Modeling and Simulation of NO$_x$ Abatement with Storage/Reduction Catalysts for Lean Burn and Diesel Engines

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Introduction

- Increasing number of vehicles
- More stringent Emission Regulations (specially in Europe and California)

**Solution:** Lean operated engines → less fuel consumption

- Demand for new types of catalytic exhaust-gas aftertreatment, e.g.
  - Diesel Particle Filter (DPF)
  - Urea-SCR
  - NO$_x$-storage catalyst (NSC)

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Exhaust-gas treatment of the E 320 BLUETEC
Introduction

Exhaust-gas treatment of the E 320 BLUETEC

Advanced DeNO\textsubscript{x} catalytic converter

Source: DaimlerChrysler
Function of the NO\textsubscript{x} Storage and Reduction Catalyst

Lean phase – O\textsubscript{2} rich

Rich phase – O\textsubscript{2} deficit
Model Specifications

- Well-defined Model Catalysts: Pt/Al₂O₃ and Pt/Ba/Al₂O₃
- Dimension: 3 cm (Width), 20 cm (Length)
- Realistic Exhaust-gas Composition:

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<tbody>
<tr>
<td>Lean</td>
<td>200</td>
<td>40</td>
<td>12</td>
<td>60</td>
<td>0.04</td>
<td>7</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>Rich</td>
<td>200</td>
<td>40</td>
<td>0.9</td>
<td>60</td>
<td>2.1</td>
<td>7</td>
<td>10</td>
<td>0.7</td>
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- Isothermal Flatbed Reactor
- NOₓ Long-Term Storage Experiments
- Lean/Rich Cycling 300s/15s and 60s/5s (realistic time scale)
- SV= 40000 h⁻¹
- T= 250 - 450°C
TEM-Images of Platinum and Barium Particles

Pt/Ba/Al₂O₃ Catalyst (aged: 4h, 700°C, 10% H₂O)
Hierarchical Modeling of a NSC

Courtesy of J. Eberspächer GmbH& Co
Simulation Program DETCHEM

Storage Mechanism
RESERVOIR
1d-Concentration profile of the storage media (transient, isothermal)

CHANNEL
2D Steady-State Profile for a Laminar Flow using Boundary-Layer-Approx.

Washcoat-Models (optional)

DETCHEM-Library
Reaction Mechanisms
Thermodynamic Properties
Transport Coefficients

Model Level

microscopic

0d
Complexity
2d / 3d

macroscopic

### Elementary-step Mechanism on Platinum

#### HC-decomposition:
- $\text{C}_3\text{H}_6 + 2* \leftrightarrow \text{C}_3\text{H}_6^*$
- $\text{C}_3\text{H}_6^* \leftrightarrow \text{C}_3\text{H}_5^* + \text{H}^*$
- $\text{C}_3\text{H}_5^* + * \leftrightarrow \text{C}_2\text{H}_3^* + \text{CH}_2^*$
- $\text{CH}_3^* + * \leftrightarrow \text{CH}_2^* + \text{H}^*$
- $\text{CH}_2^* + * \leftrightarrow \text{CH}_3^* + \text{H}^*$
- $\text{CH}^* + * \leftrightarrow \text{C}^* + \text{H}^*$
- $\text{C}_2\text{H}_3^* + \text{O}^* \leftrightarrow \text{CH}_3\text{CO}^*$
- $\text{CH}_3\text{CO}^* + * \leftrightarrow \text{CH}_3^* + \text{CO}^*$
- $\text{CH}_3^* + \text{O}^* \leftrightarrow \text{OH}^* + \text{CH}_2^*$
- $\text{CH}_2^* + \text{O}^* \leftrightarrow \text{OH}^* + \text{CH}^*$
- $\text{CH}^* + \text{O}^* \leftrightarrow \text{OH}^* + \text{C}^*$
- $\text{C}_3\text{H}_6 + * + \text{O}^* \leftrightarrow \text{C}_3\text{H}_5^* + \text{OH}^*$

#### C-O-Reaction:
- $\text{C}_3\text{H}_4^* + 4\text{O}^* + 2 * \rightarrow 3\text{C}^* + 4\text{OH}^*$
- $\text{CO} + * \leftrightarrow \text{CO}^*$
- $\text{CO}_2 + * \leftrightarrow \text{CO}_2^*$
- $\text{CO}^* + \text{O}^* \leftrightarrow \text{CO}_2^* + *$
- $\text{C}^* + \text{O}^* \leftrightarrow \text{CO}^* + *$

#### N-O-Reaction:
- $2\text{N} \rightarrow \text{N}_2 + 2$
- $\text{NO} + \text{O}^* \leftrightarrow \text{NO}_2^*$
- $\text{NO}^* + \text{O}^* \leftrightarrow \text{NO}_2^*$
- $\text{NO}^* + \text{N}^* \leftrightarrow \text{N}_2\text{O}^*$
- $\text{NO}^* + \text{H}^* \leftrightarrow \text{N}^* + \text{OH}^*$
- $\text{NO}_2^* + \text{H}^* \leftrightarrow \text{NO}^* + \text{OH}^*$


**70 Elementary-step Reactions with 35 surface species and 10 gas-phase species**

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**Hydrocarbons**

**Carbon monoxide**

**Nitric oxide**
Development of heterogeneous reaction mechanisms

Surface science studies (TPD, XPS, AES, TEM, FEM, FIM, STM, SFG …)

Analogy to gas phase kinetics, organometallics

Theory (ab-intio, DFT, BOC-MP, UBI-QEP, TS, Collision)

Mechanism (Idea)

Lab experiments (conversion, selectivity, ignition/extinction temperatures, spatial & temporal profiles, coverages)

Modeling of lab reactors (including appropriate models for gas phase kinetics and heat & mass transport)

Comparison of measured and computed data

Sensitivity analysis & Evaluation of crucial parameters

Reliable mechanism
Lean/Rich Cycle (300s/15s) and Axial Profiles for Pt/Al₂O₃

250°C

Simulation
Experiment

350°C

450°C

NO₂
NO
C₃H₆

NO Mole Fraction
NO₂ Mole Fraction
C₃H₆ Mole Fraction
Simulated Surface Coverages on Platinum

Model enables the prediction of the concentration profiles along the channel length and gives detailed insight into the surface coverages of the lean/rich phase.
Storage Reactions on Barium

- \( \text{BaCO}_3 + 2\text{NO}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{Ba(NO}_3)_2 + \text{CO}_2 \)
- \( \text{BaCO}_3 + 2\text{NO} + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{Ba(NO}_2)_2 + \text{CO}_2 \)
  \( \text{Ba(NO}_2)_2 + \text{O}_2 \rightarrow \text{Ba(NO}_3)_2 \)
- \( \text{BaCO}_3 + 3\text{NO}_2 \rightleftharpoons \text{Ba(NO}_3)_2 + \text{NO} + \text{CO}_2 \)

Modeled as Global Reactions with Shrinking Core Model, due to Diffusion Limitation during Storage Process
Shrinking Core Model with an Inactive Core

\[ R_{\text{diff}} = 4\pi r^2 \ast D_S \ast \frac{\partial C}{\partial r} \]

At the interface Nitrate-Carbonate: \( r = r_{\text{Nitrate}} \)

\[ \dot{r}_{\text{NO}_2-O_2-Ba} \ast A_{\text{Particle}} = R_{\text{diff}} \]

Shrinking Core Model with an Inactive Core

\[ \frac{1}{2} \text{BaCO}_3 + \text{NO}_2 + \frac{1}{4} \text{O}_2 \Leftrightarrow \frac{1}{2} \text{Ba(NO}_3)_2 + \frac{1}{2} \text{CO}_2 \]

\[ \dot{r}_{\text{NO}_2-\text{O}_2-\text{Ba}} = \tilde{k}_f * c_{\text{NO}_2} * c_{\text{O}_2}^{1/4} * \Theta_{\text{BaCO}_3} - \tilde{k}_b * c_{\text{CO}_2}^{1/2} * \Theta_{\text{Ba(NO}_3)_2} \]

Rate coefficients

\[ \tilde{k}_f = \frac{k_f}{1 + k_f \cdot \tau} \]

\[ \tilde{k}_b = \frac{k_b}{1 + k_f \cdot \tau} \]

\[ k_f = A_f \cdot T^\beta \cdot e^{\frac{E_{a,f}}{RT}} \]

\[ k_b = \frac{k_f}{K_{\text{eq}}^{\text{NO}_2-\text{O}_2-\text{Ba}}} = \exp\left(-\frac{\Delta_{\text{RH}}}{RT} + \frac{\Delta_{\text{RS}}}{R}\right) \]

Inhibition term:

\[ \tau = \frac{l}{D_S} * \frac{r_{\text{Nitrat}}}{r_{\text{tot}}} \]

→ Increasing inhibition term gives rise to a decreased rate coefficient
Reduction Reactions on Barium

- **Carbon Monoxide CO**
  \[
  \text{Ba(NO}_3\text{)}_2 + 3 \text{ CO} \rightarrow \text{BaCO}_3 + 2 \text{ NO} + 2 \text{ CO}_2
  \]

- **Hydrogen H\textsubscript{2}**
  \[
  \text{Ba(NO}_3\text{)}_2 + 3\text{H}_2 + \text{CO}_2 \rightarrow \text{BaCO}_3 + 2\text{NO} + 3\text{H}_2\text{O}
  \]

- **Propylene C\textsubscript{3}H\textsubscript{6}**
  \[
  \text{Ba(NO}_3\text{)}_2 + \frac{1}{3}\text{C}_3\text{H}_6 \rightarrow \text{BaCO}_3 + 2\text{NO} + \text{H}_2\text{O}
  \]

*Modeled without Shrinking Core Model, no Diffusion Limitation during Regeneration*
Parameterization of Storage/Reduction Reactions on Pt/Ba/Al₂O₃

NOₓ Long-Term Storage Experiments

Simulation
Experiment

Lean/Rich Cycling
300s/15s

→ Parameterization of the Storage Reactions on LTS Experiments and Parameterization of the Reduction Reaction on Lean/Rich Cycles
Lean/Rich Cycle (60s/5s) for Pt/Ba/Al₂O₃ at 350°C

Good agreement between simulations and experiments for both lean/rich cycling and axial profiles.
Lean/Rich Cycling (60s/5s) for Pt/Ba/Al₂O₃

- First three cycles in a row at different temperatures
- Input conditions of 2nd and 3rd are the surface coverages of the previous cycle
- Model is able to predict concentrations profiles even for incomplete regeneration (250 and 350°C)
- Problems with NO regeneration peak at 450°C
Predicted Fraction with $\text{Ba(NO}_3\text{)}_2$ on Pt/Ba/Al$_2$O$_3$ (2. Cycle)

- Predicted fractions during the 2nd lean/rich cycle along the channel length and as a function of cycling time
- Incomplete regeneration at lower temperatures
- Increasing nitrate fraction due to storage reactions
- Non-uniform nitrate distribution along the catalyst length
- Sharp decrease in the nitrate fraction indicates regeneration

$\Rightarrow$ **Model enables detailed insight into the barium nitrate distribution for a simple NSC at various temperatures**
Summary and Conclusion

Summary:
- 2d and transient Model of a NO$_x$-Storage Catalyst
- Effectiveness Factor Washcoat Model
- Realistic Exhaust-gas Composition
- Detailed Reaction Mechanism on the Noble Metal
- Shrinking Core Model for the Storage of Nitrogen Oxides on Barium

Outlook:
- Development and implementation of an Oxygen Storage Model on Ceria
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Thank You
For your Attention