Selective Catalytic Reduction of NO$_x$ with NH$_3$ over Cu-ZSM-5 – The Effect of Changing the Gas Composition

Hanna Sjövall$^a$, Richard J. Blint$^b$, Steven J. Schmiegb and Louise Olsson$^a$

$^a$Competence Centre for Catalysis
Chalmers University of Technology, Sweden

$^b$General Motors R&D Center, Chemical and Environmental Sciences Laboratory, Warren
Acknowledgements

We would like to acknowledge helpful discussions with Se Oh, Ed Bissett, Jong-Hwan Lee, Byong Cho of the General Motors Research and Development Center.
Objective

Evaluate $\text{NO}_x$ reduction of Cu-ZSM-5 with ammonia as the reductant for the development of an automotive converter kinetic model.
Catalyst preparation

<table>
<thead>
<tr>
<th>Zeolite powder</th>
<th>SiO$_2$/Al$_2$O$_3$</th>
<th>Primary crystal length (µm)</th>
<th>Copper ion exchange level (Cu/Al)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-ZSM5-27</td>
<td>27</td>
<td>1-3</td>
<td>-</td>
</tr>
<tr>
<td>Na-ZSM5-27</td>
<td>27</td>
<td>1-3</td>
<td>-</td>
</tr>
<tr>
<td>Cu-ZSM5-27</td>
<td>27</td>
<td>1-3</td>
<td>0.35</td>
</tr>
<tr>
<td>Cu-ZSM5-55</td>
<td>55</td>
<td>3-5</td>
<td>0.27</td>
</tr>
<tr>
<td>Cu-ZSM5-300</td>
<td>300</td>
<td>&lt;10</td>
<td>0.10</td>
</tr>
</tbody>
</table>

- Ion exchange from H$^+$ via Na$^+$ to Cu$^{2+}$
- **Catalysts coating:**
  - Monolith samples with $\approx$ 16.5 wt.-% washcoat
  - Washcoat composed of 80 % zeolite, 20 % binder (boehmite)
Effect of copper ion exchange

- Copper increases the overall activity
- Copper significantly increases the low temperature activity

Feed mixture:
- 500 ppm NO
- 500 ppm NH₃
- 8 % O₂

SV ≈ 18 400 h⁻¹

Sjövall et al. Accepted for publication in Appl. Catal. B: Environmental 2006
Effect of SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio

- Lower SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} (27) has the highest NO conversion
- Lower SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratios have the highest number of active sites

**Feed mixture:**
- 500 ppm NO
- 500 ppm NH\textsubscript{3}
- 8 % O\textsubscript{2}

Sjövall et al. Accepted for publication in Appl. Catal. B: Environmental 2006
Comparison to supplier catalysts

Chalmers catalyst

Chalmers Cu-ZSM-5 catalyst shows similar activity as supplier Cu-zeolite catalysts and lower N$_2$O formation

Steven J. Schmieg and Jong-Hwan Lee
SAE 2005-01-3881
NO oxidation
- Effect of water

• NO oxidation important for SCR activity
• Water inhibits the oxidation rate

Sjövall et al. Accepted for publication in Appl. Catal. B: Environmental 2006
NH$_3$ oxidation
- Effect of water

- NH$_3$ oxidation becomes important at high temperatures
- Water inhibits the oxidation rate

Sjövall et al. Accepted for publication in Appl. Catal. B: Environmental 2006
SCR activity and influence of H₂O

Water enhances the SCR activity at both high and low temperatures.

Sjövall et al. Accepted for publication in Appl. Catal. B: Environmental 2006
Effect of NH₃ concentration

- High ammonia concentrations limit the NOₓ conversion
- Water suppresses the inhibition effect

Sjövall et al. Accepted for publication in Appl. Catal. B: Environmental 2006
Effect of NO or NH$_3$ Concentration on NO$_x$ Conversion at 350°C

- A: Increasing ammonia concentrations
- B: Increasing NO concentrations
Effect of NO/NO₂ ratio

- Highest conversion is at NO/NO₂=1
- N₂O formation increases with increasing NO/NO₂ ratios

Feed mixture: 500 ppm NOₓ
500 ppm NH₃
8 % O₂
Temperature: 350°C

SV ≈ 18 400 h⁻¹
FTIR spectra of species on Cu-ZSM-5
- NO\textsubscript{x} adsorption

**Feed mixture:**
(a) 500 ppm NO
(b) 500 ppm NO and 8 % O\textsubscript{2}
(c) 500 ppm NO\textsubscript{2}

• The features between 1500 cm\textsuperscript{-1} and 1650 cm\textsuperscript{-1} can most likely be partially assigned to various nitrates
FTIR spectra of species on Cu-ZSM-5
- NH₃ adsorption

- 1458 cm⁻¹ can be assigned to NH₄⁺
- 1620 cm⁻¹ may be a combination of bands raised by both ammonia and water
- The broad feature in the 2200 – 3500 cm⁻¹ has been assigned to water
- 3600 – 3610 cm⁻¹ are assigned to OH vibrations at Brønsted acid sites

Feed mixture:
(a) 500 ppm NH₃ at 175°C
(b) 500 ppm NH₃ and 8 % O₂ at 175°C,
(c) 500 ppm NH₃ at 350°C
(d) 500 ppm NH₃ and 8 % O₂ at 350°C
FTIR spectra of species on Cu-ZSM-5
- Adsorbed species during SCR conditions at 175°C

Feed mixture:
500 ppm NO, 8 % O₂ and
300 - 700 ppm NH₃

- 300 ppm NH₃, 500 ppm NO and
8% O₂: NH₃, NH₄⁺ and NO₃⁻ on the surface
- NH₃ increases ⇒ adsorbed H₂O, NH₃ and NH₄⁺ also increases

- High NH₃ conc.: adsorbed NH₃ increases, 2200 – 3500 cm⁻¹ partly assigned to water cease to evolve, 1572 cm⁻¹ reduces: nitrite/nitrate formation decreases
⇒ NH₃ blocking effect
FTIR spectra of species on Cu-ZSM-5
- Adsorbed species during SCR conditions at 350°C

Feed mixture:
500 ppm NO, 8 % O₂ and 300 - 700 ppm NH₃

- No adsorbed ammonia on the surface, due to rapid NH₃ oxidation
- Nitrites/nitrates (1500 - 1650 cm⁻¹), water and possible OH groups on the surface
- NH₃ increases ⇒ adsorbed H₂O increases and nitrite/nitrate decreases
- No NH₃ blocking effect
FTIR spectra of species on Cu-ZSM-5 - Influence of NO/NO₂ ratio

- The three spectra are similar.
- Increased nitrite/nitrate coverage is observed with an increased NO₂ fraction.

⇒ The increased SCR activity with equimolecular amounts of NO and NO₂ can not be explained by surface species alone. It is possible that gas phase NO is needed in the SCR reaction.

Feed mixture:
(a) 500 ppm NH₃, 8 % O₂, 500 ppm NO
(b) 500 ppm NH₃, 8 % O₂, 250 ppm NO, 250 ppm NO₂
(c) 500 ppm NH₃, 8 % O₂, 500 ppm NO₂

Temperature: 350°C
Summary (1)

• Zeolite effects
  – Ion-exchange with copper greatly enhances the NO\textsubscript{x} reduction
  – \(\text{NO}_x\) conversion increases with decreasing SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio.
  – Chalmers Cu-ZSM-5 catalyst shows similar activity as supplier Cu-zeolite catalysts and lower N\textsubscript{2}O formation.

• Oxidation reactions
  – \(\text{NH}_3\) oxidation is rapid at high temperature.
  – Oxidation of NO increases with temperature and reaches equilibrium at 350\textdegree C.

• Water effects
  – Enhanced NO\textsubscript{x} reduction at both low and high temperatures.
  – Decreased NO and \(\text{NH}_3\) oxidation.

• NO/NO\textsubscript{2} ratio
  – The highest NO\textsubscript{x} conversion occurs when the concentration of NO equals NO\textsubscript{2}.
  – N\textsubscript{2}O formation increases when the NO\textsubscript{2}/NO\textsubscript{x} ratio increases.
Summary (2)

• Ammonia effects
  – At low temperature (175°C) high concentrations of ammonia blocks the NO\textsubscript{x} reduction. The inhibition is suppressed by water.
  – A high ammonia concentration compared to NO concentration results in enhanced NO\textsubscript{x} reduction at high temperature (350°C), where ammonia oxidation is rapid.

• FTIR spectroscopy
  – The adsorbed species on Cu-ZSM-5 was examined during exposure to NO, NO\textsubscript{2} or NH\textsubscript{3} and compared to the species during SCR conditions.
  – High NH\textsubscript{3} conc. at low temperature (175°C): reduces nitrite/nitrate formation ⇒ NH\textsubscript{3} blocking effect.
  – High temperature (350°C) no ammonia on the surface and no NH\textsubscript{3} blocking, due to rapid NH\textsubscript{3} oxidation.
  – The increased SCR activity with equimolecular amounts of NO and NO\textsubscript{2} can not be explained by surface species alone. It is possible that gas phase NO is needed in the SCR reaction.