Kinetic models for NH_3 SCR over Cu-ZSM-5

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Objective

Develop both global and detailed kinetic models for ammonia SCR over Cu-ZSM-5. These models were developed for use in predicting NO_x emissions from urea SCR automotive catalytic converters.

Detailed model:

- H. Sjövall, R. J. Blint and L. Olsson, submitted, 2008.
- H. Sjövall, R. J. Blint and L. Olsson, submitted, 2008.
- L. Olsson, H. Sjövall and R.J. Blint, submitted, 2008.

- H. Sjövall, R. J. Blint, E. Fridell and L. Olsson, *Appl. Catal. B: Environmental*. 64(3-4) (2006) 180.
- H. Sjövall, E. Fridell, R.J. Blint and L. Olsson, Top. Catal., 42-43 (2007) 113-117.

Global model:

- L. Olsson, H. Sjövall and R. J. Blint, *Applied Catalysis B: Environmental*, 81 (2008) 203.

Detailed kinetic model

- Three subsystems investigated separately:
  - Ammonia adsorption and desorption, ammonia oxidation
  - NO_2 adsorption and NO oxidation
  - SCR reactions

Detailed kinetic model on Cu-ZSM5
- Surface description

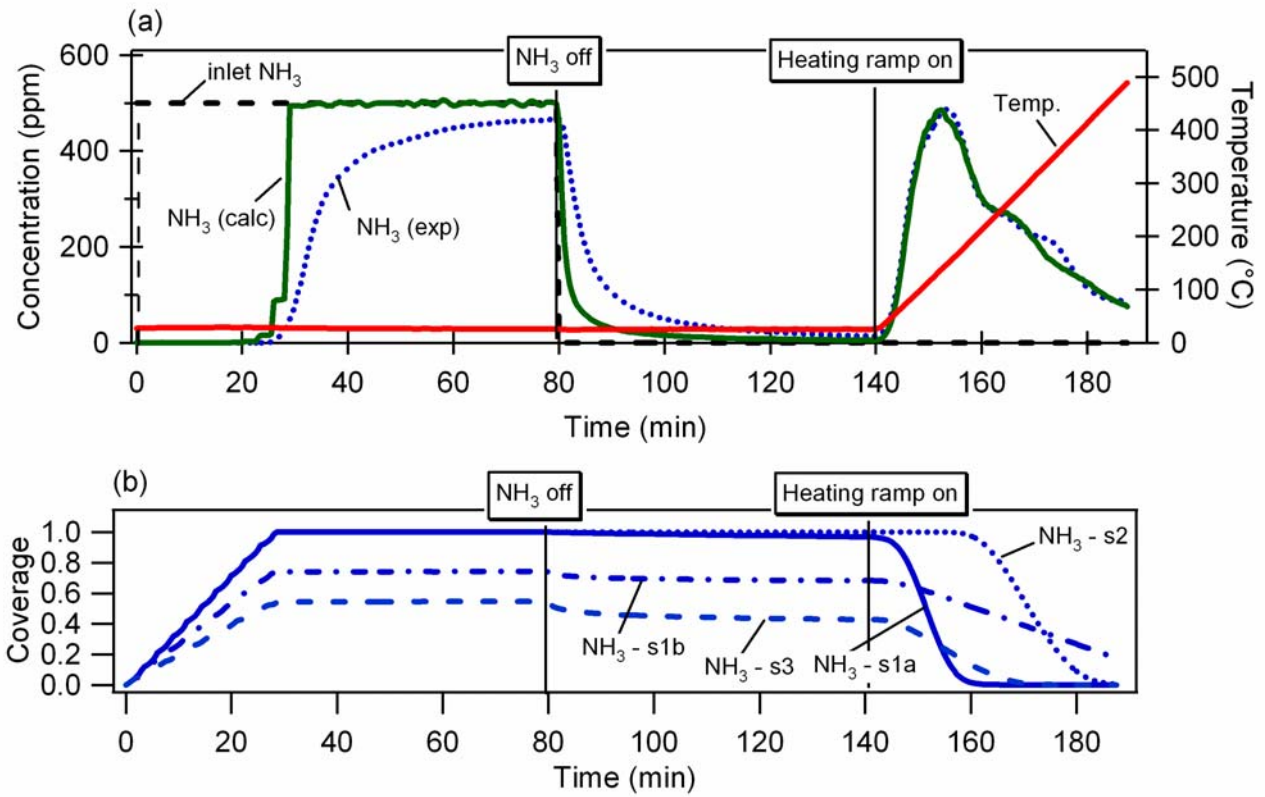
- Copper sites
  - Suggested in litterature that Cu coordinates 4 NH_3

    [Komatsu et al. J. Catal., 148 (1994) 427.]
    - S1a: The active site
    - S1b: 3 sites for storage of NH_3, H_2O, etc.
  - Brönstedt acid sites – S2
    - Investigated separately using H-ZSM5 catalyst
  - Loosley bound species: S3
    - Observed at room temperature

H. Sjövall, R.J. Blint, L. Olsson, Submitted 2008.

Detailed kinetic model on Cu-ZSM5

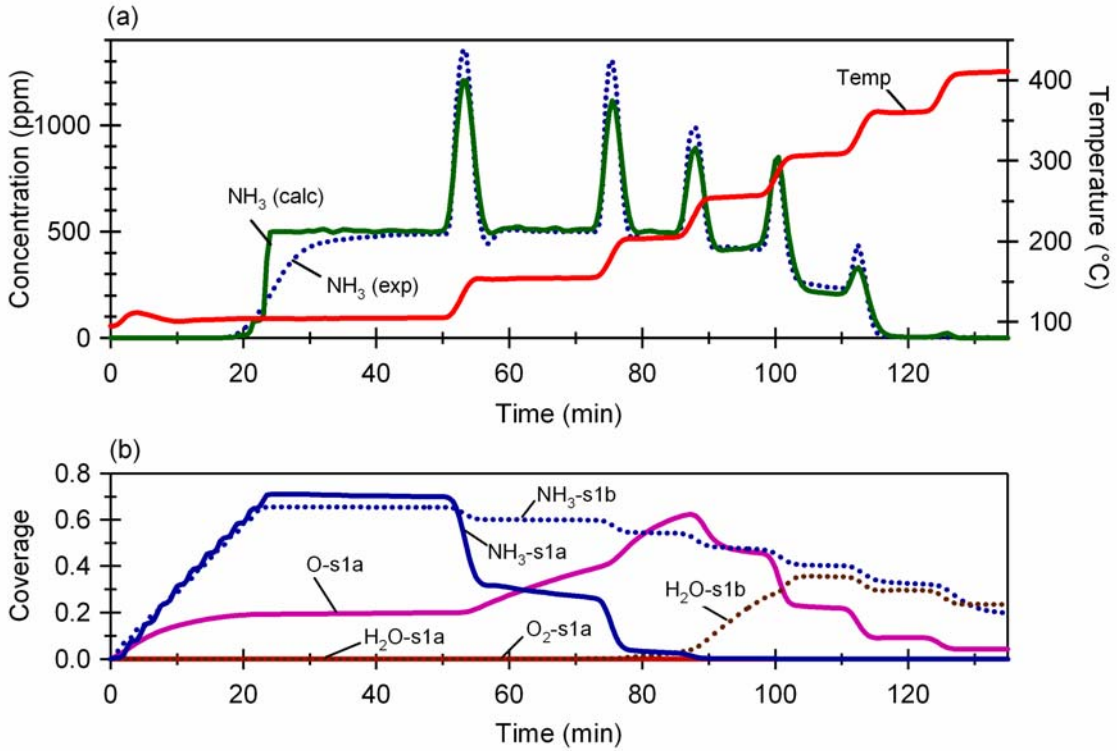
- NH_3 TPD, 30°C



- NH_3 adsorption and desorption from S1a, S1b, S2 and S3. S1=Copper, S2= Acid sites, S3=Loosley bound

H. Sjövall, R.J. Blint, L. Olsson, Submitted 2008.

Detailed kinetic model on Cu-ZSM5
- NH_3 oxidation



Feed mixture:

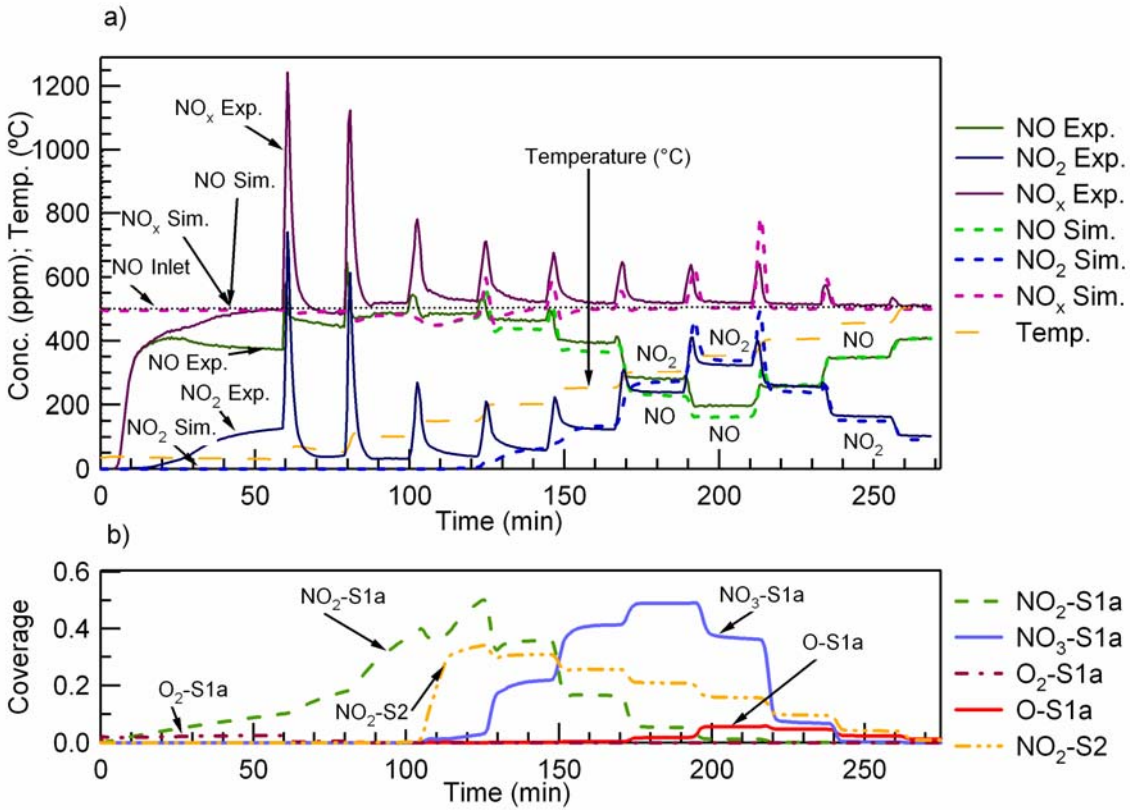
500ppm NH_3, 8 % O_2, 5 % H_2O, SV=18 400h^{-1}

- NH_3 adsorption and desorption from S1a, S1b, S2 and S3.
- Oxygen adsorption on S1a.
- NH_3 oxidation
- S1=Copper, S2= Acid sites, S3=Loosley bound

H. Sjövall, R.J. Blint, L. Olsson, Submitted 2008.

Detailed kinetic model on Cu-ZSM5

- NO oxidation



Feed mixture:

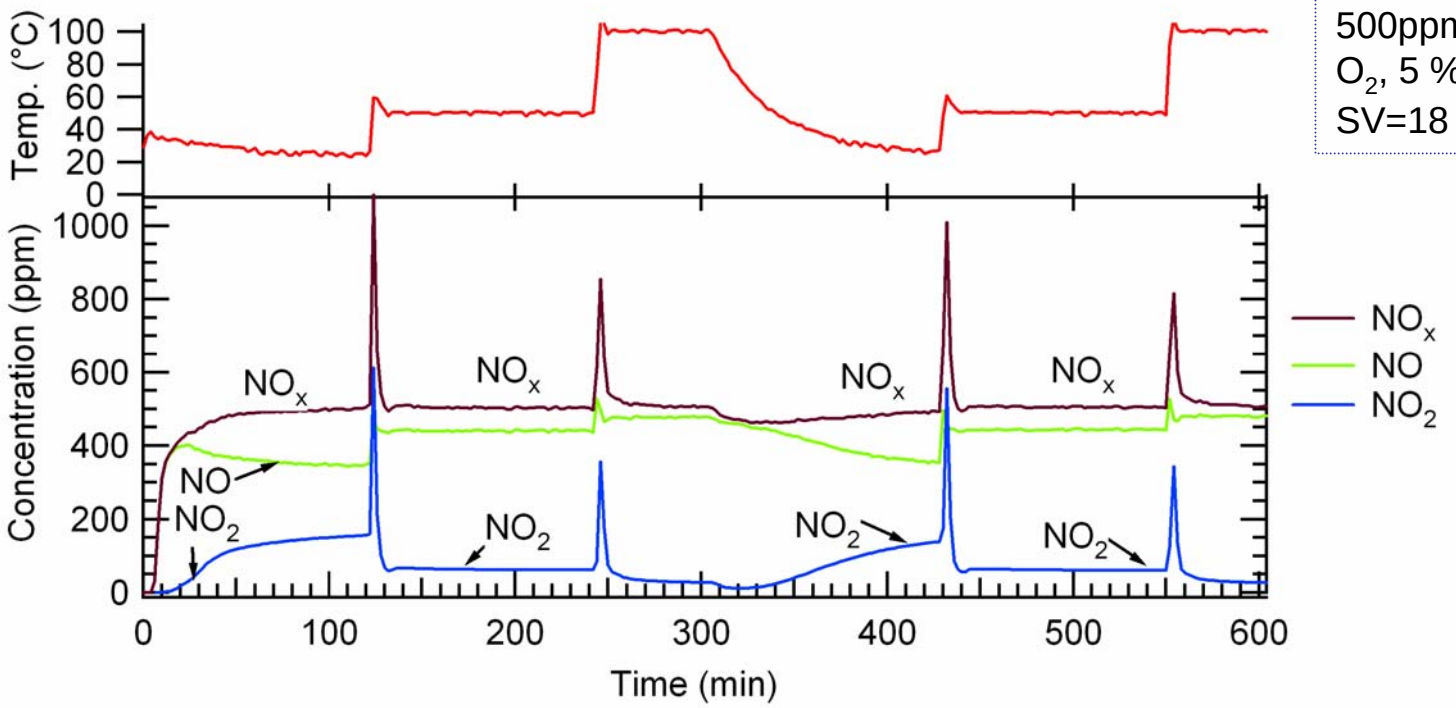
500ppm NO, 8 % O_2, 5 % H_2O, SV=18 400h^{-1}

- NO_2 adsorption and desorption from S1a, and S2.
- Oxygen adsorption on S1a
- NO oxidation
- Nitrate formation (2 steps)
- S1=Copper, S2= Acid sites

L. Olsson, H. Sjövall and R.J. Blint, Submitted 2008.

Detailed kinetic model on Cu-ZSM5

- Low temperature NO oxidation



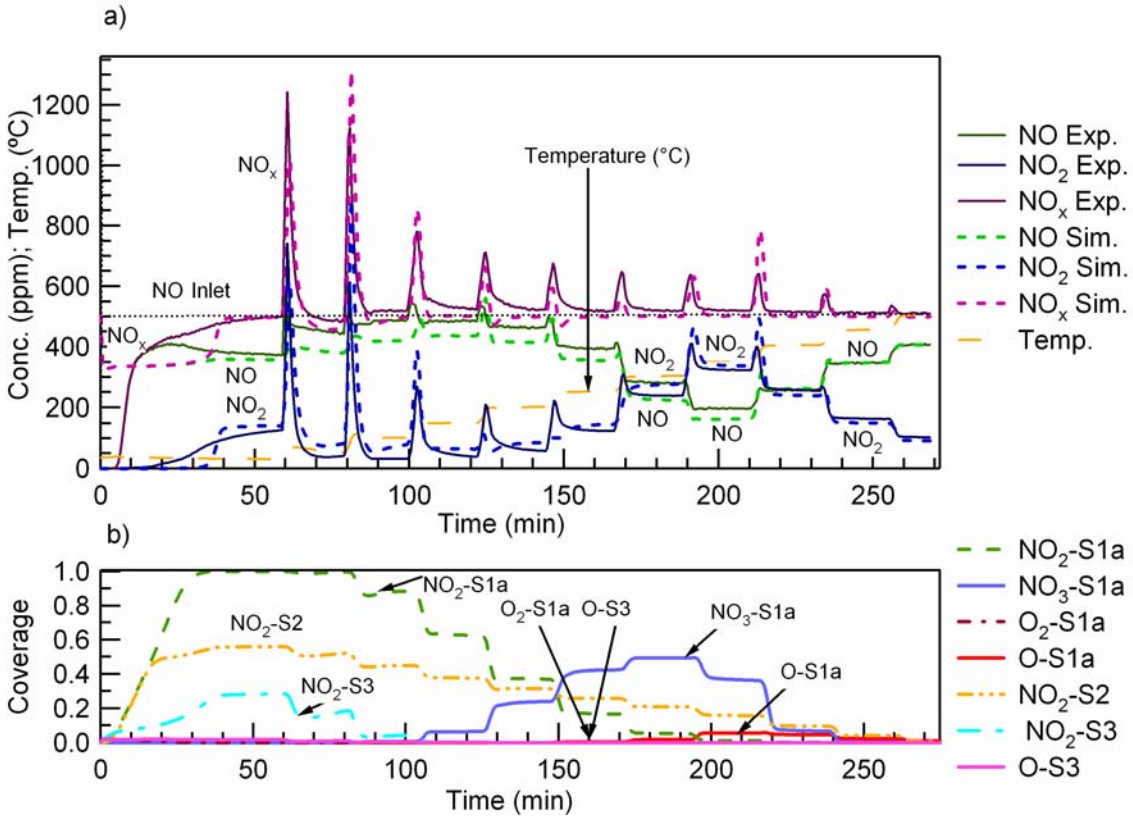
Feed mixture:

500ppm NO, 8 % O_2, 5 % H_2O, SV=18 400h^{-1}

L. Olsson, H. Sjövall and R.J. Blint, Submitted 2008.

Detailed kinetic model on Cu-ZSM5

- NO oxidation, incl. low temperature mechansim



Feed mixture:

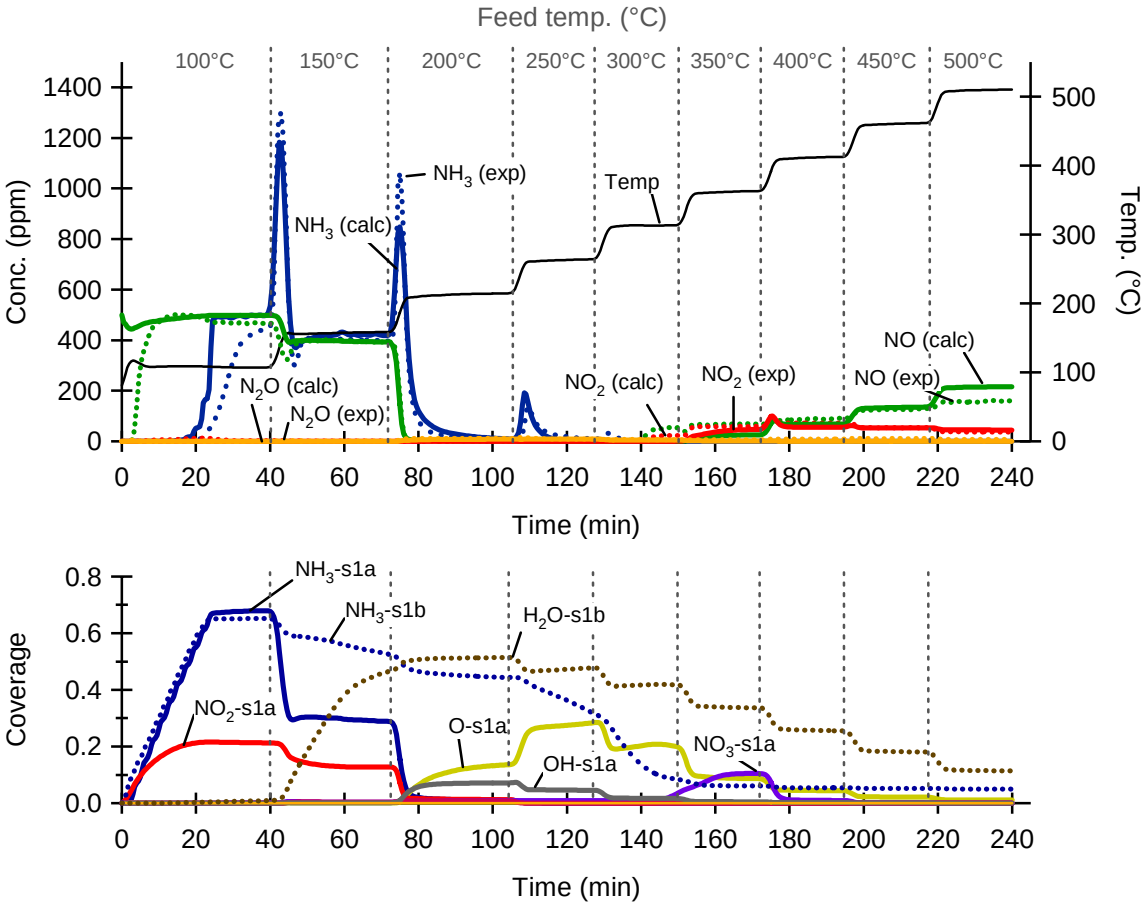
500ppm NO, 8 % O_2, 5 % H_2O, SV=18 400h^{-1}

- Low temperature mechanism:
  - NO oxidation occurs also on S3 at lower temperatures
  - O_2 desorbs easily on S3 ⇒ O-S3 decreases when increasing T ⇒ decreased NO ox.
- S1=Copper, S2= Acid sites S3=Loosley bound species

L. Olsson, H. Sjövall and R.J. Blint, Submitted 2008.

Detailed kinetic model on Cu-ZSM5

- NH_3 SCR



Feed mixture:

500ppm NO and NH_3, 8 % O_2, SV=18 400h^{-1}

- Six steps added for the SCR
- Mechansim invloves steps with HNO_2, HNO_3 and OH on the surface
- S1=Copper, S2= Acid sites, S3=Loosley bound

H. Sjövall, R.J. Blint and L. Olsson, Submitted 2008.

Detailed kinetic model on Cu-ZSM5

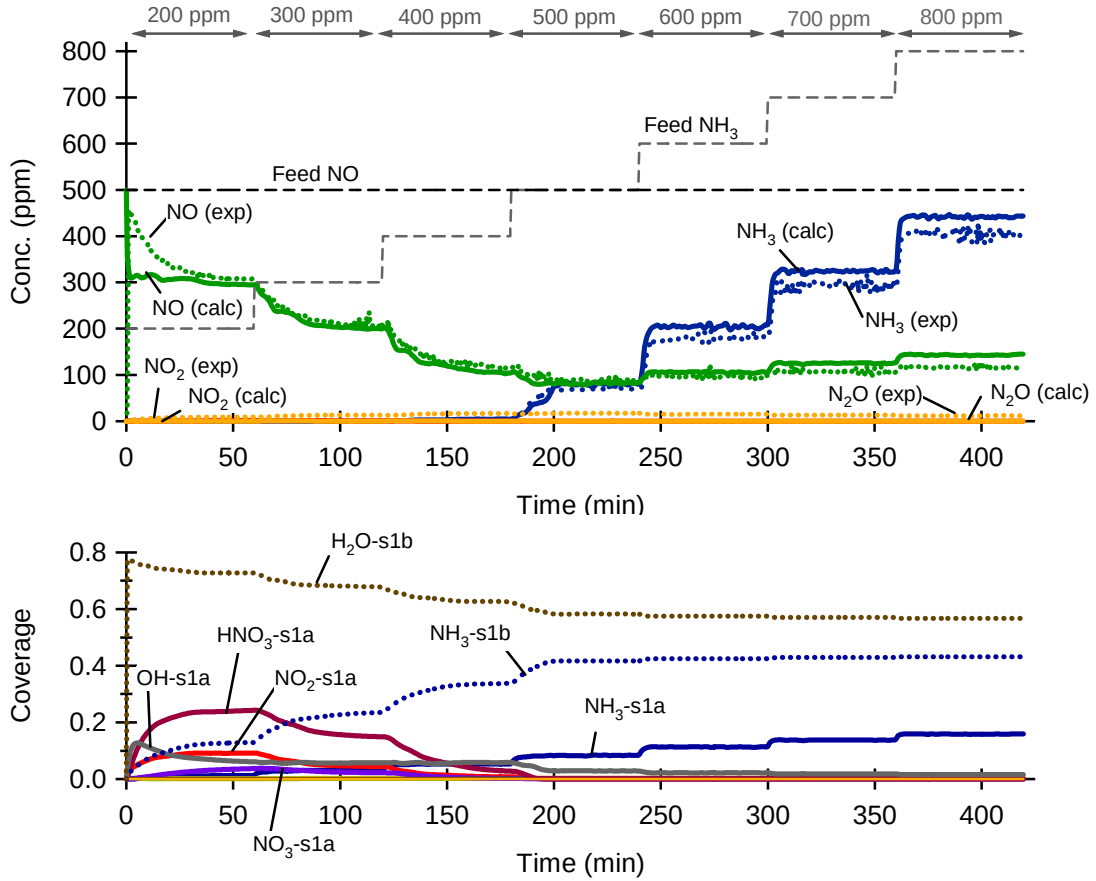
- NH_3 SCR, Validation

- Validated with 8 experiments
  - Varying NO to NO_2
  - Influence of water
  - Changing NH_3 concentration
  - Changing NO concentration
  - Changing NH_3 in the presence of $NO+NO_2$

H. Sjövall, R.J. Blint and L. Olsson, Submitted 2008.

Detailed kinetic model on Cu-ZSM5

- NH_3 SCR, Validation, Changing NH_3 conc.



Feed mixture:

500ppm NO, varying NH_3, 8 % O_2, 5 % H_2O, SV=18 400h^{-1}

H. Sjövall, R.J. Blint and L. Olsson, Submitted 2008.

Global kinetic model of NH_3 SCR over Cu-ZSM-5

Reactions for NH_3 adsorption and desorption, NH_3 oxidation and NO oxidation

$$NH_3 + S1 \overset{r1}{\leftrightarrow} NH_3 - S1$$

$$2NH_3 - S1 + 3/2O_2 \overset{r2}{\rightarrow} N_2 + 3H_2O + 2S1 \qquad NO + 1/2O_2 \overset{r3}{\longleftrightarrow} NO_2$$

Reactions for SCR

$$4NH_3 - S1 + 4NO + O_2 \overset{r4}{\rightarrow} 4N_2 + 6H_2O + 4S1$$ Standard SCR

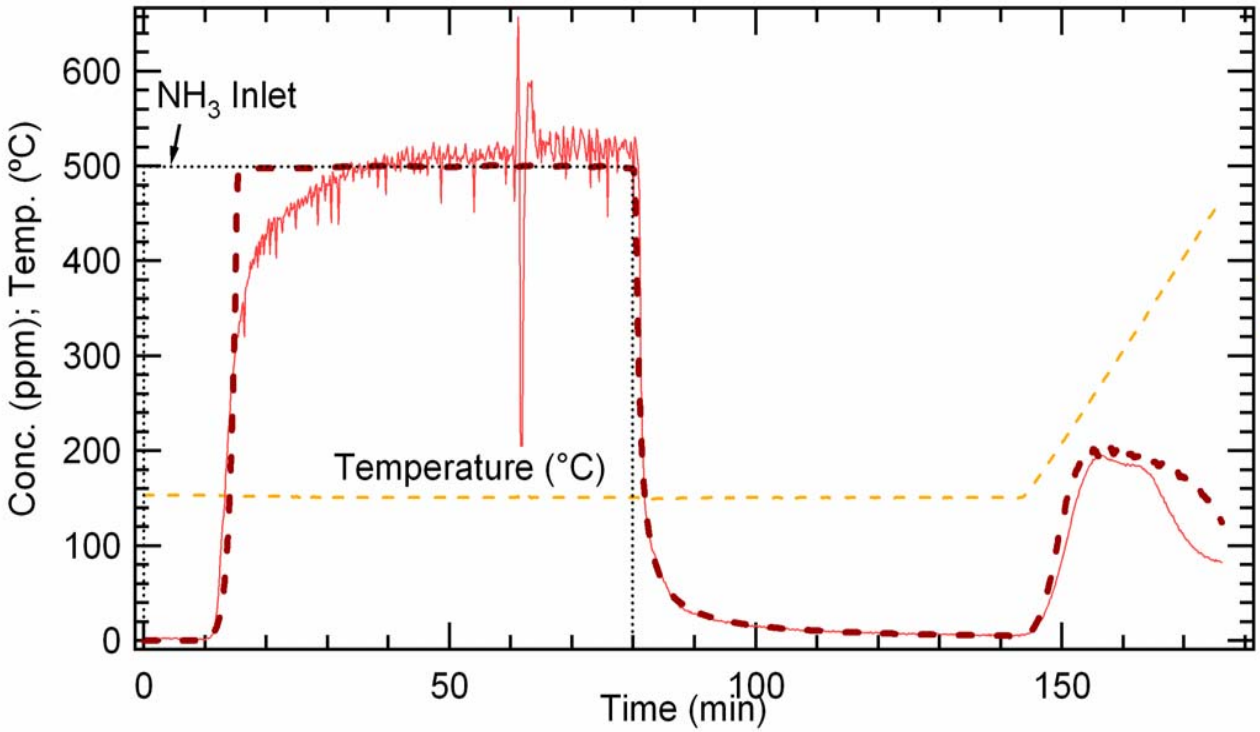
$$2NH_3 - S1 + NO + NO_2 \overset{r5}{\rightarrow} 2N_2 + 3H_2O + 2S1$$ Rapid SCR

$$4NH_3 - S1 + 3NO_2 \overset{r6}{\rightarrow} 3.5N_2 + 6H_2O + 4S1$$ NO_2 SCR

$$2NH_3 - S1 + 2NO_2 \overset{r7}{\rightarrow} N_2 + N_2O + 3H_2O + 2S1$$

L. Olsson, H. Sjövall, R.J. Blint, *Appl. Catal B 81 (2008) 203.*

Global kinetic model of NH_3 SCR over Cu-ZSM-5 -NH_3 storage



Feed mixture:

Includes 5 % H_2O, SV=18 400h^{-1}

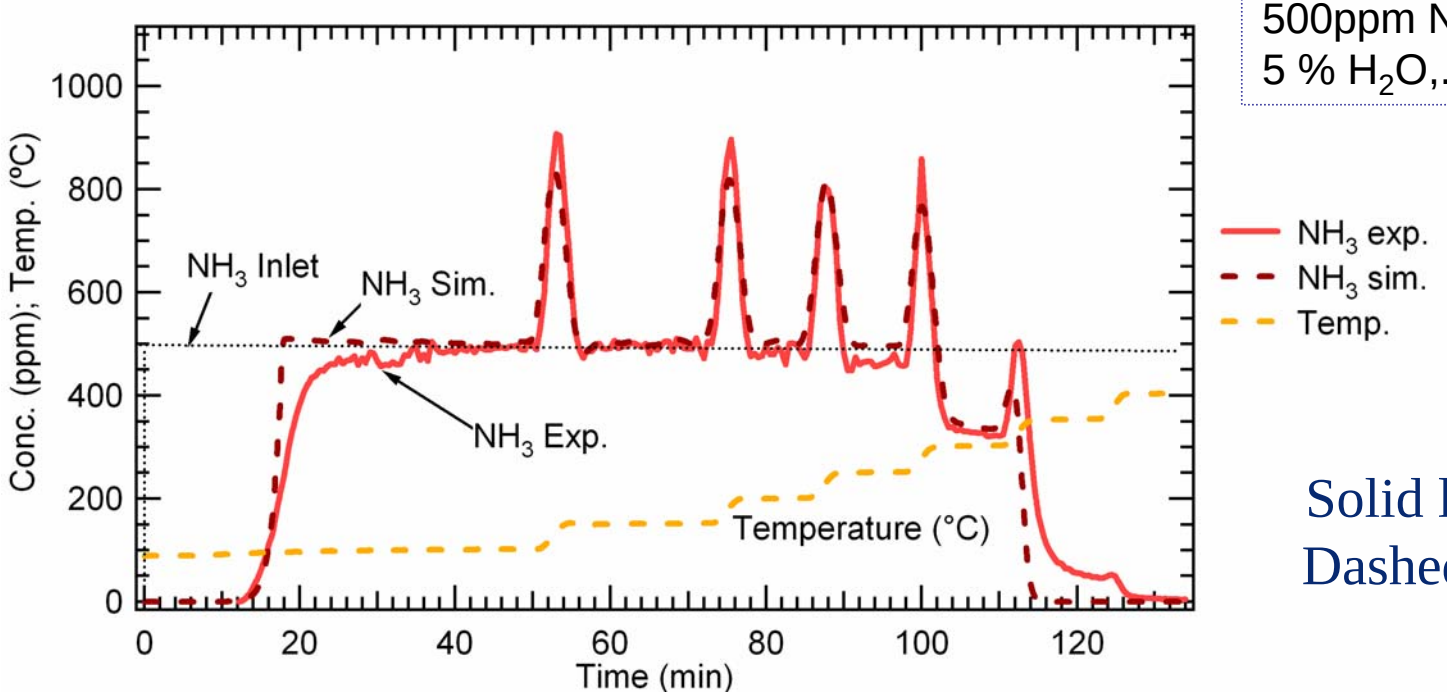
Solid lines: Exp.
Dashed lines: Sim.

L. Olsson, H. Sjövall, R.J. Blint, *Appl. Catal B 81 (2008) 203.*

Global kinetic model of NH_3 SCR over Cu-ZSM-5 -NH_3 oxidation

Feed mixture:

500ppm NH_3, 8 % O_2, 5 % H_2O,.SV=18 400h^{-1}



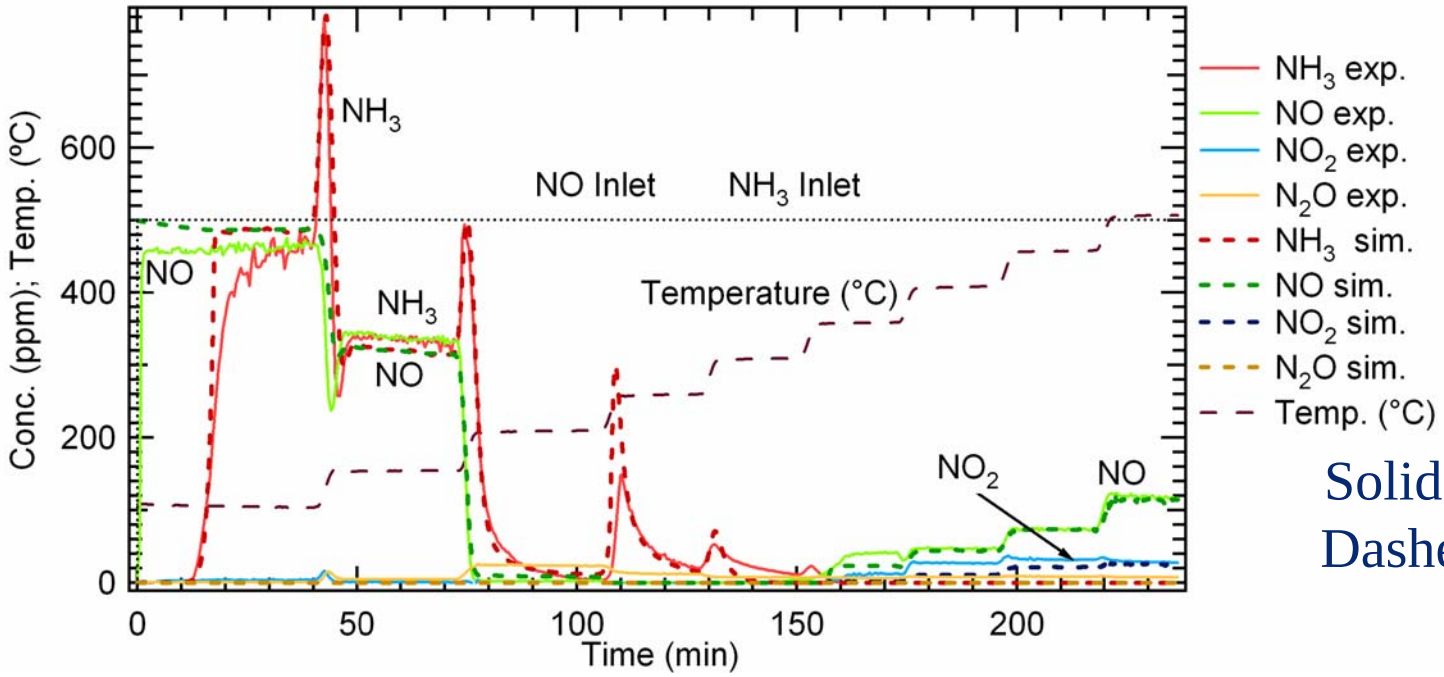
Solid lines: Exp.
Dashed lines: Sim.

L. Olsson, H. Sjövall, R.J. Blint, *Appl. Catal B 81 (2008) 203.*

Global kinetic model of NH_3 SCR over Cu-ZSM-5 -NH_3 SCR

Feed mixture:

500ppm NO and NH_3, 8 % O_2, 5 % H_2O, SV=18 400h^{-1}



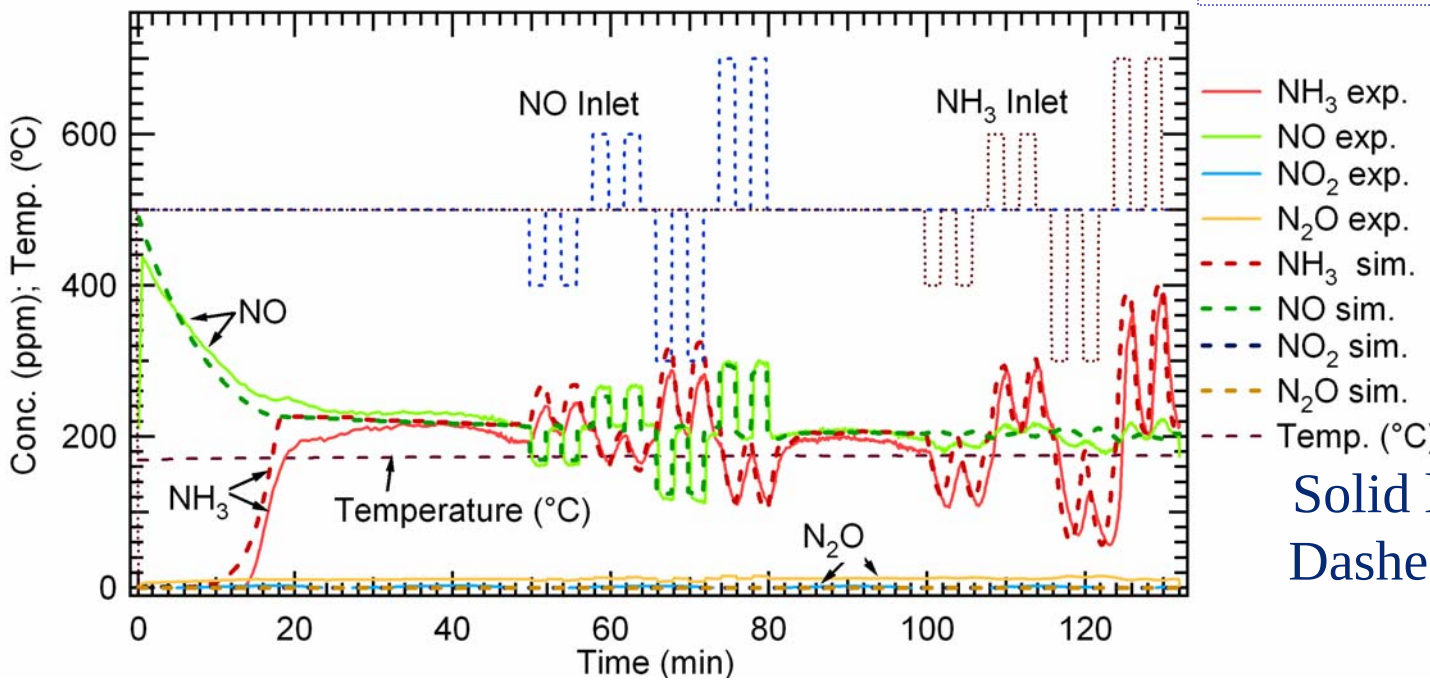
Solid lines: Exp.
Dashed lines: Sim.

L. Olsson, H. Sjövall, R.J. Blint, *Appl. Catal B 81 (2008) 203.*

Global kinetic model of NH_3 SCR over Cu-ZSM-5 -Validation at 175°C

Feed mixture:

8 % O_2, 5 % H_2O, varying NO and NH_3, SV=36 800h^{-1}



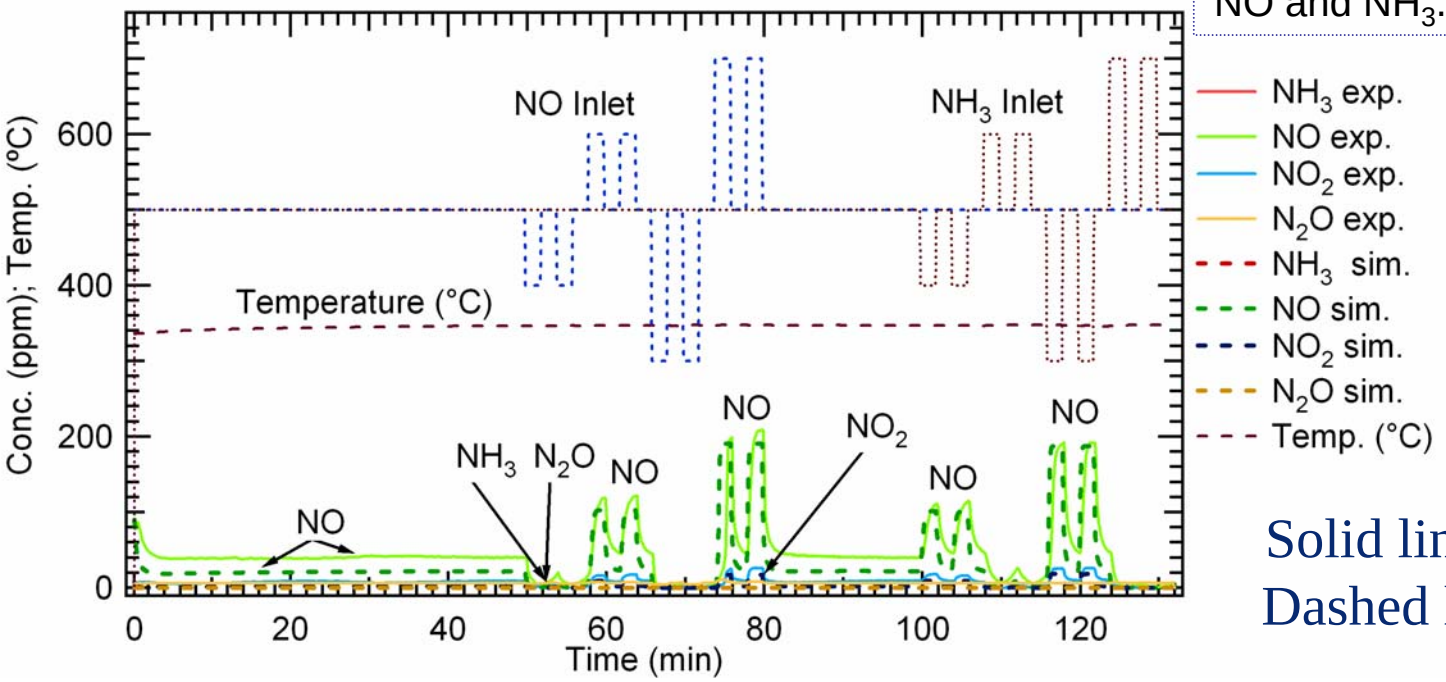
Solid lines: Exp.
Dashed lines: Sim.

L. Olsson, H. Sjövall, R.J. Blint, *Appl. Catal B 81 (2008) 203.*

Global kinetic model of NH_3 SCR over Cu-ZSM-5 -Validation at 350°C

Feed mixture:

8 % O_2, 5 % H_2O, varying NO and NH_3.SV=36 800h^{-1}



Solid lines: Exp.
Dashed lines: Sim.

L. Olsson, H. Sjövall, R.J. Blint, *Appl. Catal B 81 (2008) 203.*

Summary

- Detailed kinetic model
  - Three sub-systems investigated separately
    - NH_3 storage, NH_3 oxidation
    - NO oxidation
    - SCR
  - NH_3 storage on copper, Brönstedt acid sites and loosley bound NH_3
  - Activity for low temperature NO oxidation
  - HNO_3, HNO_2 and OH important surface species for the SCR reactions
  - Model validated with 8 experiments
- Global kinetic model
  - 7 reaction steps
    - NH_3 storage, NH_3 oxidation, NO oxidation, standard SCR, rapid SCR, NO_2 SCR, N_2O formation
    - Model validated with 6 experiments, including short transients