



CLEERS Workshop 2012, Dearborn, April 30th, 2012

Development and validation of a chemico-physically consistent mathematical model of dual-layer Ammonia Slip Catalysts

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Catalytic Processes **LCCP**



POLITECNICO DI MILANO

DAIMLER

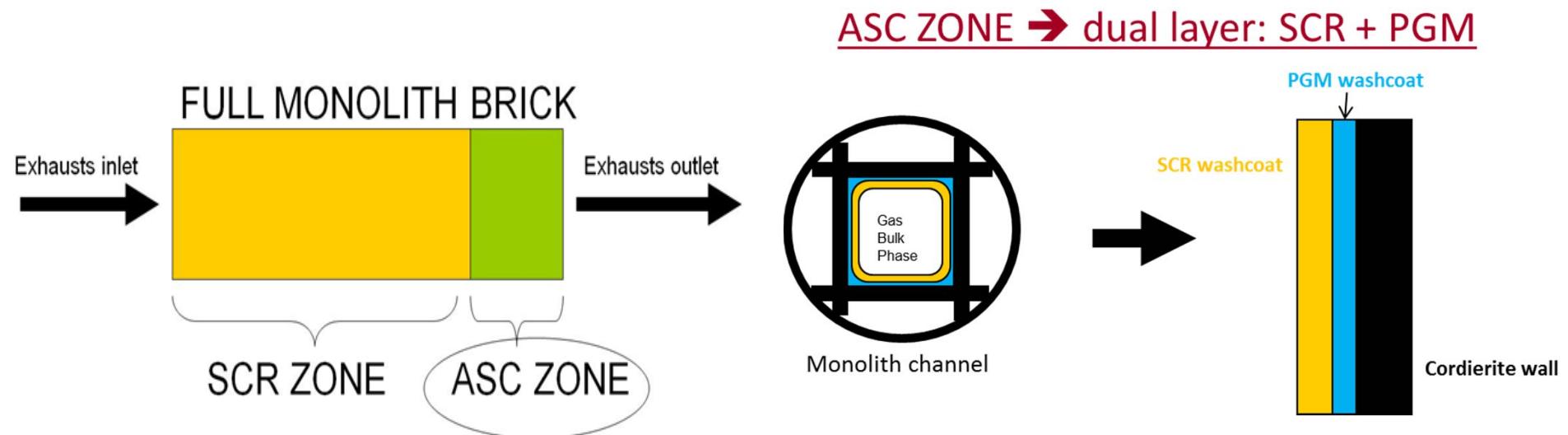
Dual Layer ASCs concept

What is the NH₃ slip: undesired release of unreacted NH₃ downstream of the SCR converters.

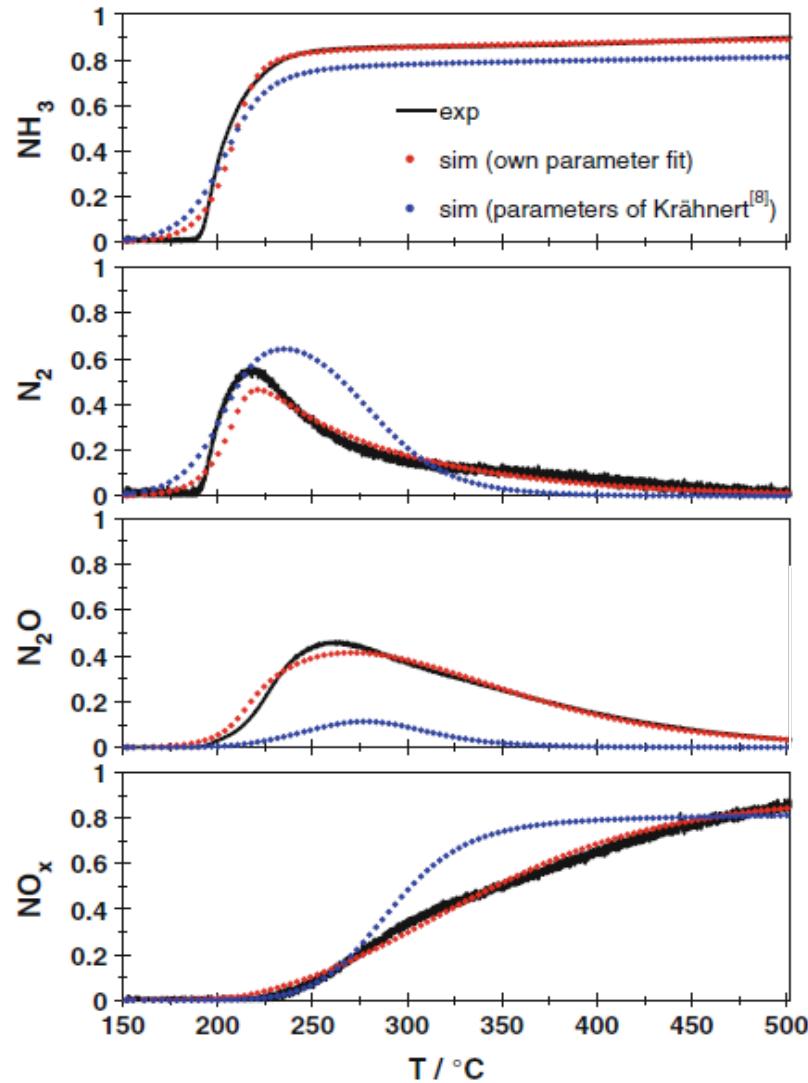
Possible causes of NH₃ slip:

- incomplete NOx conversion
- overdosing of reducing agent to favour NOx conversion
- desorption of stored NH₃ during fast heat-up transients

How to avoid it? Catalytic device downstream of the SCR converter → **ASC**



Why a Dual Layer ASC configuration?



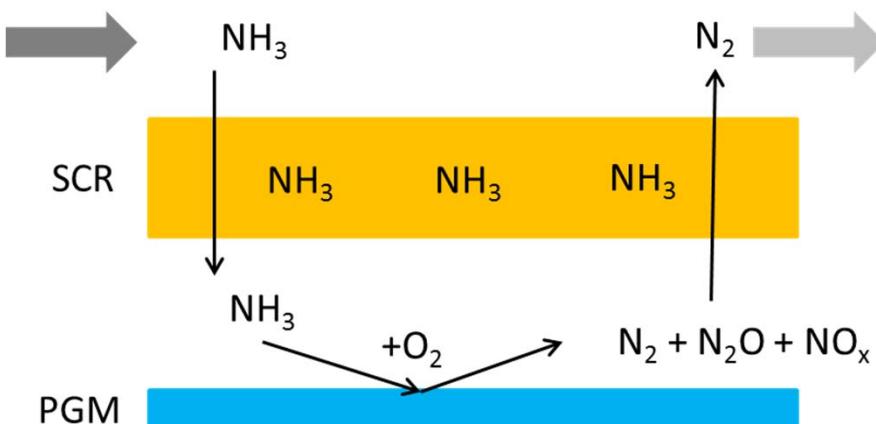
PGM catalysts have poor selectivity to N_2



N_2O and NO_x , the unselective products of the PGM layer, diffuse back in the SCR layer where they can react with NH_3 over the SCR catalyst to give N_2 !!!



NH_3 conversion & N_2 selectivity increase



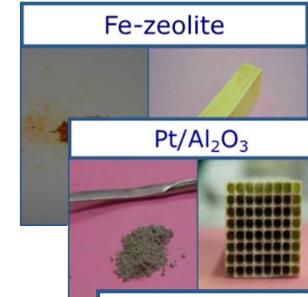
Scheuer et al., Top.Catal. 52 (2009) 847

Scheuer et al., App.Catal. B: Environmental 111– 112 (2012) 445

Goal/Outline

Development of a chemico-physically consistent mathematical model of a dual-layer ASC monolith

1. Kinetic study and model validation of the SCR component

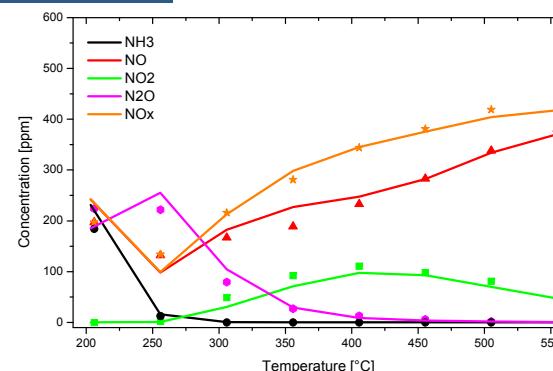
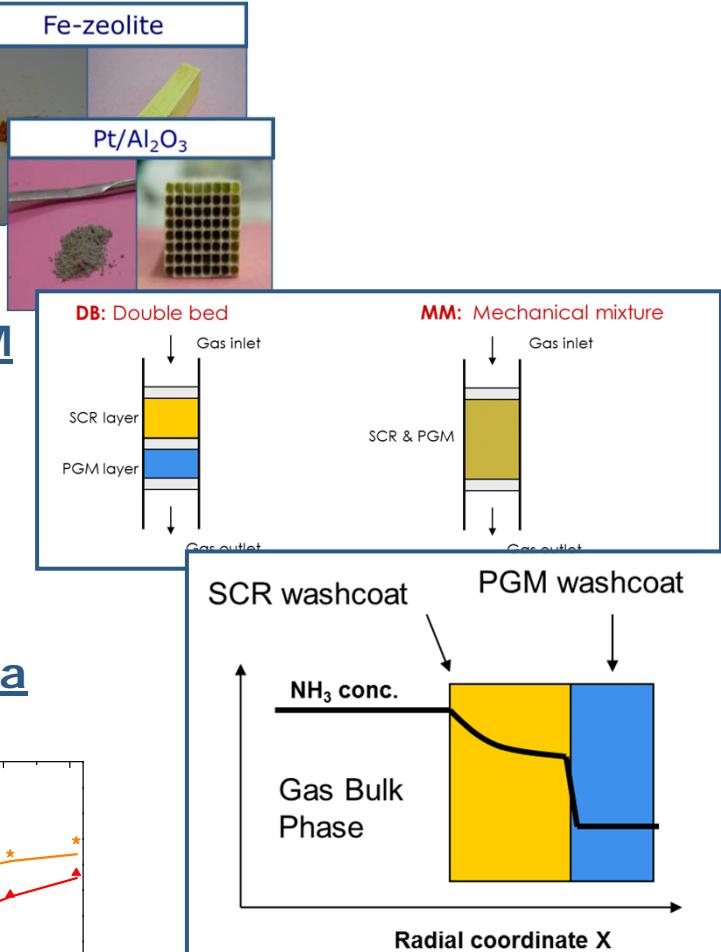


2. Kinetic study and model validation of the PGM component

3. Kinetic study of the combined SCR+ PGM components

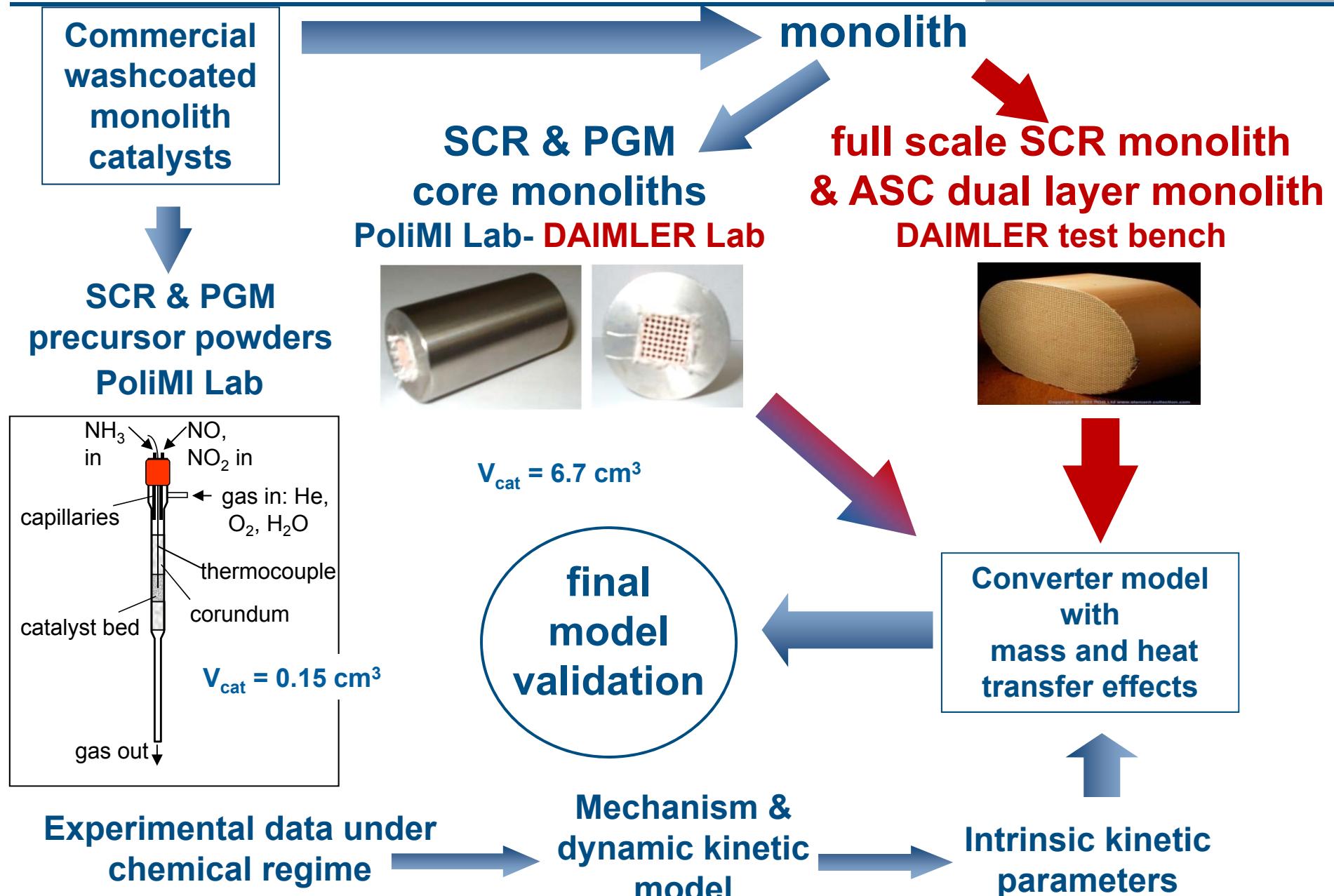
4. Development of the dual-layer monolith model

5. Validation against lab- and full scale data from dual-layer monolith data

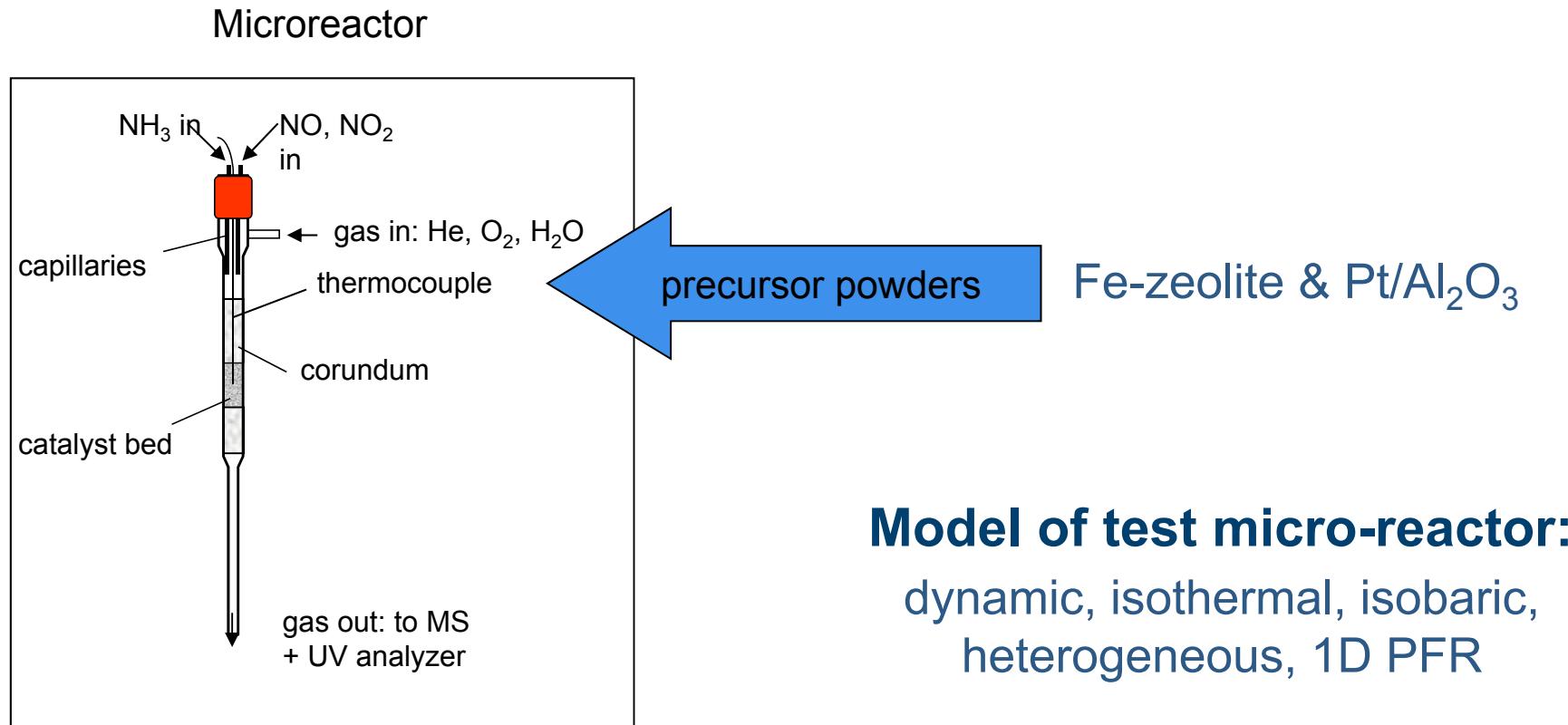


Approach & Methods

Approach & Methods



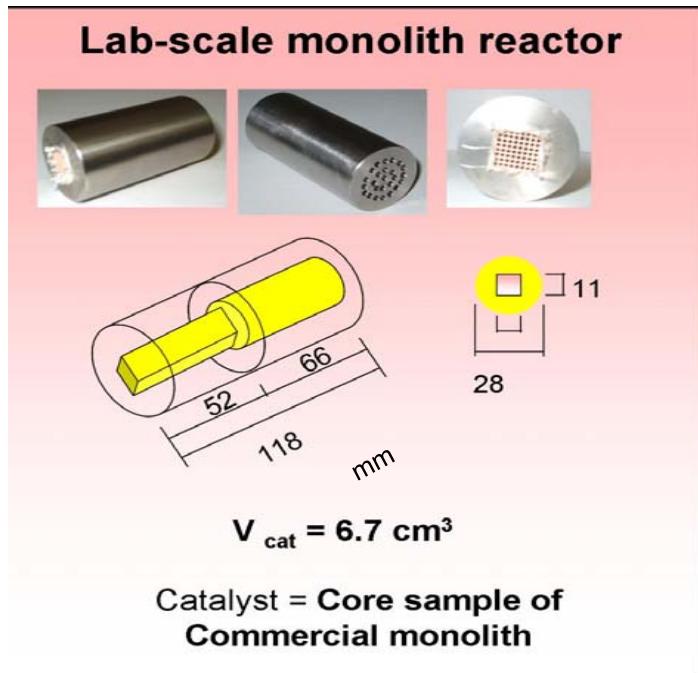
Microreactor scale



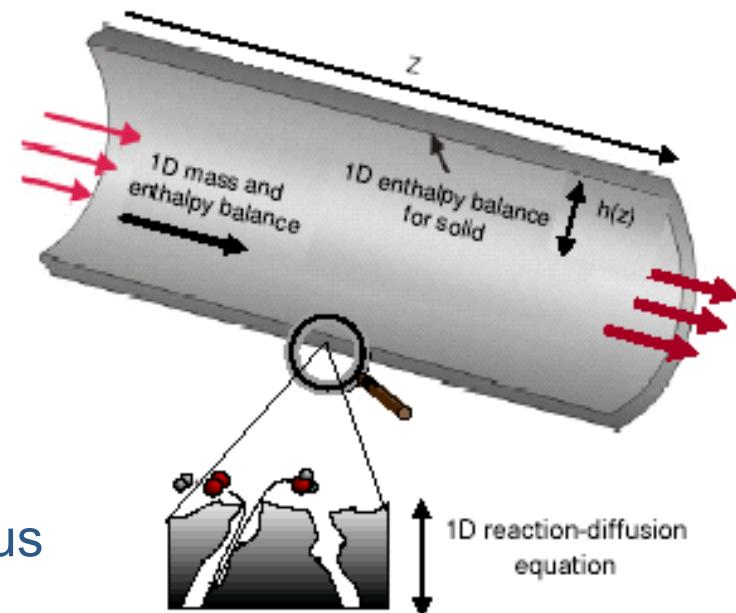
Lab-scale tests in microreactor afford:

- no diffusional limitations
- isothermal operation
- N-balances
- fast transients

Monolith scale



Fe-zeolite washcoated monoliths
PGM washcoated monoliths
ASC dual layer washcoated monoliths



Model of monolithic SCR converters:

- extruded/washcoated monoliths → the 1D+1D model accounts also for intraporous diffusion within the catalytic layers.
- modeling of one representative channel.
- 1D mass and enthalpy balances for gas and solid.

Tronconi et al., IEC Res. 37 (1998), 2341

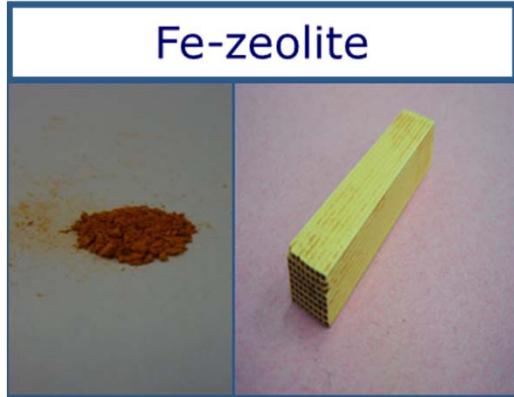
Chatterjee et al., SAE technical paper 2005-01-0965

Chatterjee et al., SAE technical paper 2006-01-0468

Goal/Outline

Development of a chemico-physically consistent mathematical model of a dual-layer ASC monolith

1. Kinetic study and model validation of the SCR component



- Experimental study over powdered catalyst (chemical regime)
- Identification of the reaction scheme
- Development of a global kinetic model
- Estimation of the kinetic parameters
- Model validation at the monolith scale

Kinetic scheme

Kinetic investigation analyzing the effect of operative conditions
(temperature, species concentrations, GHSV, steady-state vs. transients) on:

NH₃

NH₃/O₂

NO/O₂ – NO₂/O₂

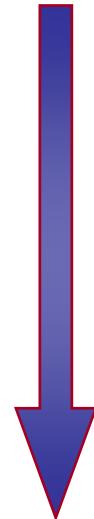
NH₃/NO/O₂

NH₃/NO₂/O₂

NH₃/NO-NO₂/O₂

N₂O/NO-NO₂

N₂O/NH₃



1. NH₃ adsorption/desorption $NH_3 \leftrightarrow NH_3^*$
2. NH₃ oxidation to N₂ $2NH_3^* + 3/2O_2 \rightarrow N_2 + 3H_2O$
3. NH₃ oxidation to NO $2NH_3^* + 5/2O_2 \rightarrow 2NO + 3H_2O$
4. NO oxidation to NO₂ $NO + 1/2O_2 \rightarrow NO_2$
5. Standard SCR $NH_3^* + NO + 1/4O_2 \rightarrow N_2 + 3/2H_2O$
6. High-T Standard SCR $NH_3 + NO + 1/4O_2 \rightarrow N_2 + 3/2H_2O$
7. Ammonium nitrate formation $2NH_3^* + 2NO_2 \rightarrow NH_4NO_3^* + N_2 + H_2O$
8. Ammonium nitrate sublimation $NH_4NO_3^* \rightarrow (NH_3^*) + (HNO_3) \rightarrow NH_4NO_{3(s)}$
9. N₂O formation $2NH_3^* + 2NO_2 \rightarrow N_2 + N_2O + 3H_2O$
10. NO₂-SCR → N₂ $8NH_3^* + 6NO_2 \rightarrow 7N_2 + 12H_2O$
11. Fast SCR $2NH_3^* + NO + NO_2 \rightarrow 2N_2 + 3H_2O$
12. N₂O reduction by NO $N_2O + NO \rightarrow N_2 + NO_2$
13. N₂O-SCR $2NH_3^* + 3N_2O \rightarrow 2N_2 + 3H_2O$

Kinetic scheme

Kinetic investigation analyzing the effect of operative conditions (temperature, species concentrations, GHSV, steady-state vs. transients) on:

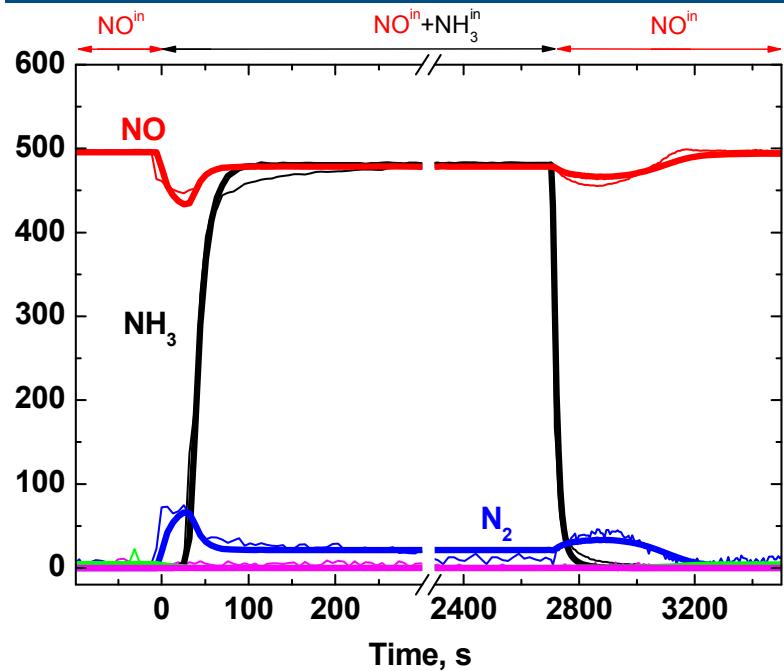


Specific rate for Standard SCR
hysteresis effects and kinetic
scheme accounting also for N₂O
decomposition /reactivity

1. NH₃ adsorption/desorption $\text{NH}_3 \leftrightarrow \text{NH}_3^*$
2. NH₃ oxidation to N₂ $2\text{NH}_3^* + 3/2\text{O}_2 \rightarrow \text{N}_2 + 3\text{H}_2\text{O}$
3. NH₃ oxidation to NO $2\text{NH}_3^* + 5/2\text{O}_2 \rightarrow 2\text{NO} + 3\text{H}_2\text{O}$
4. NO oxidation to NO₂ $\text{NO} + 1/2\text{O}_2 \rightarrow \text{NO}_2$
5. Standard SCR $\text{NH}_3 + \text{NO} + 1/4\text{O}_2 \rightarrow \text{N}_2 + 3/2\text{H}_2\text{O}$
6. High-T Standard SCR $\text{NH}_3 + \text{NO} + 1/4\text{O}_2 \rightarrow \text{N}_2 + 3/2\text{H}_2\text{O}$
7. Ammonium nitrate formation $2\text{NH}_3^* + 2\text{NO}_2 \rightarrow \text{NH}_4\text{NO}_3^* + \text{N}_2 + \text{H}_2\text{O}$
8. Ammonium nitrate sublimation $\text{NH}_4\text{NO}_3^* \rightarrow (\text{NH}_3^*) + (\text{HNO}_3) \rightarrow \text{NH}_4\text{NO}_{3(s)}$
9. N₂O formation $2\text{NH}_3^* + 2\text{NO}_2 \rightarrow \text{N}_2 + \text{N}_2\text{O} + 3\text{H}_2\text{O}$
10. NO₂-SCR → N₂ $8\text{NH}_3^* + 6\text{NO}_2 \rightarrow 7\text{N}_2 + 12\text{H}_2\text{O}$
11. Fast SCR $2\text{NH}_3^* + \text{NO} + \text{NO}_2 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O}$
12. N₂O reduction by NO $\text{N}_2\text{O} + \text{NO} \rightarrow \text{N}_2 + \text{NO}_2$
13. N₂O-SCR $2\text{NH}_3^* + 3\text{N}_2\text{O} \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O}$

SCR catalyst: kinetics derivation over powders

Hysteresis effect with NH₃ surface coverage

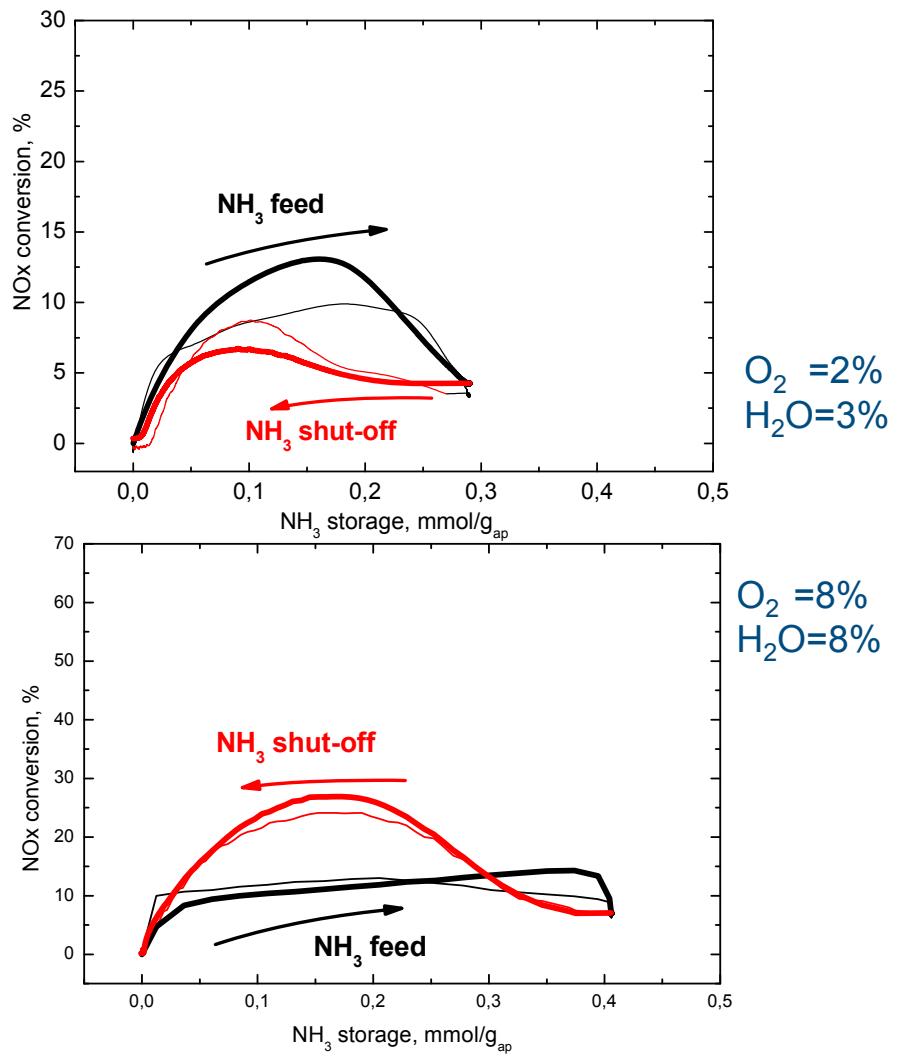


Standard SCR

$$r_{NO} = \exp \left[k_{NO}^o - E_{NO} \left(\frac{1000}{T} - \frac{1000}{473} \right) \right] C_{NO} \theta_{NH_3} (1 - \sigma_{NH_3})$$

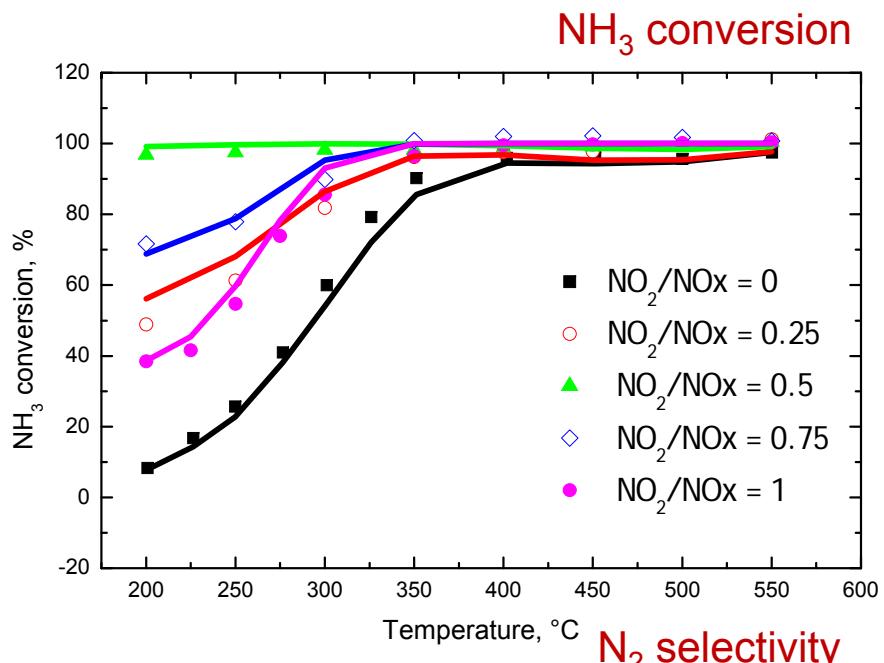
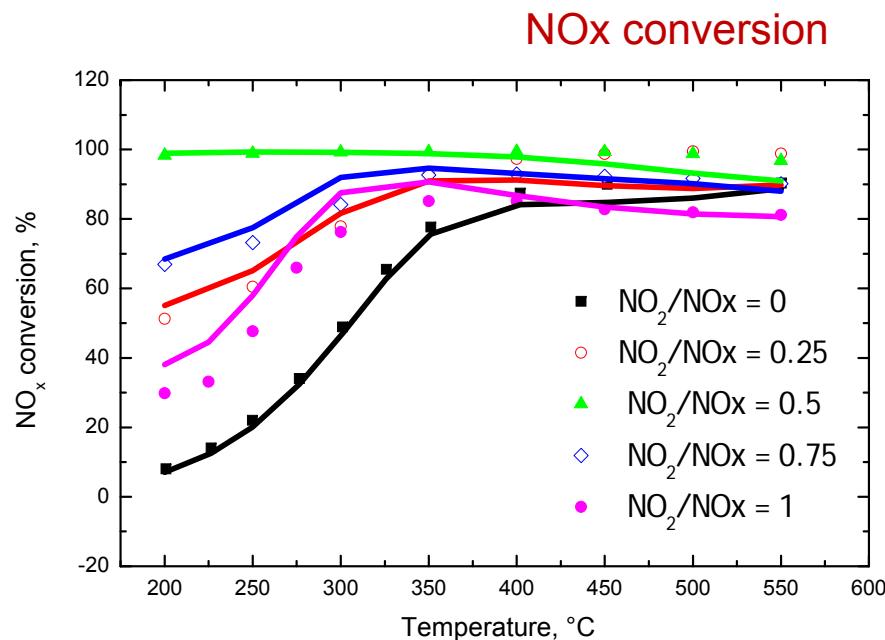
Experimental conditions:
 NH₃=NO= 500 ppm
 O₂= 2-8%; H₂O= 3-8%
 T=200°C

Thin lines = experimental
 Thick lines = kinetic fit

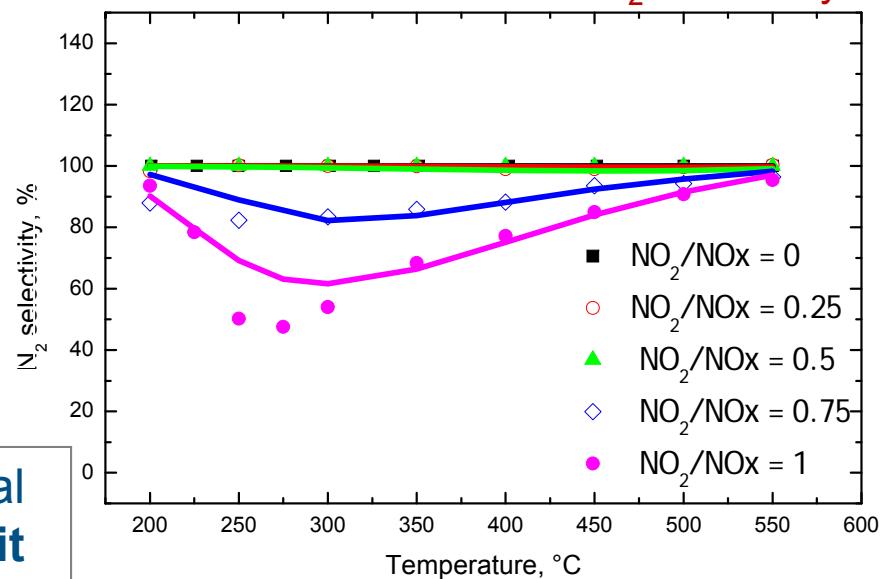


**Good reproduction
 of hysteresis effects**

NO-NO₂/NH₃-O₂ reacting system: steady state data



N₂ selectivity

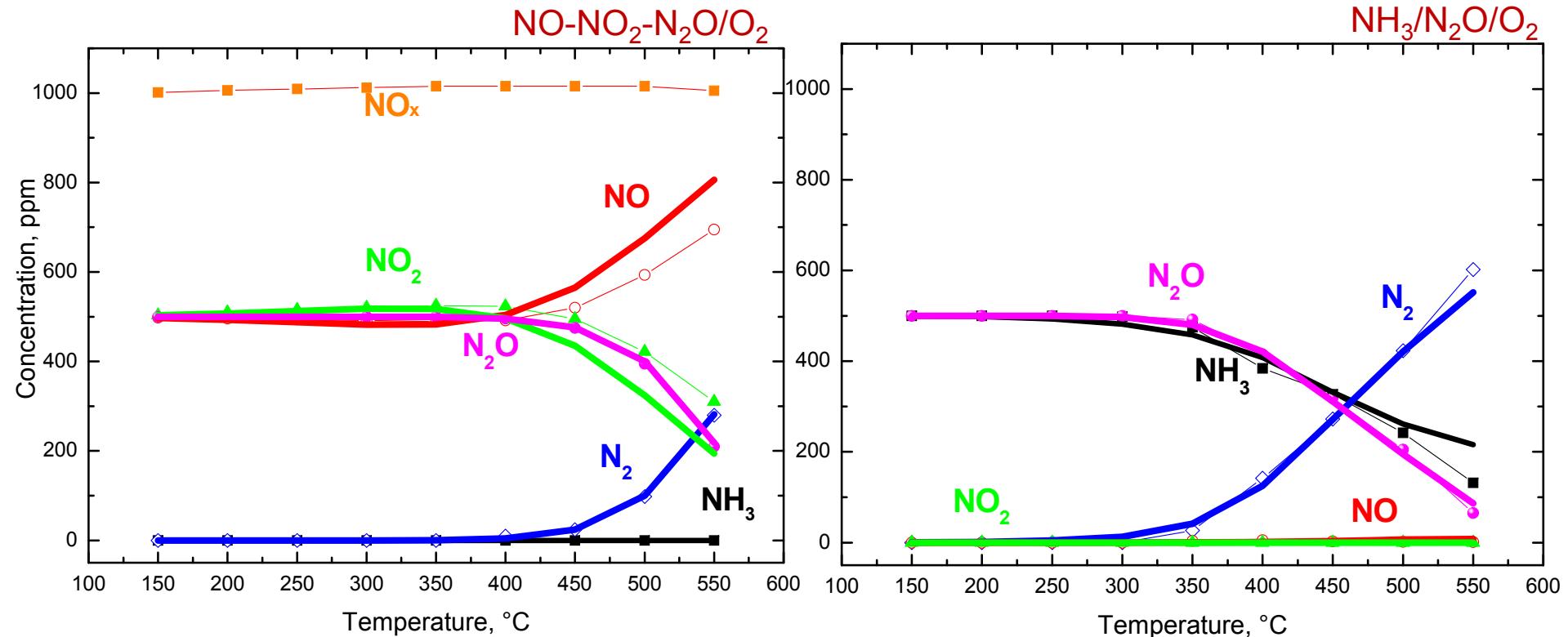


**Good reproduction of data
for $200 < T < 550^\circ\text{C}$ and
 $0 < \text{NO}_2/\text{NOx} < 1$**

Experimental conditions:
 $\text{NH}_3 = \text{NO}_x = 500 \text{ ppm}$
 $\text{O}_2 = 8\%; \text{H}_2\text{O} = 8\%$

Symbols = experimental
Thick lines = kinetic fit

NO-NO₂-N₂O/NH₃-O₂ reacting system: steady state data



N₂O decomposition to N₂ in the presence of NO_x and reaction with ammonia above 300°C captured by the model.

Experimental conditions:
NH₃=N₂O=NO=NO₂=500 ppm
O₂=8%; H₂O=8%

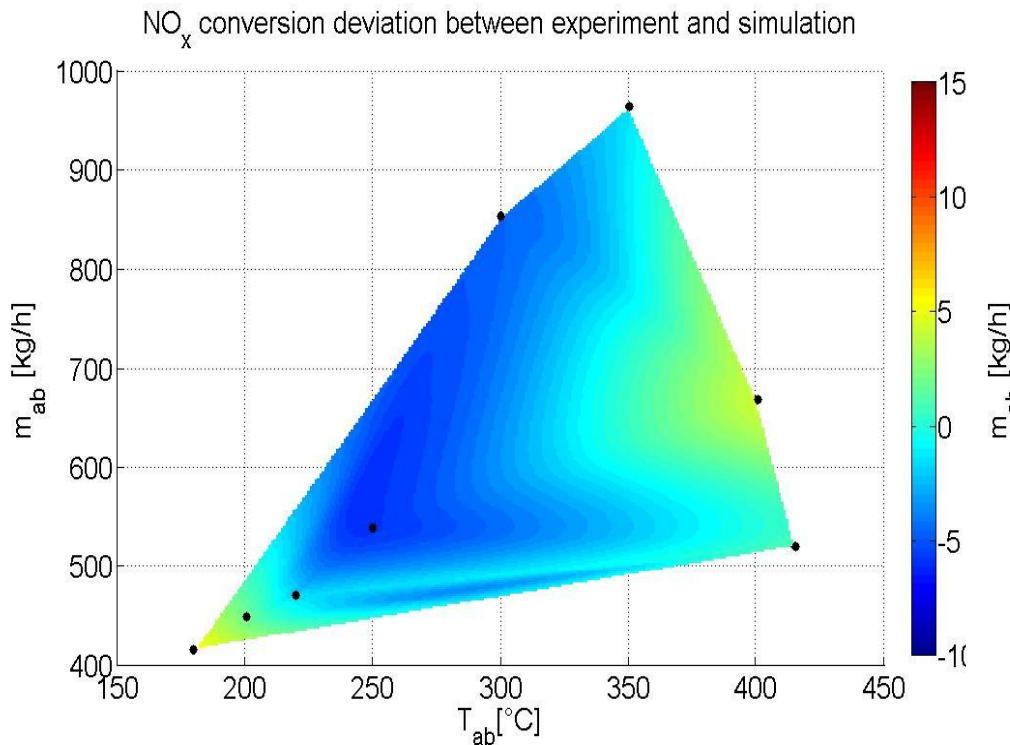
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Kaucký et al., J. Catal. 238 (2006) 293.
Pérez-Ramírez et al., J. Catal. 208 (2002) 211
Devadas et al., App. Catal. B-Environ. 67 (2006) 187
Coq et al., J. Catal. 195 (2000) 298

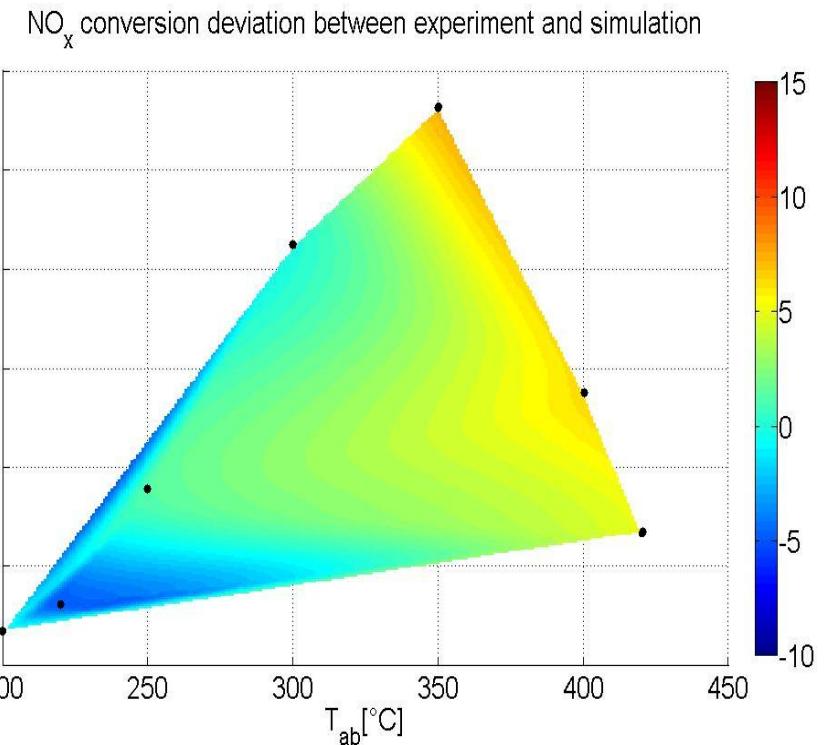
SCR catalyst: model validation over test bench full scale monoliths

Validation maps

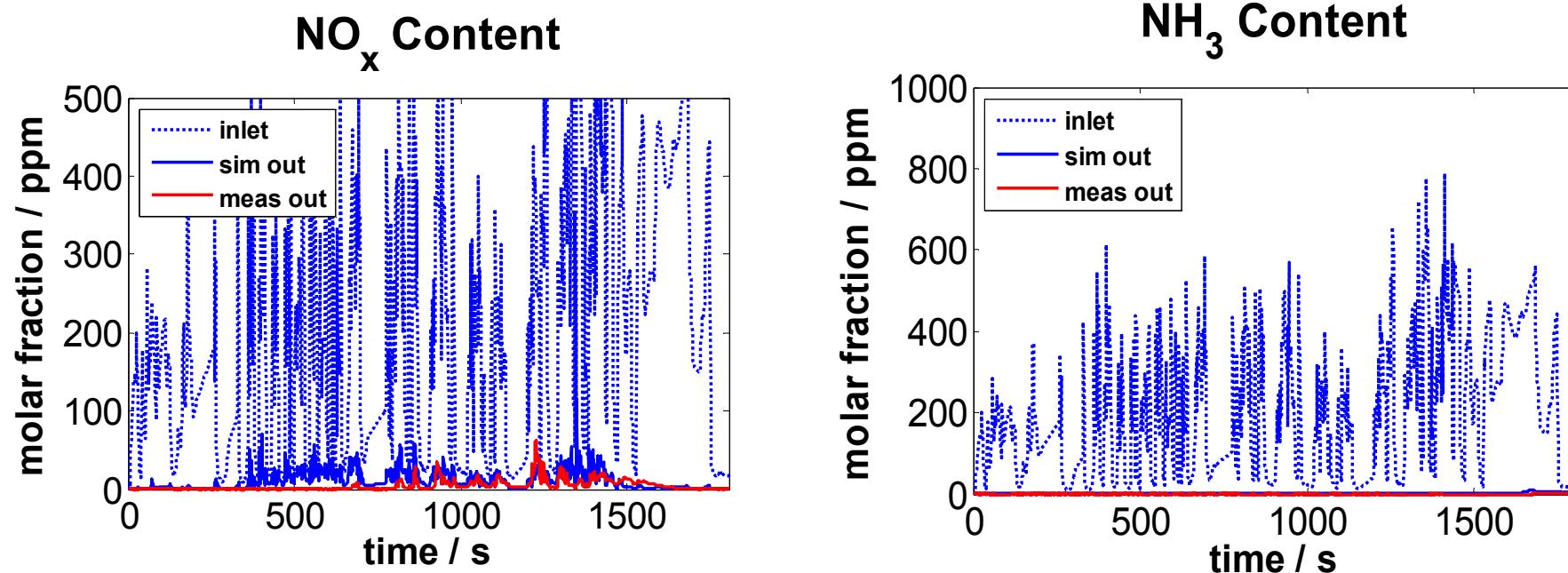
12" monolith sample



15" monolith sample



**Deviation in NOx conversions simulations vs. experimental
are within $\pm 5\%$ error in the whole T & mass flow rate fields.**

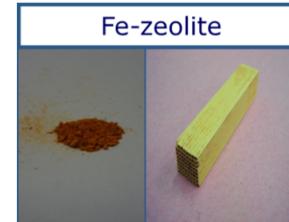


**Model prediction under realistic transient conditions in
good agreement with the experimental behavior.**

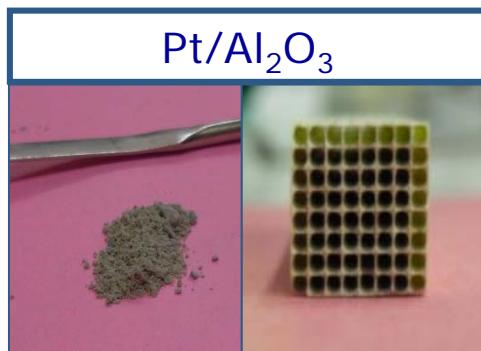
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2. Kinetic study and model validation of the PGM component



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Kinetic modeling of PGM component

Kinetic investigation analyzing the effect of operative conditions
(temperature, species concentrations, GHSV, steady-state vs. transients) on:



NH₃

NH₃/O₂

NO/O₂ – NO₂/O₂

NH₃/NO/O₂

NH₃/NO₂/O₂

NH₃/NO-NO₂/O₂

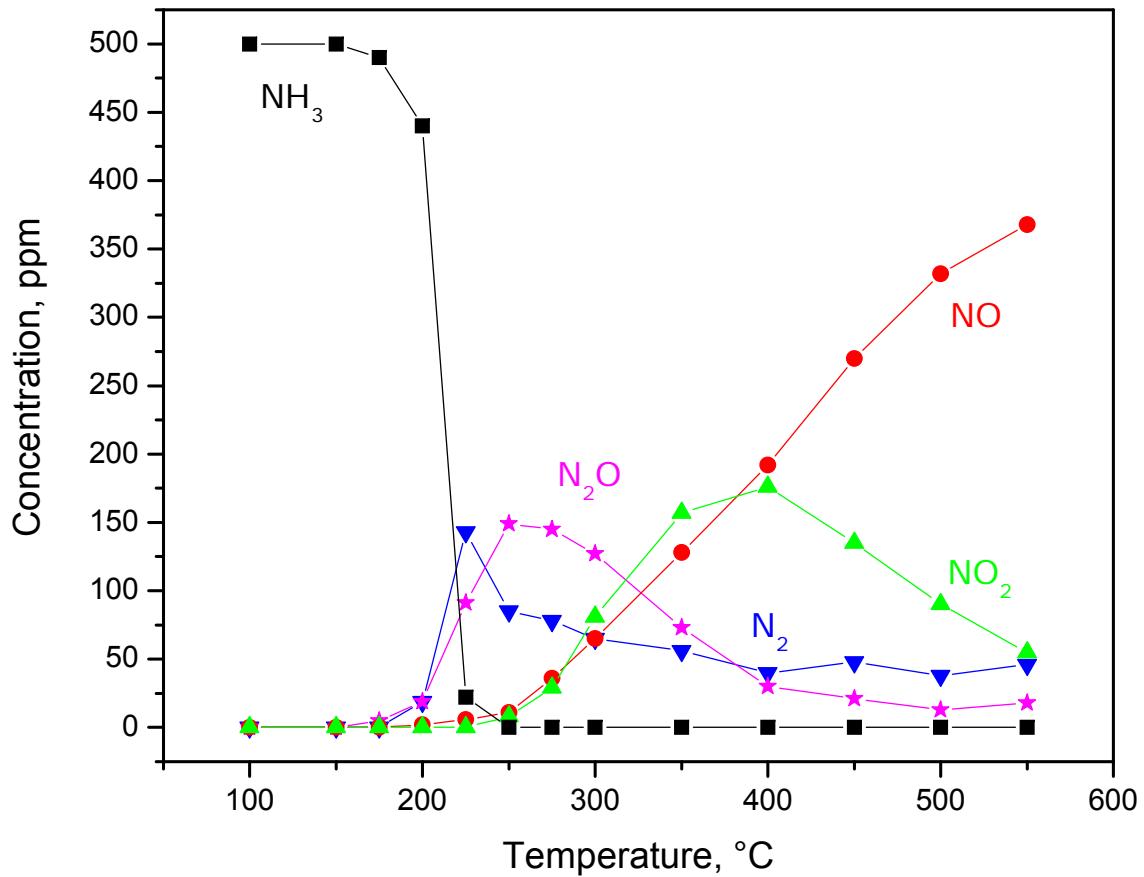
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2. NH₃ oxidation to N₂ (INHIBITED BY NO₂)
 $2NH_3^* + 3/2 O_2 \rightarrow N_2 + 3H_2O$
3. NH₃ oxidation to NO (INHIBITED BY NO₂)
 $2NH_3^* + 5/2 O_2 \rightarrow 2NO + 3H_2O$
4. NO oxidation to NO₂ (INHIBITED BY NO₂)
 $NO + 1/2 O_2 \rightarrow NO_2$
5. Unselective Standard SCR (INHIBITED BY NO₂)
 $NH_3^* + NO + 3/4 O_2 \rightarrow N_2O + 3/2 H_2O$
6. N₂O Formation
 $2NH_3^* + 2NO_2 \rightarrow N_2 + N_2O + 3H_2O$
7. NO₂-SCR
 $8NH_3^* + 6NO_2 \rightarrow 7N_2 + 12H_2O$

Global kinetic model of NH₃ slip
PGM catalysts accounting also
for NO₂ reactivity and inhibition
effects

Colombo et al., manuscript in preparation

PGM catalyst: kinetics derivation over powders

NH₃/O₂ reacting system



Experimental conditions:

NH₃= 500 ppm

O₂= 8%; H₂O= 8%

Steep reaction light-off between 200-225°C

Modest production of nitrogen, with significant formation of N₂O between 200-300°C, and NO_x at T>300°C

NH₃ oxidation



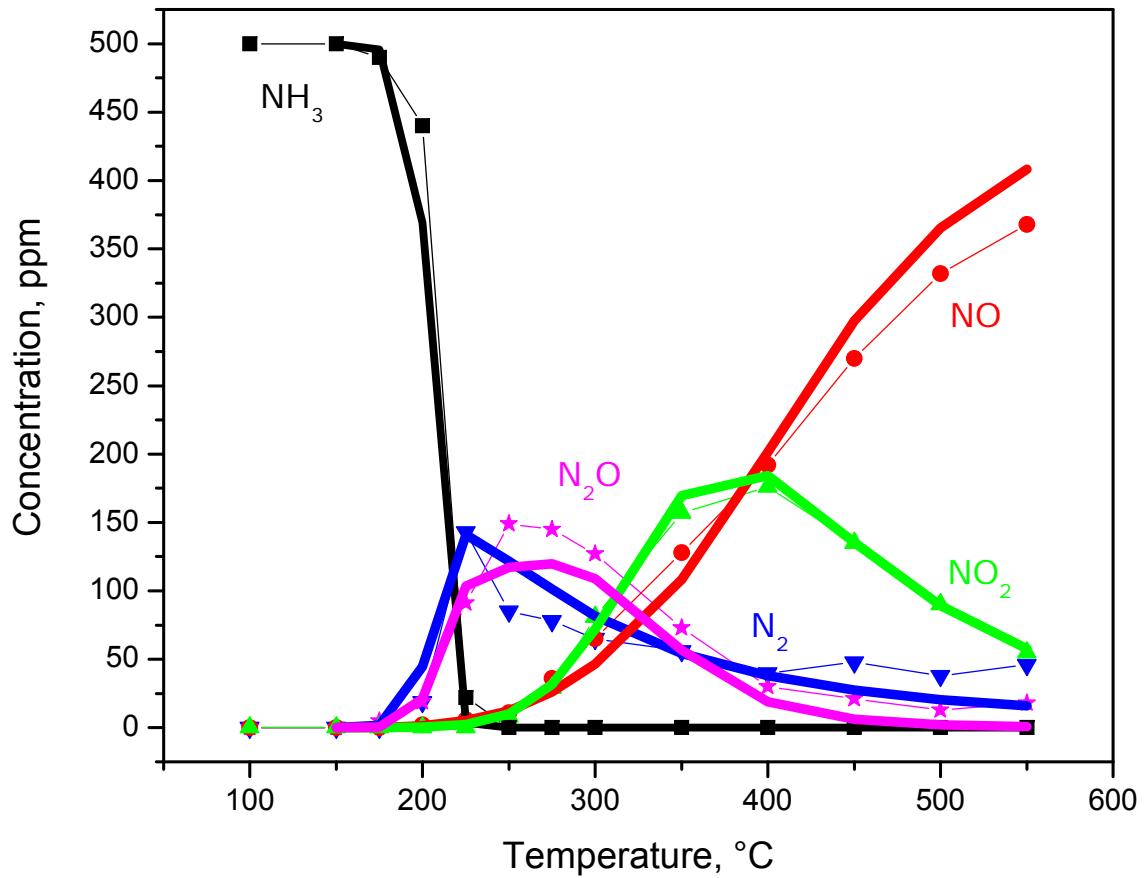
NO oxidation



NH₃/NO/O₂ reactivity



NH₃/O₂ reacting system



Experimental conditions:
NH₃= 500 ppm
O₂= 8%; H₂O= 8%

Symbols = experimental
Thick lines = kinetic fit

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NH₃ oxidation



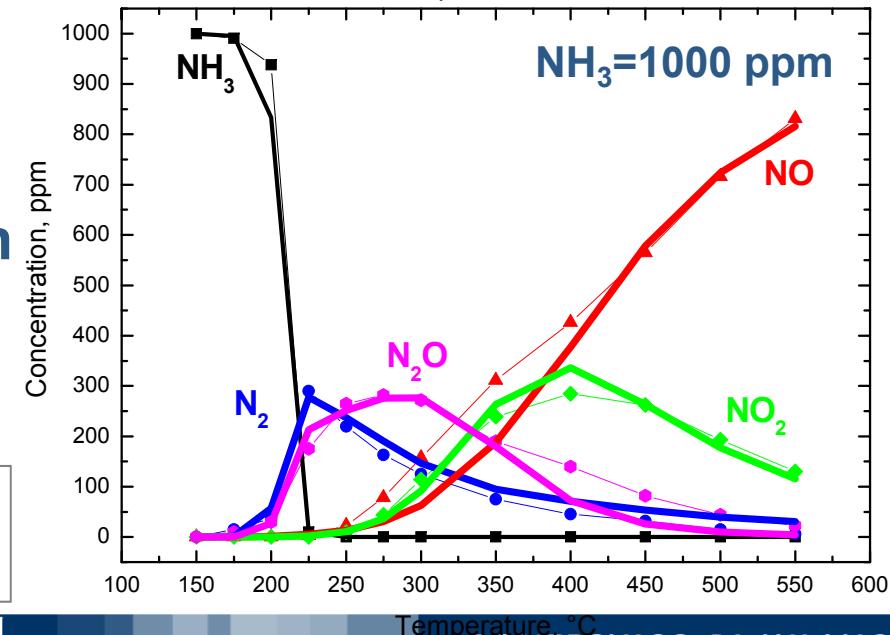
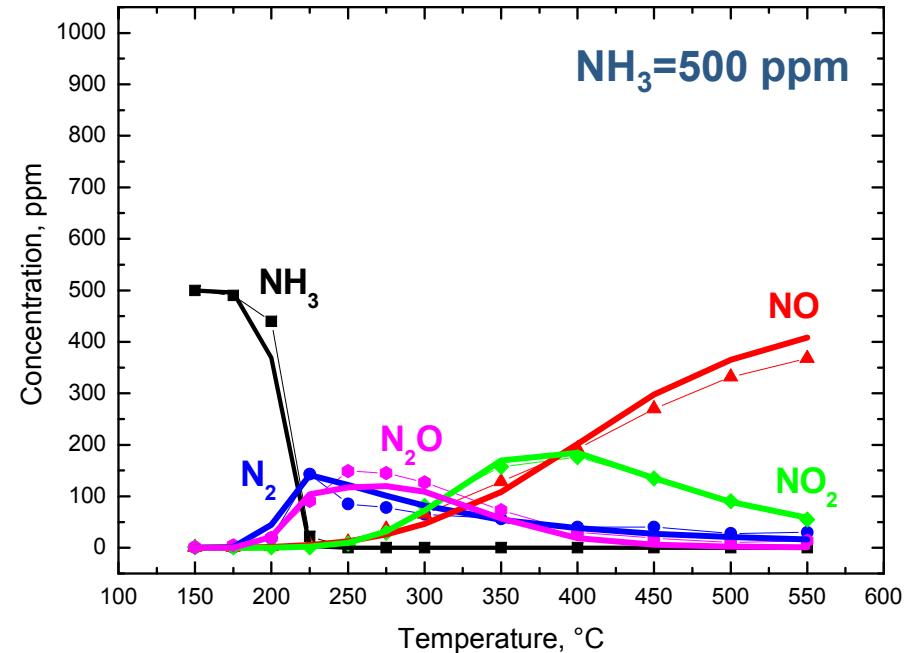
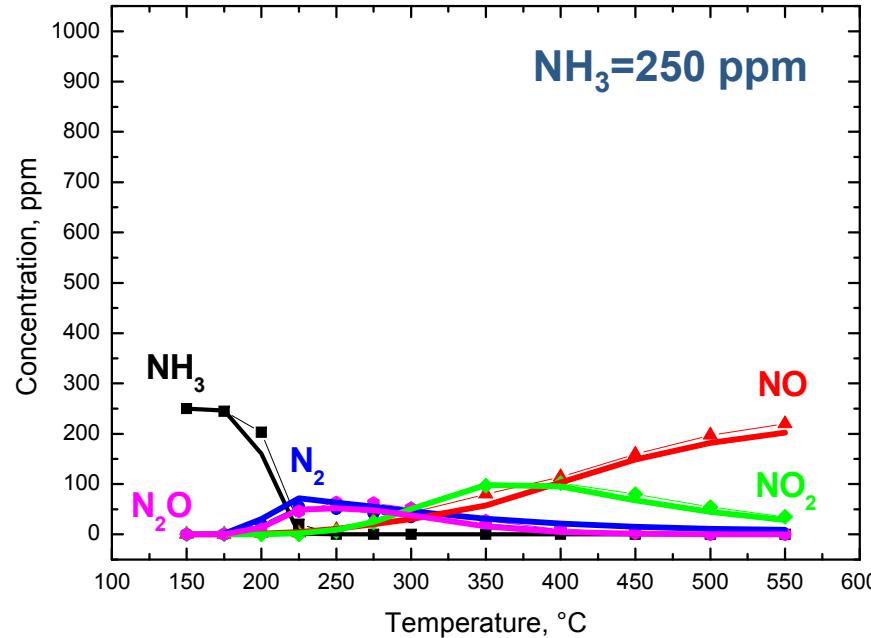
NO oxidation



NH₃/NO/O₂ reactivity



NH₃/O₂ reacting system: effect of NH₃ concentration

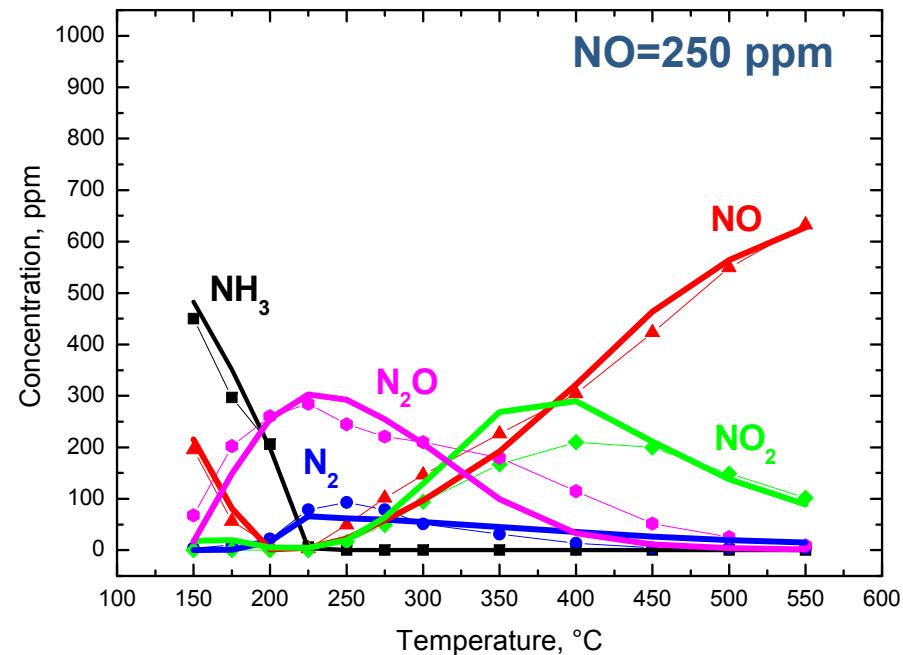
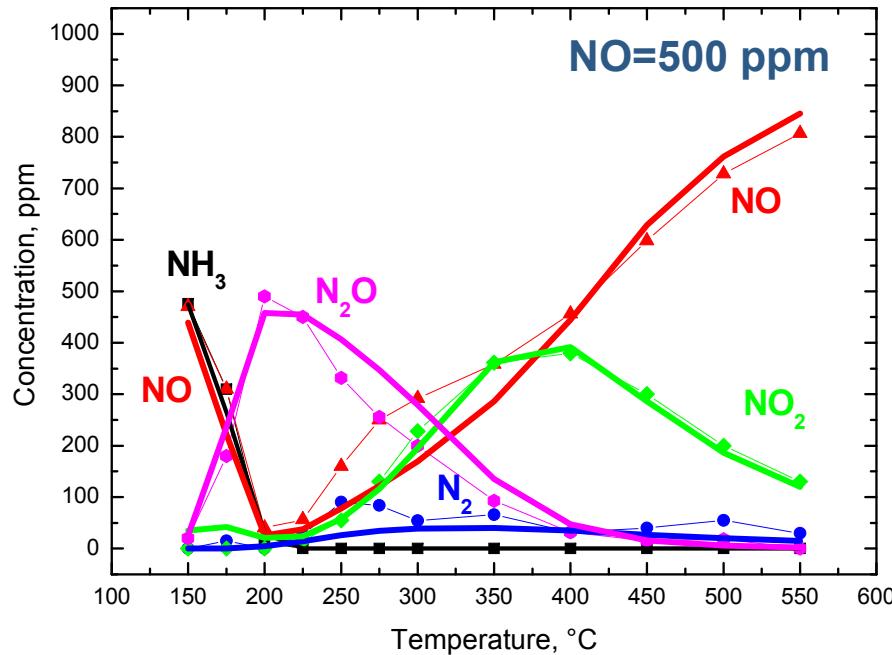


- Similar activity
- Slightly higher N₂O production with growing NH₃ concentration
- Good reproduction of NH₃/O₂ reacting system

Experimental conditions:
NH₃ = 250-500-1000 ppm
O₂ = 8%; H₂O = 8%

Symbols = experimental
Thick lines = kinetic fit

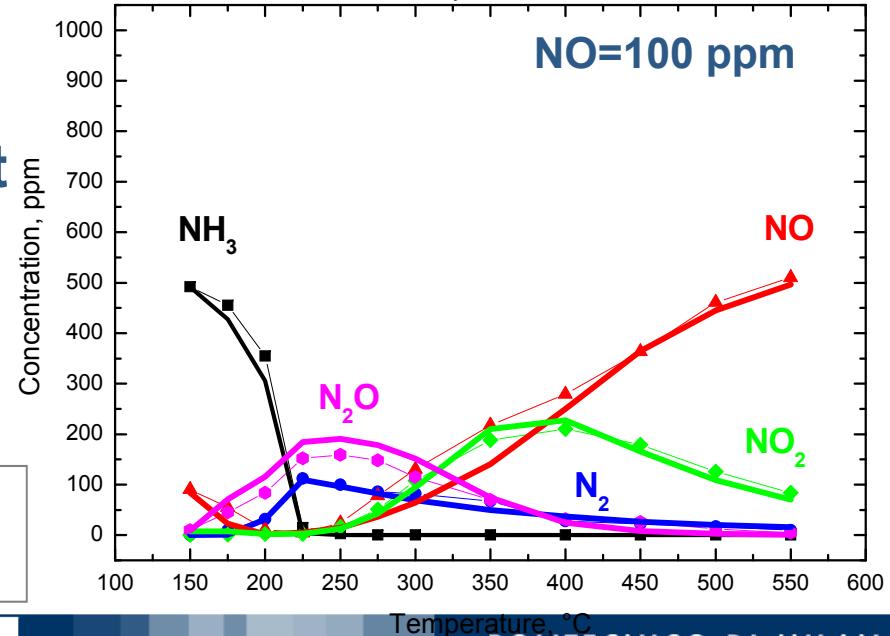
$\text{NH}_3/\text{NO}/\text{O}_2$ reacting system: effect of NO concentration



- Higher production of N₂O on increasing the NO feed content
- Good reproduction of NH₃/NO/O₂ reacting system

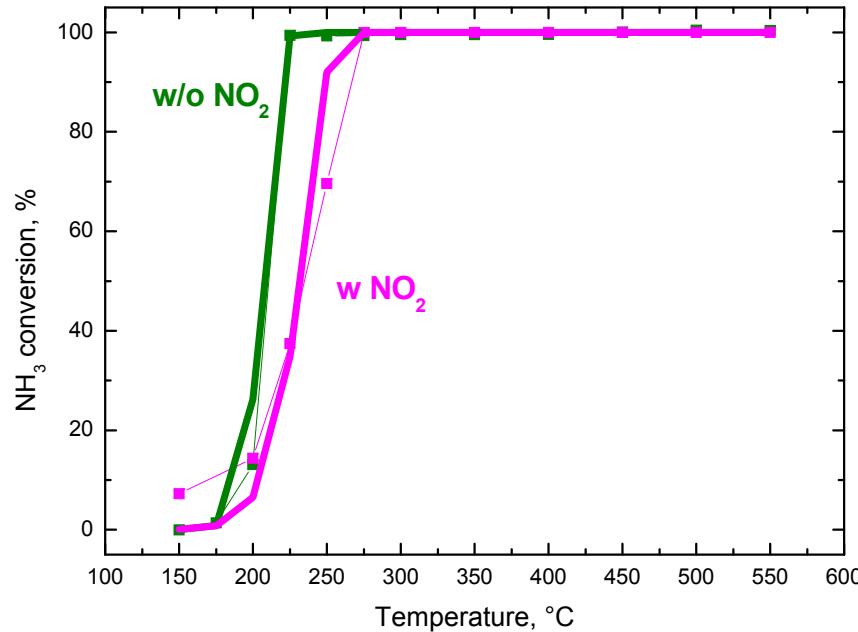
Experimental conditions:
NH₃ = 500 ppm
NO = 100-250-500 ppm
O₂ = 8%; H₂O = 8%

Symbols = experimental
Thick lines = kinetic fit

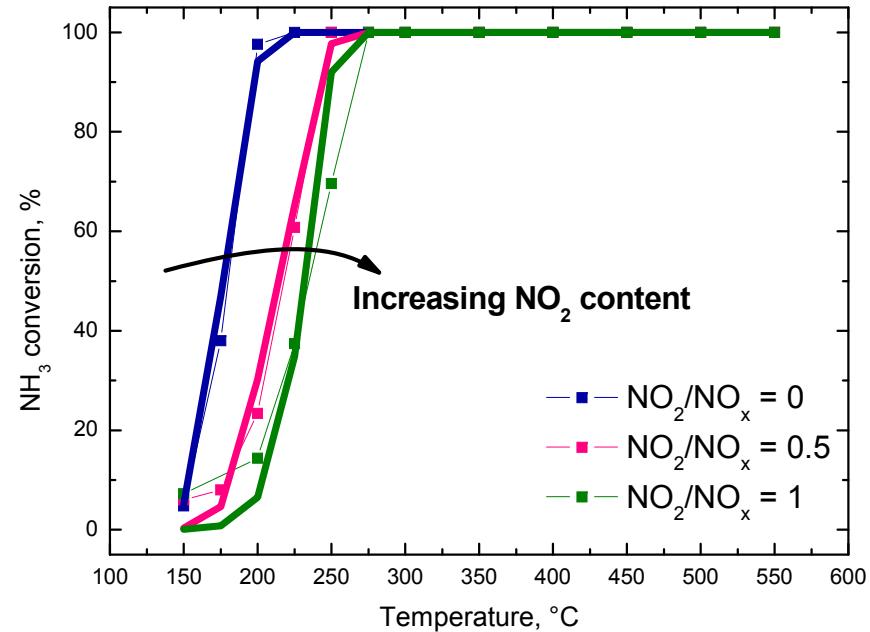


$\text{NH}_3/\text{NO}_2/\text{O}_2$ reacting system: NO_2 inhibition on NH_3 oxidation

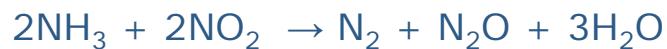
$\text{NH}_3 + \text{NO}_2$



$\text{NH}_3 + \text{NOx}$



NH_3/NO_2 reactivity



Experimental conditions:

NH₃=500 ppm

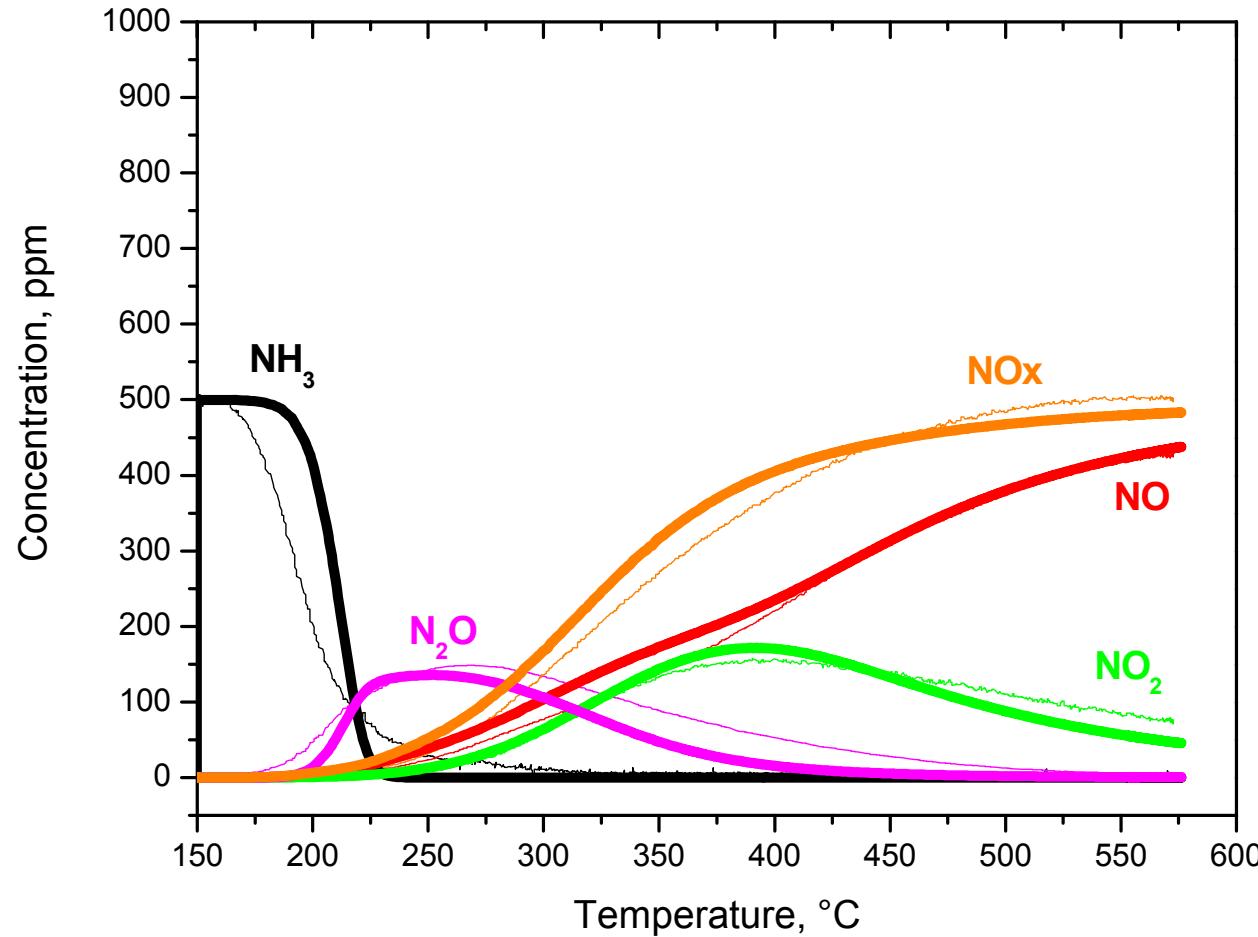
NO_x= 500 ppm

O₂= 8%; H₂O= 8%

Symbols = experimental
Thick lines = kinetic fit

PGM catalyst: model validation over lab-scale monoliths

NH₃ / O₂ reacting system



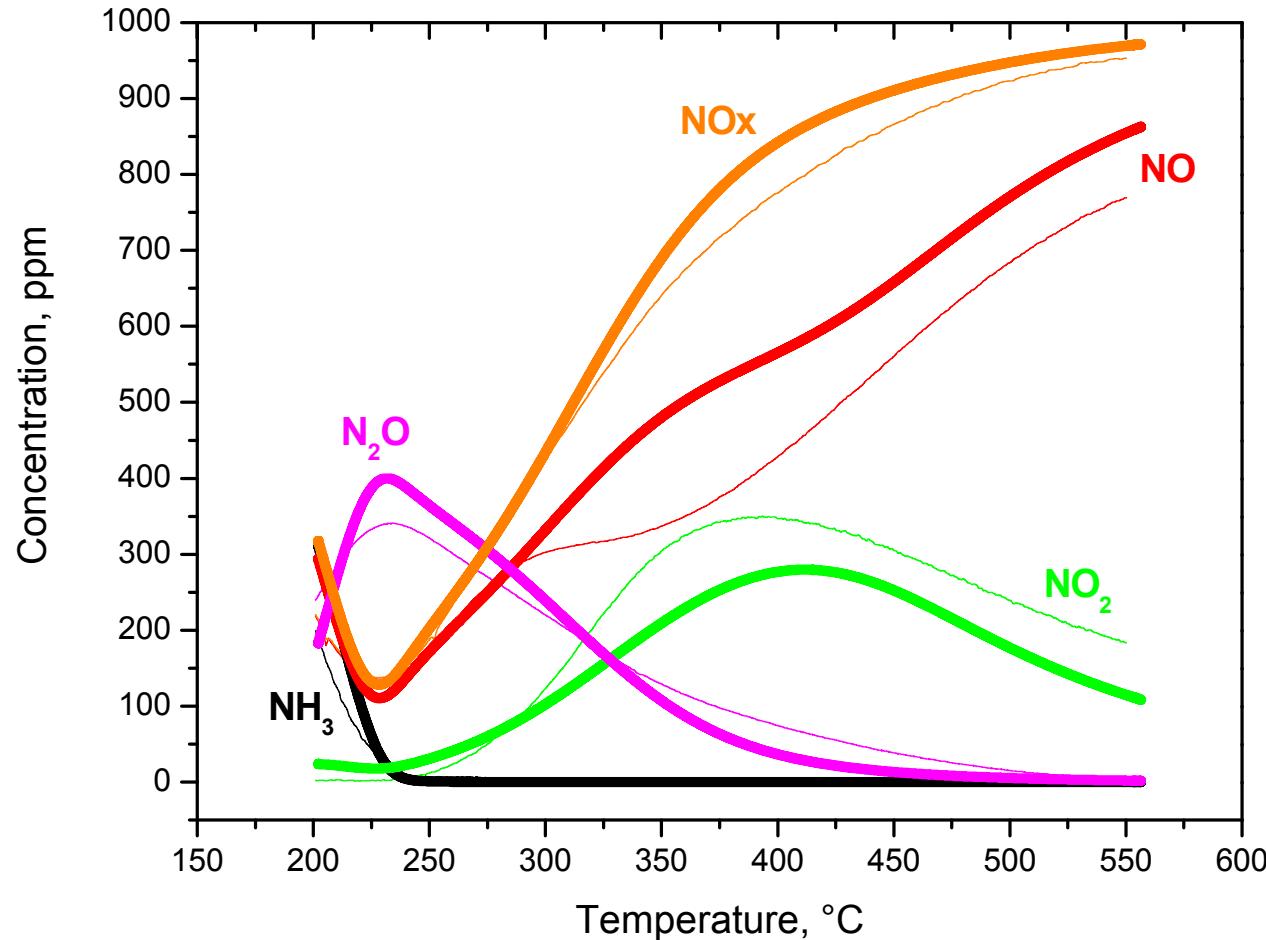
Model predictions in good agreement with the experimental behavior.

Experimental conditions:

NH₃=500 ppm
O₂= 8%; H₂O= 8%; CO₂=8%
T ramp=2°C/min

Thin lines= experimental
Thick lines = simulations

NH₃ /NO/O₂ reacting system



Model predictions in good agreement with the experimental behavior.

Experimental conditions:

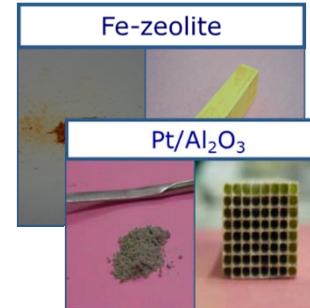
NH₃=NO=500 ppm
O₂= 8%; H₂O= 8%; CO₂=8%
T ramp=2°C/min

Thin lines= experimental
Thick lines = simulations

Goal/Outline

Development of a chemico-physically consistent mathematical model of a dual-layer ASC monolith

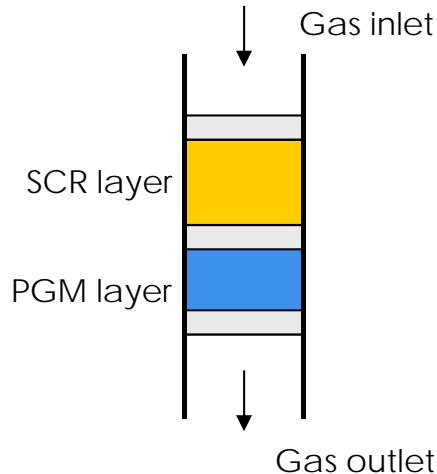
1. Kinetic study and model validation of the SCR component



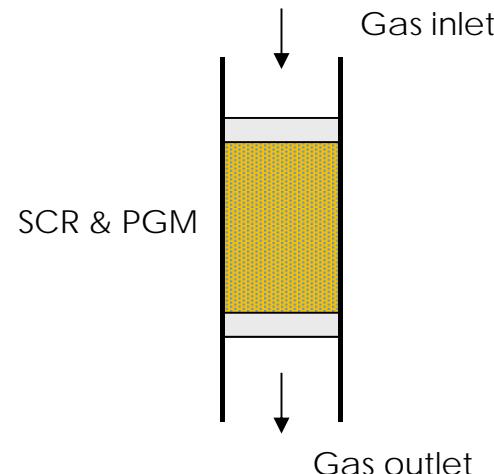
2. Kinetic study and model validation of the PGM component

3. Kinetic study of the combined SCR + PGM components

DB: Double bed



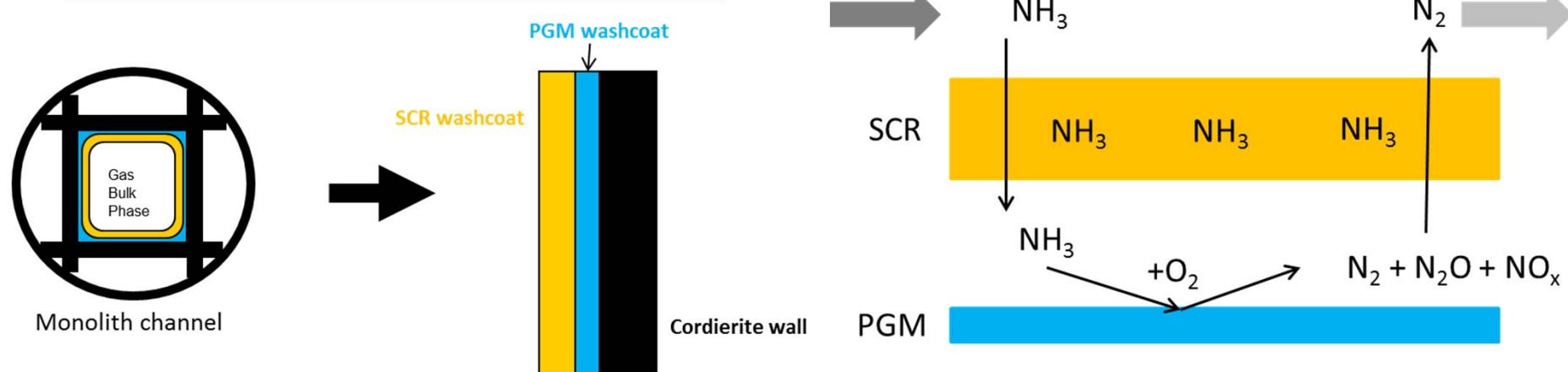
MM: Mechanical mixture



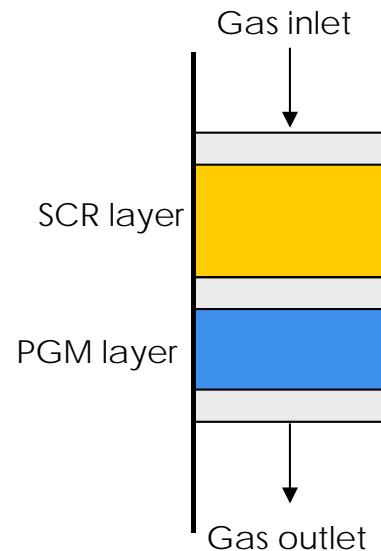
- Experimental study of two different SCR+PGM configurations
- Identification of potential interactions between the cat. systems
- Predictive simulation of the experimental runs

Reactor configurations of the combined SCR+ PGM components

ASC ZONE → dual layer: SCR + PGM

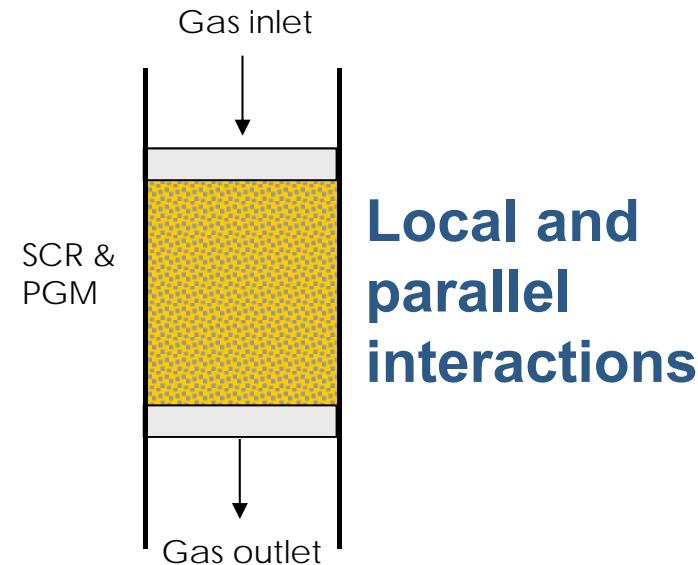


DB: Double bed



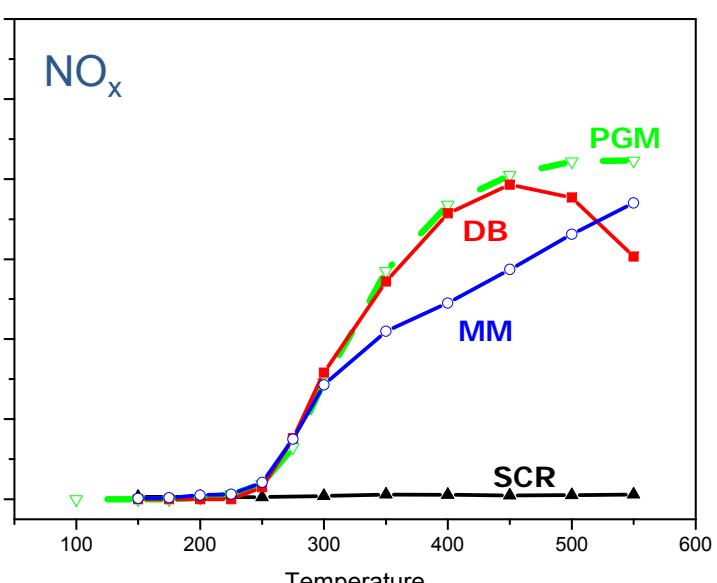
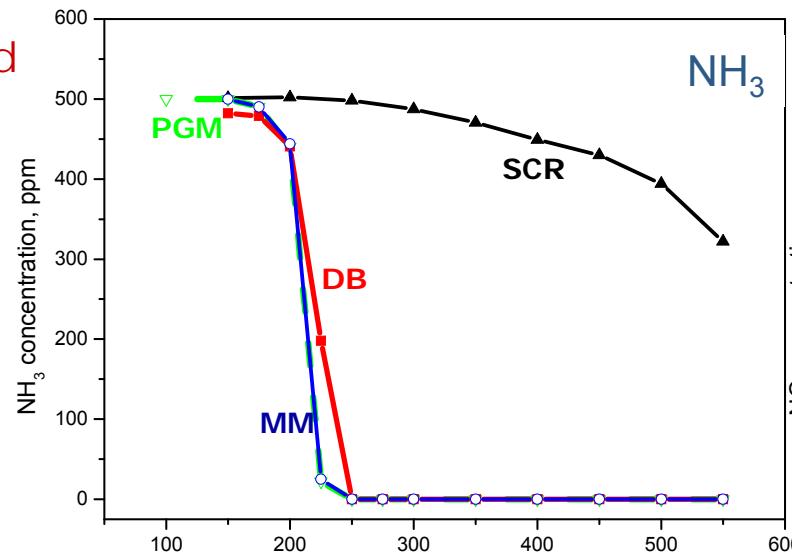
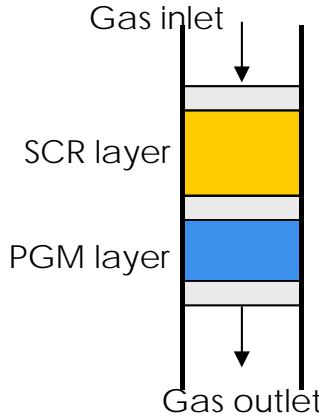
Sequential interactions

MM: Mechanical mixture



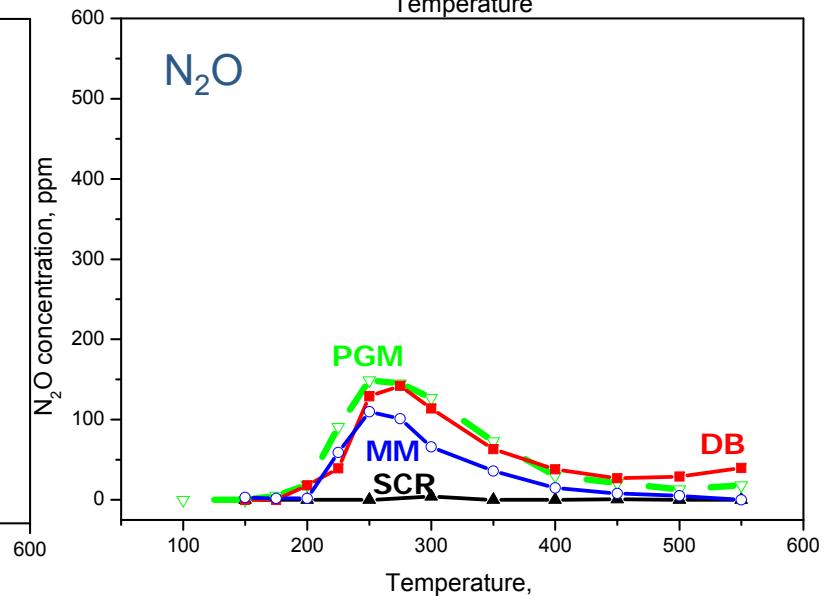
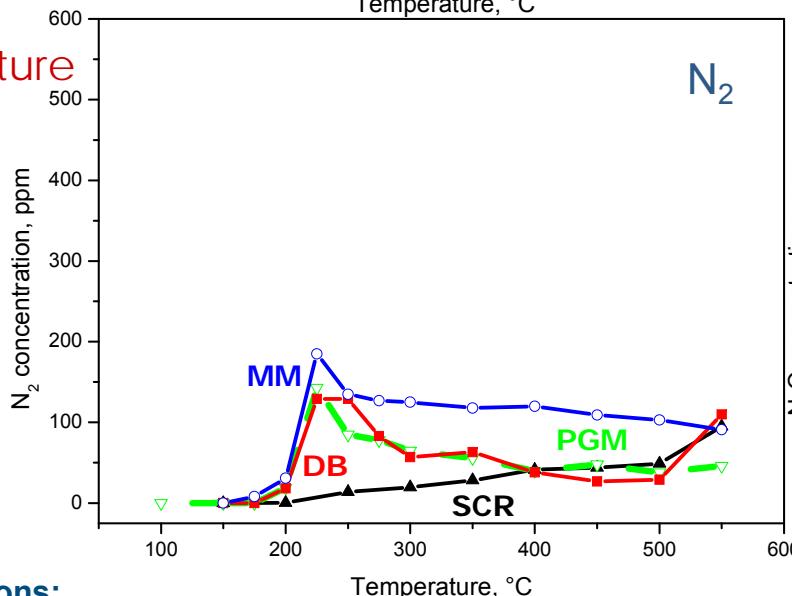
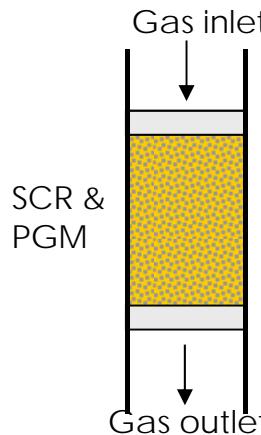
NH₃ / O₂ reacting system

DB: Double bed



MM:

Mechanical mixture



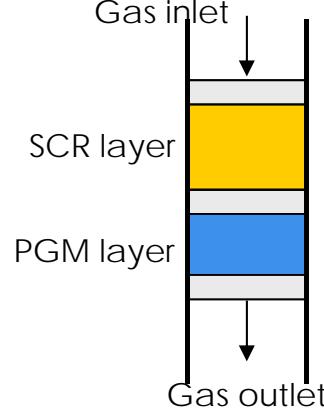
Experimental conditions:

NH₃= 500 ppm

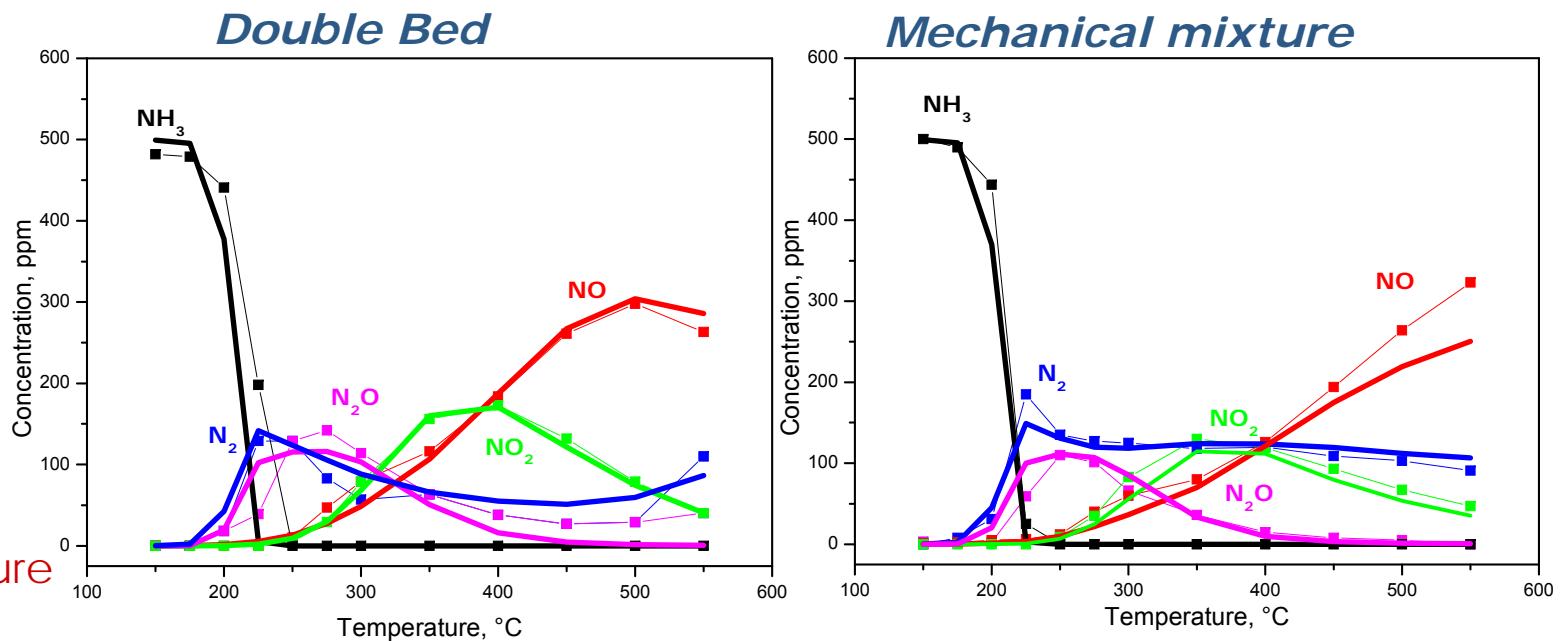
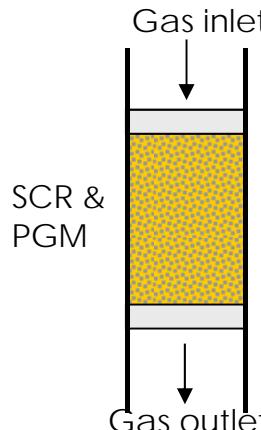
O₂= 8%; H₂O= 8%

NH₃ / O₂ reacting system

DB: Double bed



MM:
Mechanical mixture



Better N₂ selectivity observed over the MM configuration, nicely predicted by the model by superimposing the PGM and the SCR kinetics.

Experimental conditions:

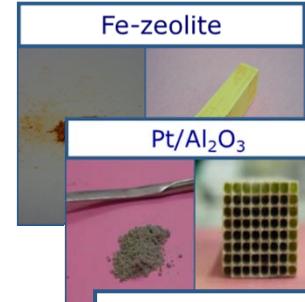
NH₃= 500 ppm
O₂= 8%; H₂O= 8%

Symbols = experimental
Thick lines = simulations

Goal/Outline

Development of a chemico-physically consistent mathematical model of a dual-layer ASC monolith

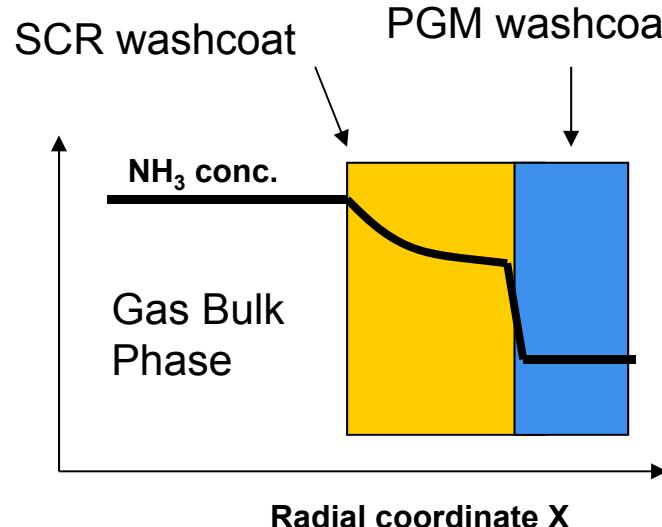
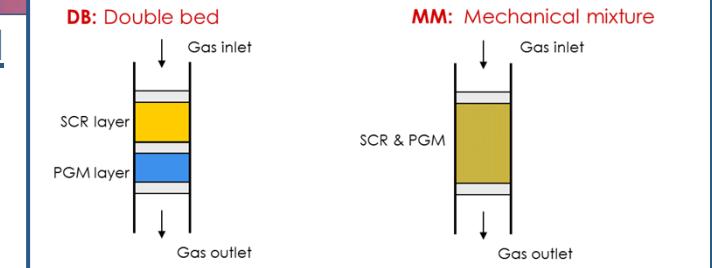
1. Kinetic study and model validation of the SCR component



2. Kinetic study and model validation of the PGM component

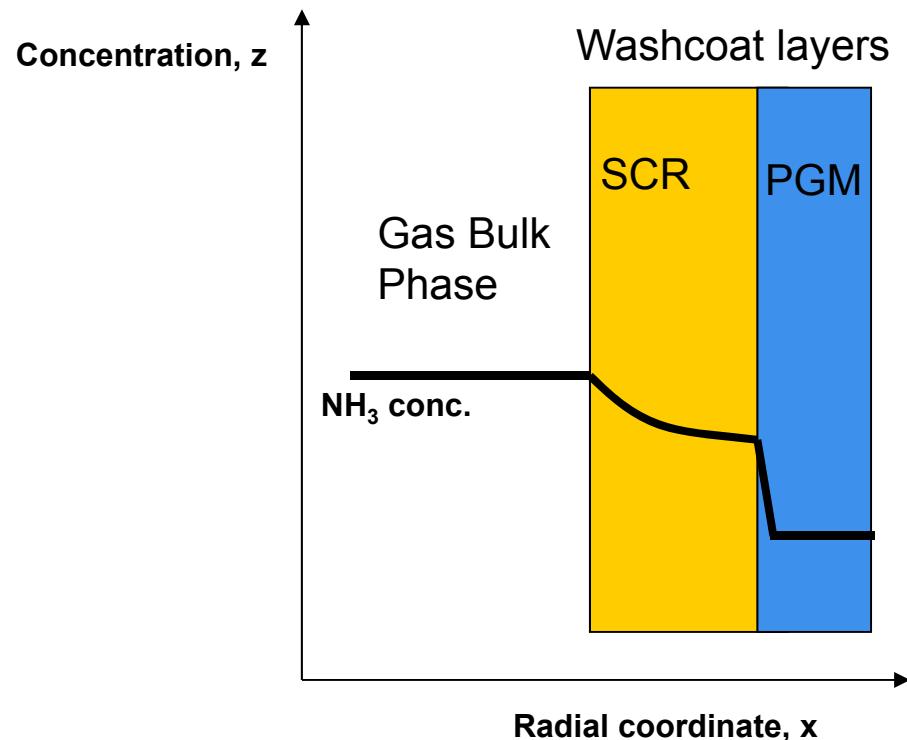
3. Kinetic study of the combined SCR + PGM components

4. Development of the dual-layer monolith model



Modeling of dual-layer NH₃ slip monolith catalyst

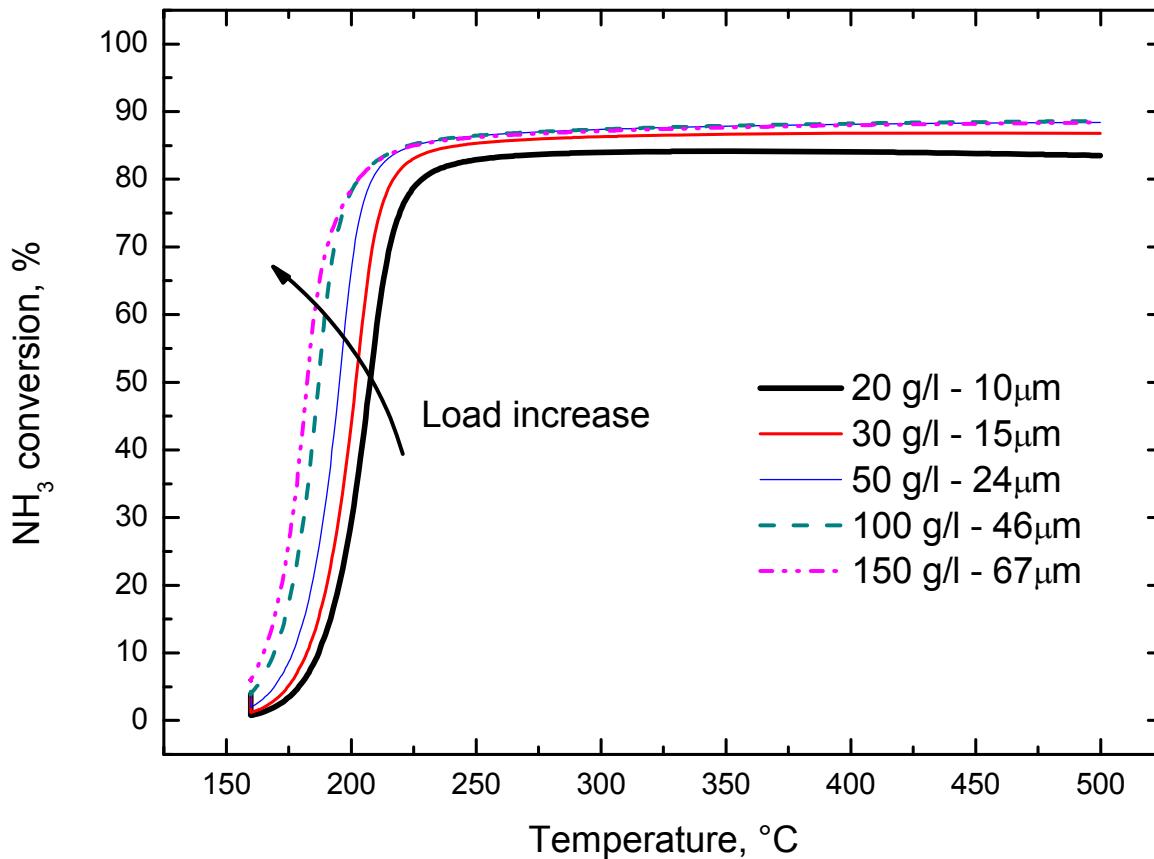
EXPECTED CONCENTRATION PROFILES



Is it necessary to model
reaction/diffusion in both
catalytic layers?

Modelling of PGM layer

PGM layer: effect of washcoat load



Chemical regime
only below 225-
250 $^{\circ}\text{C}$

Simulated conditions:

NH_3 = 300 ppm

O_2 = 5%

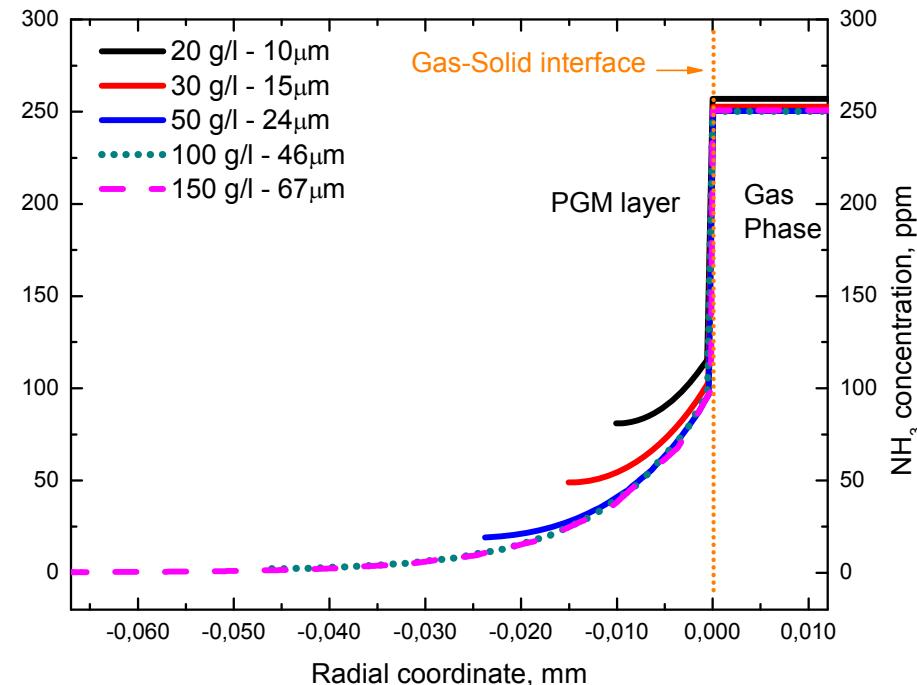
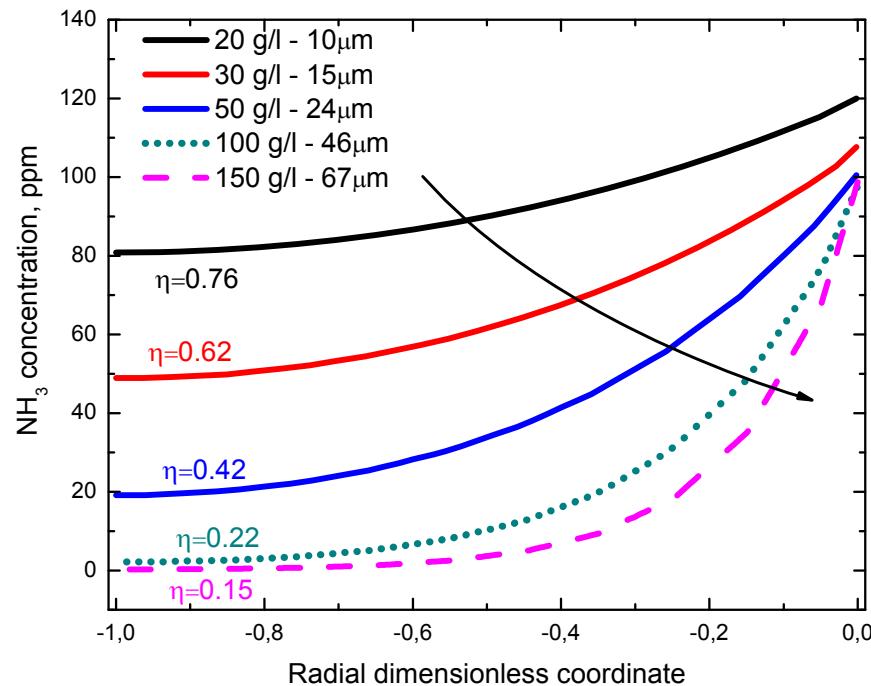
GHSV = 300'000 h^{-1}

Colombo et al., Chem. Eng. Sci. 75 (2012) 75

PGM layer: effect of washcoat load

T=300°C,

z = 5 mm from monolith entrance



Only the first 15-20 μm of PGM catalyst are effectively working

Simulated conditions:

NH_3 = 300 ppm

O_2 = 5%

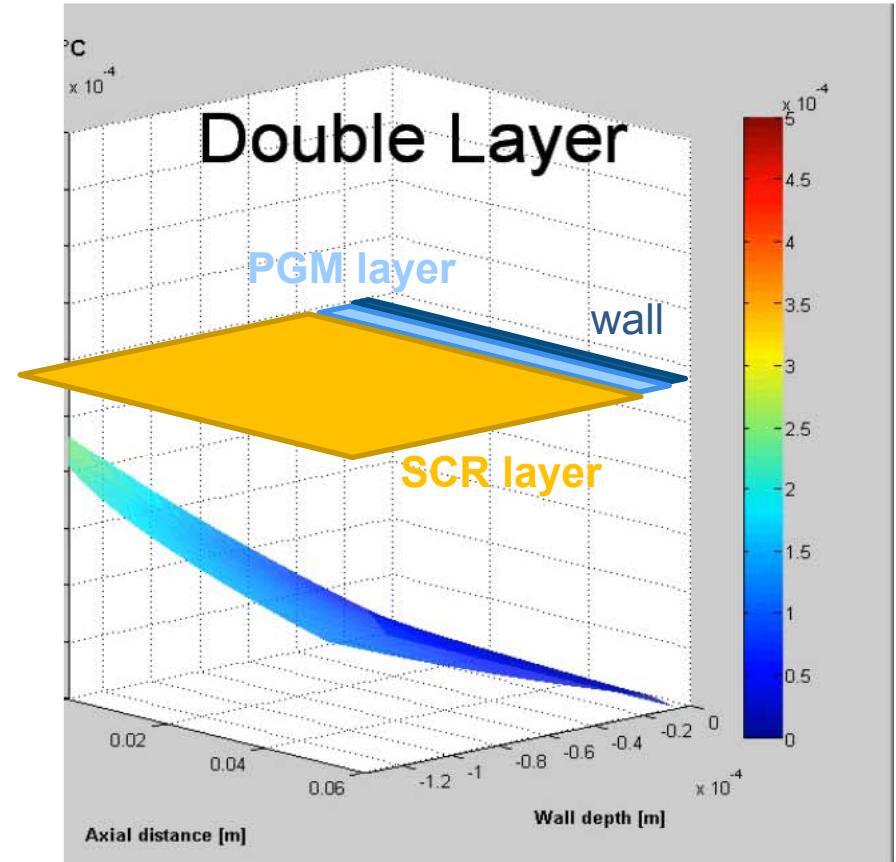
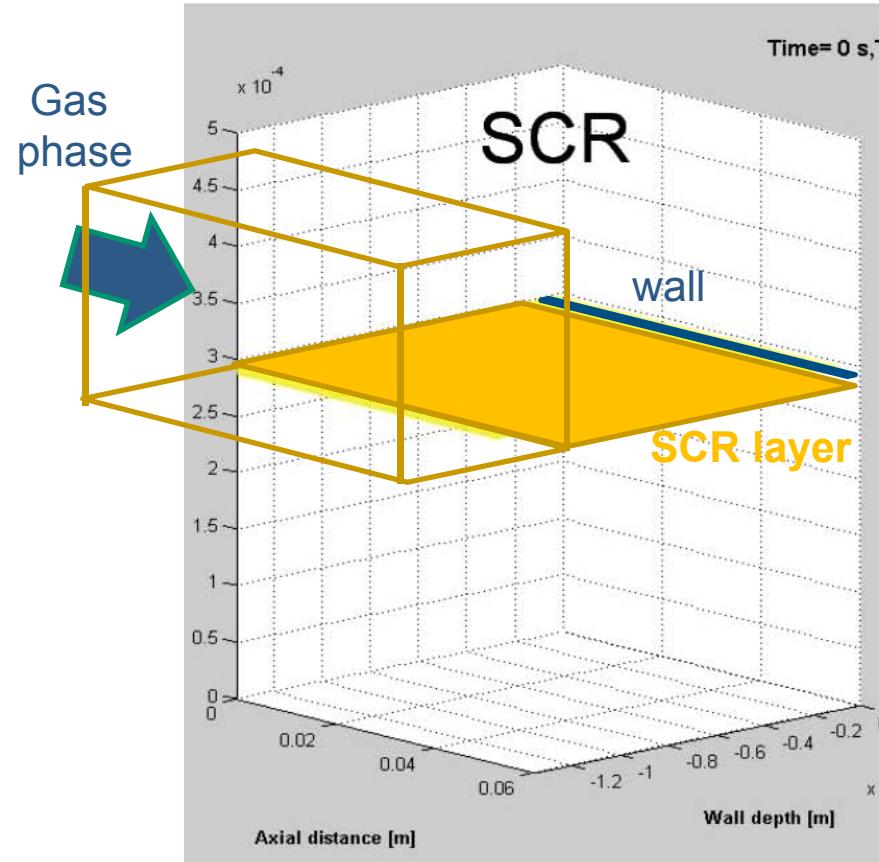
GHSV = 300'000 h⁻¹

Colombo et al., Chem. Eng. Sci. 75 (2012) 75

Modelling of SCR layer

SCR layer: effect of PGM addition

NO concentration profiles in $\text{NH}_3/\text{NO}/\text{O}_2$ reacting system



Simulated conditions:

$\text{NH}_3 = \text{NO} = 300 \text{ ppm}$

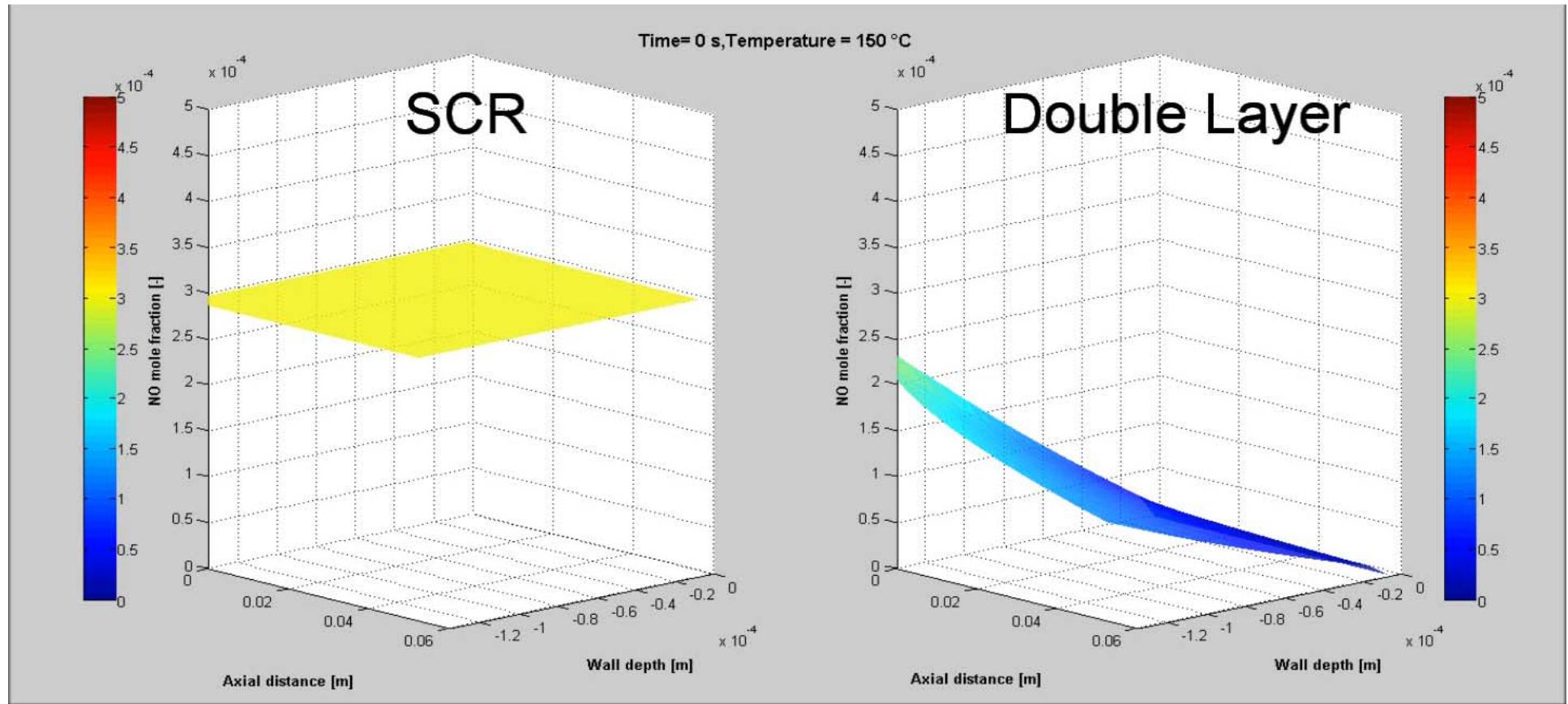
$\text{O}_2 = 5\%$

$\text{GHSV} = 300'000 \text{ h}^{-1}$

Colombo et al., Chem. Eng. Sci. 75 (2012) 75

SCR layer: effect of PGM addition

NO concentration profiles in $\text{NH}_3/\text{NO}/\text{O}_2$ reacting system



Simulated conditions:

$\text{NH}_3 = \text{NO} = 300 \text{ ppm}$

$\text{O}_2 = 5\%$

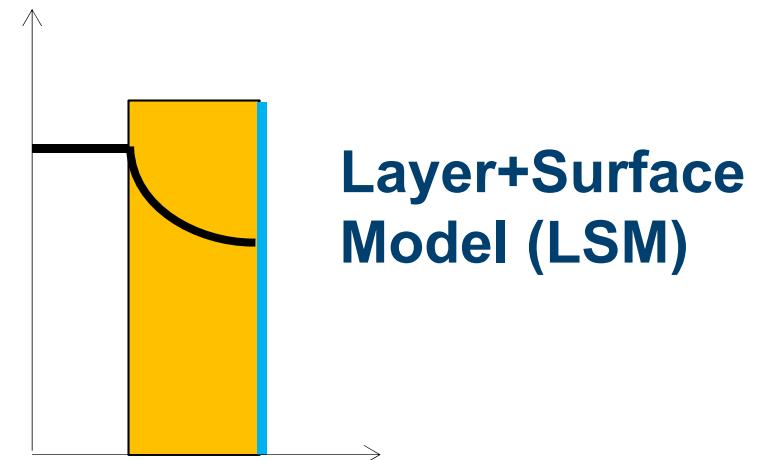
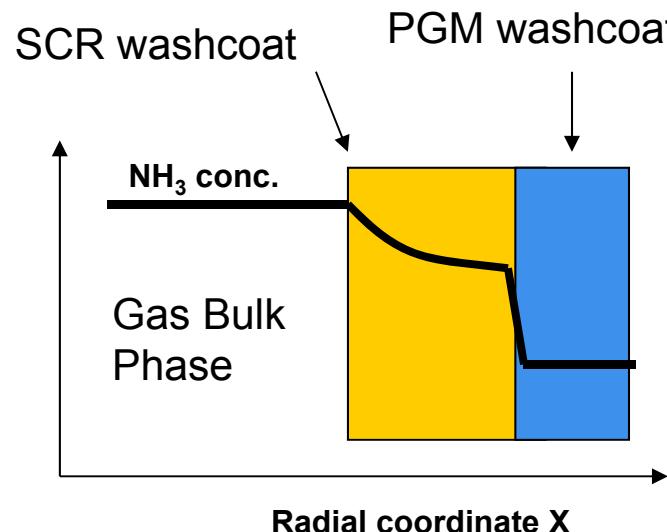
GHSV = $300'000 \text{ h}^{-1}$

Colombo et al., Chem. Eng. Sci. 75 (2012) 75

Is it necessary to model reaction/diffusion in both catalytic layers?

SCR layer → **YES!!!**

PGM layer → **NO**



Layer+Surface Model (LSM)

Reaction/diffusion within
the SCR washcoat layer

$$0 = D_{eff,i} \frac{\partial^2 C_i^*}{\partial x^{*2}} + S_W^2 R_i$$

Inner boundary condition

SCR only

Dual-layer ASC

$$\left. \frac{\partial C_i^*}{\partial x^*} \right|_{SCR \text{ Washcoat / wall}} = 0$$

No flux

$$\left. \frac{D_{eff,i}}{S_w} \cdot \frac{\partial C_i^*}{\partial x^*} \right|_{SCR \text{ Washcoat / PGM Washcoat}}$$

Flux continuity at SCR/PGM
interface

$$= R_{Surf,i}^{PGM} \left[\frac{mol}{m^2 \cdot s} \right]$$

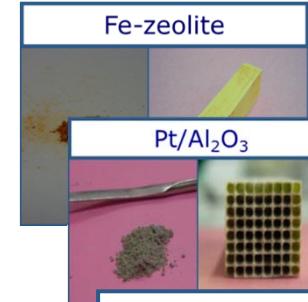
Kinetics from powdered catalyst

Colombo et al., Chem. Eng. Sci. 75 (2012) 75

Goal/Outline

Development of a chemico-physically consistent mathematical model of a dual-layer ASC monolith

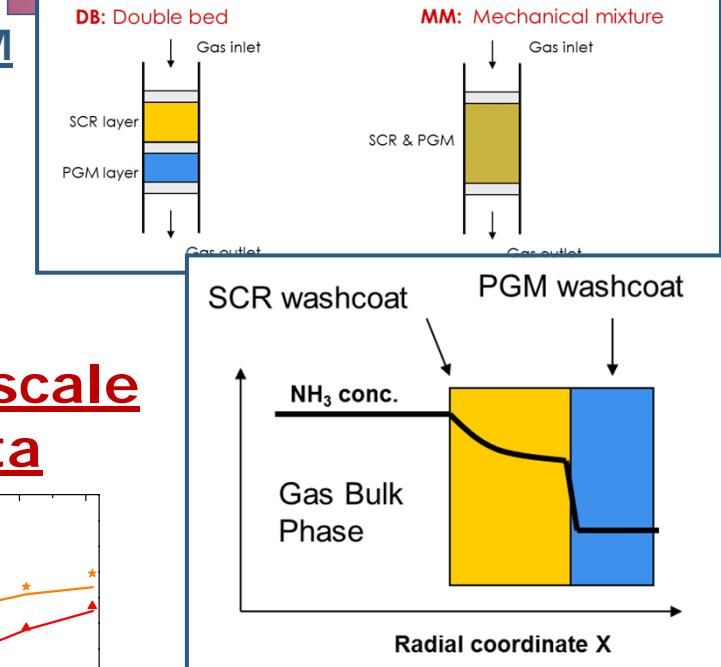
1. Kinetic study and model validation of the SCR component



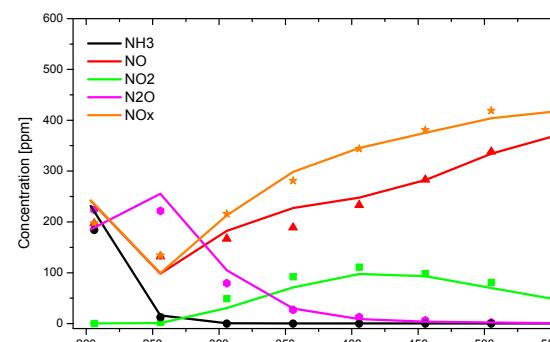
2. Kinetic study and model validation of the PGM component

3. Kinetic study of the combined SCR+ PGM components

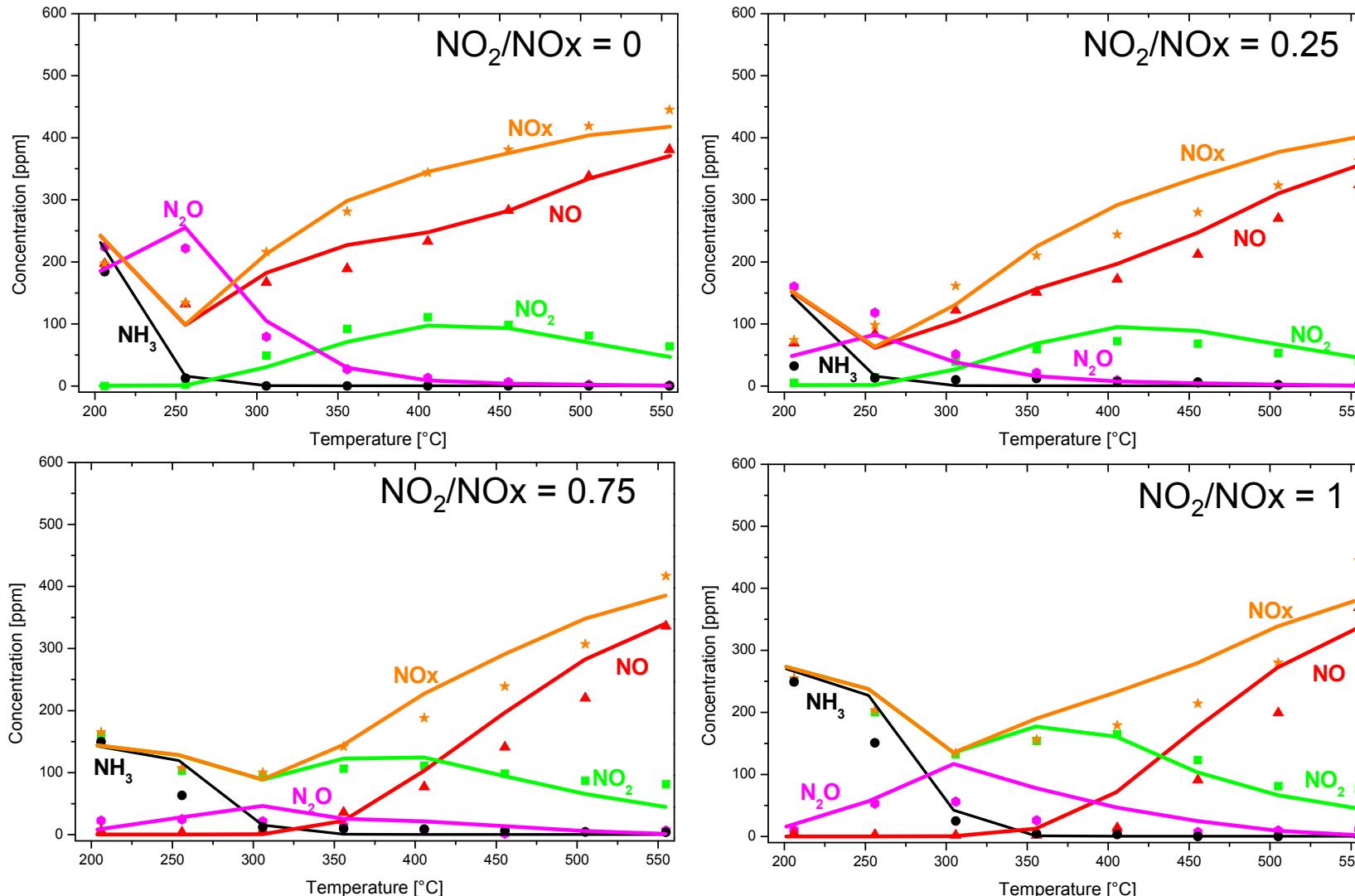
4. Development of the dual-layer monolith model



5. Validation against lab- and full scale data from dual-layer monolith data



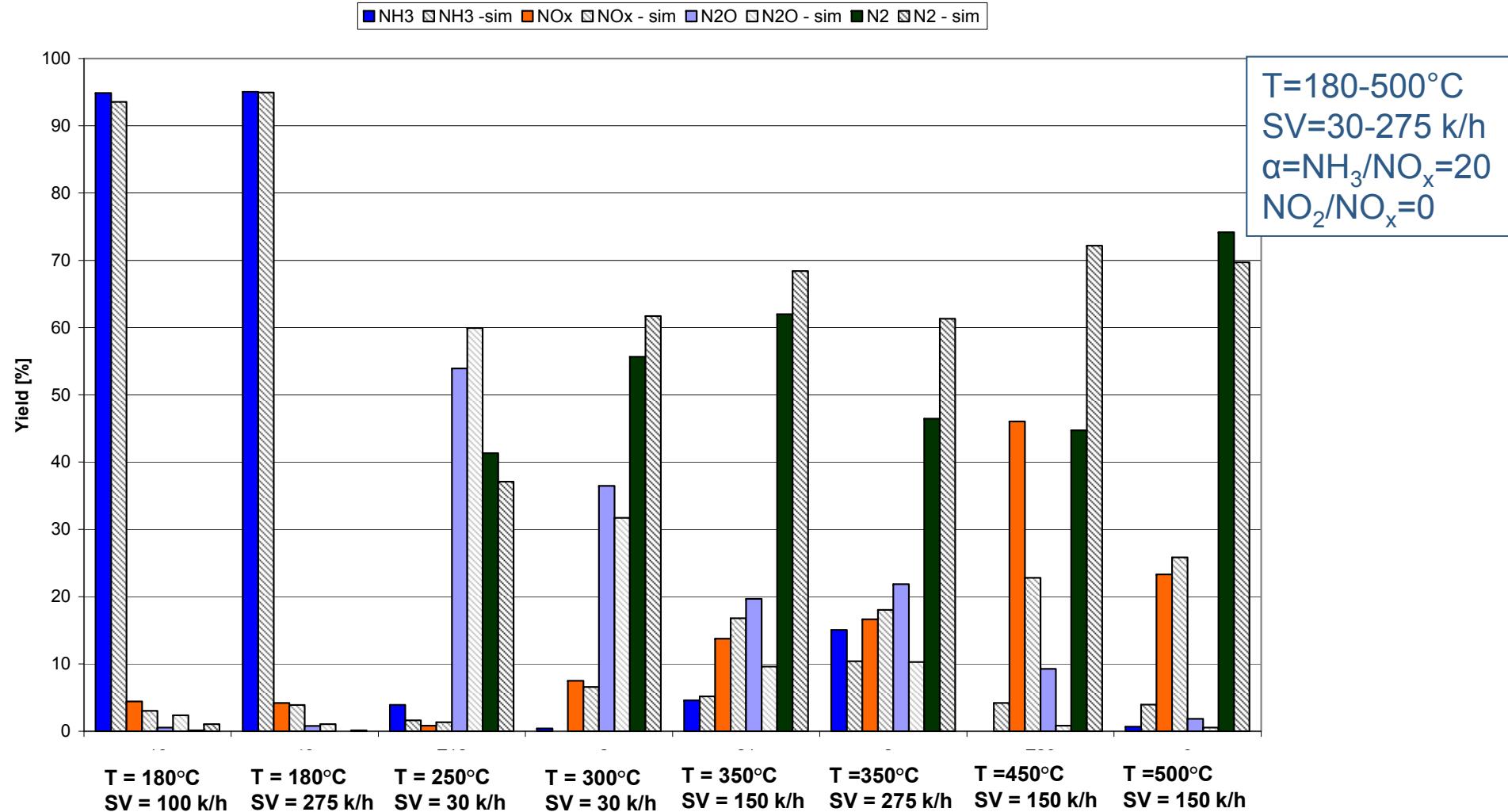
Model validation against lab-scale ASC monolith data



Model predictions under realistic transient conditions in good agreement with the experimental behavior.

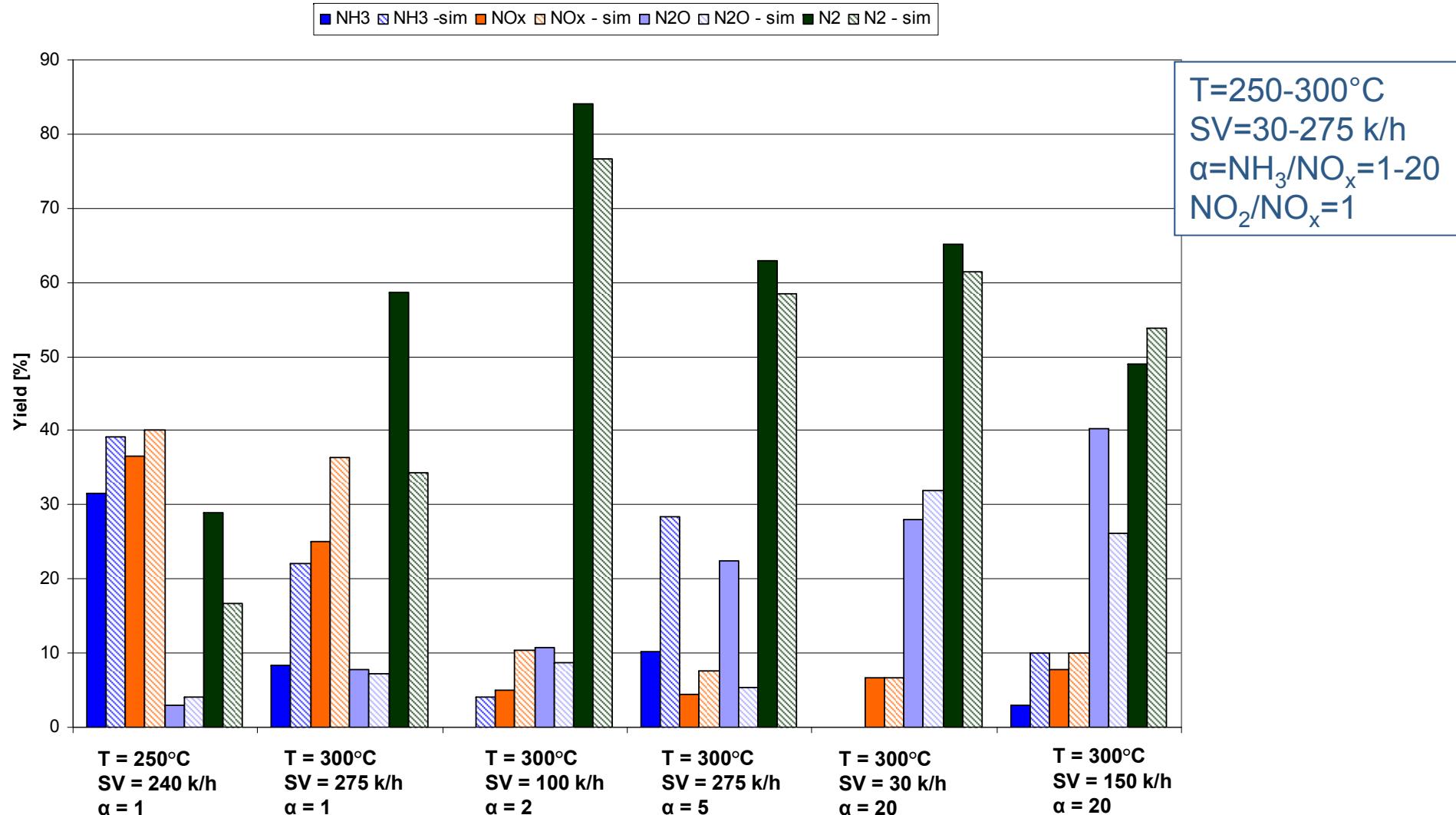
Model validation against DOE data over the full scale ASC monolith

DOE data: T=180-500°C, SV=30-300 k/h, NO₂/NO_x=0-1, α =NH₃/NO_x=0-20



Model validation against DOE data over the full scale ASC monolith

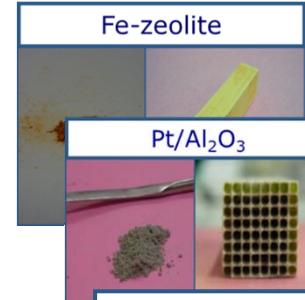
DOE data: T=180-500°C, SV=30-300 k/h, NO₂/NO_x=0-1, $\alpha=\text{NH}_3/\text{NO}_x=0-20$



Goal/Outline

Development of a chemico-physically consistent mathematical model of a dual-layer ASC monolith

1. Kinetic study and model validation of the SCR component

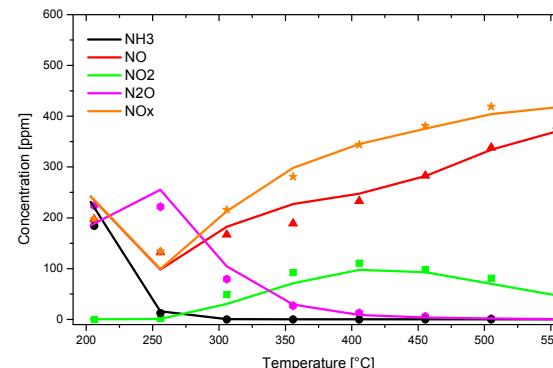
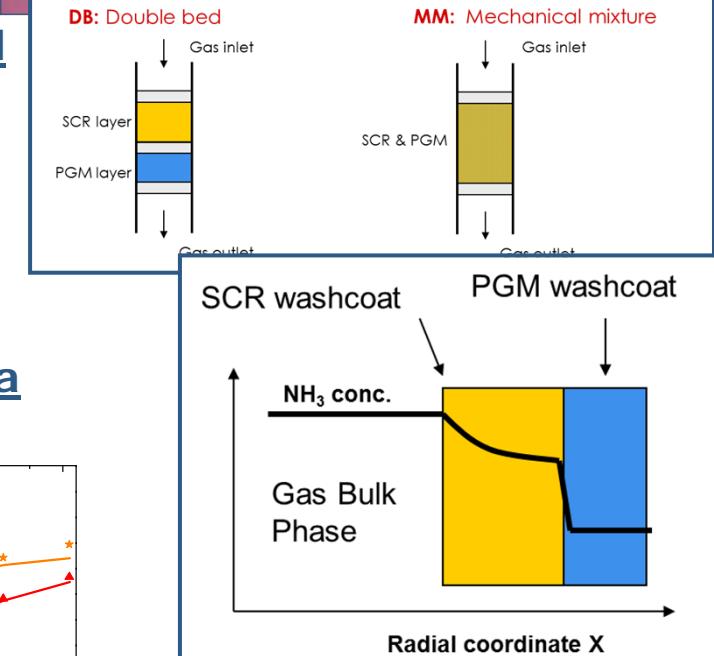


2. Kinetic study and model validation of the PGM component

3. Kinetic study of the combined SCR+ PGM components

4. Development of the dual-layer monolith model

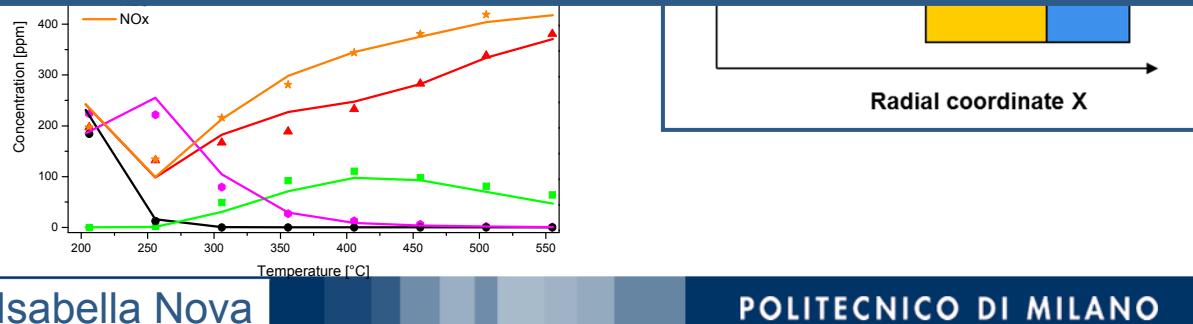
5. Validation against lab- and full scale data from dual-layer monolith data



Goal/Outline

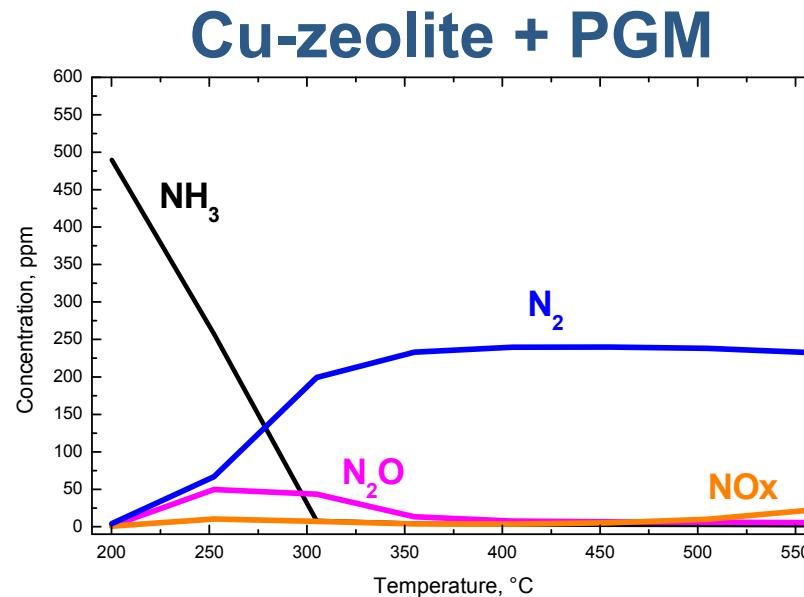
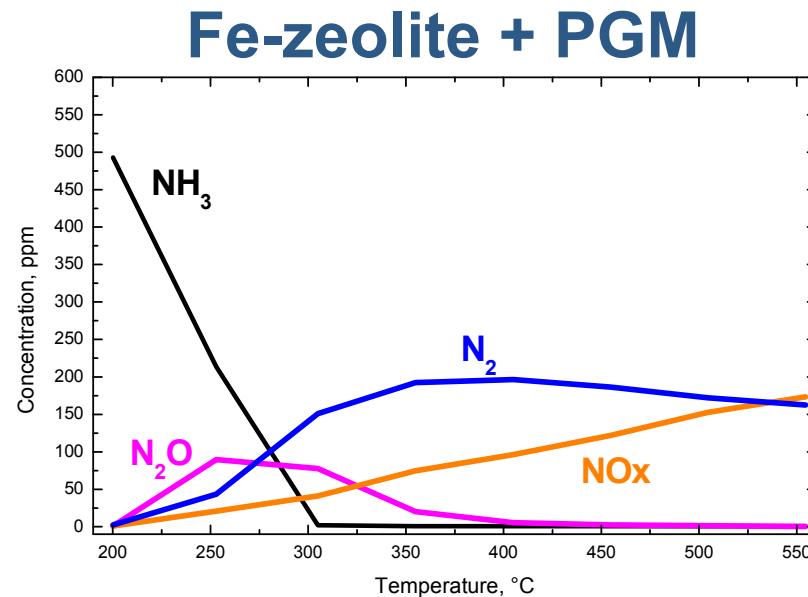
Development of a chemico-physically consistent mathematical model of a dual-layer ASC monolith

The model is now used in the automotive development process at DAIMLER to simulate the behaviour of ASC catalysts...e.g. to compare Fe- and Cu-based ASC catalysts, to optimize the ASC performances...



Fe- vs. Cu-zeolite based dual-layer NH₃ slip catalysts

Effect of SCR component on ASC activity and selectivity



Cu-zeolite exhibits similar NH₃ oxidation activity and lower selectivity to NOx and to N₂O in the whole T-range.

Simulated conditions:

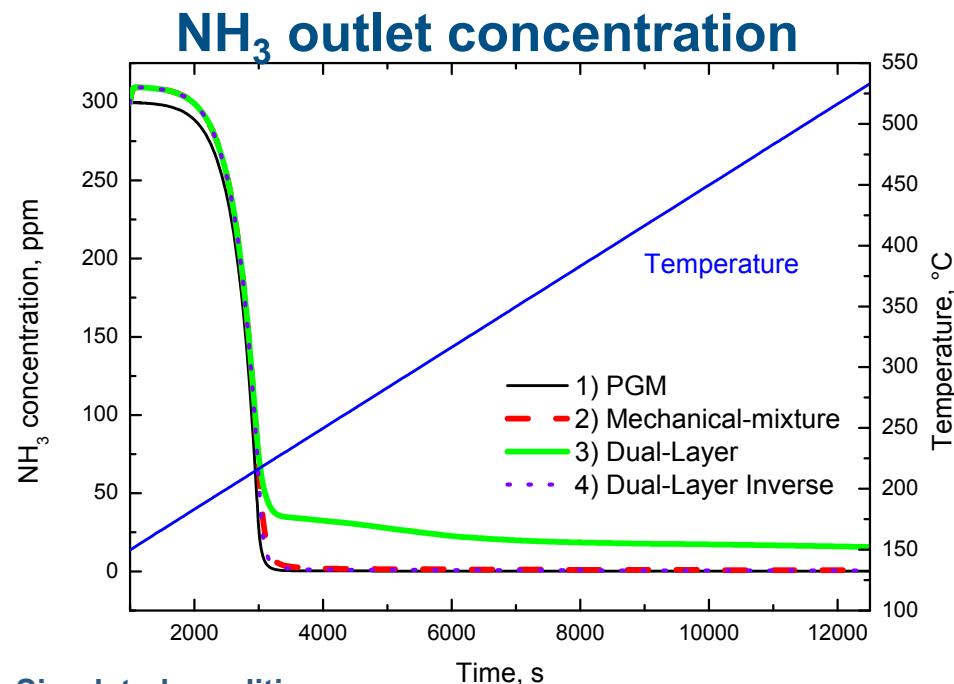
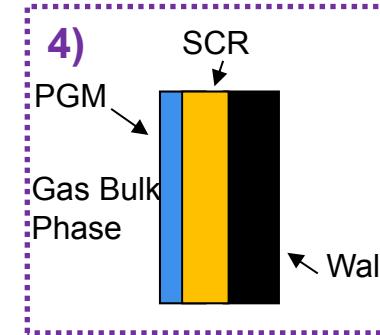
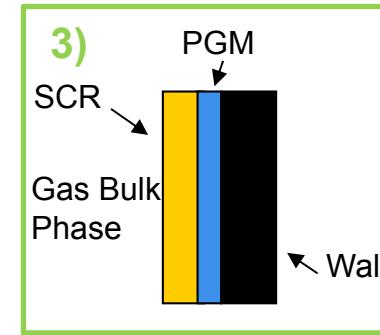
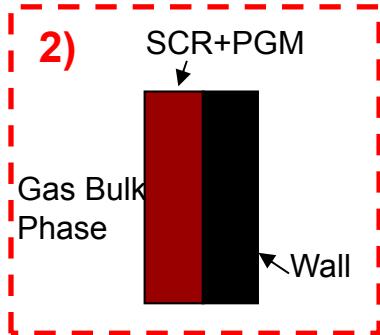
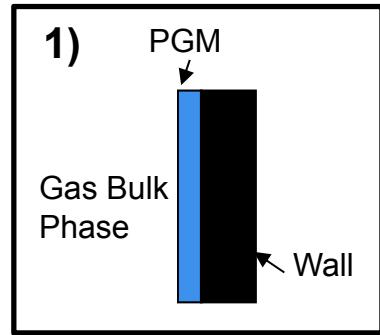
NH₃ = 500 ppm

O₂ = H₂O = 8%

GHSV = 100'000 h⁻¹

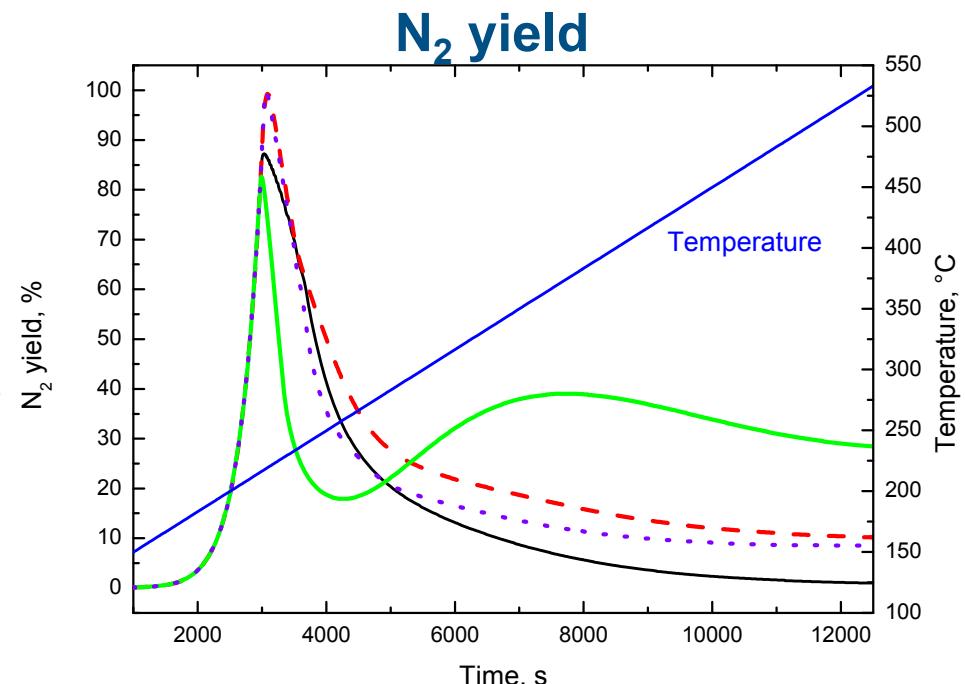
Optimization of ASC performance

Evaluation of NH_3 oxidation activity and selectivity for different SCR+PGM configurations



Simulated conditions:

Fe-zeolite, $\text{NH}_3 = 300 \text{ ppm}$, $\text{O}_2 = 5 \%$, $\text{H}_2\text{O} = 6 \%$, GHSV = $100'000 \text{ h}^{-1}$

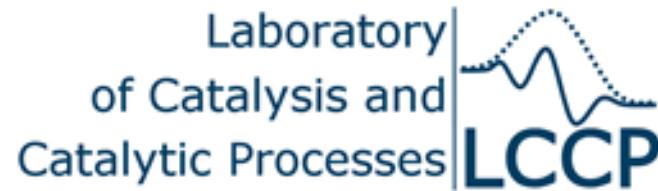


Colombo et al., Topics in catalysis, submitted

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DAIMLER



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G.C. Koltsakis



LABORATORY OF APPLIED THERMODYNAMICS



Thank you for your attention!



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

Politecnico di Milano