A novel approach to the modeling of dual-layer ammonia slip catalysts

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Outline

- Introduction
  - Dual layer Ammonia Slip Catalysts (ASCs) concept
- Kinetic models
  - Fe-zeolite SCR kinetics (SAE 2007-01-1136)
  - NH_3 oxidation kinetics on Pt/Al_2O_3 (Top.Catal.52-2009-1847)
- Dual-layer simulation approach
  - Mathematical model
  - Simulation results for NH_3/O_2 and $NH_3/NO/O_2$ reacting systems
    - SCR only catalyst
    - PGM only catalyst
    - Dual-layer catalyst

    } → Steady state concentrations; Intralayer concentration profiles
- Layer+Surface approach
  - Mathematical model
  - Comparison with Dual-layer approach for NH_3/O_2 and $NH_3/NO/O_2$ reacting systems

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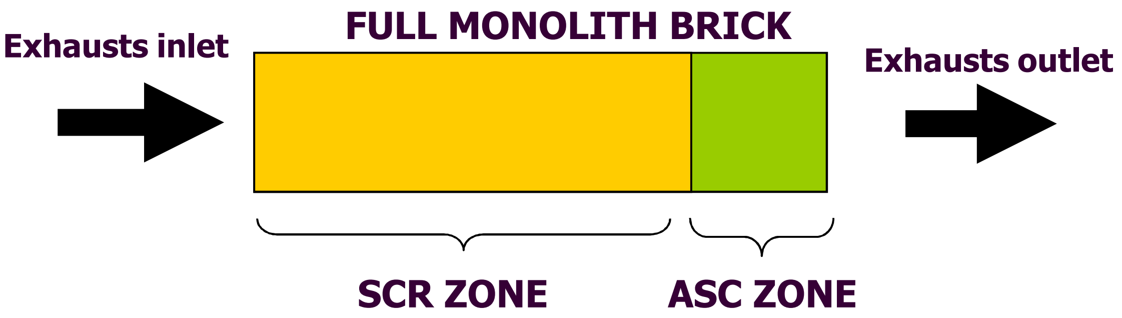
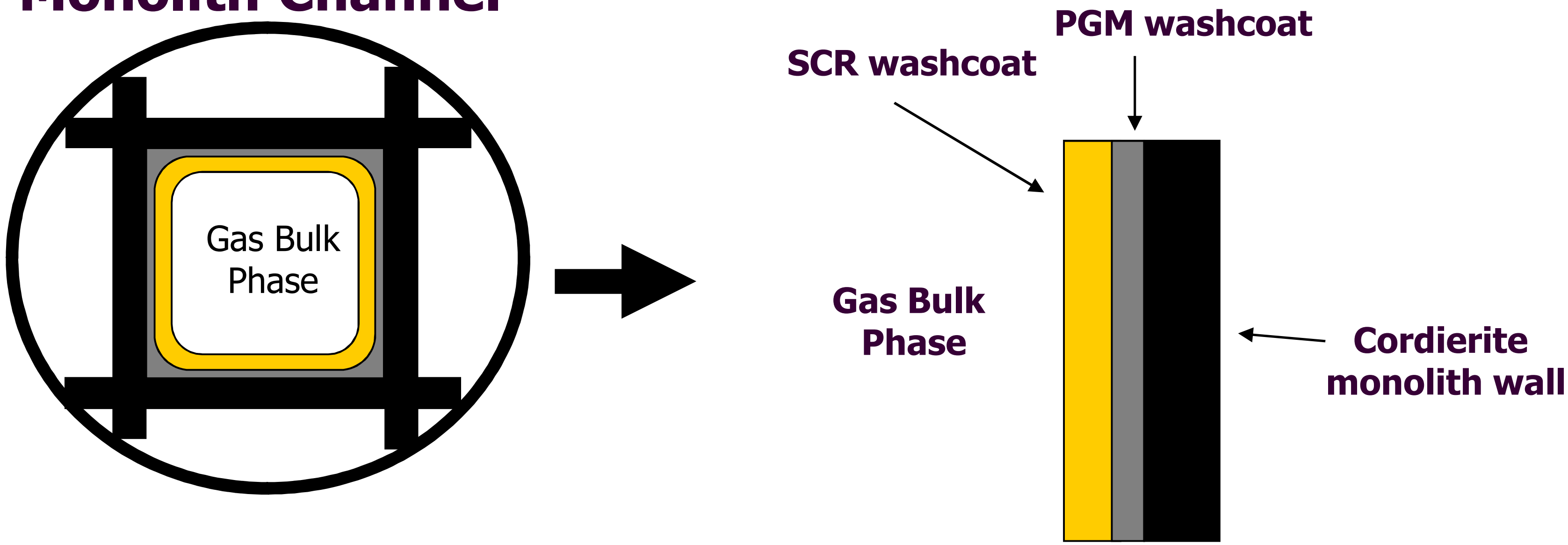
Dual Layer ASCs concept*

System configuration



ASC ZONE → double coated : SCR + PGM

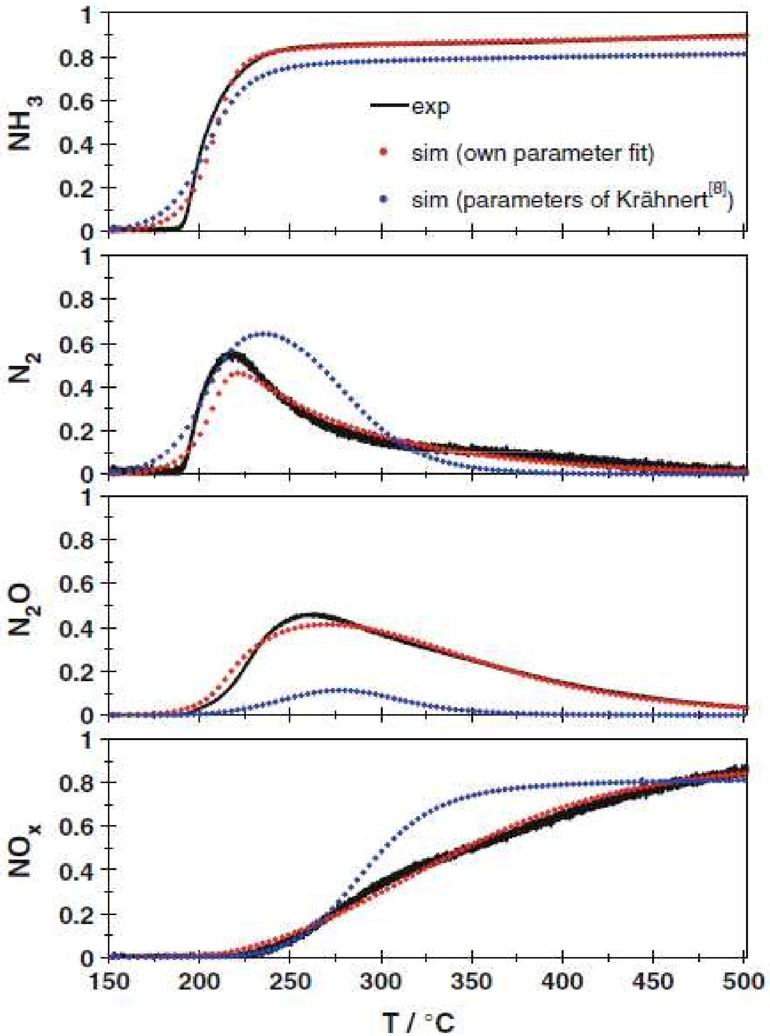
Monolith Channel



* Scheuer et al. ICEC 2010, Beijing,China, September 12th-15th 2010

Dual layer ASCs concept

Why a dual layer system?



PGM catalysts have poor selectivity to N_2

↓

The unselective oxidation products are N_2O and NOx, which have to diffuse back in the SCR layer

↓

NOx can react with NH_3 over the SCR catalyst to give N_2!!!

↓

Both NH_3 conversion & selectivity to N_2 increase

- **Scheuer et al. Top.Catal. 52-2009-1847**
- **Scheuer et al. ICEC 2010, Beijing,China, September 12th-15th 2010**

Kinetic Models

Literature reaction schemes & rate equations

- Fe-zeolite SCR kinetics → Chatterjee et al. SAE 2007-01-1136
- NH_3 oxidation on Pt/Al_2O_3 → Scheuer et al. Top.Catal. 52-2009-1847

Fe-zeolite SCR kinetics

1. Ammonia Adsorption/Desorption

   $NH_3 \Leftrightarrow NH_3^*$

(1) $$r_{ads} = k_{ads} C_{NH_3} (1 - \theta_{NH_3})$$

(2) $$r_{des} = k_{des}^{o} \exp\left[-\frac{E_{des}^{\circ}}{RT} (1 - \alpha \theta_{NH_3}) \right] \cdot \theta_{NH_3}$$

2. Ammonia oxidation

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

(3) $$r_{ox} = k_{ox}^{o} \exp[-\frac{E_{ox}}{RT}] \theta_{NH_3}$$

3. NO oxidation

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

(4) $$r_{NO\,ox} = k_{NOox}^{o} \exp\left(-\frac{E_{NOox}}{RT} \right) \left(C_{NO} \sqrt{P_{O_2}} - \frac{C_{NO_2}}{K_{NO_2}^{eq}} \right)$$

4. Standard-SCR

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

(5) $$r_{NO} = \frac{k_{NO}^{0} \exp[-\frac{E_{NO}}{R} (1/T - 1/473)] C_{NO} \theta_{NH3}}{1 + K_{NH3} \frac{\theta_{NH3}}{1 - \theta_{NH3}}} \left(\frac{p_{O2}}{0.02} \right)^{\beta}$$

5. Fast-SCR

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

(6) $$r_{Fast} = k_{Fast}^{o} \exp\left(-\frac{E_{Fast}}{R} \left(\frac{1}{T} - \frac{1}{473} \right) \right) \frac{C_{NO_2}}{\varepsilon + C_{NO_2}} C_{NO} \theta_{NH_3}$$

Chatterjee et al. SAE 2007-01-1136

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NH_3 oxidation on Pt/Al_2O_3

1. Ammonia Adsorption/desorption

   $NH_3 + b \Leftrightarrow NH_3\text{-}b$

2. Oxygen adsorption/desorption

   $O_2 + 2a \Leftrightarrow 2\ O\text{-}a$

3. NO adsorption/desorption

   $NO + a \Leftrightarrow NO\text{-}a$

4. NH_3 activation

   $NH_3\text{-}b + 1.5\ O\text{-}a \rightarrow N\text{-}a + 1.5\ H_2O + 0.5\ a + b$

5. N_2 formation

   $2\ N\text{-}a \rightarrow N_2 + 2\ a$

6. NO formation

   $N\text{-}a + O\text{-}a \rightarrow NO\text{-}a + a$

7. N_2O formation

   $NO\text{-}a + N\text{-}a \rightarrow N_2O + 2\text{-}a$

- 2 different adsorption sites (a & b)
- 3 adsorbed species (NH_3, O_2, NO)

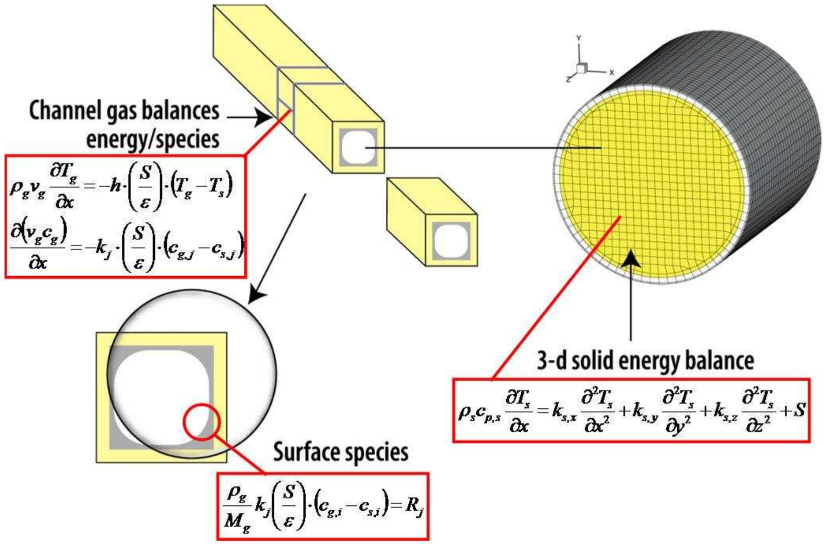
$$r_j = k_j^o \exp\left(-\frac{E_j}{RT}\right) \cdot \prod_{i=1}^{NSS} \theta_i^{\nu_{i,j}} \cdot \prod_{i=1}^{NGS} C_i^{\nu_{i,j}} \cdot C_{Pt}$$

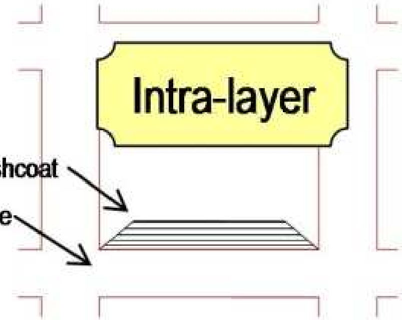
Scheuer et al. Top.Catal. 52-2009-1847

Dual-Layer (DL) approach

Mathematical Model

axisuite						
software module	functionality / reactor type	3-way catalyst	diesel oxidation catalyst	lean NO_x trap	selective catalytic reduction	diesel particulate filter
axicat	flow-through	✓	✓	✓	✓	n/a
axitrap	wall-flow	n/a	✓	✓	✓	✓
axifoam	deep-bed	n/a	✓	✓	✓	✓
axiheat	exhaust pipe	single-wall	double-wall	insulating material	flanges	reacting flow





Washcoat:

$$-D_j \frac{\partial}{\partial x}\left(f_x \frac{\partial y_j}{\partial x}\right) = \frac{f_x}{c_m}\sum_k c_{j,k} R_k$$

Channel gas species balance:

$$\frac{\partial}{\partial z}(v_1 y_{1,j}) = \frac{1}{df_{-w}} k_{1,j}(y_{1s,j} - y_{1,j}) \qquad k_{i,j} = \frac{Sh\cdot D_{mol,j}}{d_i}$$

Boundary conditions:

$$-D_j f_{-w} \frac{\partial y_j}{\partial x}\bigg|_{1s} = -df_{-w}^{\;2} \frac{\partial}{\partial z}(v_1 y_{1,j}) \qquad \frac{\partial y_j}{\partial x}\bigg|_{2s} = 0$$

Channel/1st layer — 2nd layer/substrate

1st layer/2nd layer → $y_j\big|_{x=w_1/w_2} = y_j\big|_{x=w_2/w_1}$

Isothermal conditions assumed

Koltsakis & Stamatelos A. M., *Appl. Catal B.*, 1997.
Pontikakis et al., Top. In Catal, 2001
Tsinoglou & Koltsakis, Proc. IMechE, 2007

Catalysts configuration and properties

Monolith geometrical properties:

- Cells density = 400 CPSI
- Wall thickness = 7 mils

SCR catalyst

- Load=175 g/l[1]
- Average washcoat thickness ≈140 µm

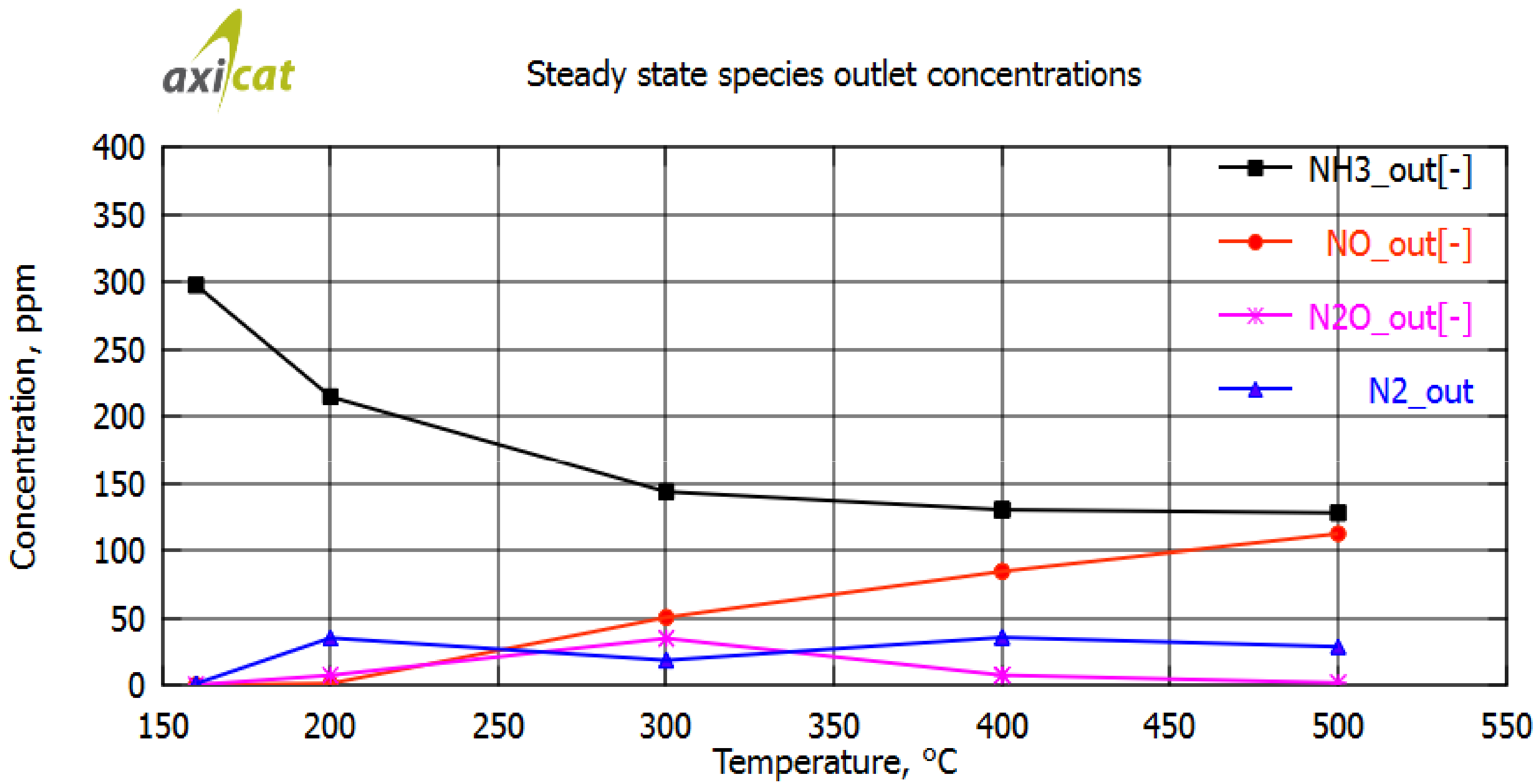
PGM catalyst

- Load = 20 g/l
- Average washcoat thickness ≈ 10µm[2]

The SCR washcoat load/thickness affects in opposite ways N_2 selectivity and NH_3 conversion → optimization problem[3]
NOT the aim of the present work

[1] Chatterjee et al. SAE 2007-01-1136
[2] Scheuer et al. Top.Catal. 52-2009-1847
[3] Scheuer et al. ICEC 2010, Beijing,China, September 12th-15th 2010

DL simulation results: NH_3/O_2



Simulated conditions:

300 ppm NH_3, 5%O_2, GHSV = 300’000 h^{-1}

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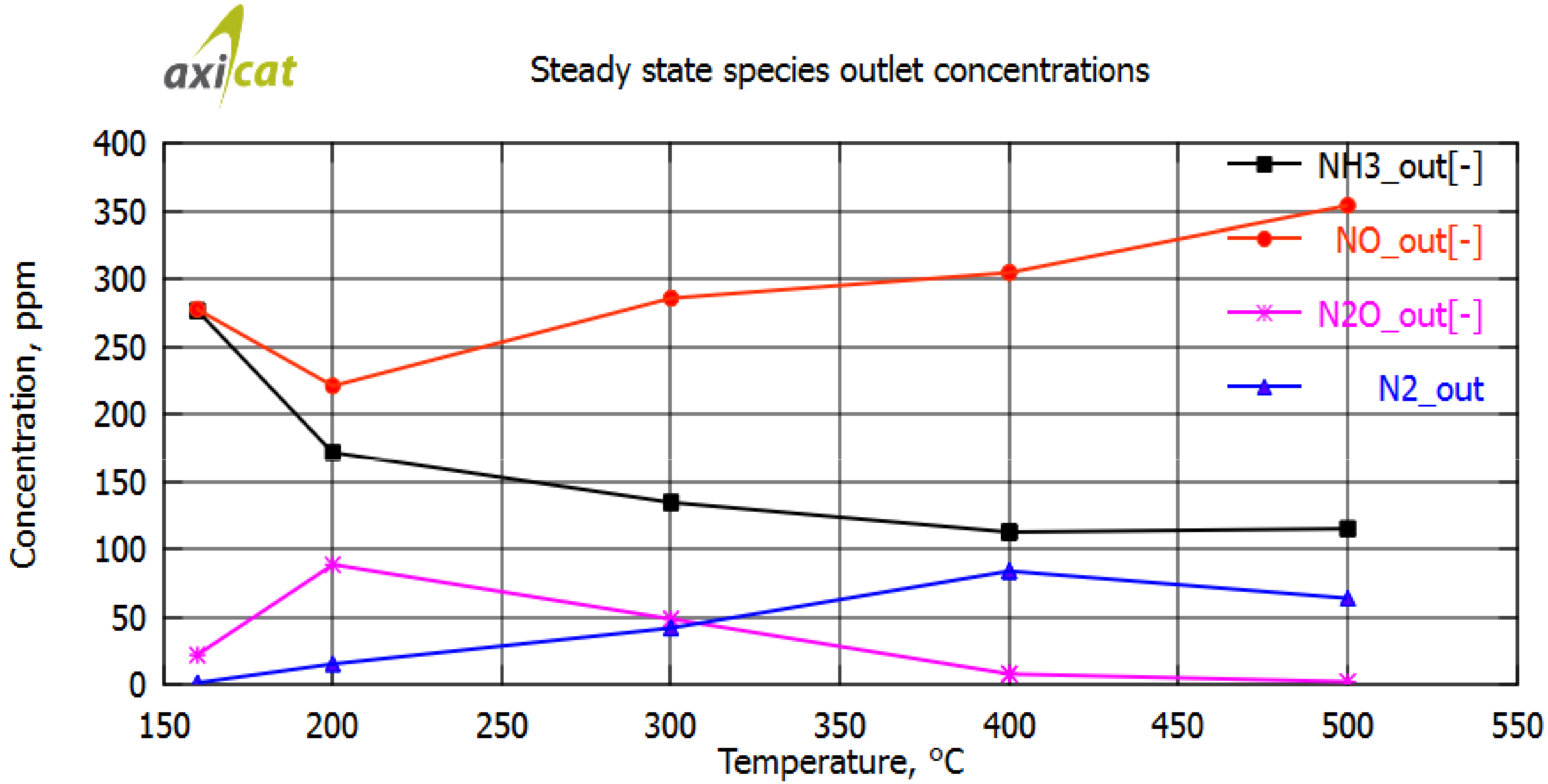
DL simulation results: $NH_3/NO/O_2$



Decrease of N_2 selectivity at low temperatures

Simulated conditions:

300 ppm NH_3, 300 ppm NO, 5%O_2, GHSV = 300’000 h^{-1}

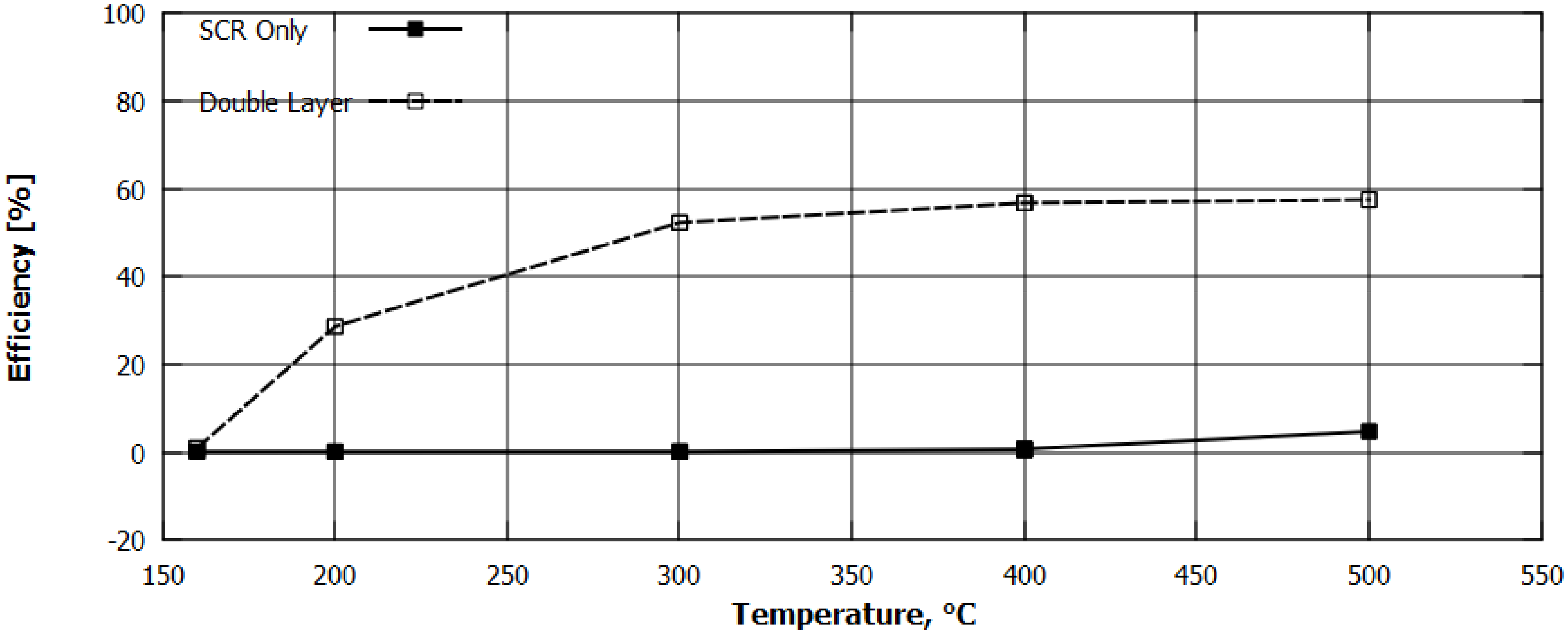
Is it necessary to model reaction/diffusion in both catalytic layers?

SCR Layer

SCR layer: effect of PGM addition

NH_3/O_2 reacting system

Steady state NH_3 conversion efficiency



Significant increase of NH_3 conversion with PGM addition

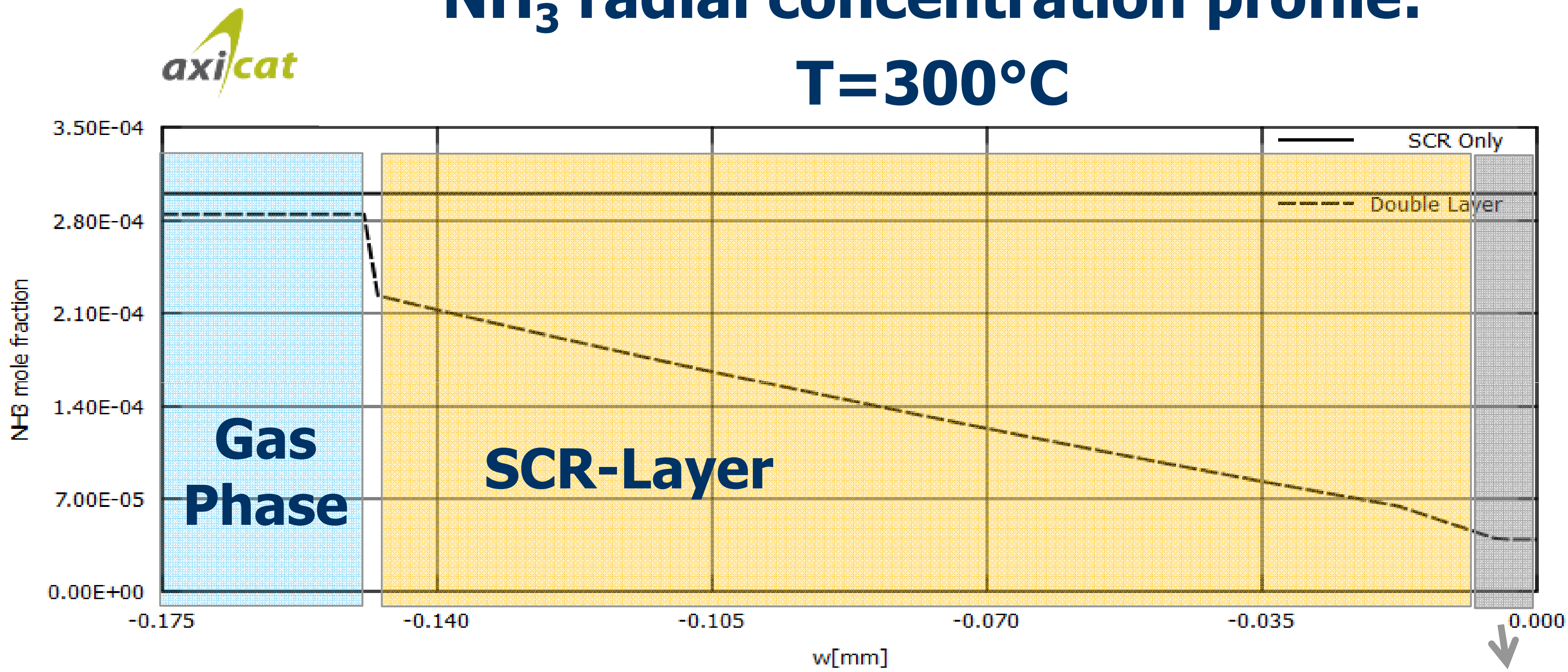
Simulated conditions:
300 ppm NH_3, 5%O_2, GHSV = 300'000 h^{-1}

SCR layer: effect of PGM addition

NH_3/O_2 reacting system

NH_3 radial concentration profile:

T=300°C



PGM-Layer

PGM presence drastically modifies SCR intralayer concentration profile!!

Significant SCR intralayer gradients!!

Colombo, Nova, Tronconi: Paper in preparation

Simulated conditions:

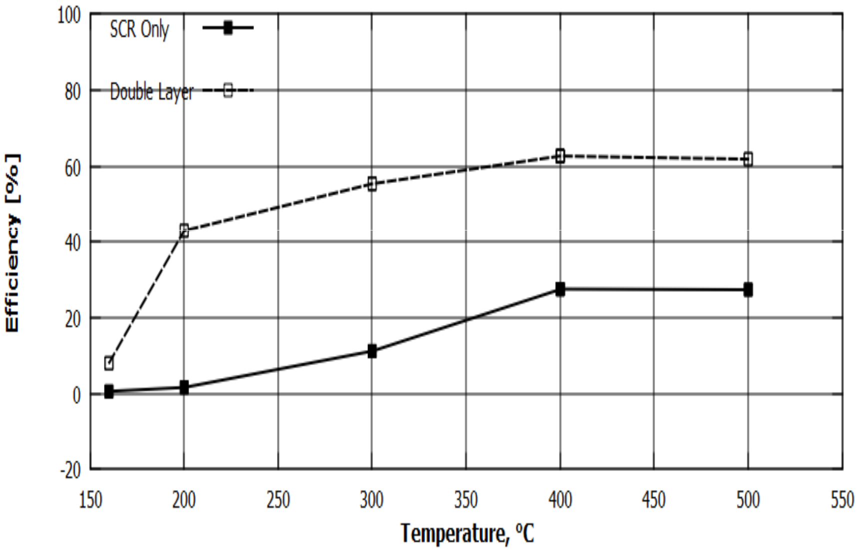
300 ppm NH_3, 5%O_2, GHSV = 300'000 h^{-1}

SCR layer: effect of PGM addition

$NH_3/NO/O_2$ reacting system

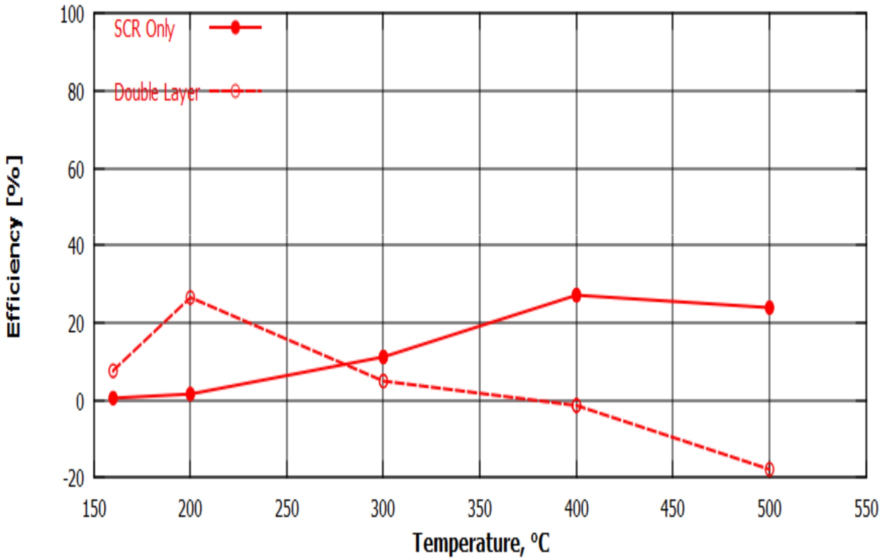
Steady state NH_3 & NO conversion efficiencies

NH_3 conversion



Significant increase of NH_3 conversion with PGM addition

NO conversion



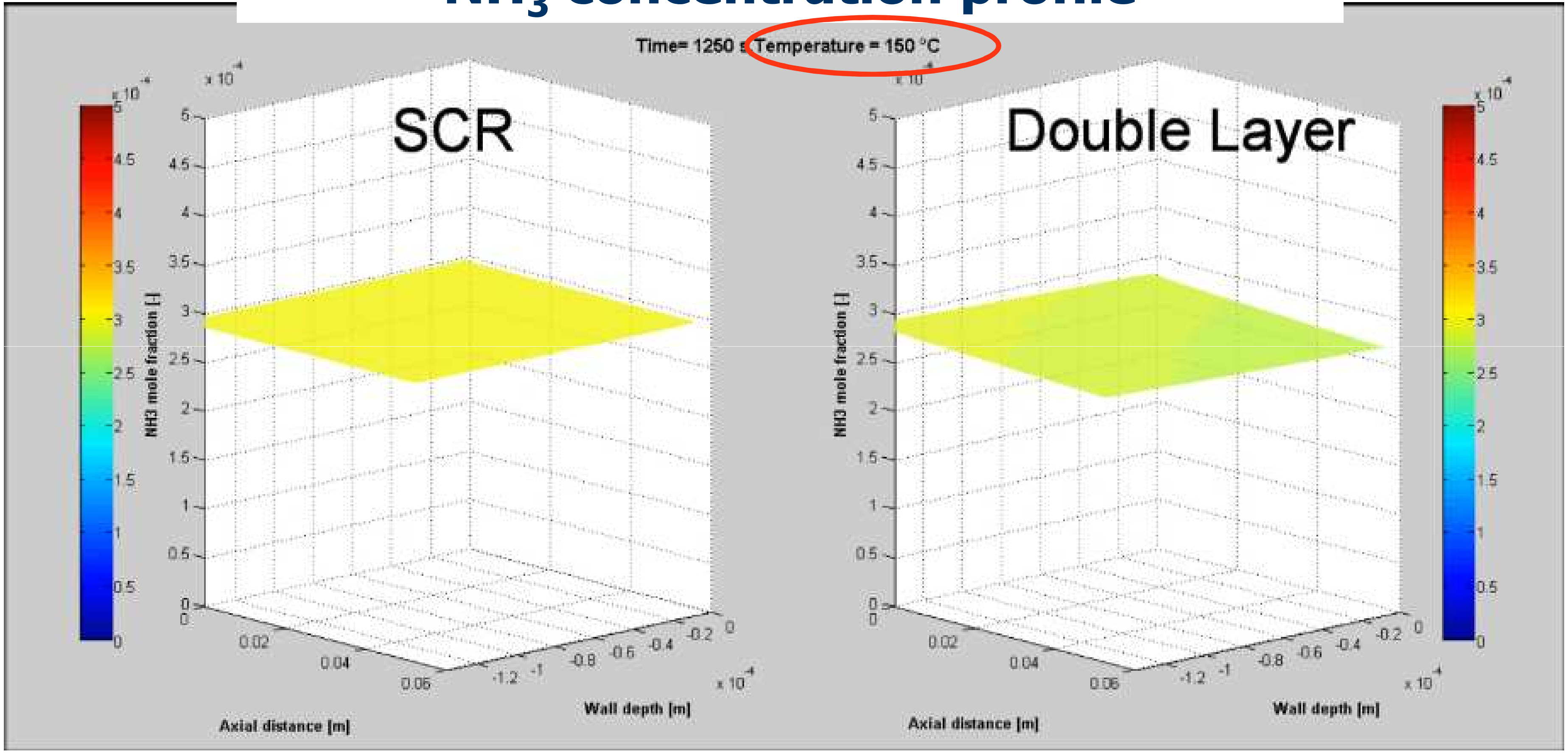
PGM addition strongly influences also NO conversion

Simulated conditions:

300 ppm NH_3, 300 ppm NO, 5%O_2, GHSV = 300'000 h^{-1}

SCR layer: effect of PGM addition

$NH_3/NO/O_2$ reacting system
NH_3 concentration profile



Colombo, Nova, Tronconi: Paper in preparation

Simulated conditions:

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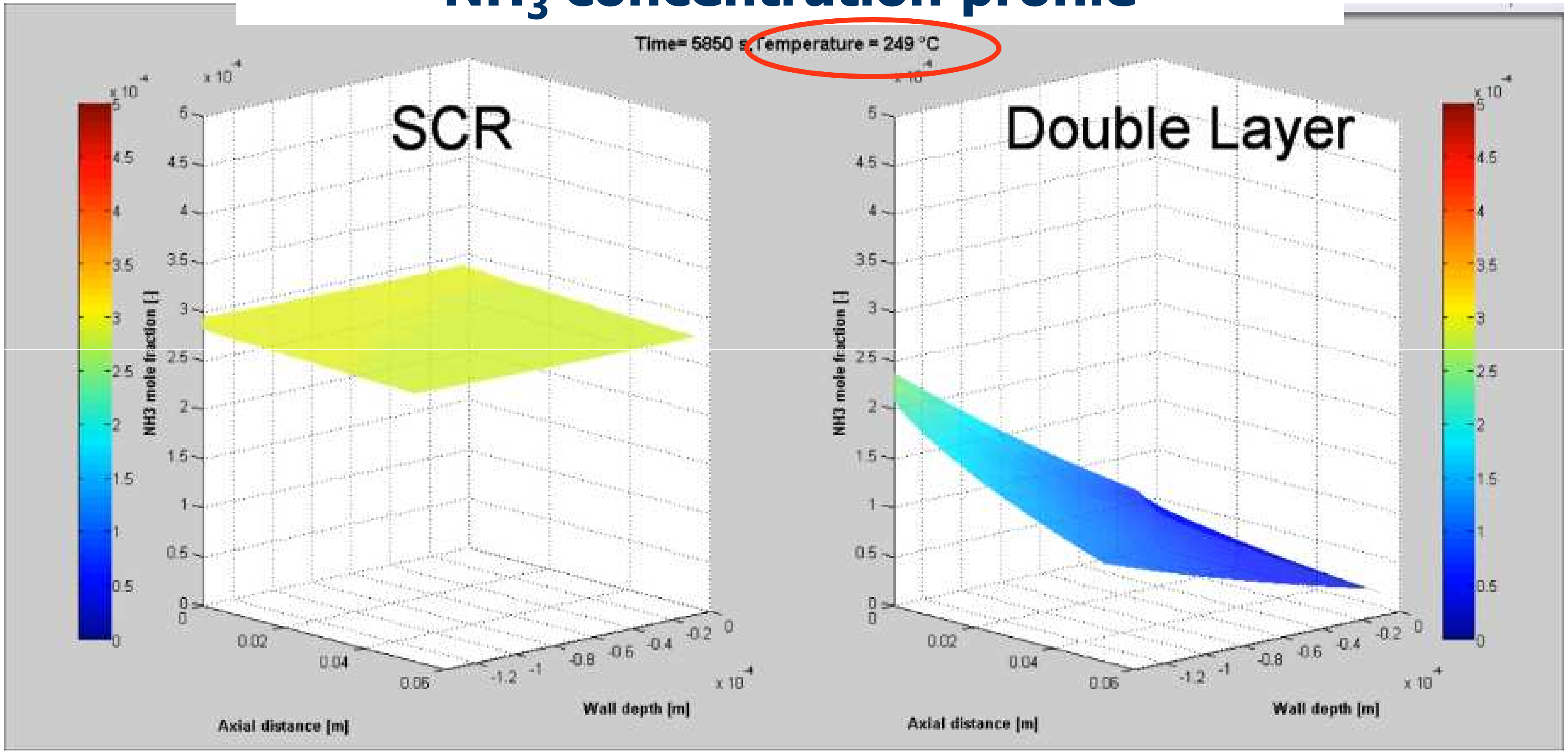
SCR layer: effect of PGM addition

$NH_3/NO/O_2$ reacting system
NH_3 concentration profile



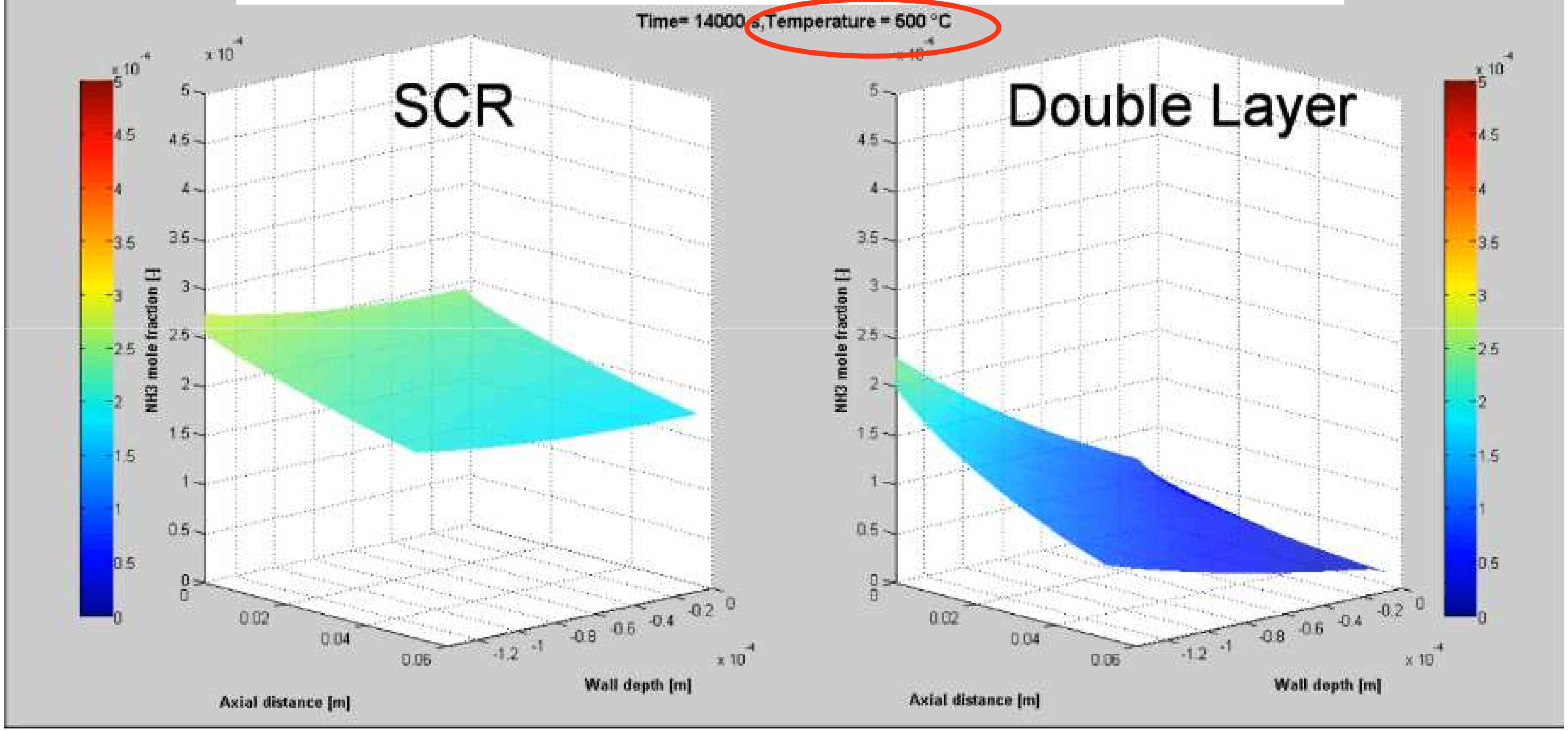
Colombo, Nova, Tronconi:
Paper in preparation

Simulated conditions:

300 ppm NH_3, 300 ppm NO, 5%O_2, GHSV = 300'000 h^{-1}

SCR layer: effect of PGM addition

$NH_3/NO/O_2$ reacting system
NH_3 concentration profile



Colombo, Nova, Tronconi: Paper in preparation

Simulated conditions:

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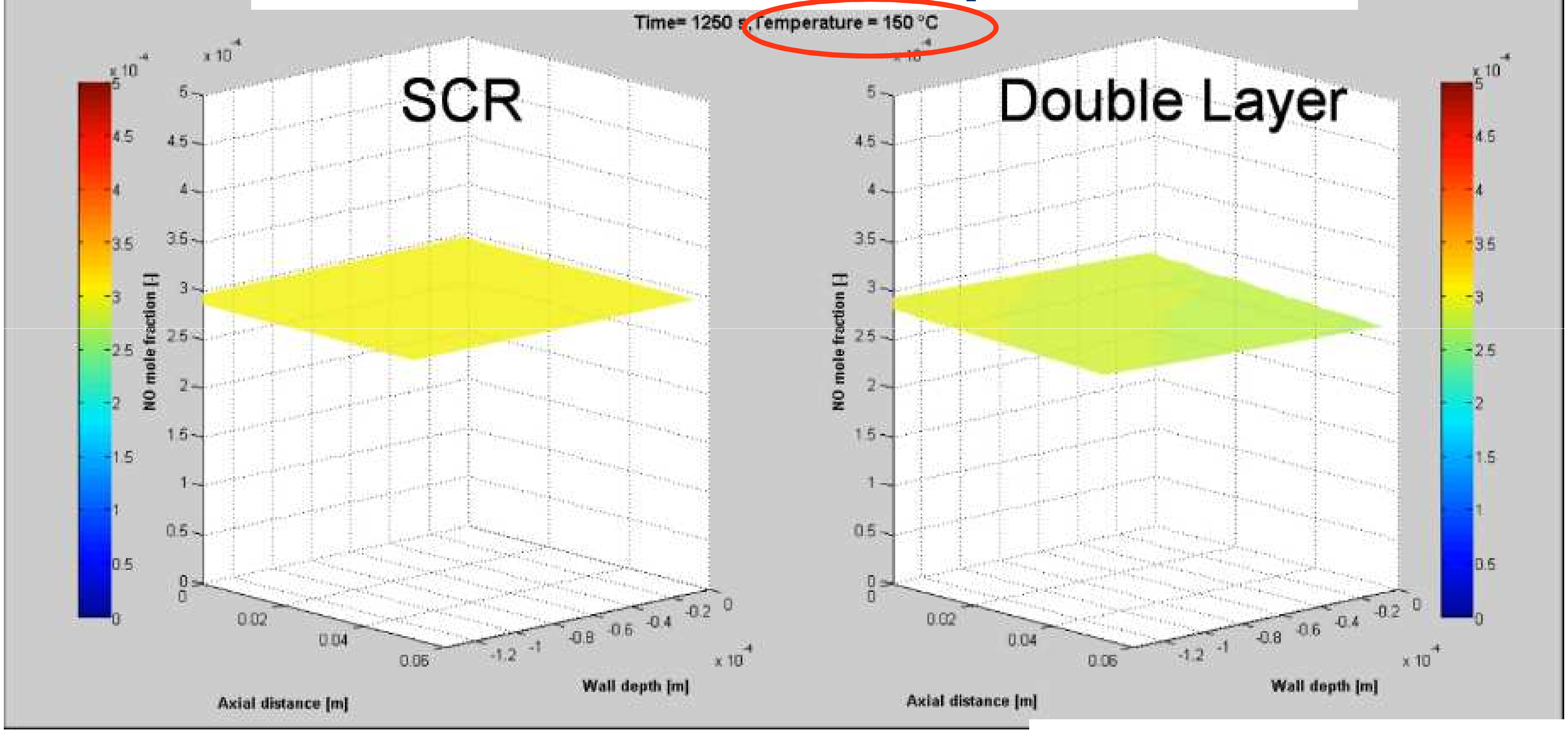
SCR layer: effect of PGM addition

$NH_3/NO/O_2$ reacting system
NO concentration profile



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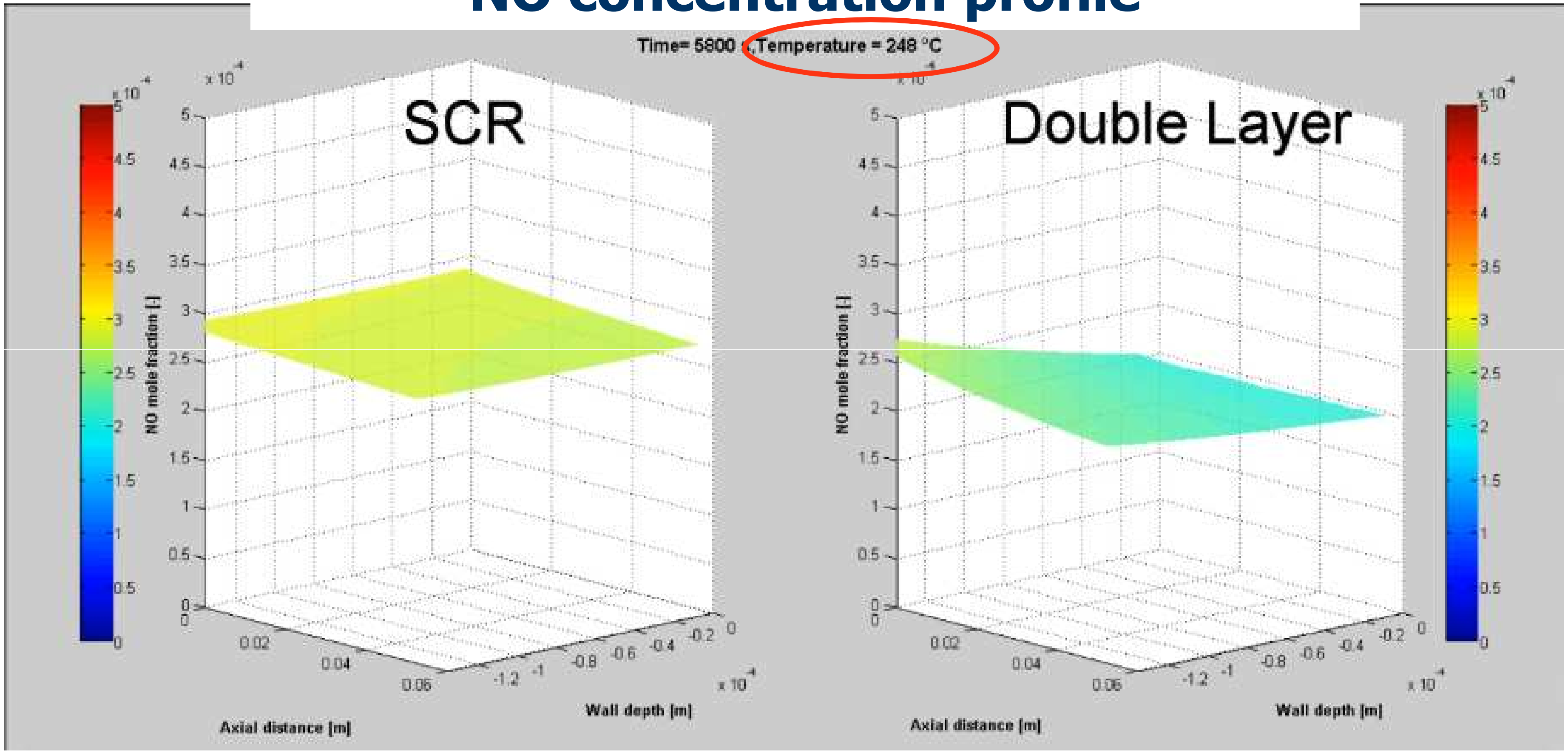
SCR layer: effect of PGM addition

$NH_3/NO/O_2$ reacting system
NO concentration profile



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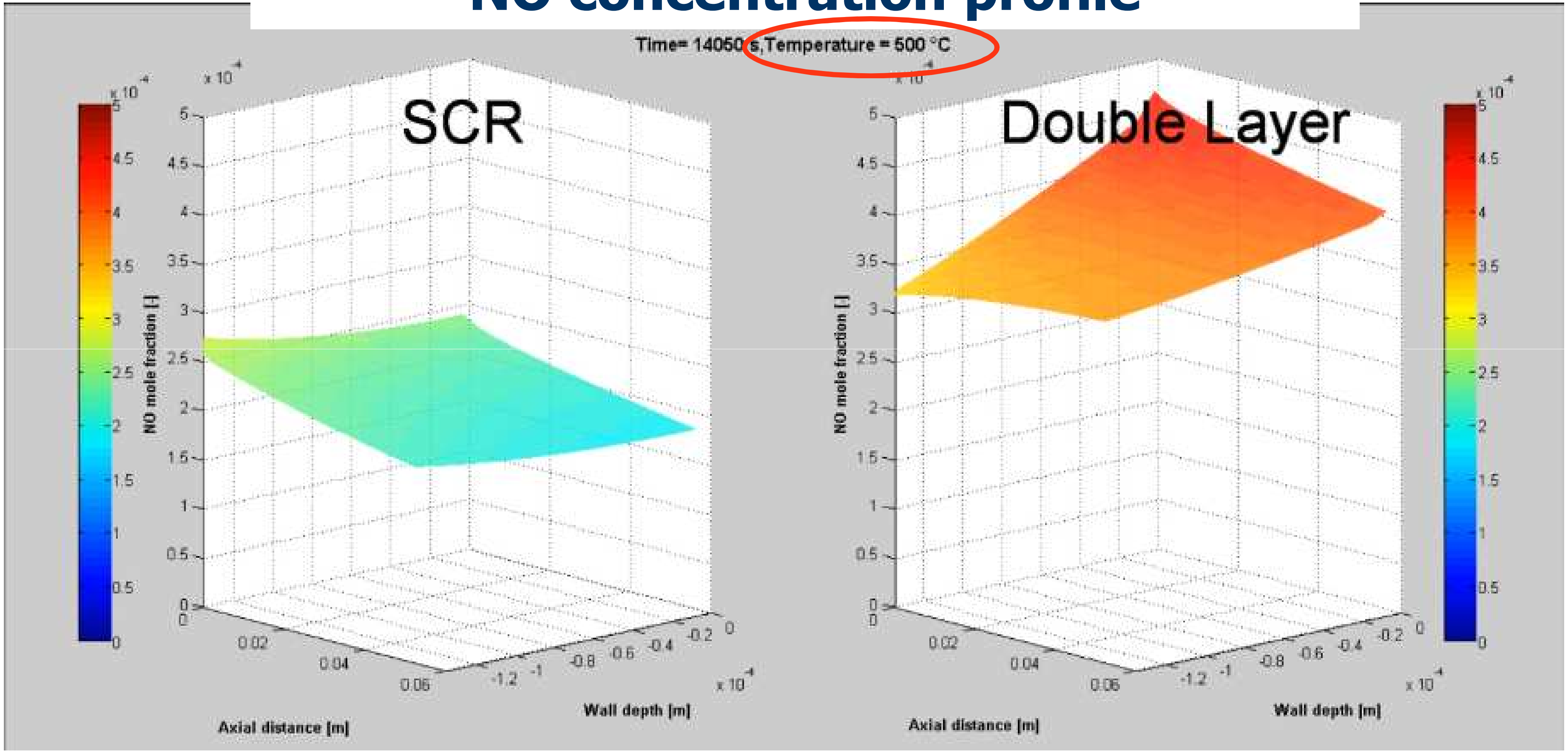
SCR layer: effect of PGM addition

$NH_3/NO/O_2$ reacting system

NO concentration profile



Colombo, Nova, Tronconi: Paper in preparation

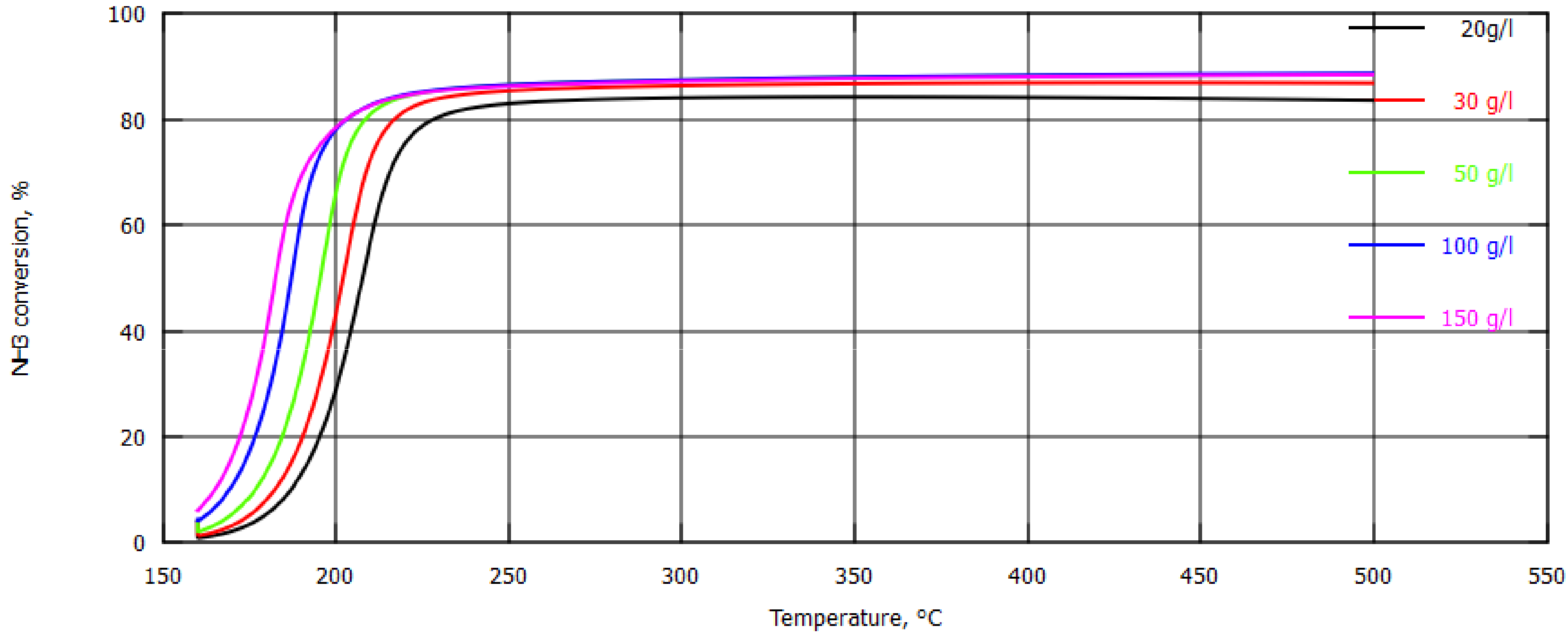
Simulated conditions:

300 ppm NH_3, 300 ppm NO, 5%O_2, GHSV = 300’000 h^{-1}

PGM Layer

PGM layer: washcoat load effect on NH_3 conversion

Steady state NH_3 conversion efficiency

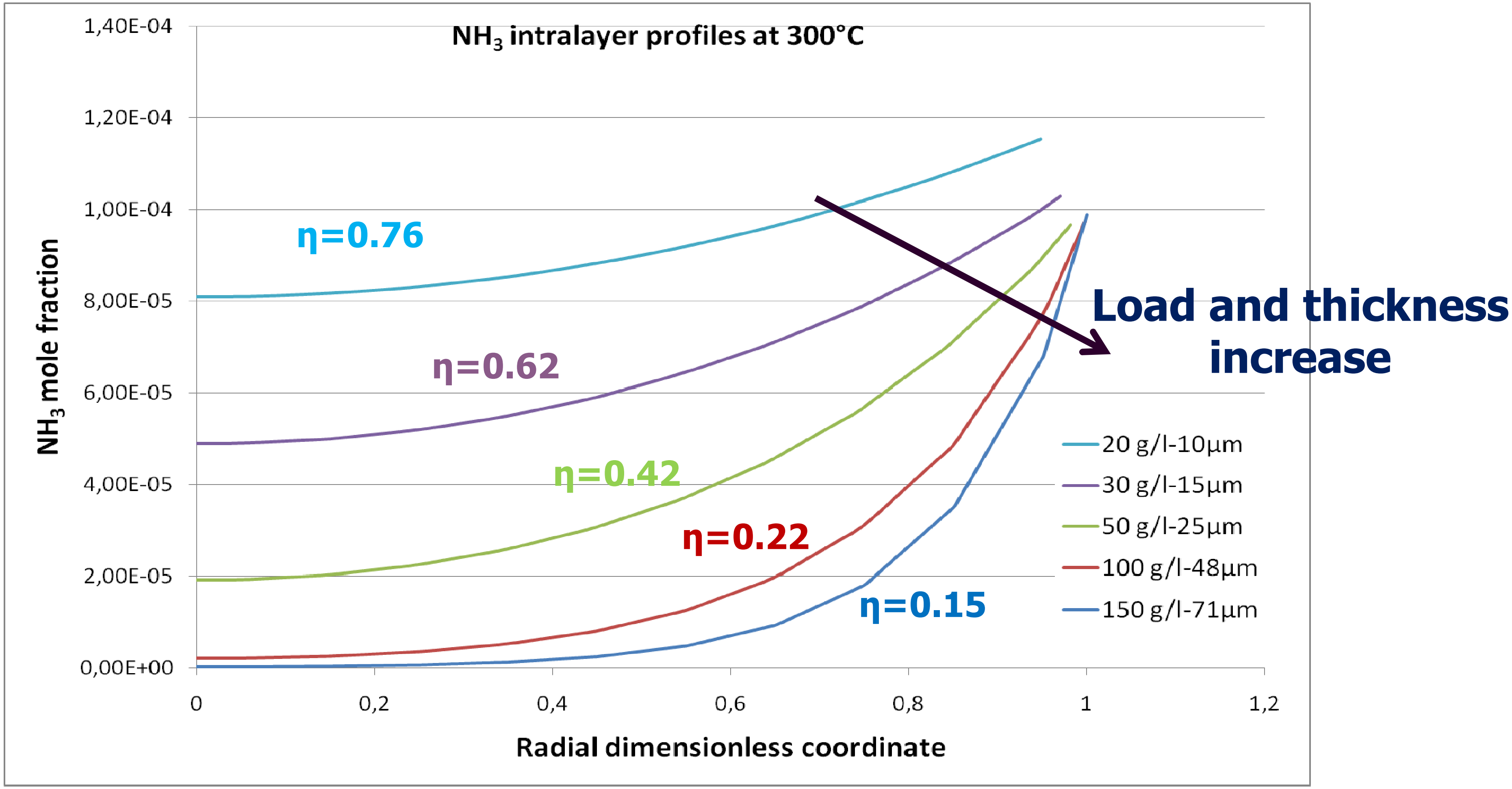


The increase of the washcoat load has little or no effect above 250°C

Simulated conditions:

300 ppm NH_3, 5%O_2, GHSV = 300’000 h^{-1} ;PGM only catalyst

PGM layer: catalyst effectiveness



Internal diffusion control for higher washcoat loads/thickness

Simulated conditions:

300 ppm NH_3, 5%O_2, GHSV = 300'000 h^{-1} ;PGM only catalyst

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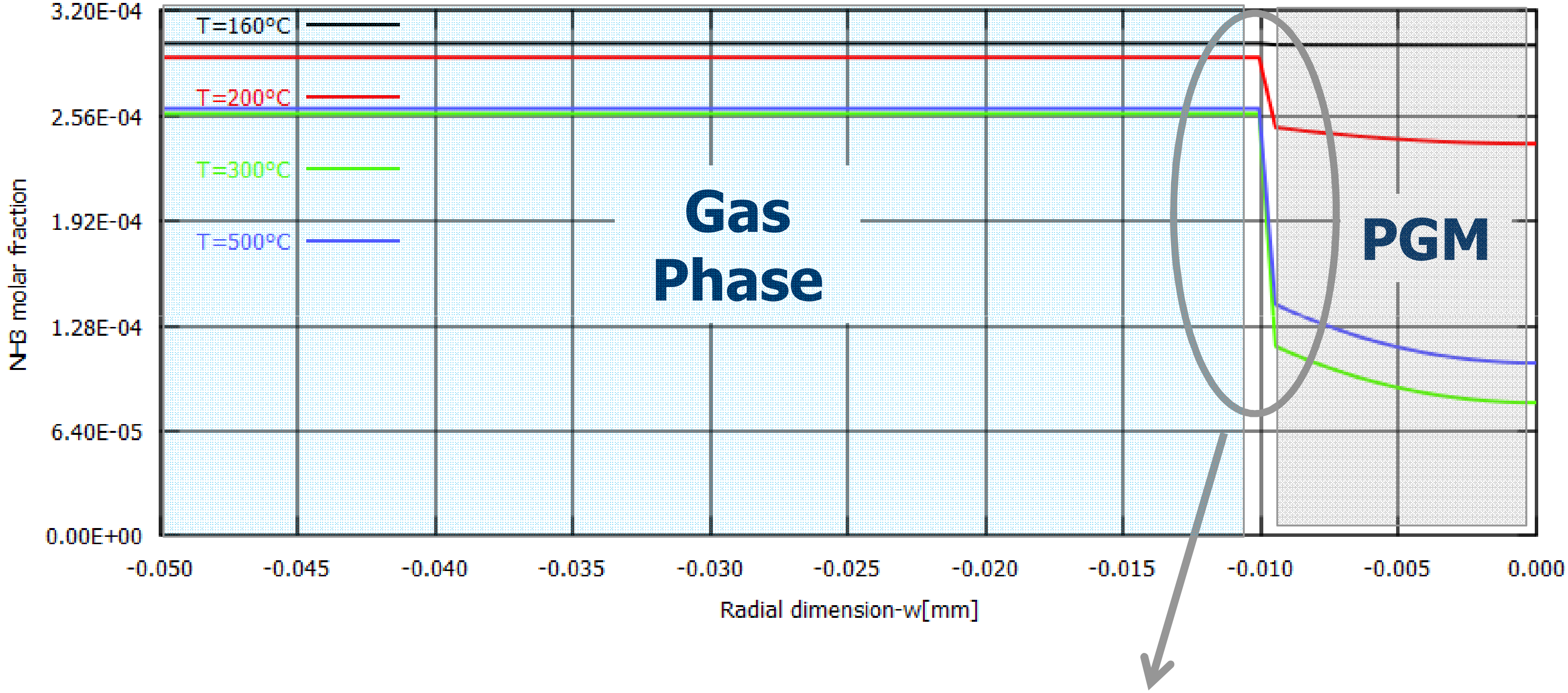
PGM layer: role of interphase mass transfer

NH_3 radial concentration profile



Significant contribution of external mass transfer

Simulated conditions:

300 ppm NH_3, 5%O_2, GHSV = 300’000 h^{-1} ;PGM only catalyst

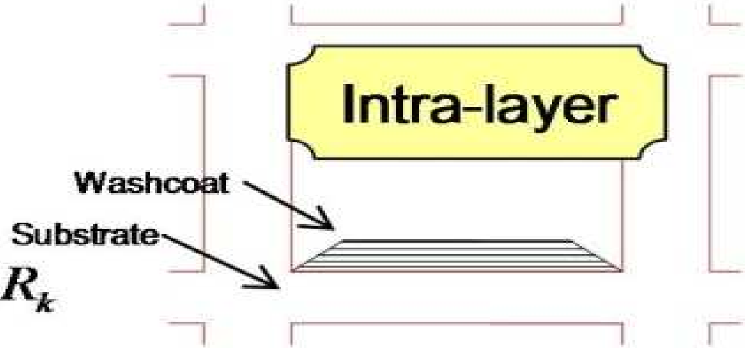
Is it necessary to model reaction/diffusion in both catalytic layers?

SCR layer → YES!!!

PGM layer → NO???

Layer+Surface (LS) approach

Mathematical Model



Washcoat:

$$-D_j \frac{\partial}{\partial x}\left(f_x \frac{\partial y_j}{\partial x} \right) = \frac{f_x}{c_m} \sum_k c_{j,k} R_k$$

Channel gas species balance:

$$\frac{\partial}{\partial z}\left(v_1 y_{1,j}\right) = \frac{1}{df_{-w}} k_{1,j}\left(y_{1s,j} - y_{1,j}\right), \qquad k_{i,j} = \frac{Sh \cdot D_{mol,j}}{d_i}$$

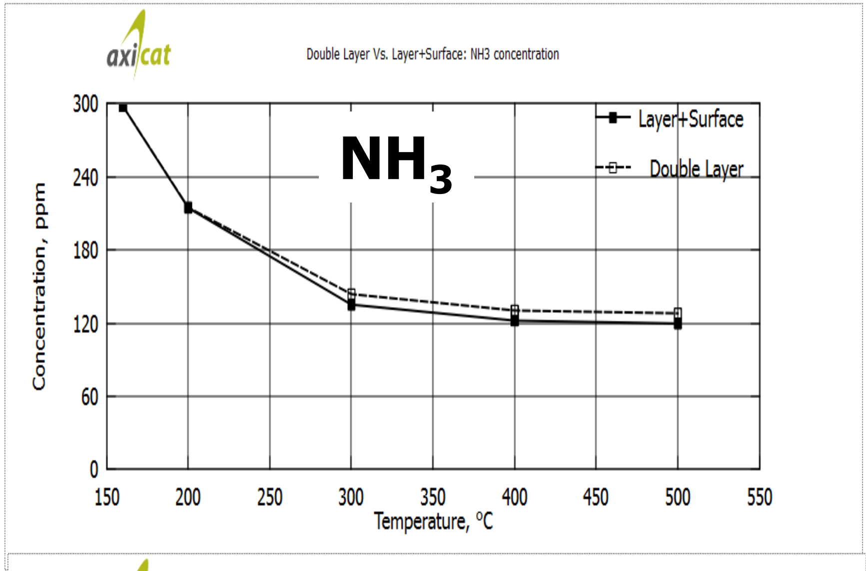
Boundary conditions:

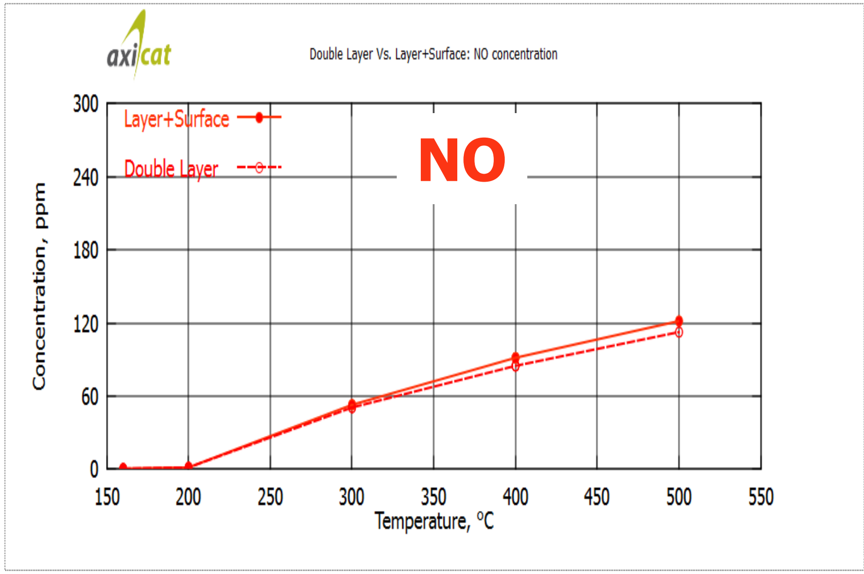
$$-D_j f_{-w} \left.\frac{\partial y_j}{\partial x}\right|_{1s} = -df_{-w}{}^2 \frac{\partial}{\partial z}\left(v_1 y_{1,j}\right)$$ → Channel/1st layer

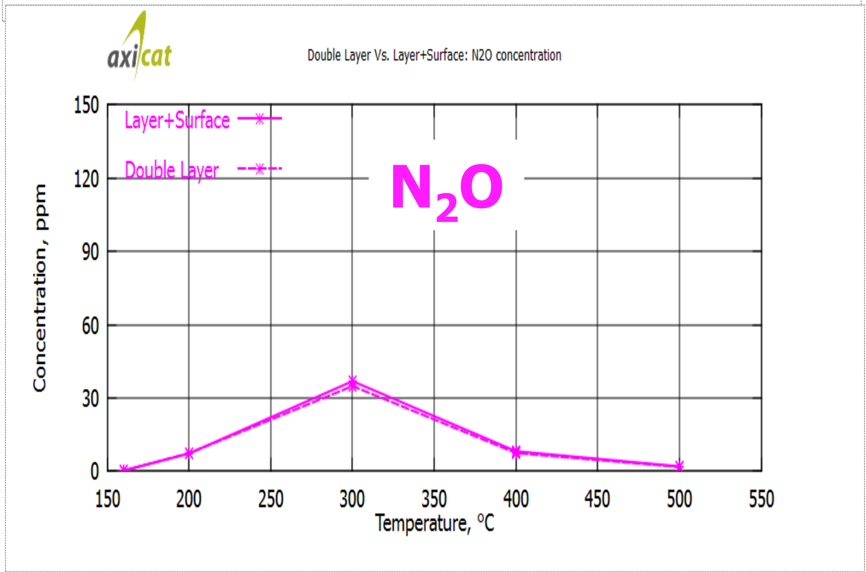
$$\left.\frac{\partial y_j}{\partial x}\right|_{2s} = -\frac{1}{D_j \cdot c_m} \sum_k c_{j,k} R_k^{PGM}$$ → 1st layer/2nd layer

$$R_k^{PGM} = R_{k,Vol}^{PGM} \cdot \frac{V}{S}$$ → **PGM rates are espressed as $mol/m^2/s$**

LS Vs. DL simulation results: NH_3/O_2







Negligible deviations between LS & DL simulations

Simulated conditions:

300 ppm NH_3, 5%O_2, GHSV = 300'000 h^{-1}

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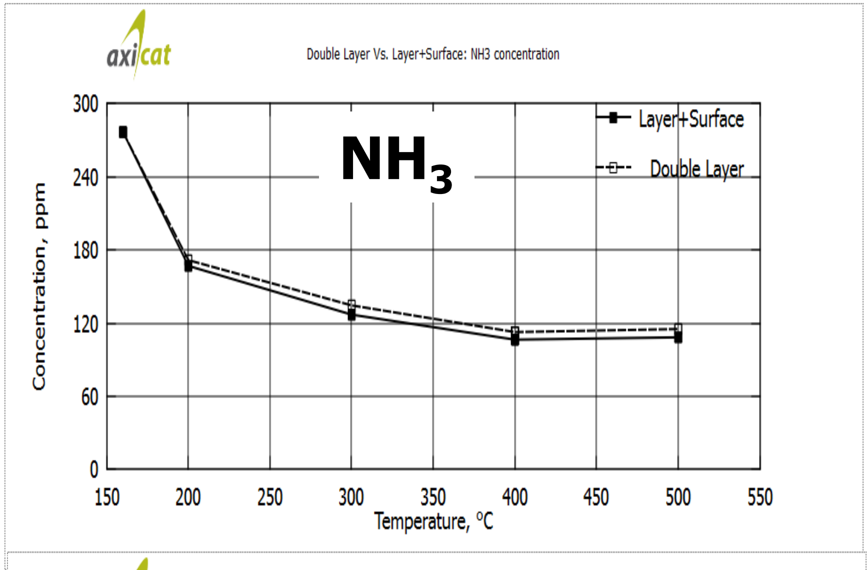
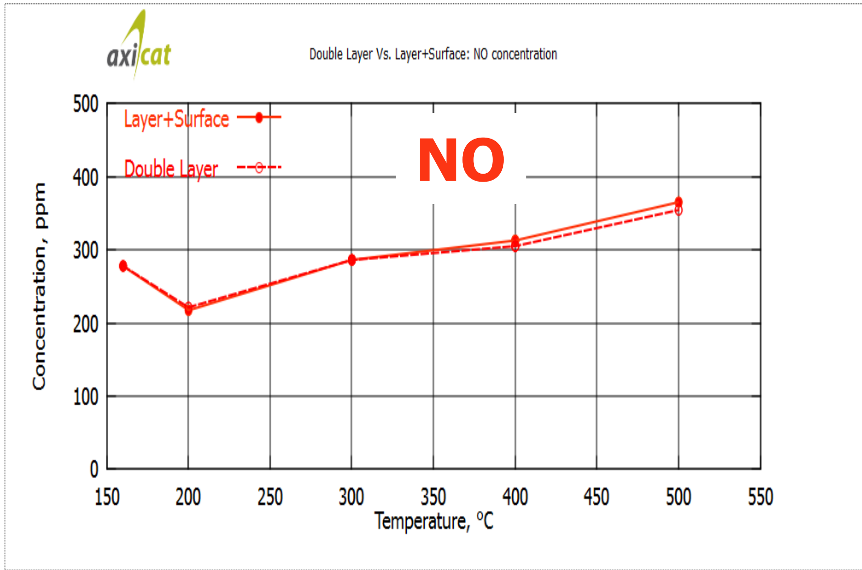
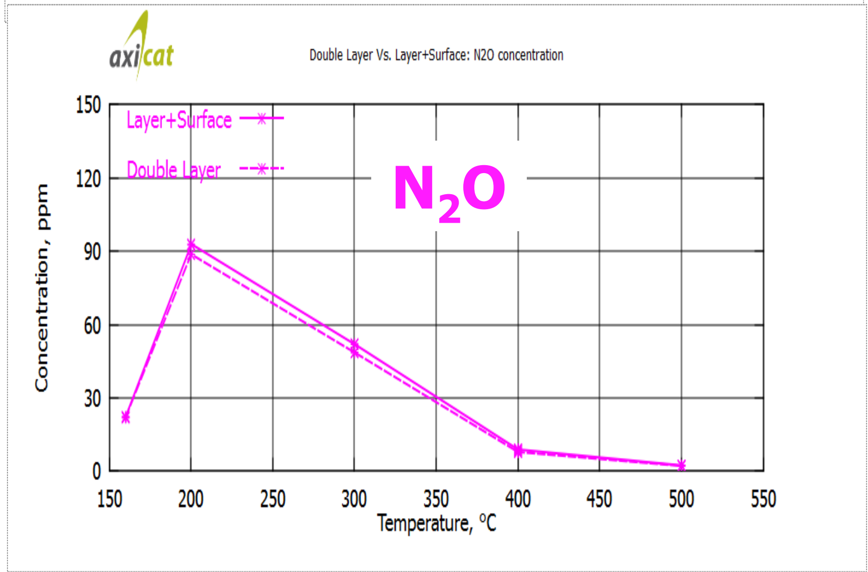
LS Vs. DL simulation results: $NH_3/NO/O_2$







Negligible deviations between LS & DL simulations

Simulated conditions:

300 ppm NH_3, 300 ppm NO, 5%O_2, GHSV = 300’000 h^{-1}

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Conclusions

1. The addition of a PGM layer beneath the SCR one leads to significant concentration gradients within the SCR layer

   ↓

   Modeling reaction/diffusion within the SCR layer is crucial
   → only a few SCR models in the literature do that
   (e.g. Chatterjee et al SAE 2007-01-1136)

2. The **PGM layer can be modeled as a catalytic surface**:
   - Extremely high reaction rates over PGM
   - Surface approach: the whole catalytic volume is concentrated at the surface → extraction of the kinetics possible with an extremely thin layer (10μm)
   - With higher loads/washcoat thickness catalyst effectiveness at T>250°C drops→ only the catalyst surface is active

3. The simplified Layer+Surface approach has been **successfully validated** against the complete Dual-Layer model

Thank you for your kind attention

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http://lat.eng.auth.gr/

http://www.lccp.polimi.it/

http://www.exothermia.com/