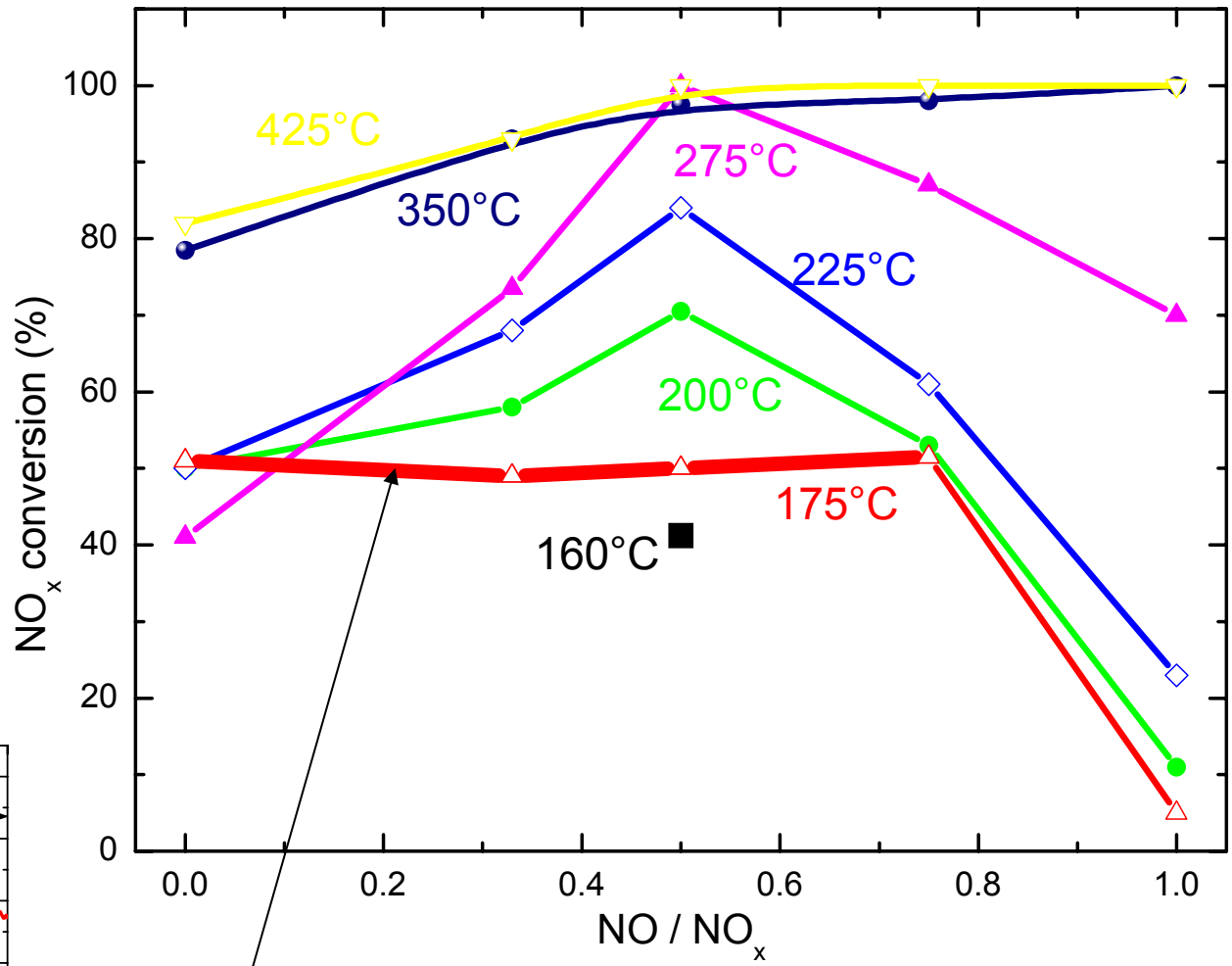
C_{O2} = 2 %

C_{H2O} = 1%

T = 160 - 425°C

$NO/NO_x = 0 \rightarrow 1$





Focus on effect of NO/NO_2 at 175 °C

I. Nova et al., Catal. Today 114 (2006) 3

C. Ciardelli et al., Appl.Catal. B: Environm. 70 (2007) 80

TRM $NO\text{-}NO_2/NH_3$ @ 175°C

Operating conditions:

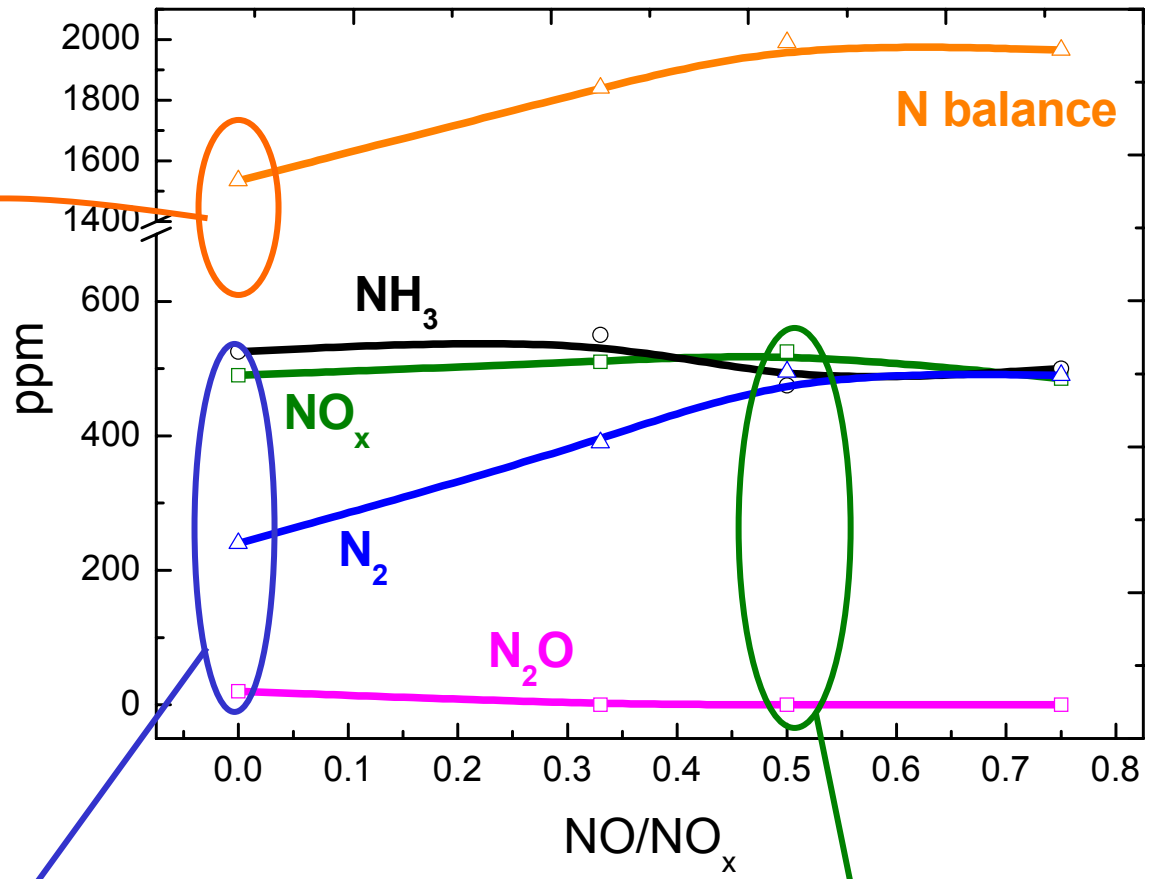
- 1000 ppm NH_3
- 1000 ppm NO_x
- 1% H_2O
- 2% O_2
- T = 175 °C

GHSV = 210,000 h^{-1}

lack of 500 ppm in the N-balance

↓

250 ppm NH_4NO_3



NH_4NO_3 formation

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

"Fast" SCR

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

Chemistry of $NO\text{-}NO_2/NH_3$

NO_2/NH_3

$[NH_4NO_2] \rightarrow N_2 + 2H_2O$

NH_3^{ads}

$2NO_2 \leftrightarrow N_2O_4 + H_2O \leftrightarrow HONO + HNO_3$

NH_3^{ads}

NH_4NO_3

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

$NO\text{-}NO_2/NH_3$

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

$NH_4NO_3 \leftrightarrow NH_3 + HNO_3$

NO

$HONO + NO_2$

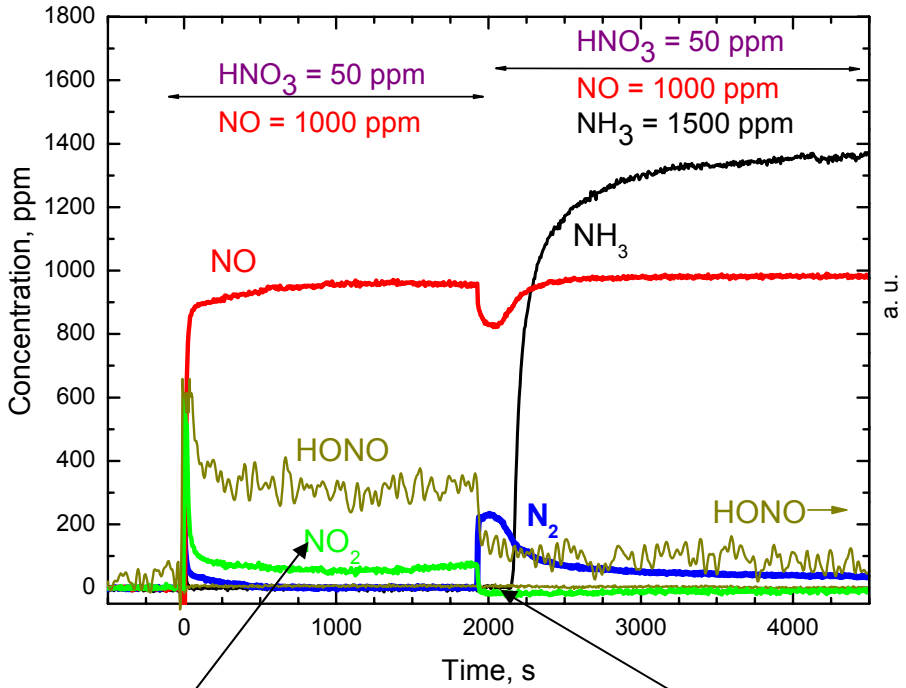
NH_3^{ads}

$[NH_4NO_2] \rightarrow N_2 + 2H_2O$

$NH_4NO_3 + NO \rightarrow N_2 + NO_2 + 2H_2O$

I. Nova, C. Ciardelli, E. Tronconi, D. Chatterjee, B. Bandl-Konrad, *Catal. Today*, **114** (2006), 3.
C. Ciardelli, I. Nova, E. Tronconi, D. Chatterjee, B. Bandl-Konrad, *Chem. Commun.* **23** (2004), 2718.
Also: Yeom, Sachtler et al., J. Catal. **231** (2005) 181 over BaNa-Y zeolite

Fast SCR mechanism: NO + HNO_3 reaction



Conditions :

- C_{O2} = 0 %; C_{H2O} = 1%
- C_{NH3} = 1500 ppm
- C_{NO} = 1000 ppm
- Feed stream saturated with HNO_3 + H_2O @ 42°C
- T = 200 °C

$$HNO_3 + NO \rightarrow HONO + NO_2$$

Converted NO ≅ Produced NO_2

$$HNO_3 + NO \rightarrow HONO + NO_2$$
$$HONO + NH_3 \rightarrow N_2 + 2H_2O$$
$$NO_2 + NH_3 \rightarrow \tfrac{1}{2}\, NH_4NO_3 + \tfrac{1}{2}\, N_2$$

NO reduces HNO_3, but NH_3 is necessary to arrive at N_2

I. Nova, C. Ciardelli, E. Tronconi, D. Chatterjee, B. Bandl-Konrad, *Catal. Today*, **114** (2006), 3

V-based catalyst: $NH_3 + NO/NO_2/O_2$ System

Kinetic analysis

Kinetic analysis

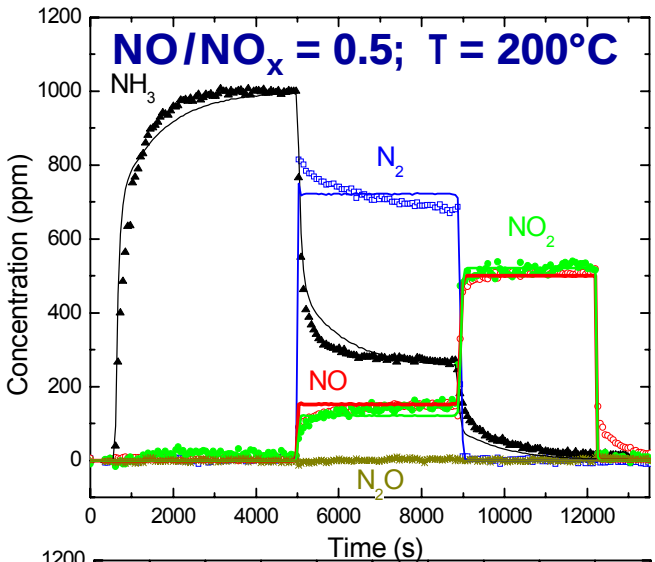
Reactions considered:

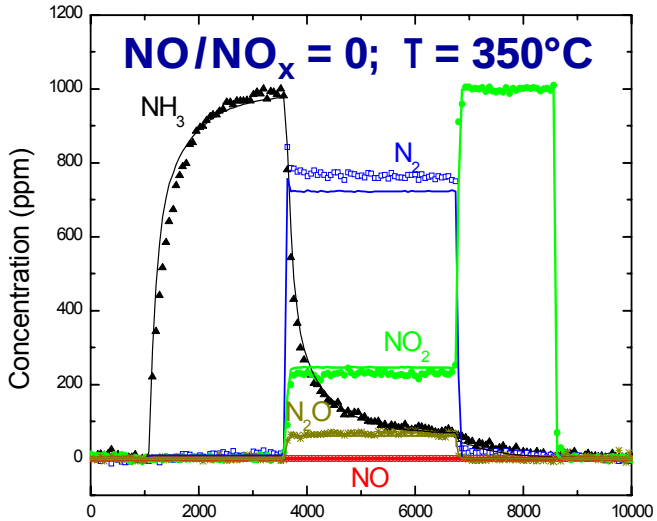
$NH_3 \leftrightarrow NH_3^*$	(NH_3 ads./des.)
$NH_3 + 3/4\ O_2 \rightarrow ½\ N_2 + \mathbf{3/2}\ H_2O$	(NH3 oxidation)
$NH_3 + NO + ¼\ O_2 \rightarrow N_2 + \mathbf{3/2}\ H_2O$	(standard SCR)
$NH_3 + \mathbf{3/4}\ NO_2 \rightarrow \mathbf{7/8}\ N_2 + \mathbf{3/2}\ H_2O$	(NO2-SCR)
$2NO_2 + H_2O \leftrightarrow HNO_2 + HNO_3$	(NO_2 disproportion)
$HNO_2 + NH_3^* \rightarrow N_2 + 2H_2O$	(NH_4NO_2 decomposition)
$HNO_3 + NO \leftrightarrow HNO_2 + NO_2$	(HNO_3 reduction by NO)
$HNO_3 + NH_3^* \leftrightarrow NH_4NO_3^*$	(nitrate adsorption)
$NH_4NO_3^* \rightarrow N_2O + 2\ H_2O$	(N_2O formation)

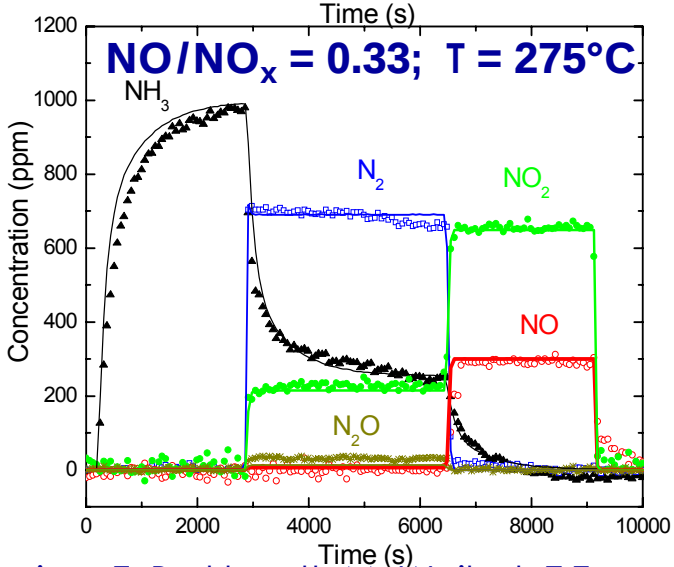
D. Chatterjee, T. Burkhardt, M. Weibel, E.Tronconi, I. Nova, C. Ciardelli, *SAE technical paper* 2006-01-0468.

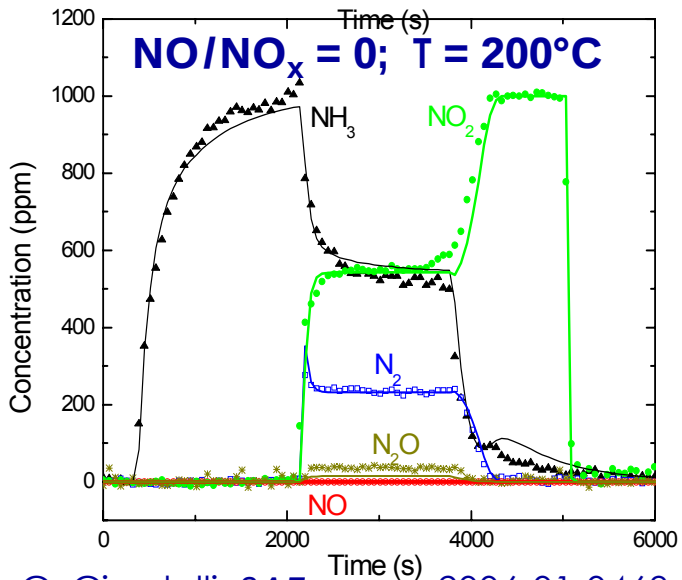
Fit results

Global fit of more than 50 kinetic runs: 160 < T < 450°C; 92000 < GHSV < 210000 h^{-1}; 2% < O_2 < 6%; 0 < NO/NO_x < 1



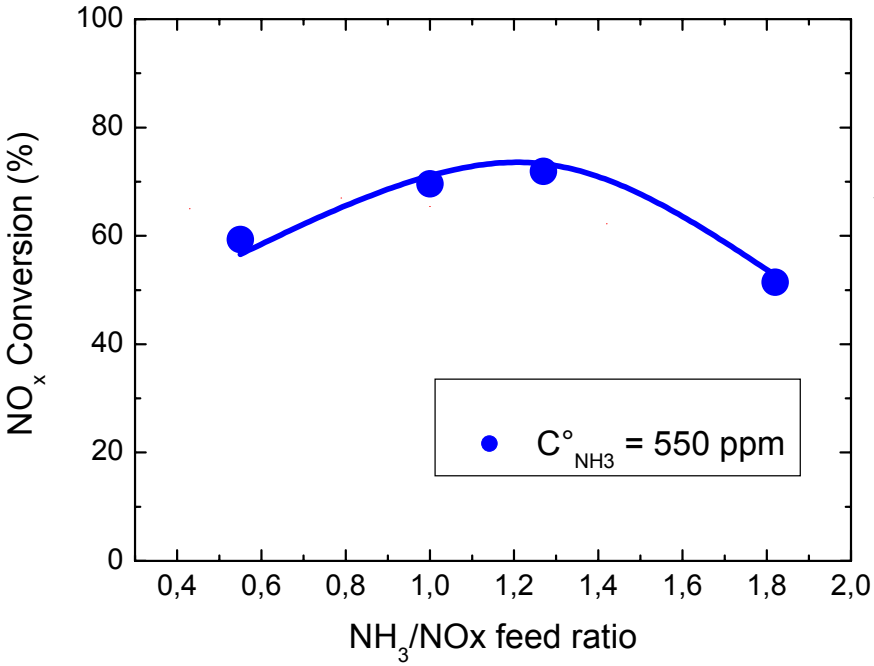






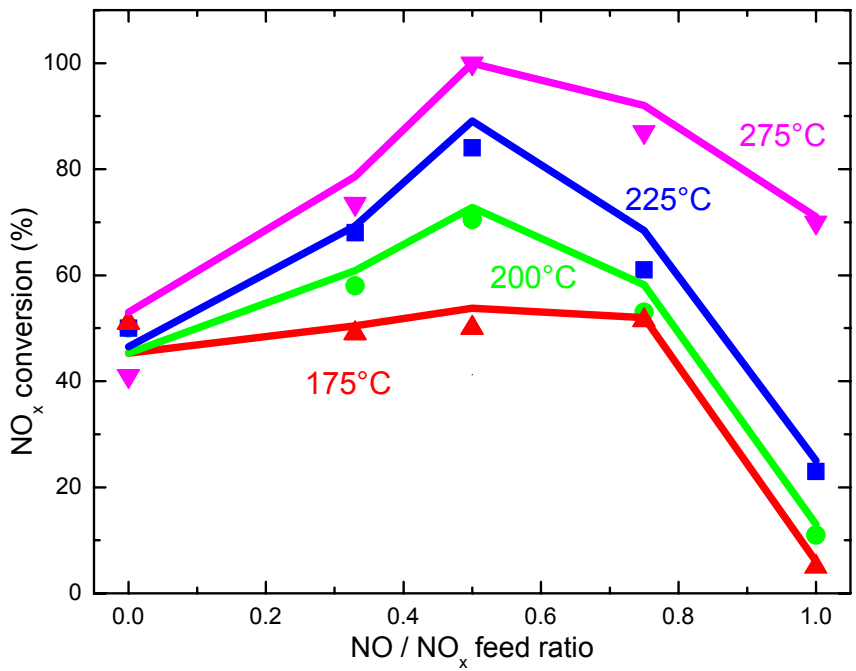
D. Chatterjee, T. Burkhardt, M. Weibel, E.Tronconi, I. Nova, C. Ciardelli, *SAE paper* 2006-01-0468.

Fit results: influence of NH_3/NO_x & NO/NO_x



Conditions:
GHSV = 210,000 h^{-1};
T = 200 °C;
C_{O2} = 2 %; C_{H2O} = 1%;
NO/NO_x = 0.5

Conditions:
GHSV = 210,000 h^{-1};
C_{O2} = 2 %; C_{H2O} = 1%;
NH_3/NO_x = 1



Fit results: dynamic features

$NH_3 + NO/NO_2/O_2$

GHSV = 210,000 h^{-1};

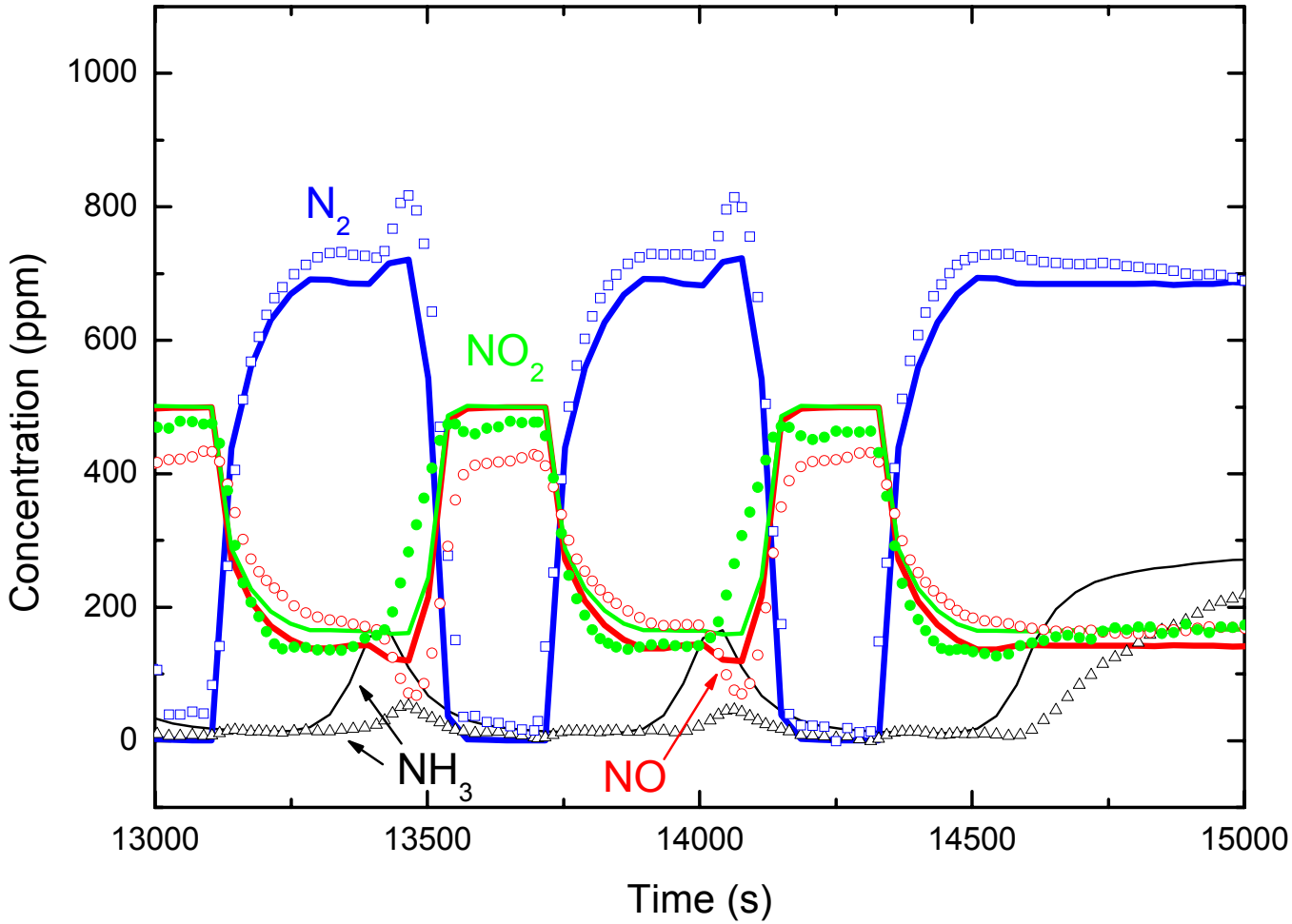
C_{NH3} = 1000 ppm;

$C_{NO} = C_{NO2}$ = 500 ppm;

C_{H2O} = 1%;

C_{O2} = 2%;

T = 200°C

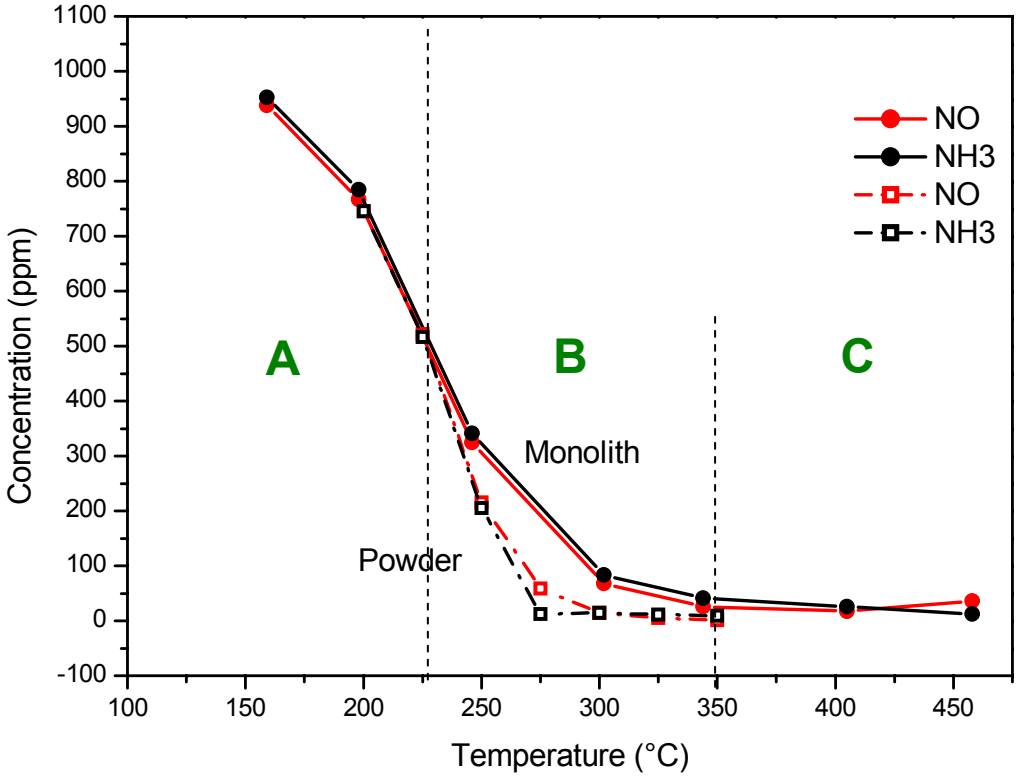


SCR dynamics are governed by ads/des of both NH_3 and nitrates!

Influence of NO_2 on SCR dynamics has to be taken into account in the Urea DCU

V-based catalyst: Modeling & Scale-up

Standard SCR reaction: Monolith vs. Powder



Notes:

Zone A: T < 225°C

Kinetic control

Zone B: 225 < T < 350 °C

Mass transfer control

monolith less active than powder

Zone C: T> 350 °C

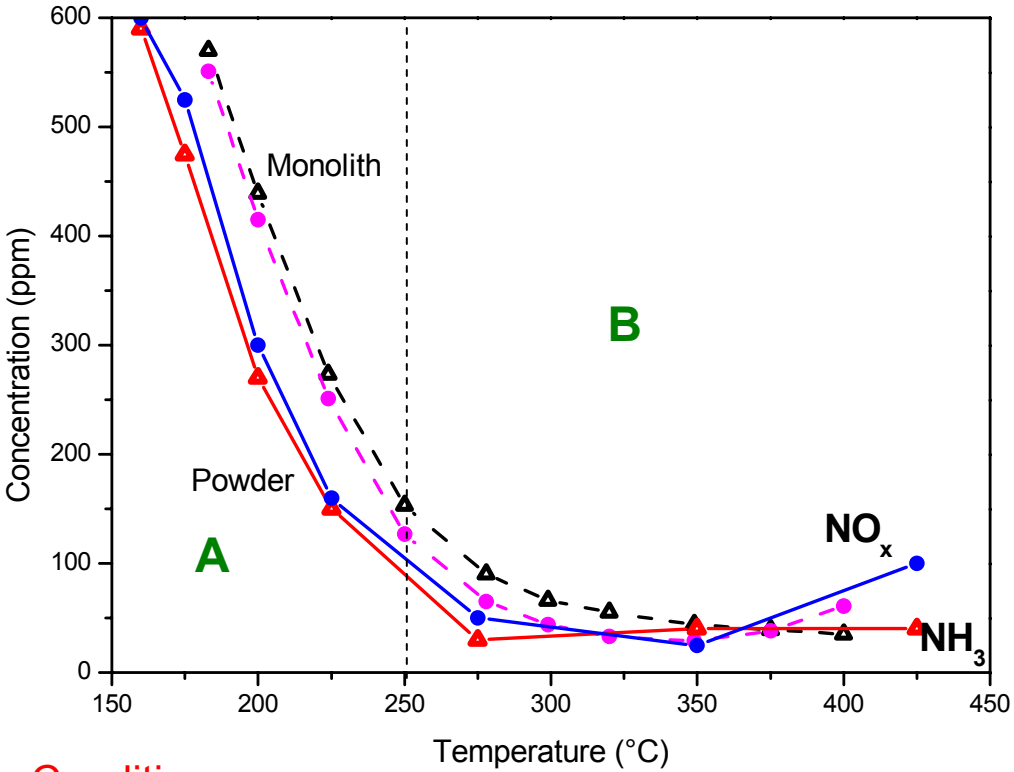
total conversion

Conditions:

- NH_3:NO = 1000:1000 ppm
- Cat. Mass= 12.8g Monolith – 0.16g Powder
- GHSV= 46000 Ncc/(h*g) Monolith (= 36000 h^{-1})
  = 45000 Ncc/(h*g) Powder
- O_2 = 2% H_2O = 1%

Role of diffusional resistances in monolithic converters

Fast SCR reaction: Monolith vs. Powder



Conditions:

- NH_3:NO:NO_2 = 1000:500:500 ppm
- Weight: 12.8g Monolith – 0.16g Powder
- GHSV: 105000 Ncc/(h*g) Monolith (= 82000 h^{-1})
  105000 Ncc/(h*g) Powder
- O_2 = 2% H_2O = 1%

Notes:

Kinetic control never prevails over monolith because reaction is fast even at low T

Zone A T < 250 °C

Mass transfer control:

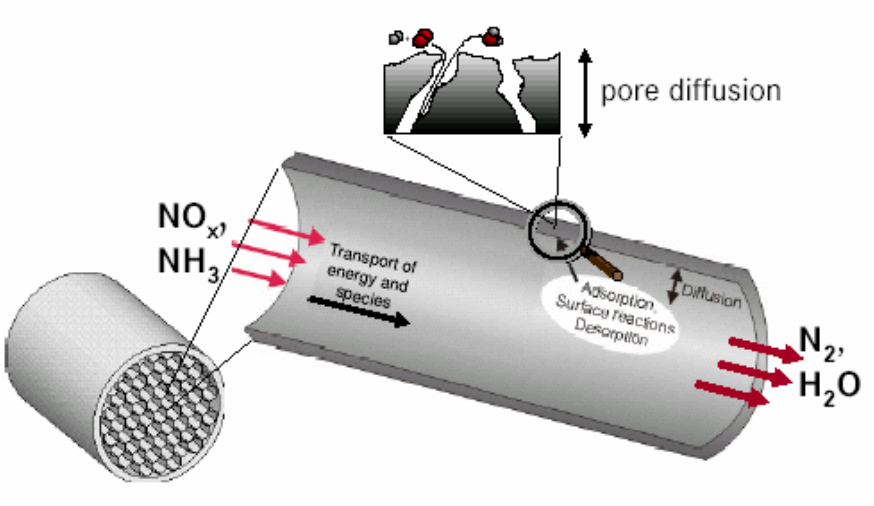
monolith less active than powder

Zone B T > 250 °C

Total conversion over both catalysts in spite of different mass transfer behavior
Possible role of gas-phase reactions in monolith?

Role of diffusional resistances in monolithic converters

Monolithic SCR Converter Model



- Extruded monoliths → the 1D+1D model accounts also for intraporous diffusion within the catalytic substrate.

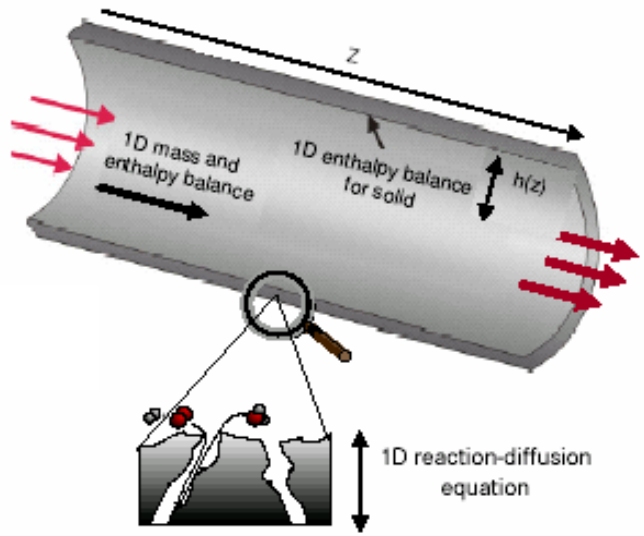
-Modeling of one representative channel.

-1D mass and enthalpy balances for gas and solid phase.

- Gas-solid mass and heat transport by means of transfer coefficients, h(z).

- 1D reaction-diffusion equations to account for diffusional limitations within the catalytic wall

- Evaluation of effective diffusivities $D_{eff,j}$ from morphological data according to a modified "random pore" model (Wakao-Smith).



E. Tronconi et al., IEC Res. 37 (1998) 2341
D. Chatterjee et al., *SAE technical paper* 2005-01-0965
D. Chatterjee et al., *SAE technical paper* 2006-01-0468

Monolithic Reactor Model

Transient, two-phase, single channel, 1D+1D mathematical model of SCR honeycomb reactors

Mass and enthalpy balances:

Gaseous species: j = 1,NCG

Adsorbed species: m=1,NCA

In the gas phase:

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

$$\frac{\partial T_g}{\partial t} = -\frac{v}{L}\frac{\partial T_g}{\partial z} - \frac{4}{d_h} h\left(T_g - T_s\right)/(\rho_g C_p)$$

In the solid phase:

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

$$\frac{\partial T_s}{\partial t} = \frac{h\left(T_g - T_s\right) - \sum_{j=1}^{NCG} \Delta H_j R_{eff,j}}{\rho_s C_{p,s} S_W}$$

$$\Omega_m \frac{\partial \vartheta_m}{\partial t} = R_m$$

Gas – solid continuity:

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

$$R_{eff,j} = -\frac{D_{eff,j}}{S_W}\frac{\partial C_j^*}{\partial x}\Big|_W$$

D. Chatterjee, T. Burkhardt, B. Bandl-Konrad, T.Braun, E.Tronconi, I. Nova, C. Ciardelli, *SAE technical paper* 2005-01-965

Validation – Full monolith scale

Engine test bench measurements with different SCR catalyst configurations:

- Catalyst Volumes: 25L, 32L, 43L

- Monolith diameter of 5.66"

- Catalyst Cell densities: 200 cpsi, 300cpsi

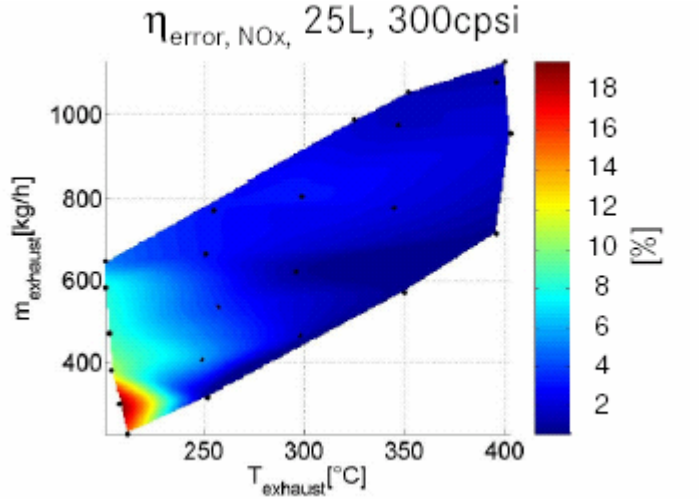
- Wall thickness: 0.32 mm

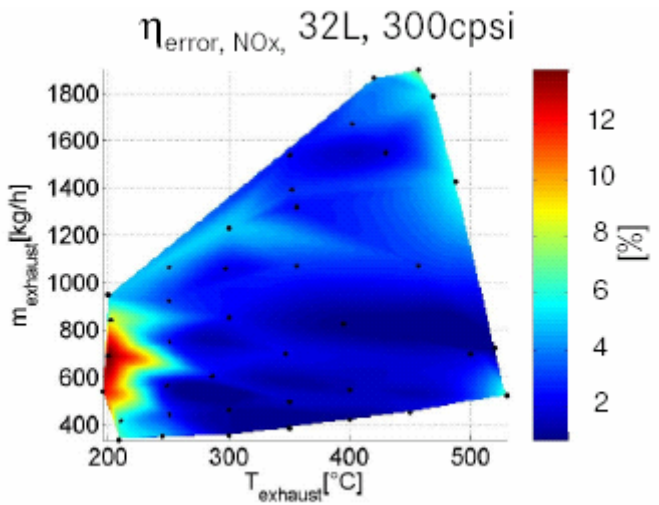
-Overall 100 constant engine operating points have been measured.

- Error quantification for a single operating point by means of the mean error:

$$\eta_{error,NO_x} = \frac{\int_0^{t_{end}} \sqrt{\left(\eta_{NO_x,sim.}(t) - \eta_{NO_x,\exp.}(t)\right)^2}\, dt}{t_{end}}$$

Case of no DOC

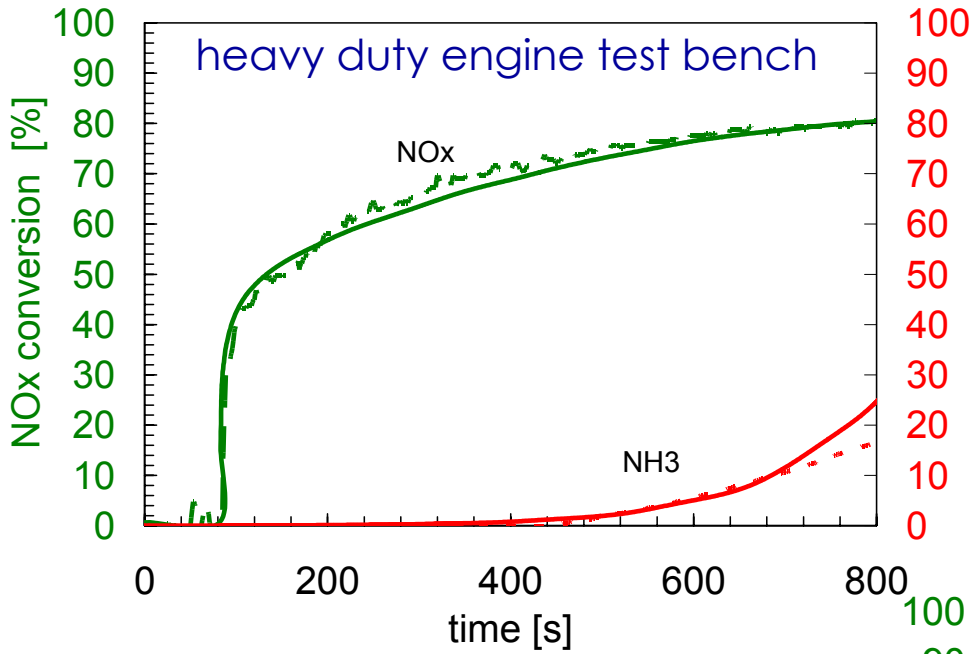




✓ Mean error for $\mathbf{h}_{NOx}$ is typically lower than 4%.

✓ Model is validated for a wide range of operating conditions.

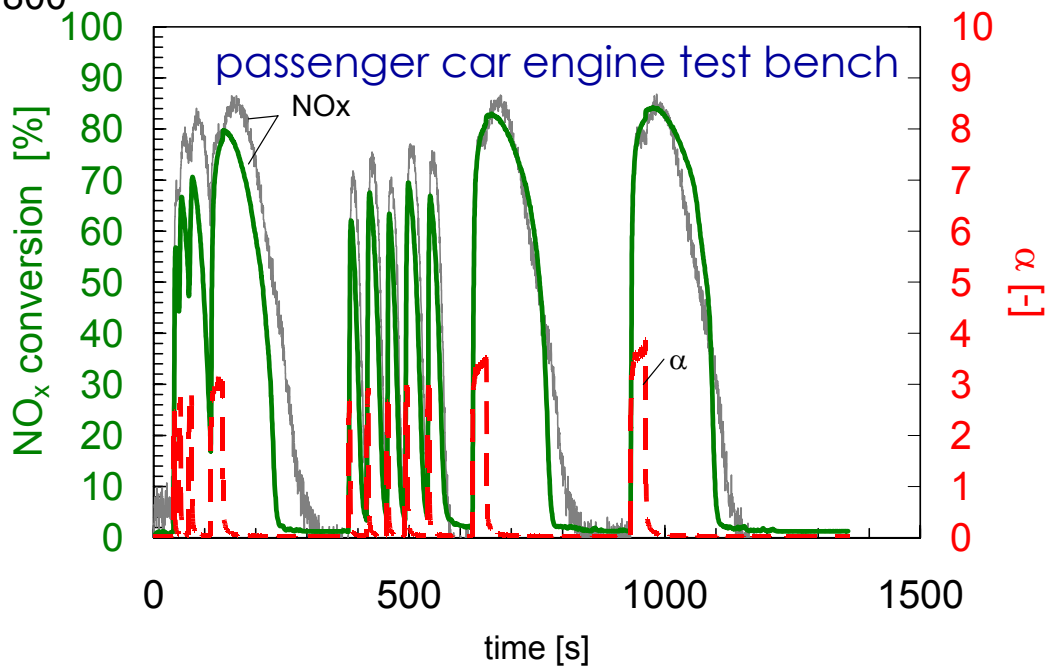
Validation – Full monolith scale



$T_{exh.}$ = 220 °C, NO_2/NO_x = 16%, 25L catalyst, 300cpsi, GHSV = 21700h-1 and α = 1.29

With DOC

(*) D. Chatterjee, T. Burkhardt, M. Weibel, E.Tronconi, I. Nova, C. Ciardelli, *SAE technical paper* 2006-01-0468.



$T_{exh.}$ = 229°C, NO_2/NO_x = 44%, GHSV = 73200h-1. , catalyst 1.8L, 300cpsi

Validation with test bench data reveals a good prediction quality of the model.

Modeling of Integrated Aftertreatment Systems

Intrinsic kinetics

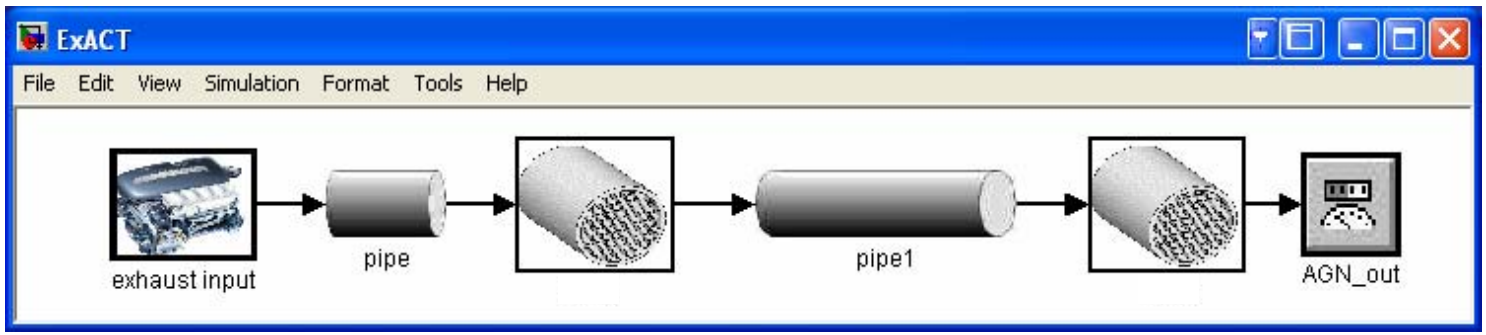
↓

2-D (1D+1D) model of SCR monolithic converters

↓

DaimlerChrysler-ExACT

Exhaust Gas Aftertreatment Components Toolbox



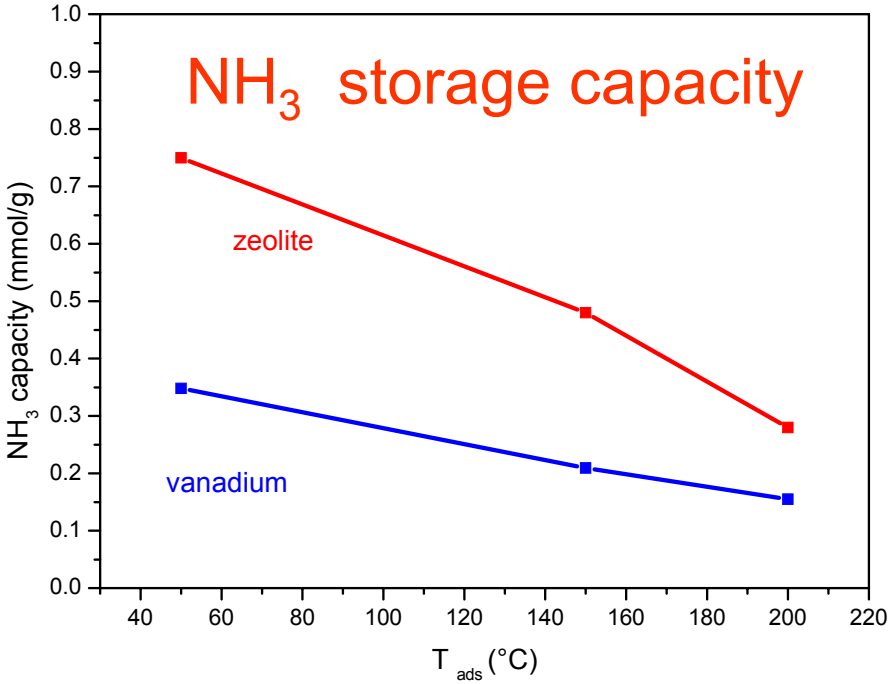
- Simulation of full transient test-cycles
- Catalyst sizes/geometry pre-selection
- Assessment of variations in engine out parameters on catalyst performance
- Optimization of operating and control strategy

D. Chatterjee, 9th CLEERS Workshop, 2006

Fe-Zeolite catalyst: SCR reactivity & chemistry

work in progress

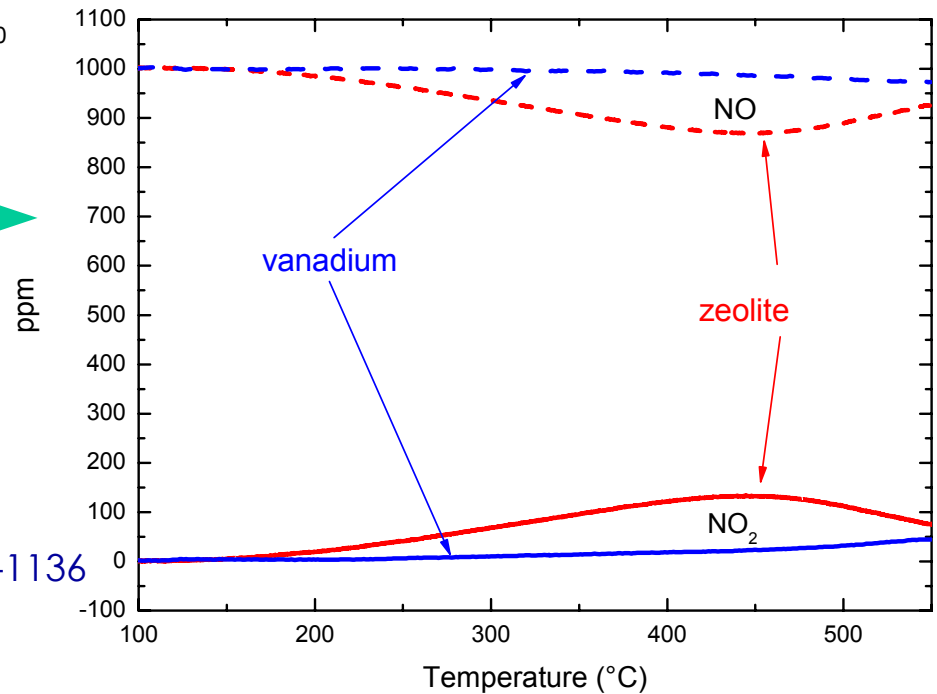
Zeolite- vs. V-based catalyst



Washcoated monolith catalyst crushed to powder

- Higher storage capacity of zeolite cat.

NO/O_2

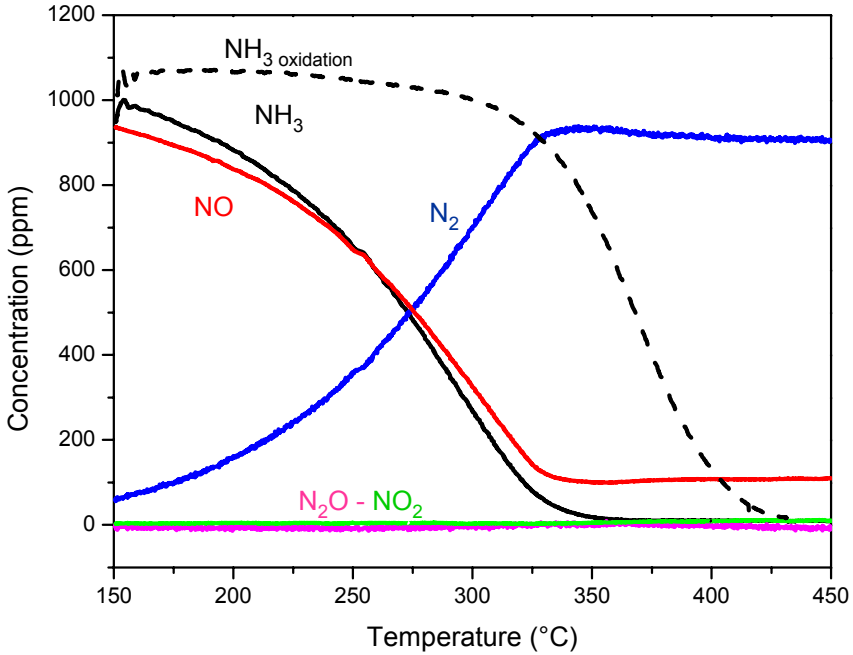


- NO oxidation activity observed over the zeolite cat.

D. Chatterjee, T. Burkhardt, M. Weibel, I. Nova, A. Grossale, E.Tronconi, *SAE technical paper* 2007-01-1136

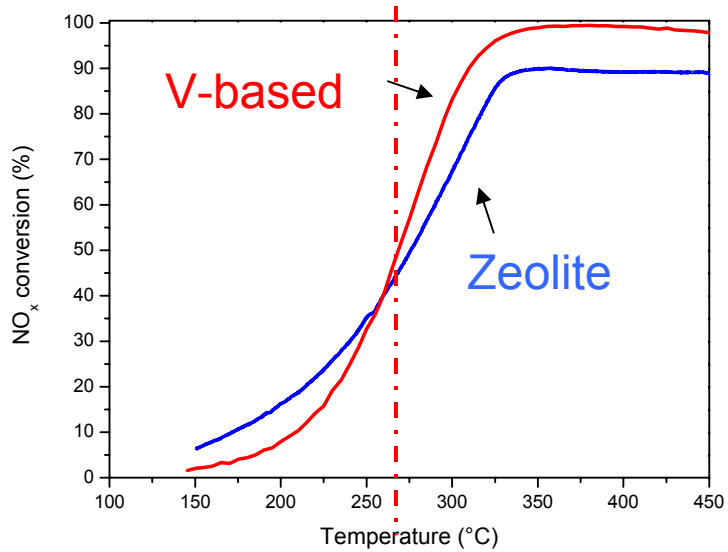
NO\NH$_3$ – O$_2$ system: Std. SCR reaction

Zeolite



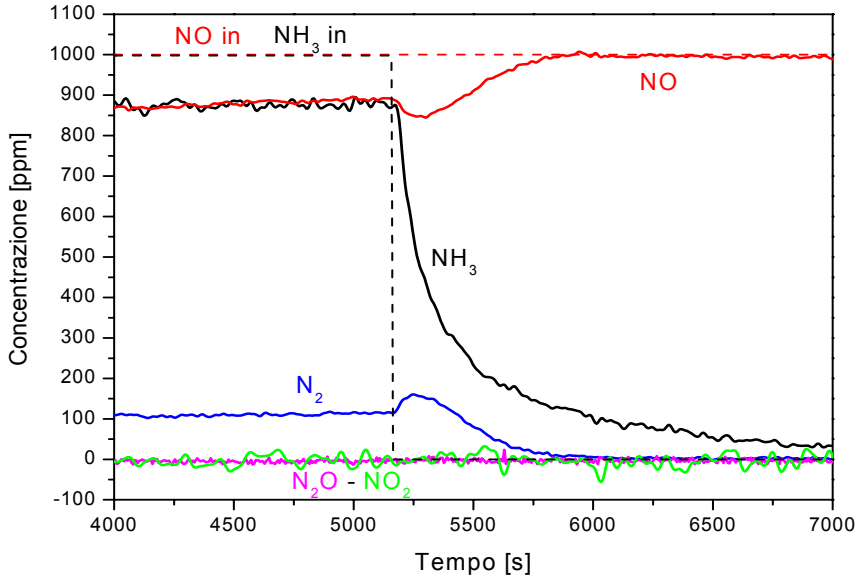
- Zeolite active in the SCR reaction
  - 100% N_2 selectivity
  - @ T> 275°C NH_3 conversion > NO
    - → NH_3 oxidation
  - @ high T NO is not totally converted
    - → NH_3 oxidation

Zeolite vs. V-based cat. NO_x conversion



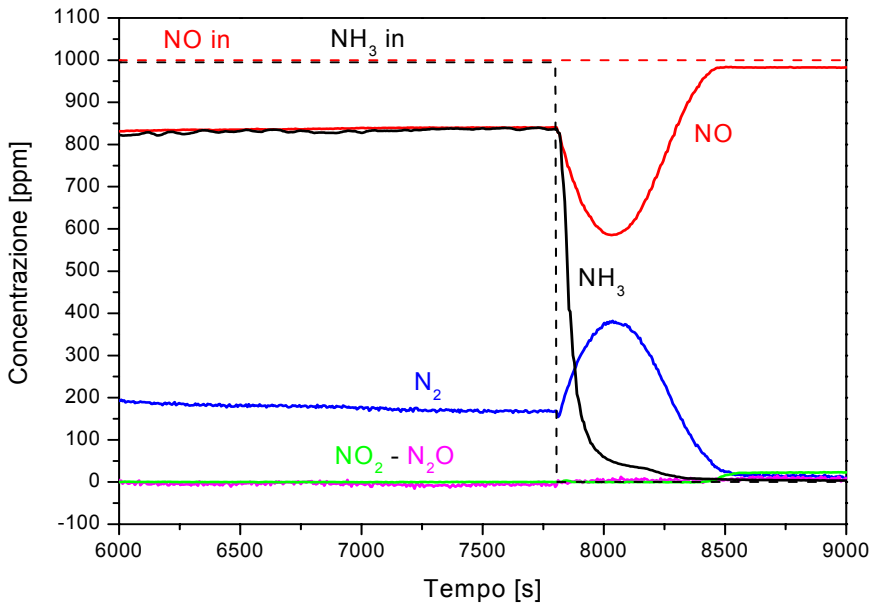
- Zeolite is more active below 270°C
- @ High T the V-based cat. exhibits 100% NO_x conversion

Standard SCR: *Zeolite vs. V-based catalyst*



NH_3+NO /O_2 , T = 200°C :
similar dynamic features
due to NH_3 inhibition

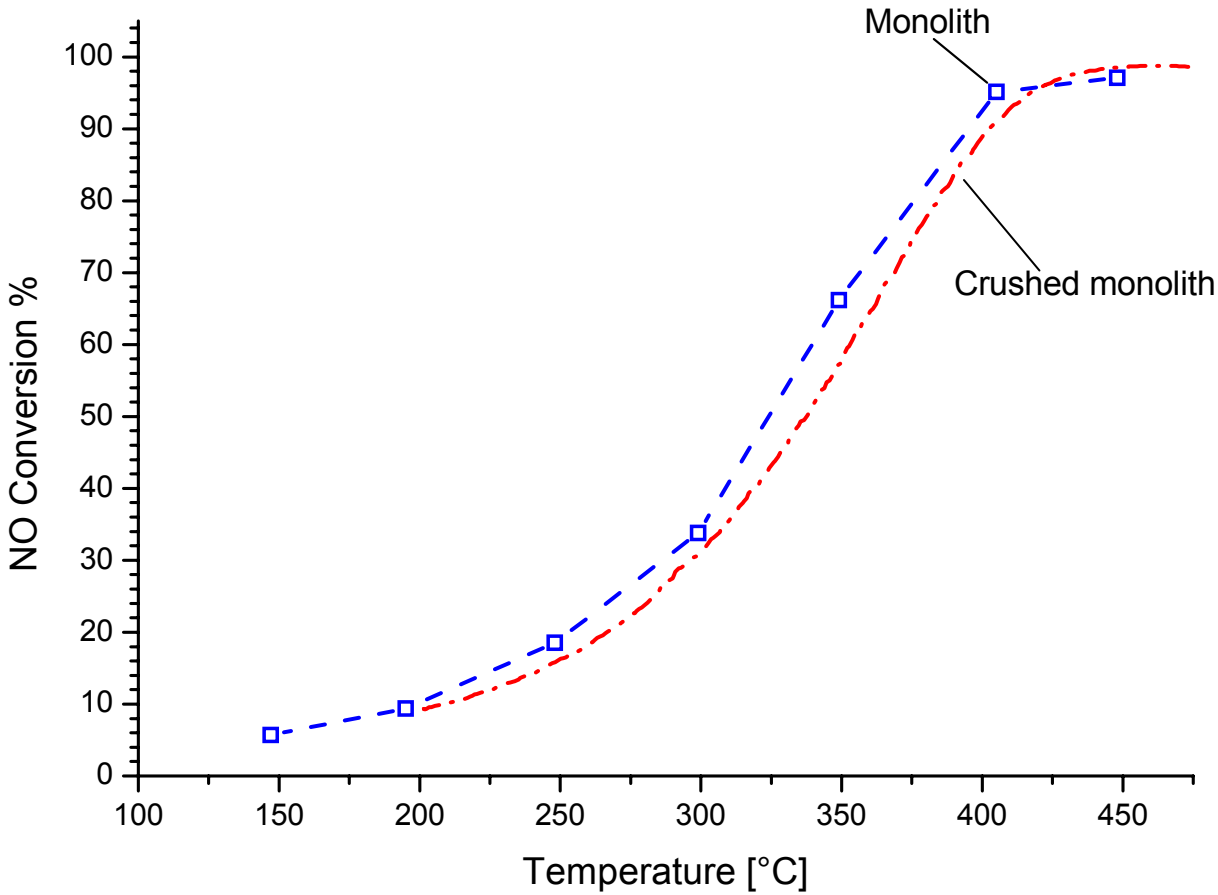
Vanadium:
optimum NH_3 coverage = 26%



Zeolite (washcoat powder):
optimum NH_3 coverage = 17%

Std SCR on Fe-Zeolite: Monolith vs. powder

GHSV=170000 [Ncc/(h*g)]



Monolith
Q= 4200 Ncc/min
mcat = 1.42 g (active ph.)

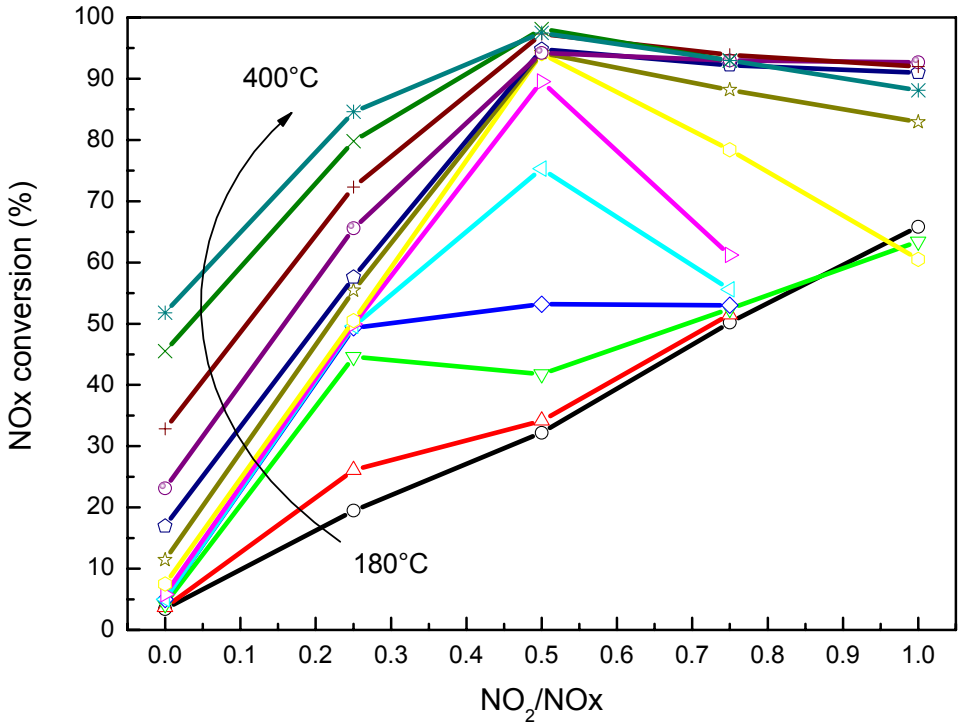
Crushed Monolith
Q= 120 Ncc/min
mcat = 0.042 g (active ph.)

No apparent role of diffusional limitations

D. Chatterjee, T. Burkhardt, M. Weibel, I. Nova, A. Grossale, E.Tronconi, *SAE technical paper* 2007-01-1136

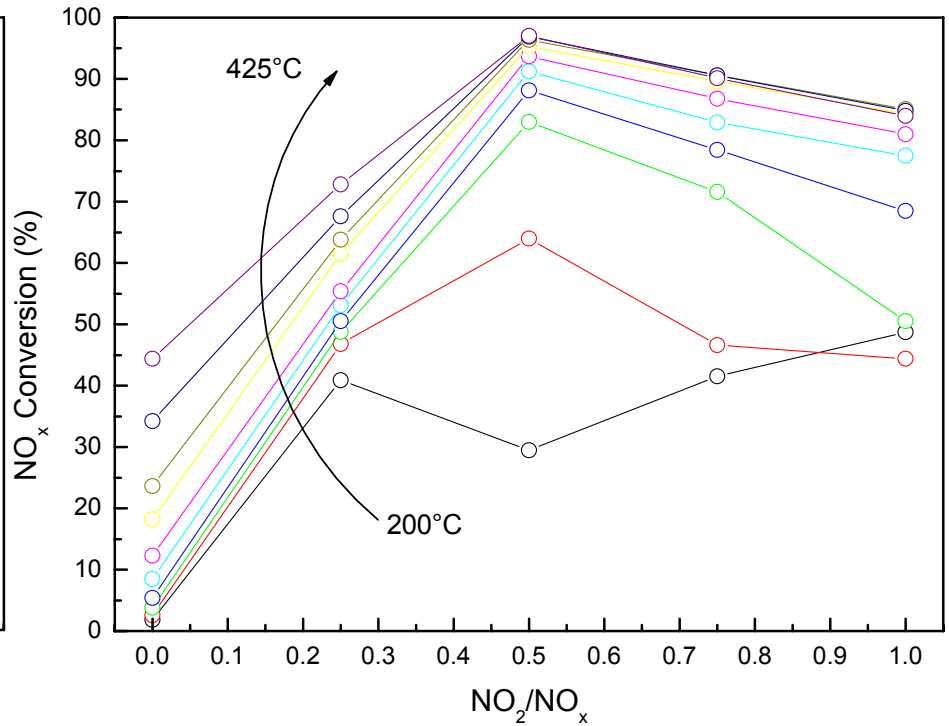
$NO\text{-}NO_2\backslash NH_3$ – O_2 system: Fast SCR

Crushed monolith



Mcat = 0.021 g (active ph.)
GHSV 789000 Ncc/(hg)
O2 = 2%, H2O = 1%
1000:500:500 NH_3:NO:NO_2

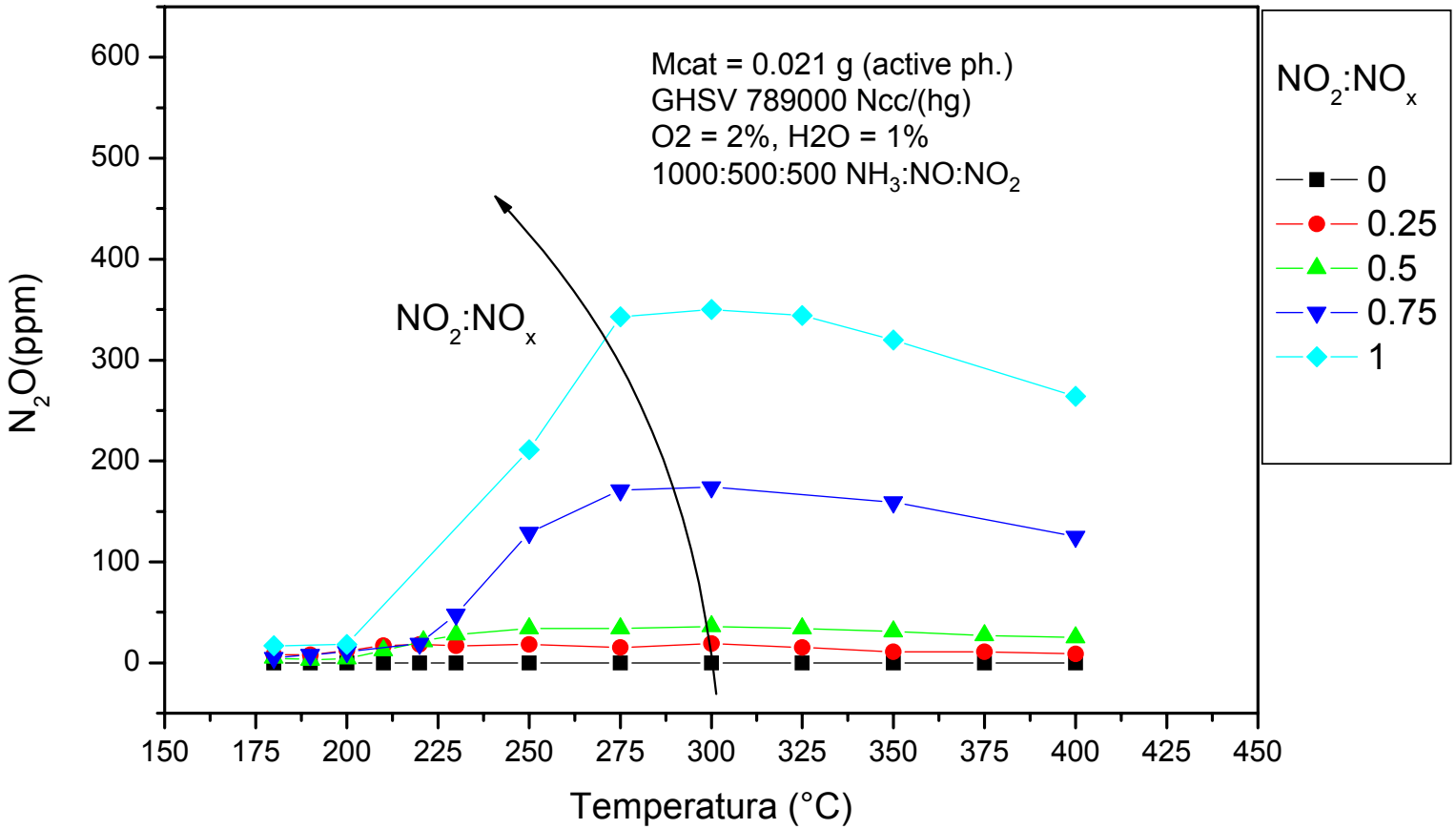
Monolith



M_{cat} = 0.86 g (active ph.)
GHSV 788000 Ncc/(hg)
O_2 = 2%, H_2O = 1%
1000:500:500 = NH_3:NO:NO_2

- ✓ Low T behavior dominated by NO_2 reactivity: max NO_x conversion for NO_2/NO_x= 1 (NH_4NO_3 formation)
- ✓ High T: max NO_x conversion for NO_2/NO_x = 1/2

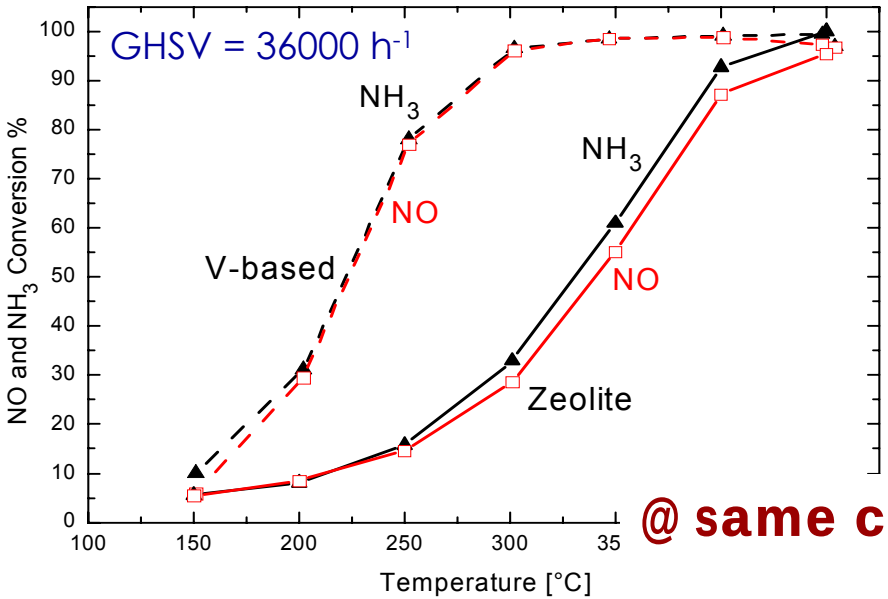
Effect of NO_2/NOx on N_2O formation



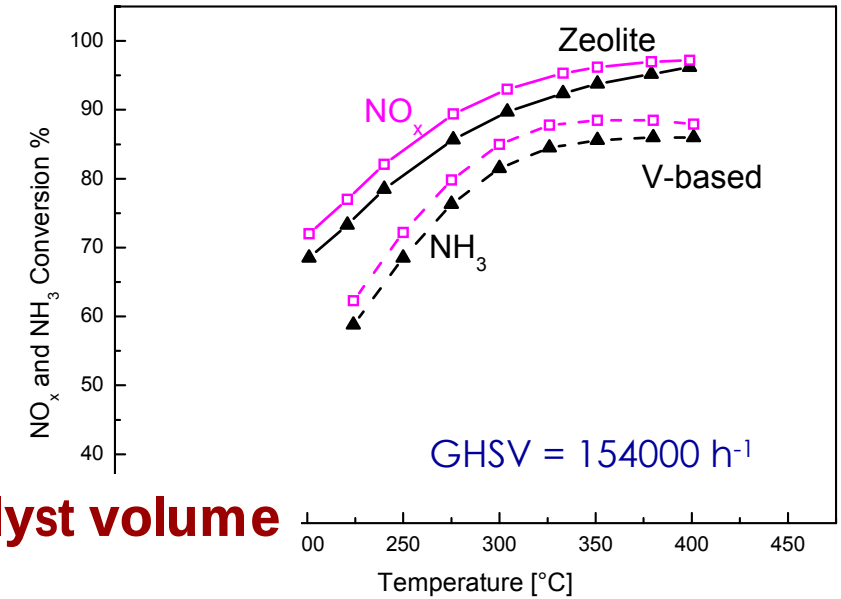
✓ N_2O formation favored by $NO_2/NO_x > 1/2$

V-based vs. Zeolite-based monolith catalyst

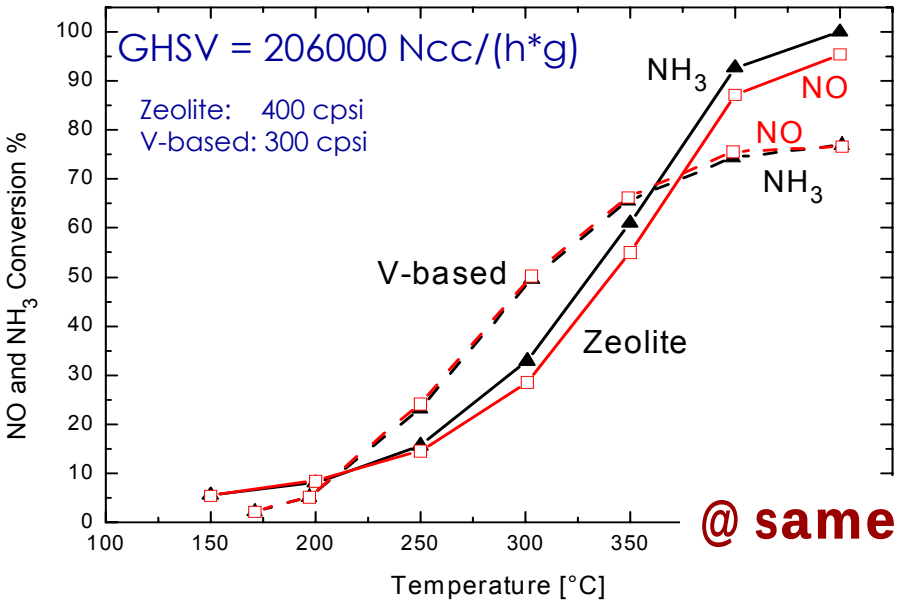
NH_3+NO/O_2



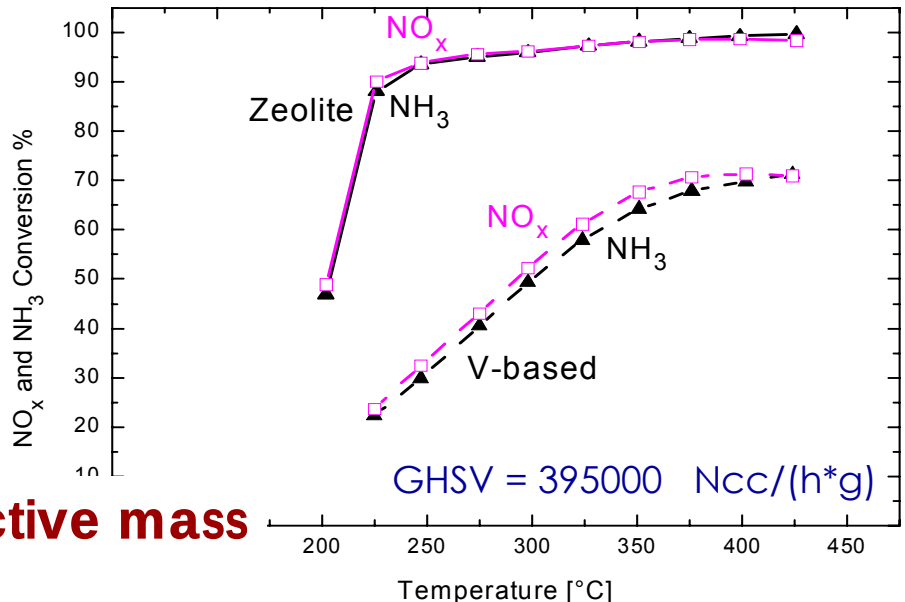
$NH_3+NO+NO_2/O_2$



@ same catalyst volume



@ same active mass



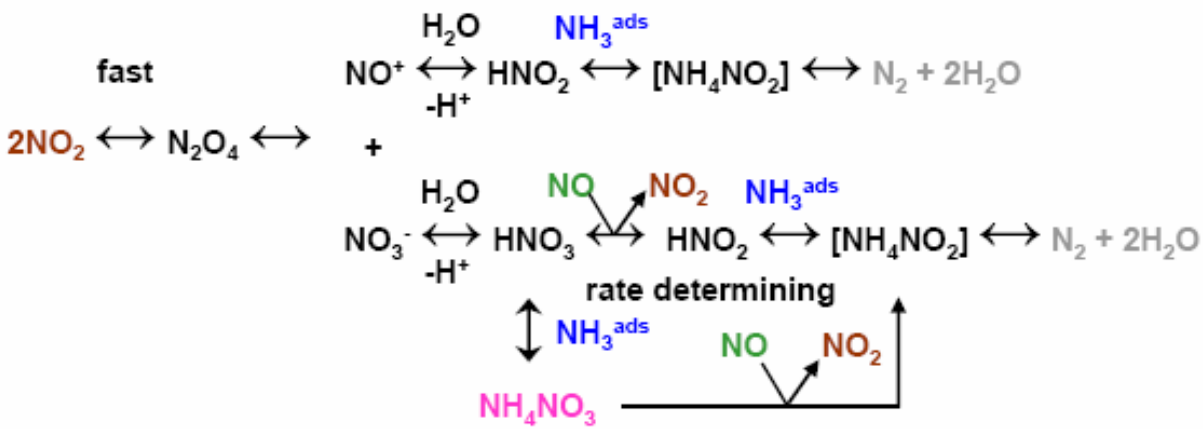
Proposed chemistry similar to V- catalysts?

Reaction Scheme for NO/NO_2 SCR over Metal-Exchanged Zeolites

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

NH_3 + Brønsted acid site $\rightarrow$ NH_4^+

NH_3 + acidic site $\rightarrow$ NH_3^{ads}



O. Kroecher,1st MinNOx Conference, Berlin, February 2007

Summary and Conclusions

I. NH_3 SCR on V-based catalyst:

- ✓ **Low-T dynamics controlled by:**
  - NH_3 adsorption/desorption/reaction
  - NH_3 inhibition effects on NOx reactivity
  - storage/release of surface nitrates
- ✓ **Transient behavior quantitatively described by mechanistic kinetic model**
- ✓ **Account of transport phenomena in monolithic converter model permits predictive scale-up of kinetics across five orders of magnitude**

II. NH_3 SCR on Fe-zeolite catalyst :

- ✓ **Chemistry similar to V-based catalyst:**
  same rate expressions can be used
- ✓ **Washcoat diffusion of minor importance**
- ✓ **Higher NO_2 sensitivity at low T and NO2/NOx < 50%**
- ✓ **Mechanistic and kinetic analysis in progress**
  preliminary kinetics presented at SAE 2007

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