

A Multi-Site Kinetic Model for NH_3 -SCR over Cu/SSZ-13

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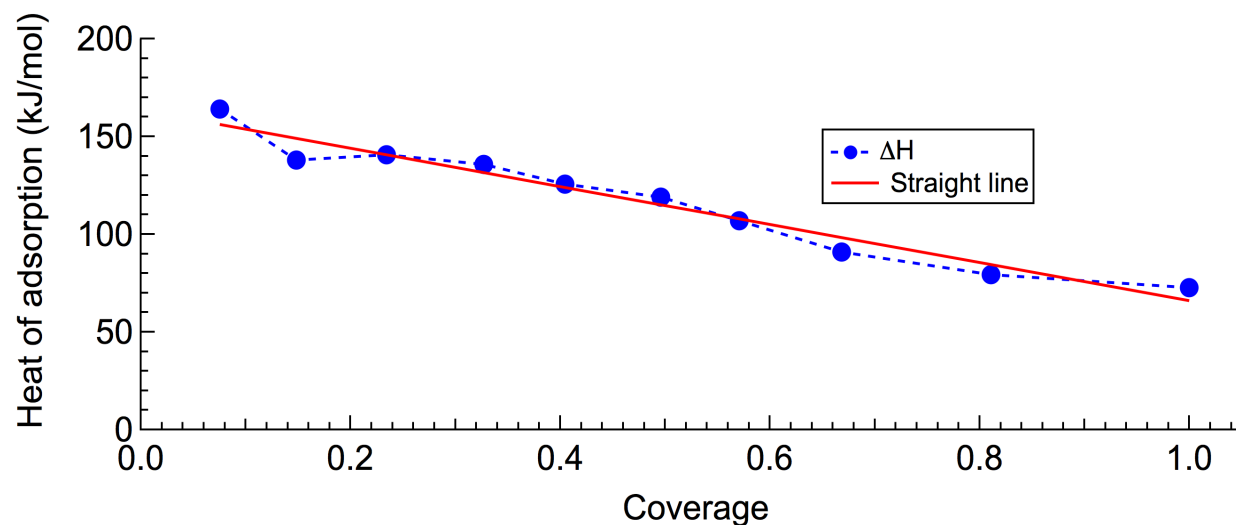
^bCummins Inc., Columbus, Indiana

Objective

The objective of this study was to develop a kinetic model for ammonia SCR over Cu/SSZ-13 in a broad temperature interval from 100 to 600°C.

Heat of adsorption of NH₃ on Cu-SSZ-13 using micro-calorimetry

- Total flow: 20 ml/min
- Catalyst mass: 100 mg
- Ammonia adsorption using 1000 ppm at each temperature
- 500, 450, 400, 350, 300, 250, 200, 150, 100, 50°C



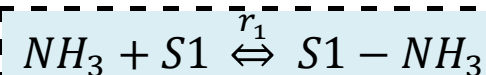
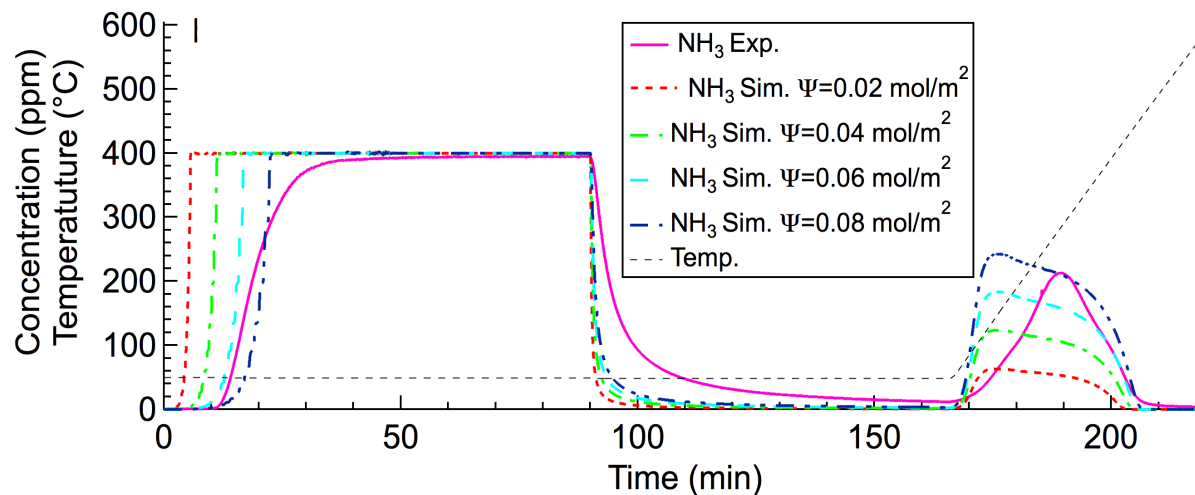
Heat of adsorption:
 $163.4 * (1 - 0.596 * \theta_{\text{NH}_3})$

Olsson et al., Appl. Catal. B: Environmental, 174 (2015) 212.

Kinetic model, NH₃ TPD at 50°C

- Heat of adsorption: $163.4 \cdot (1 - 0.596 \cdot \theta_{\text{NH}_3})$

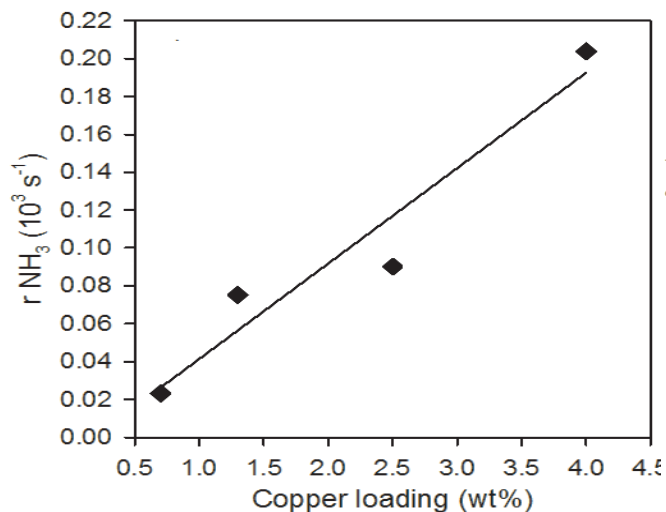
- Total flow: 3500 ml/min (30 300 h⁻¹)
- Monolith: 2 cm in length, 2.1 cm in diameter
- Ammonia adsorption using 400 ppm NH₃ + 5 % H₂O



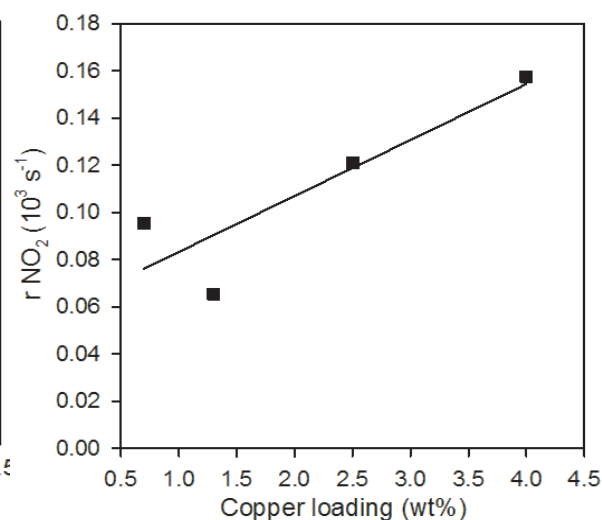
Olsson et al., Appl. Catal. B: Environmental, 174 (2015) 212.

Reaction rates versus Cu loading, Cu/BEA

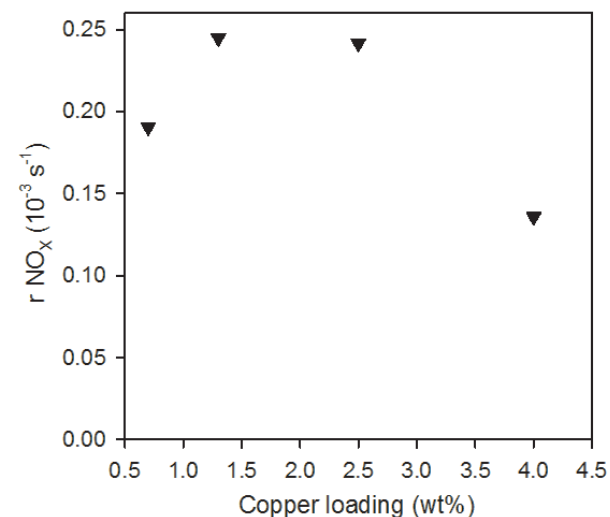
Ammonia oxidation



NO oxidation



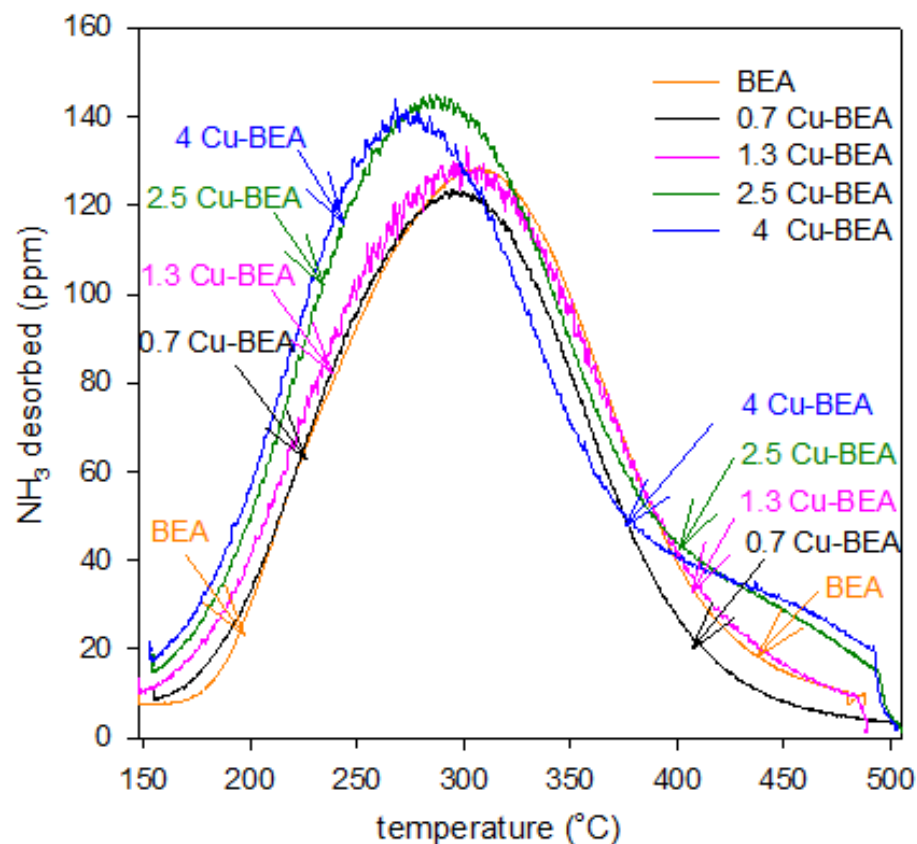
Ammonia SCR



- **Over-exchanged Cu sites are more active for ammonia and NO oxidation**
- **Low and medium loaded Cu-BEA are more active for SCR**
- **→ 2 different Cu sites**

Mihai et al. J. of Catalysis, 311 (2014) 170.

Ammonia TPD, for different Cu loading, Cu/BEA



Adsorption: 400 ppm NH₃, 5% H₂O in Ar, 150°C
Desorption: 5% H₂O in Ar, temperature ramp 10°C/min

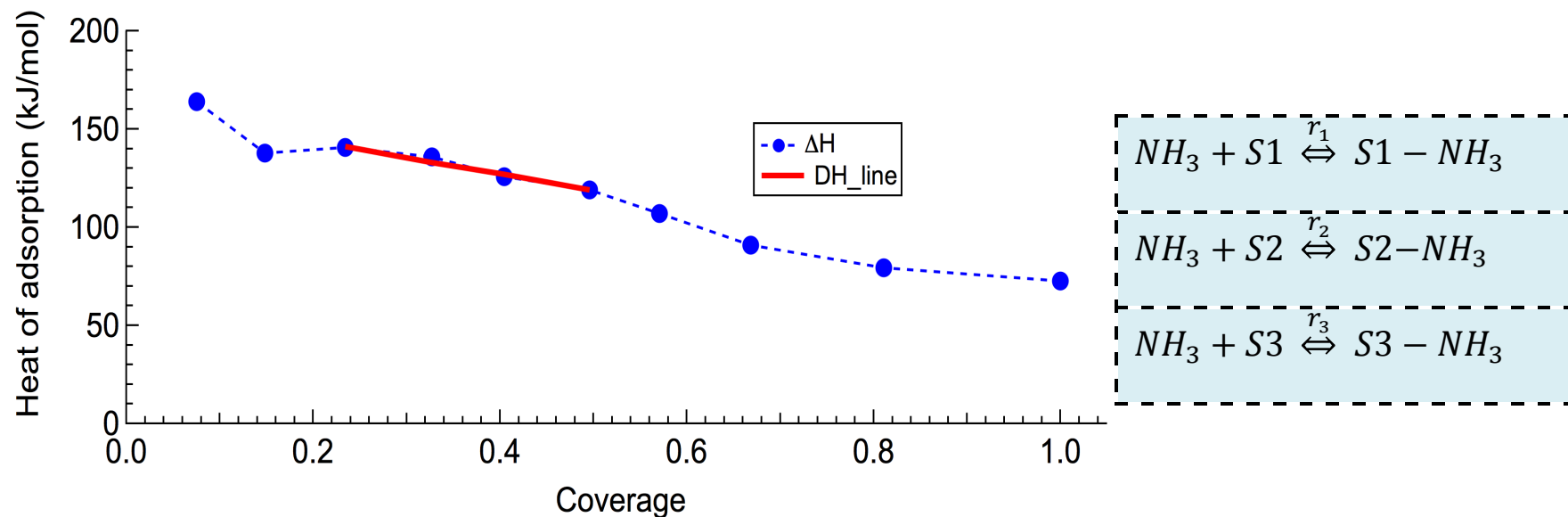
Mihai et al., J. of Catal. 311 (2014) 170.

Site description

- **S1: Copper in the six-membered rings. Lumped together with Brönsted acid sites.**
 - Main NH₃ desorption peak
- **S2: Copper in the larger cages. Lumped together with Brönsted acid sites.**
 - High temperature shoulder in the NH₃ desorption peak
- **S3: Sites for physisorption of ammonia**
 - NH₃ desorption at low temperature.

Olsson et al., Appl. Catal. B: Environmental, 174 (2015) 212.

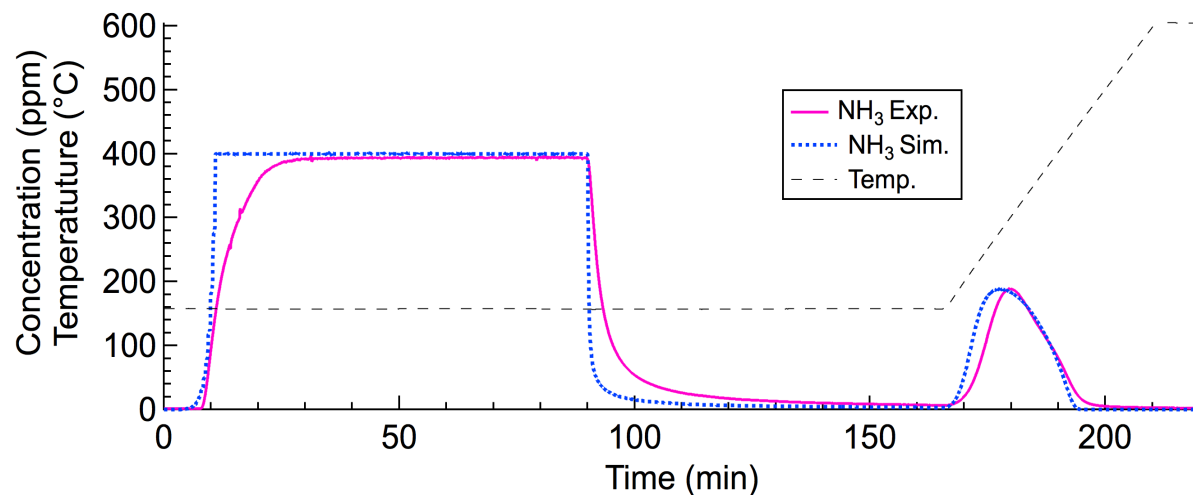
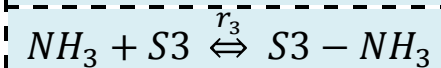
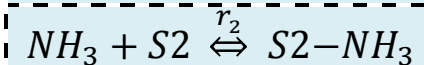
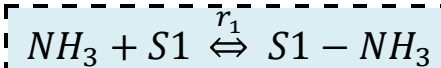
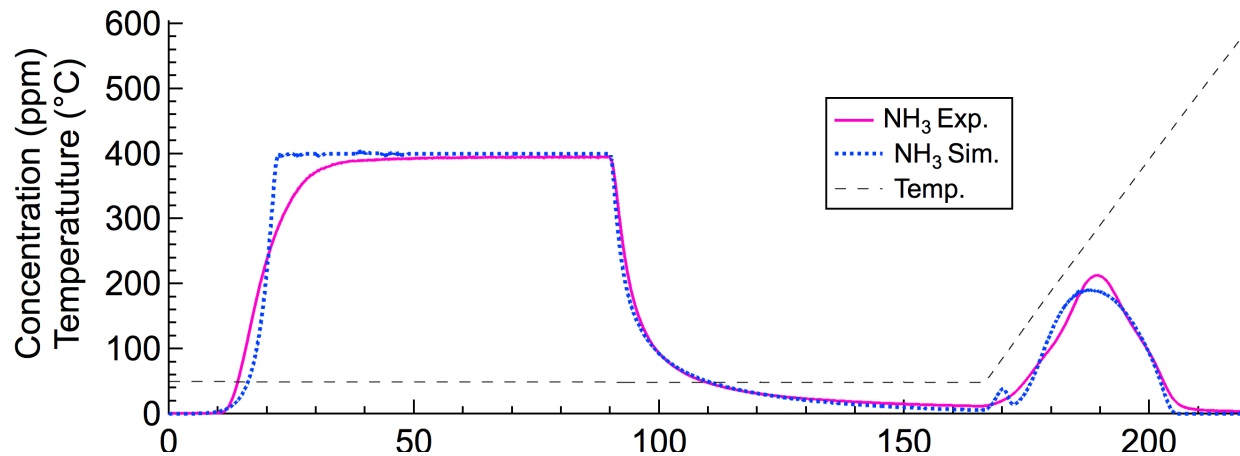
Micro calorimetry and storage model



- S1: Heat of adsorption: $149.0 \cdot (1 - 0.20 \cdot \theta_{NH_3})$
- S2: Heat of adsorption: 137.8 kJ/mol (from DSC 450°C)
- S3: Heat of adsorption: 72.6 kJ/mol (from DSC 50°C)

Olsson et al., *Appl. Catal. B: Environmental*, 174 (2015) 212.

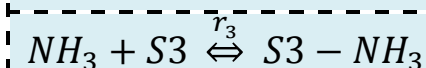
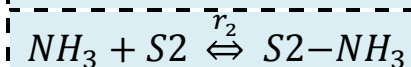
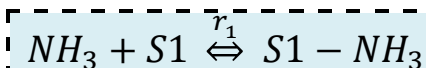
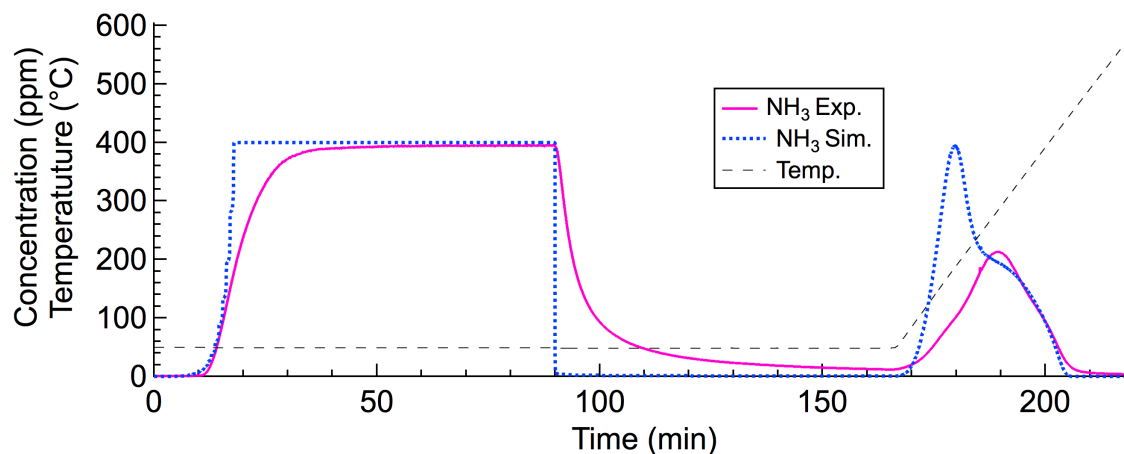
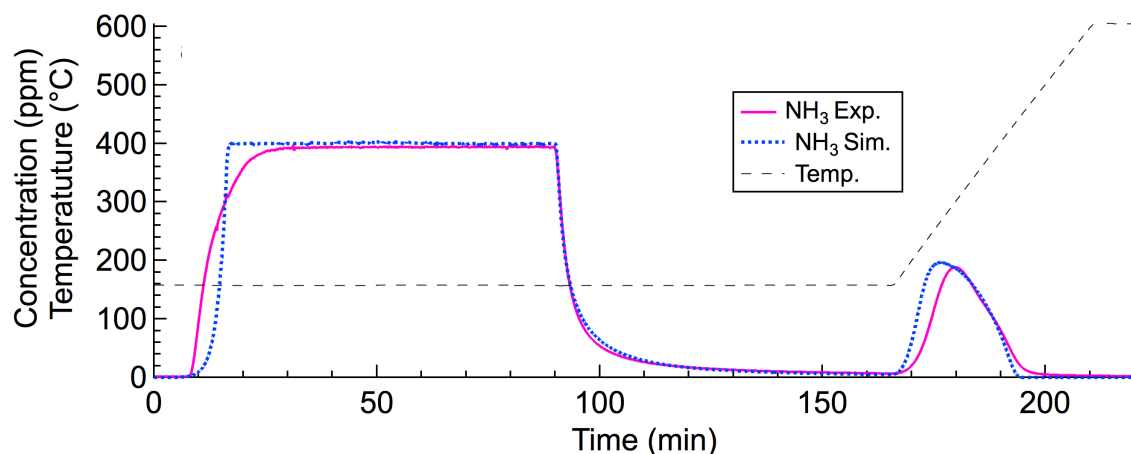
Kinetic model of NH₃ TPD



- ΔH S1:
149.0*(1-0.20* θ_{NH_3})
- ΔH S2: 137.8 KJ/mol
(from DSC 450°C)
- ΔH S3: 72.6 kJ/mol
(from DSC 50°C)

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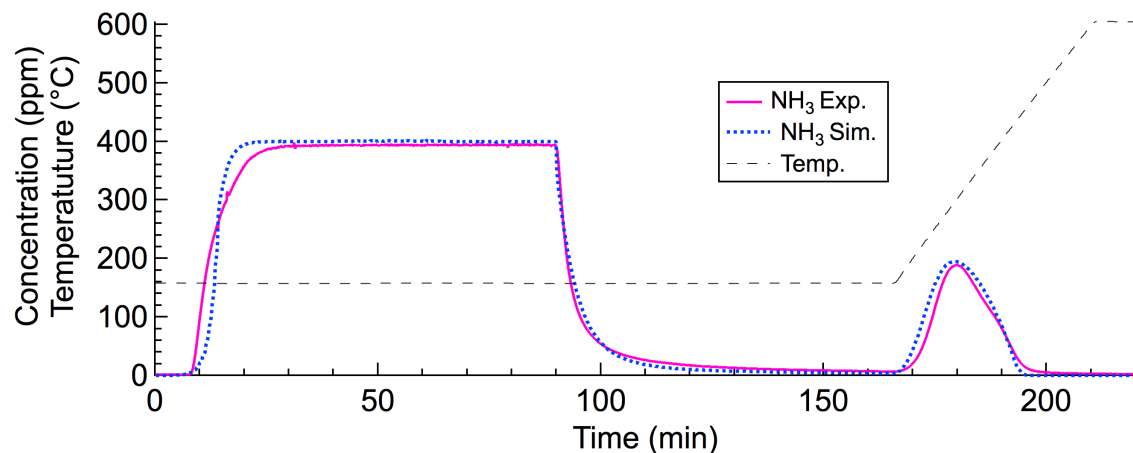
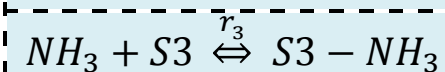
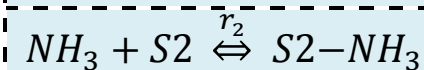
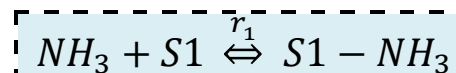
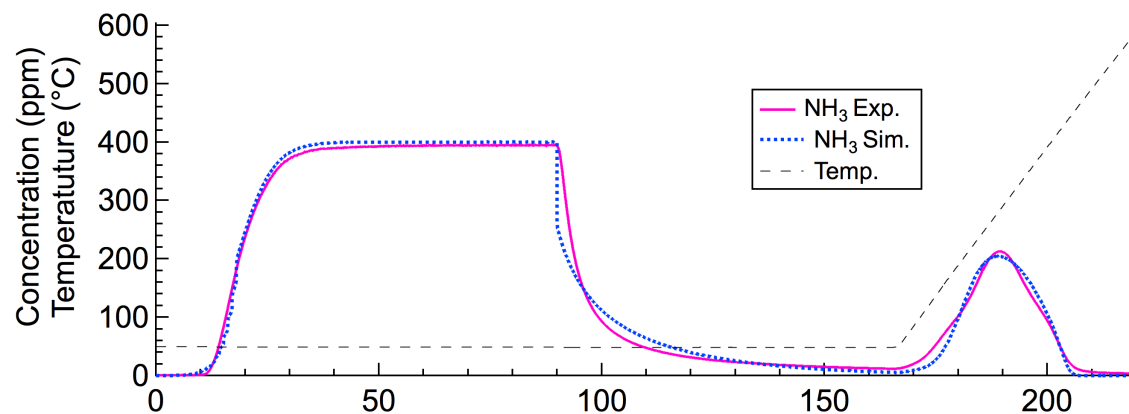
Kinetic model of NH₃ TPD



- ΔH S1:
149.0*(1-0.20* θ_{NH_3})
- ΔH S2: 137.8 KJ/mol
(from DSC 450°C)
- ΔH S3: 90.8 kJ/mol
(from DSC 150°C)

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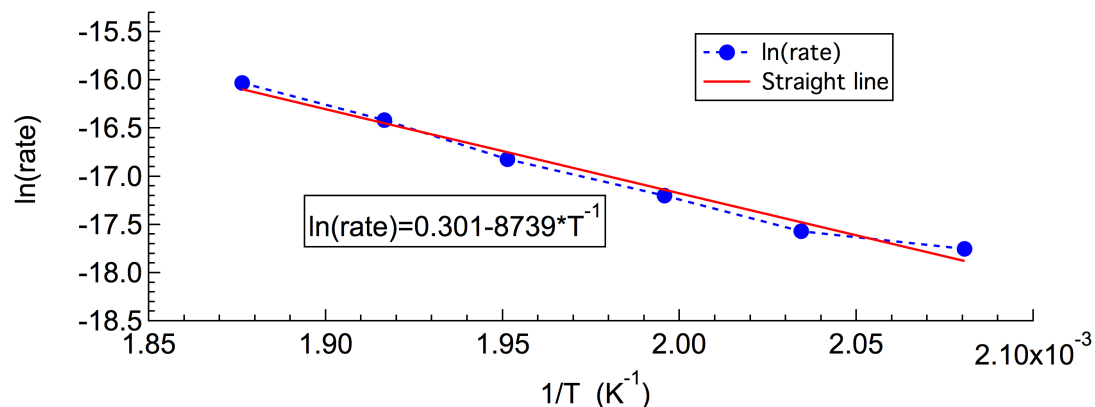
Kinetic model of NH₃ TPD



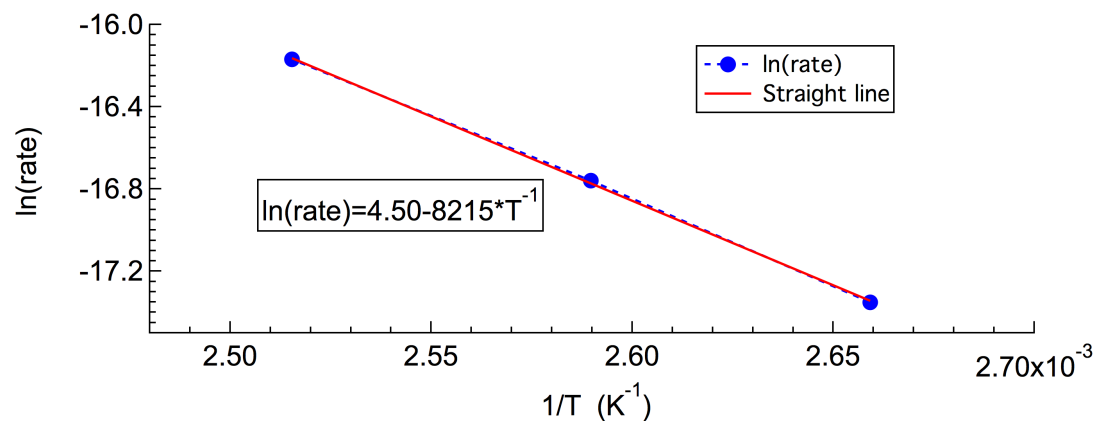
- ΔH S1:
149.0*(1-0.20* θ_{NH_3})
- ΔH S2: 137.8 kJ/mol
(from DSC 450°C)
- ΔH S3: 18.6 kJ/mol
(fitted)

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Arrhenius plots



NH_3 oxidation:
72.7 kJ/mol

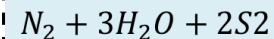
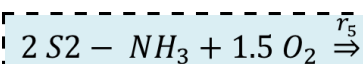
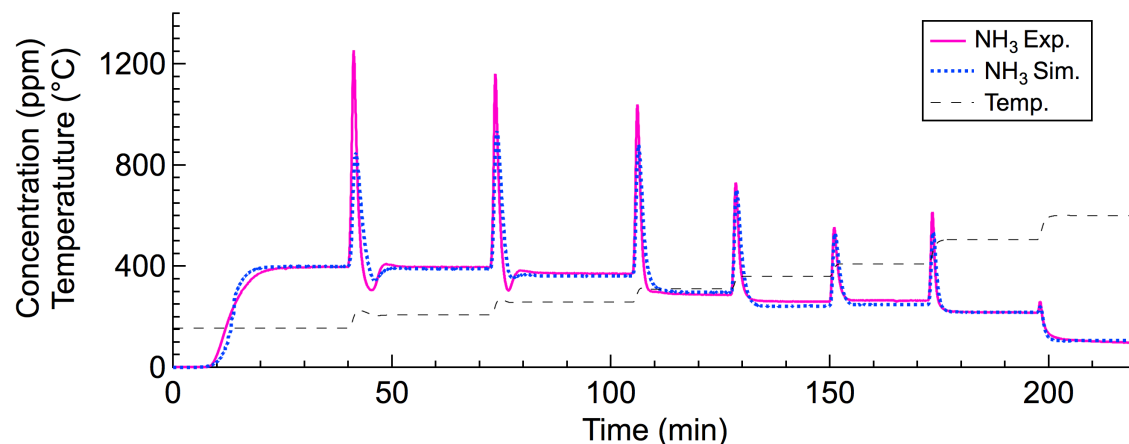
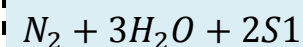
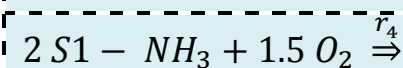
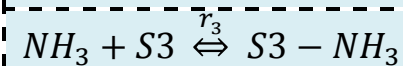
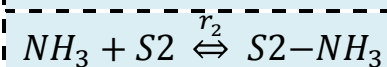
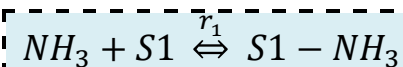
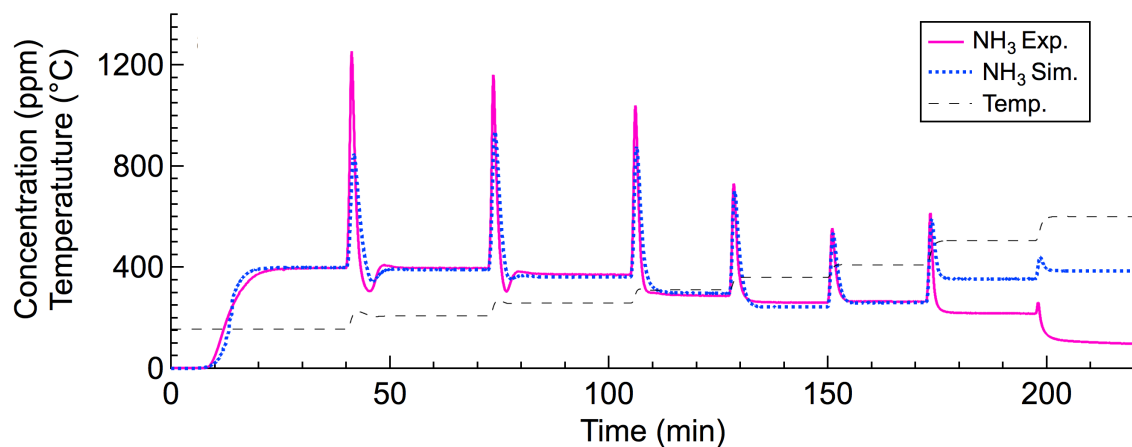


SCR:
68.3 kJ/mol

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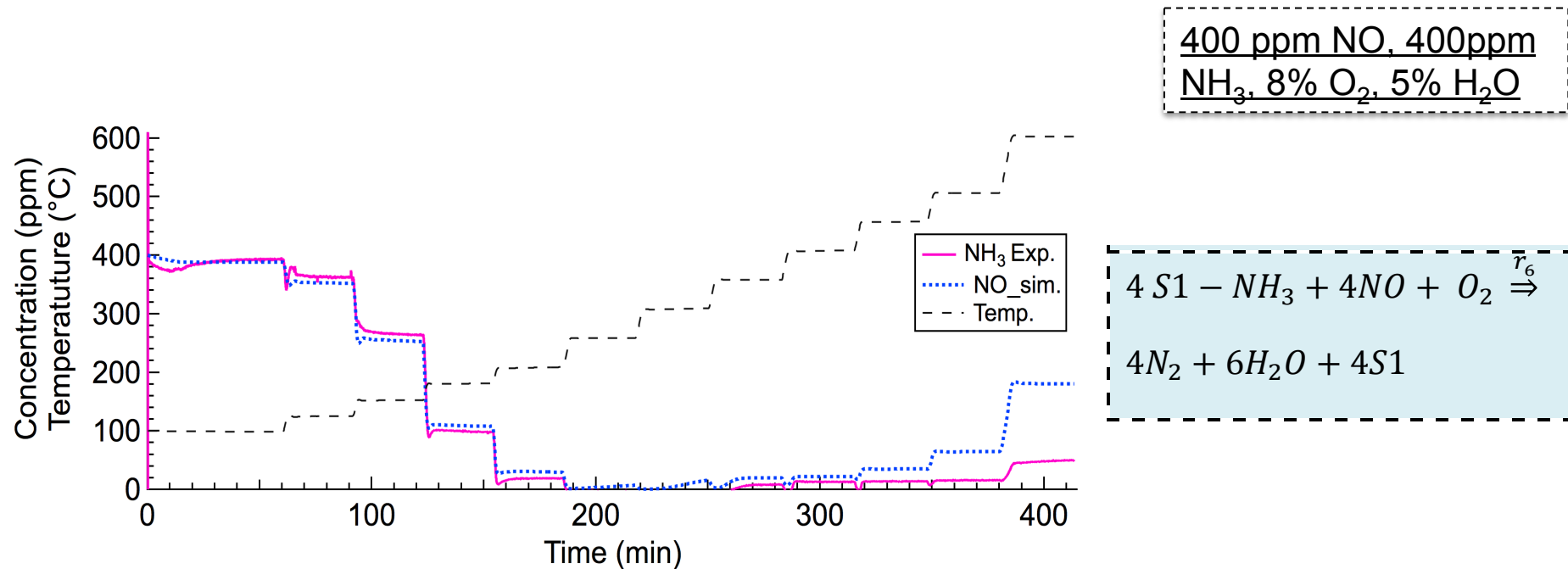
Ammonia oxidation

400ppm NH₃, 8% O₂,
5% H₂O



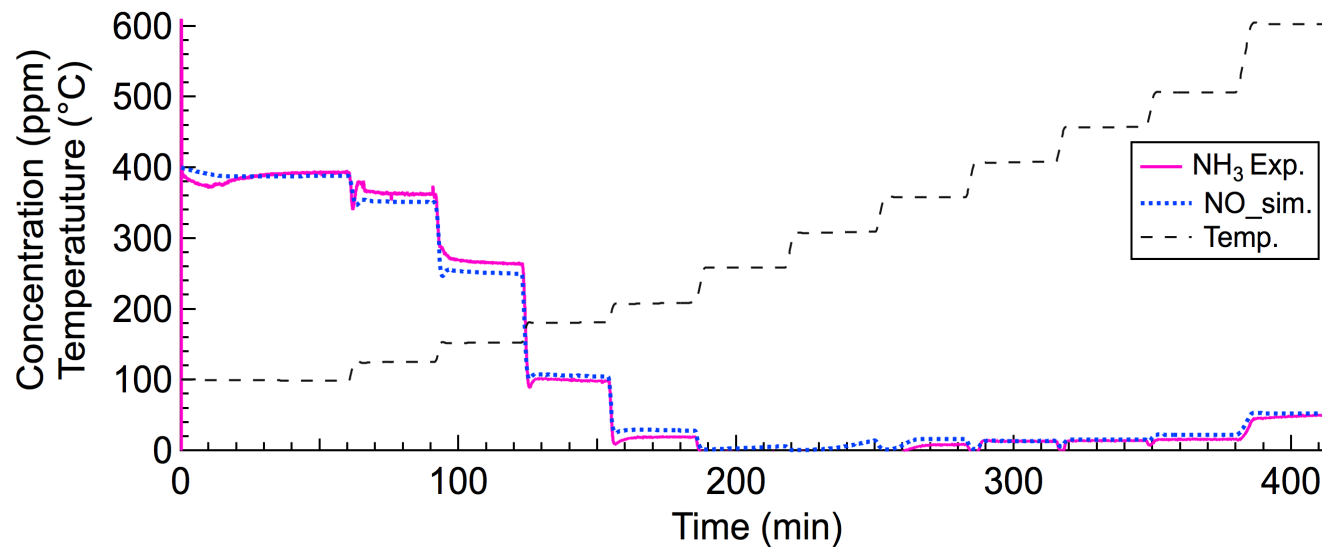
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Ammonia SCR

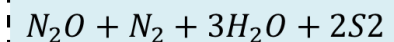
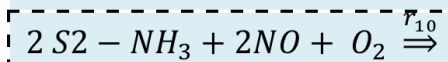
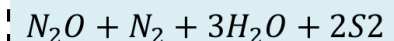
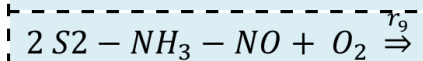
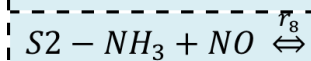
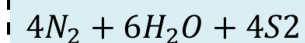
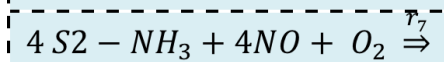
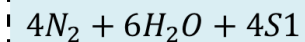
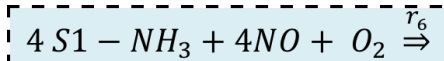


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Ammonia SCR

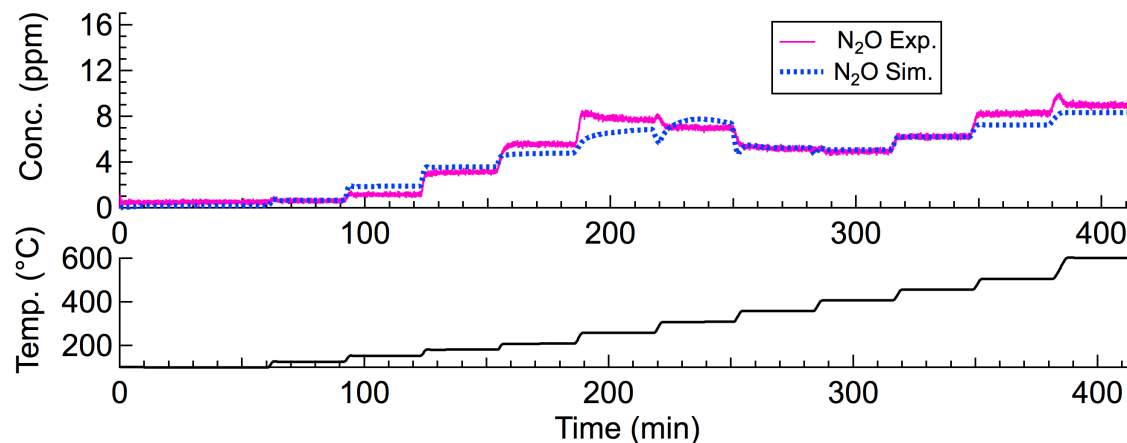
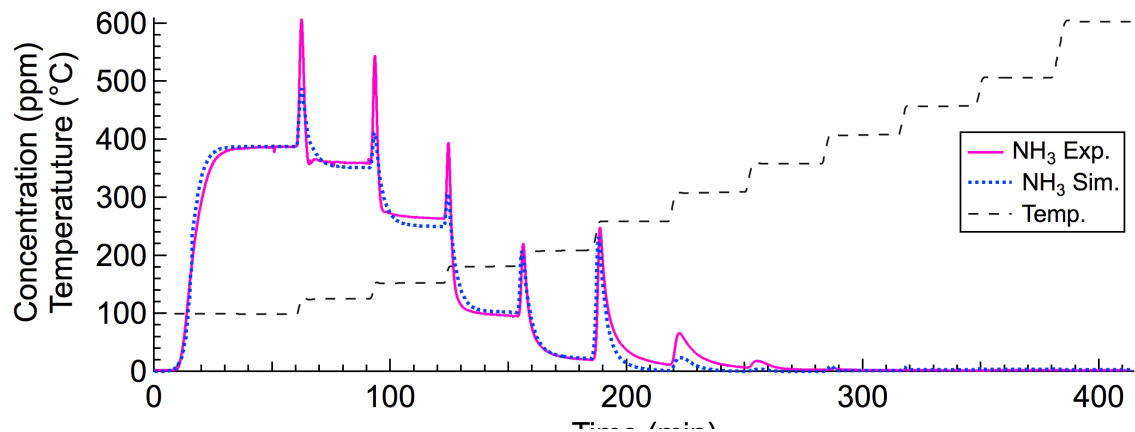


400 ppm NO, 400ppm
NH₃, 8% O₂, 5% H₂O

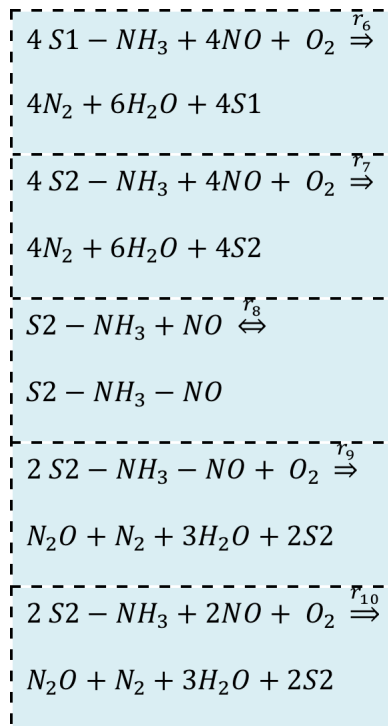


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Ammonia SCR




400 ppm NO, 400ppm
NH₃, 8% O₂, 5% H₂O



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Conclusions

- A kinetic model for NH_3 -SCR over Cu/SSZ-13 catalyst was developed. Three-sites were needed.
- Site description:
 - S1: Cu in the six-membered rings. Lumped together with Brønsted acid sites.
 - S2: Cu in the larger cages. Lumped together with Brønsted acid sites.
 - S3: Sites for physisorption of ammonia
- The main SCR reaction in the model occurs on S1 sites and the main ammonia oxidation reaction on S2 sites.
- NH_3 oxidation: The conversion slightly decreased from 350 to 400°C  reaction occurring at low temperature with low rate needed to be introduced on S1.
- An extra step was needed for ammonia-SCR on S2, to describe SCR at high temperature.

Acknowledgements

- This work was carried out at the Competence Centre for Catalysis, Chalmers University of Technology and at Cummins Inc.
- Cummins Inc. and Swedish Research Council is gratefully acknowledged for the financial support.