Model Development and its Application for a Cu-CHA Catalyst

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CLEERS 2019: September 17-19th, 2019, Ann Arbor, USA

18.09.2019
Cu-CHA Challenge: Ammonium Nitrate

"One challenge of SCR catalysts at temperatures below 200°C is that ammonium nitrate accumulates on Cu-zeolite catalysts."

– US DOE 2017 Annual Merit Review
Cu-CHA Challenge: Ammonium Nitrate

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Overview of Presentation

- SCR mechanism with nitrates
- Validate predicted amount of amm. nitrate
- Demonstrate increased SCR performance due to nitrate buffer
- Model predictability for a wide range of driving cycles (no additional calibration)
Goal: Extend Model to Include Nitrates

Current Model: Adsorption of Ammonia

- NH₃ (Ammonia)
- NH₄NO₃ (Ammonium Nitrate)

Ammonia Storage (*)

Extension: Adsorption of Nitrates

- NO₂
- NO
- HNO₃
- NO₃⁻[NH₃]
- Cu²⁺-OH
- Cu⁺

Sim (--) Exp (-)

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Mechanism

Fast SCR

Model captures steady state data

Ammonium nitrate inhibits activity at steady state

\[ 2\text{NH}_3 + 2^* \leftrightarrow 2\text{NH}_3^* \]

\[ 2\text{NO}_2 + 2\text{Cu}^{2+} - \text{OH} \leftrightarrow \text{Cu}^{2+} - \text{ONO} + \text{Cu}^{2+} - \text{NO}_3^- + \text{H}_2\text{O} \]

\[ \text{Cu}^{2+} - \text{NO}_3^- + \text{NO} \leftrightarrow \text{NO}_2 + \text{Cu}^{2+} - \text{ONO} \]

\[ 2\text{Cu}^{2+} - \text{ONO} + 2\text{NH}_3^* \rightarrow 2\text{N}_2 + 2\text{H}_2\text{O} + 2\text{Cu}^{2+} - \text{OH} + 2^* \]

\[ 2\text{NH}_3 + \text{NO} + \text{NO}_2 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O} \]
Transient NO$_2$ SCR

Model captures transients due to ammonia and nitrate storage
Predictive Simulation of WHTC

Hot WHTC, 43% NO₂/NOₓ

- Mechanism applied to driving cycle without any reparameterization
- Model predicts cumulated emissions
Predictive Simulation of WHTC

Hot WHTC, 43% NO₂/NOₓ

Space Velocity

Fast SCR

Why does so little Amm. Nitrate form during WHTC?
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How much AN forms during steady state?

Method from Ruggeri et al. (2018)

\[
\text{NH}_4\text{NO}_3 + \text{NO} \rightarrow \text{NO}_2 + 2\text{H}_2\text{O} + \text{N}_2 \quad \lambda_1
\]

\[
\text{NO} + \text{NO}_2 + 2\text{NH}_3 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O} \quad \lambda_2
\]

\[
\text{NO}_{\text{in}} - \text{NO}_{\text{out}} = \lambda_1 + \lambda_2
\]

\[
\text{NO}_{2,\text{out}} = \lambda_1 - \lambda_2
\]

\[
\text{AN react} = \lambda_1
\]
How much AN forms during steady state?

**Steady State AN Formation at 200°C, α = 1**

\[ \text{Cul}^2+ - \text{OH} + \text{NO} + \text{NH}_3^+ \rightarrow \text{N}_2 + 2\text{H}_2\text{O} + \text{Cu}^+ \]
How much AN forms during cold WHTC?

1st Cold WHTC, 60% NO₂/NOₓ

- Exp. Inlet (0.73 g)
- Exp. Outlet (0.02 g)
- Model Outlet (0 g)

2nd Cold WHTC, 60% NO₂/NOₓ

- Exp. Inlet (0.53 g)
- Exp. Outlet (0.14 g)
- Model Outlet (0.17 g)

Complete ammonium nitrate titration here
WHTC Performance at Engine, SGB, Sim.

5.9%
WHTC Performance at Engine, SGB, Sim.
How much AN forms during cold WHTC?

1st Cold WHTC, 60% NO$_2$/NO$_x$

- Exp. Inlet (0.73 g)
- Exp. Outlet (0.02 g)
- Model Outlet (0 g)

- Exp. Inlet (0.53 g)
- Exp. Outlet (0.14 g)
- Model Outlet (0.17 g)

- Exp. Inlet (1.24 g)
- Exp. Outlet (0.16 g)
- Model Outlet (0.16 g)

- Exp. Outlet (0.09 g)
- Model Outlet (0.10 g)

Complete ammonium nitrate titration here

19 mol/m$^3$ amm. nitrate measured
How much AN forms during cold WHTC?

1st Cold WHTC, 60% NO₂/NOₓ

- Used driving cycle test bench to validate that little ammonium nitrate forms during cold WHTCs with high NO₂/NOₓ
Overview of Presentation

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Changing NO$_2$/NO$_x$ Conditions

- 25% NO$_2$/NO$_x$
- 75% NO$_2$/NO$_x$
- 25% NO$_2$/NO$_x$

(A) Concentration (ppm)

(B) NO$_x$ Conversion (%)
Changing NO$_2$/NO$_x$ Conditions

3 minute step change, 200°C

![Graph showing NO and NO$_2$ concentrations over time](image)

![Diagram showing chemical reactions](image)

![Graph showing ammonium nitrate concentration vs. NO$_2$/NO$_x$ ratio](image)
Changing NO$_2$/NO$_x$ Conditions

30 second step change, 200°C
Why does little AN form during WHTC?

- Cu-CHA can act as a buffer during fluctuating NO₂/NOₓ ratios
- Little ammonium nitrate forms owing to fluctuating NO₂/NOₓ conditions
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Driving Cycle Prediction at Engine: ETC

NH₃ Exp: 96.4%
NH₃ Sim: 92.3%

NOₓ Exp: 98.6%
NOₓ Sim: 96.3%
Driving Cycle Prediction at Engine: WNTE

- NH₃ Exp: 90.2%
  NH₃ Sim: 86.7%

- NOₓ Exp: 99.1%
  NOₓ Sim: 97.1%
Driving Cycle Prediction

**Graph 1:**
- Y-axis: NO\textsubscript{x} Conv. (%)
- X-axis: Engine Model
- Data points for SGB Model and Engine Model are shown for different engine models.

**Graph 2:**
- Y-axis: N\textsubscript{2}O Out (g)
- X-axis: Test cycles (cWHTC1, cWHTC1, hWHTC 1, hWHTC 2, hWHTC 3, WNTE 3, FTP 3, ETC 3)
- Data points for SGB: WC Loading A (400/4) and Engine (WC Loading B, 600/3) are shown.
Driving Cycle Prediction

Ammonia Dosing Strategy

<table>
<thead>
<tr>
<th>NOx Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp.</td>
</tr>
<tr>
<td>α = 1.2</td>
</tr>
<tr>
<td>NH₃ Dosing</td>
</tr>
</tbody>
</table>

- Model applied to optimize entities of look-up table for simple feedback controller
- Model predicts increase in NOₓ conversion for new dosing strategy

Ammonia dosing strategy published as:
Summary & Conclusions

• Developed dual-site mechanism that captures SCR dynamics

• Demonstrated & validated that a minimal amount of ammonium nitrate forms during WHTC compared to steady state
  • Ammonium nitrate is not inhibitive during driving cycles
  • Nitrates act as buffer during fluctuating NO₂/NOₓ conditions

• Model predicts wide range of driving cycles for Cu-CHA catalysts (different washcoat loadings & cpsi) without any additional recalibration
Acknowledgements

Collaboration
• Dr. Robert E. Hayes (University of Alberta)
• Dr. Martin Votsmeier (Umicore AG & Co. KG)
• Dr. Alexander Scheuer (Umicore AG & Co. KG)

Funding
• NSERC Collaborative Research and Development (CRD) program (Canada)
• Umicore AG & Co. KG