Storage of NH_3 and H_2O over Fe-zeolite based urea-SCR catalysts

SKARLIS Stavros
CLEERS workshop 2011

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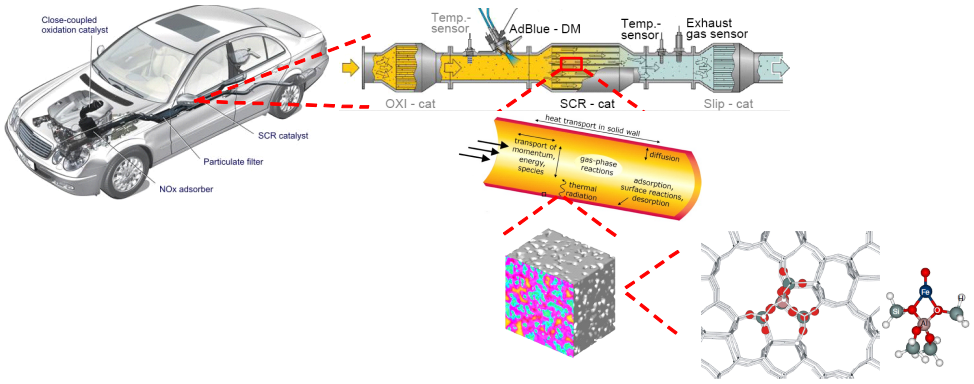
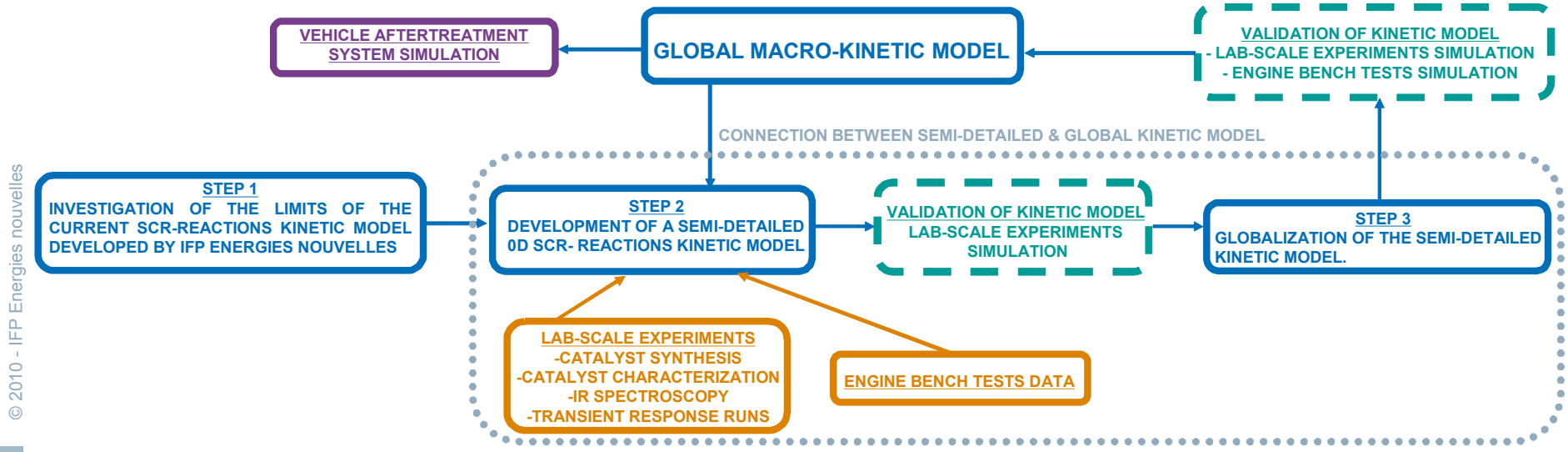
- **Doctoral Research Context and Methodology**
- Adsorption of NH_3 over Fe-zeolites
- Approaches towards the modeling of the NH_3 storage
- The single site approach
- The four sites approach
- Competitive storage between NH_3 and H_2O
- Evaluation of the methodologies and conclusions

Doctoral Research Context and Methodology

Aim of the thesis: The development of a **global macrokinetic model** for **Urea-SCR**, **Fe-Zeolite** based catalysts for engine aftertreatment system simulation .



Methodology:



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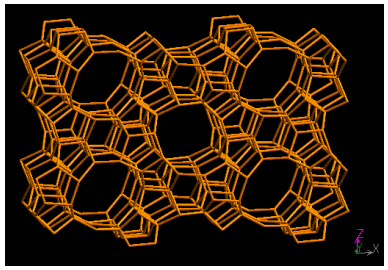
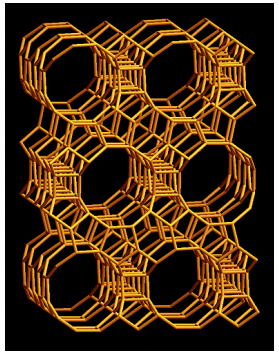
Adsorption of NH_3 over Fe-zeolites (1/2)

- **Zeolites:** Alumina (Al_2O_3) – silicate (SiO_2) natural or synthetic materials.

- The Fe-based, urea-SCR catalysts:
  - **High performance at a broad range of temperatures (150 – 550 °C)**
  - **Resistance to hydrothermal ageing**
  - **Deactivation at temperatures above 600 °C, under the presence of H_2O.**

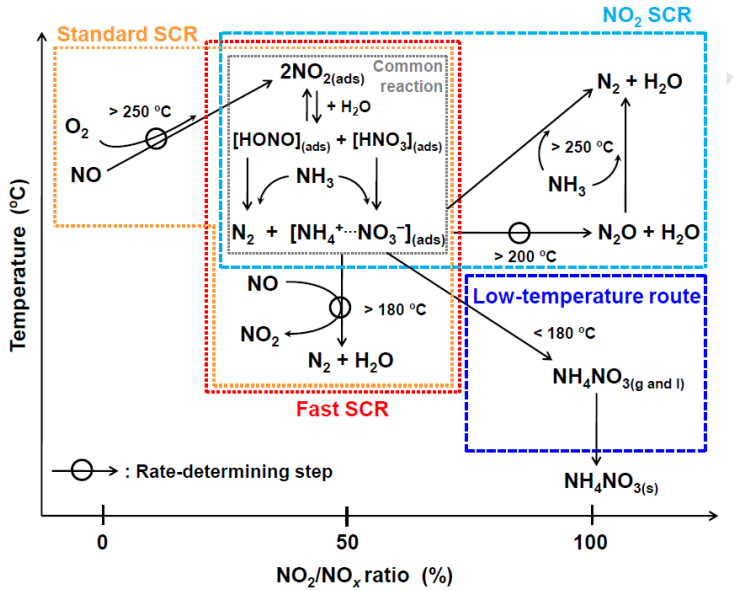


ZSM5 (MFI) zeolite



BETA zeolite

http://www.iza-structure.org/databases



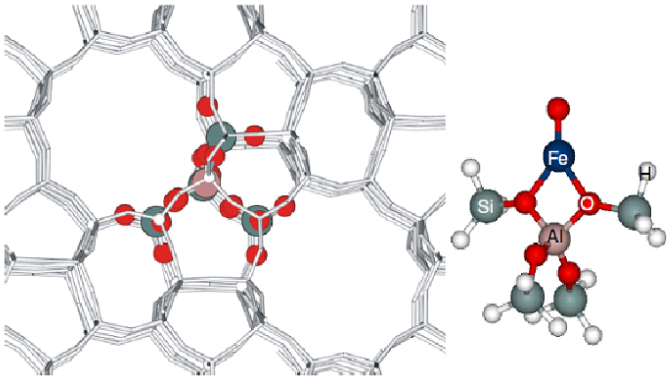
Catalysis A, General, doi: 10.1016/j.apcata.2010.09.034

Adsorption of NH_3 over Fe-zeolites (2/2)

- NH_3 is believed to be adsorbed over different types of surface species

- Surface sites for NH_3 storage over a Fe-ZSM5 catalyst:
  - **Metal sites**
  - **Brönsted and Lewis acid sites**
  - **Sites for weak physisorption**

- The metal sites can be:
  - **Fe^{3+} cations**
  - **$(FeO)_n$ species**
  - **Fe_2O_3 bulky clusters**



Heyden, (2005) Dissertation, Hamburg Univ.

- **The acidity of the Lewis sites varies significantly**

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Approaches towards the modeling of the NH_3 storage (1/2)

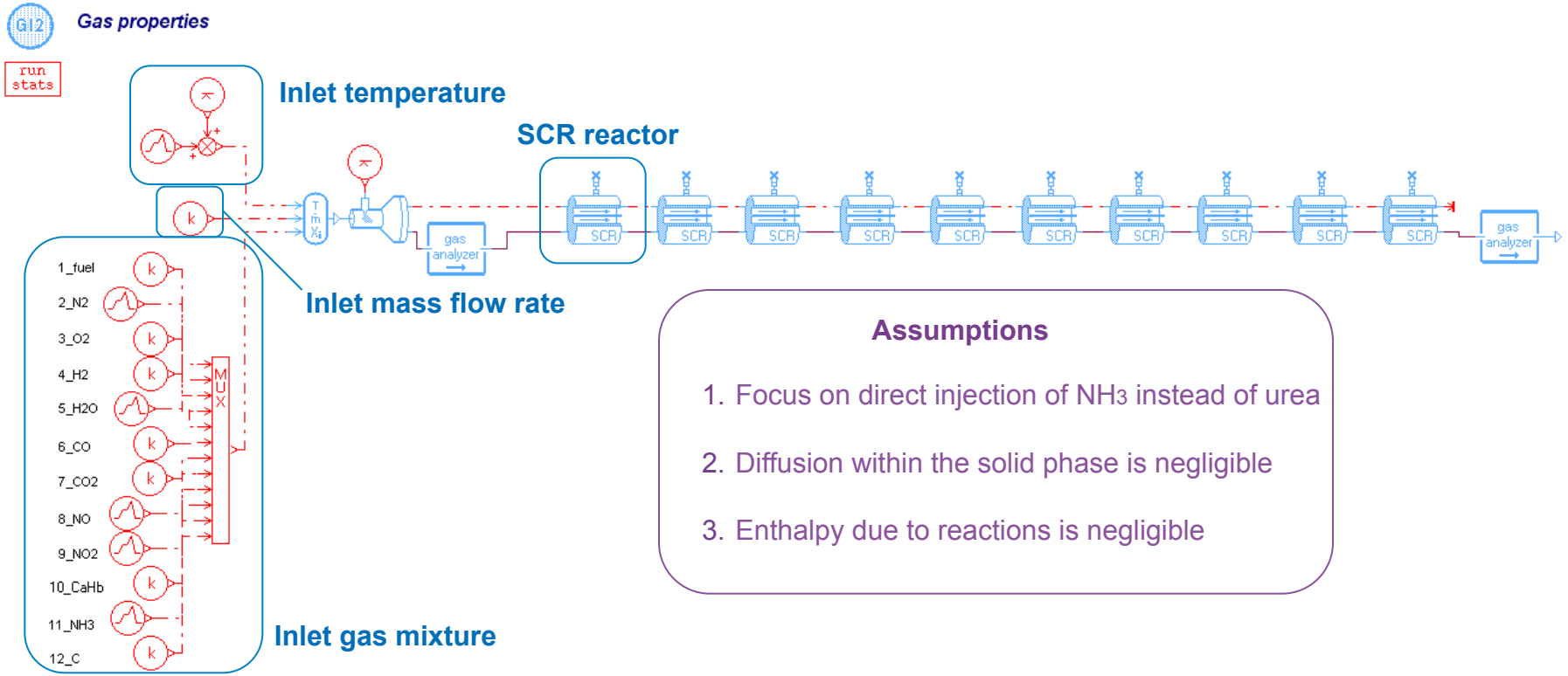
- Approaches tested:
  - Adsorption of NH_3 over a single surface site
  - Adsorption of NH_3 over four different surface sites
  - Competitive adsorption of H_2O and NH_3 over four surface sites

- Sources:
  - A. Cat. B: Env., 81 (2008) 203-217, L. Olsson
  - J. Phys. Chem. C 2009, 113,1393-1405, H. Sjövall

- Methodology:
  - Reproduction of the model – The original model is oriented to Cu-zeolite based, urea-SCR catalysts.
  - Extension of the model over Fe-zeolite based urea-SCR catalysts, applying various operating conditions.

Approaches towards the modeling of the NH_3 storage (2/2)

- **Simulation:** Development of the kinetic model of the **IFP-Exhaust** library, included in the commercial simulation platform **AMESim®**.
  - **Heat transfer model**
  - **Mass transfer model**
  - **Kinetic model**



Assumptions

1. Focus on direct injection of NH_3 instead of urea
2. Diffusion within the solid phase is negligible
3. Enthalpy due to reactions is negligible

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The single site approach (1/2)

- **Source:** A. Cat. B: Env., 81 (2008) 203-217, L. Olsson
- Description of the NH_3 storage over **Cu-based** catalysts
- Reaction rate expressions:

$$R_{ads,NH_3} = k_{ads,NH_3} \cdot C_{NH_3} \cdot (1 - \theta_{NH_3})$$

$$k_{ads,NH_3} = A_{ads,NH_3} \cdot \exp\left(-\frac{E_{ads,NH_3}}{R \cdot T_s}\right)$$

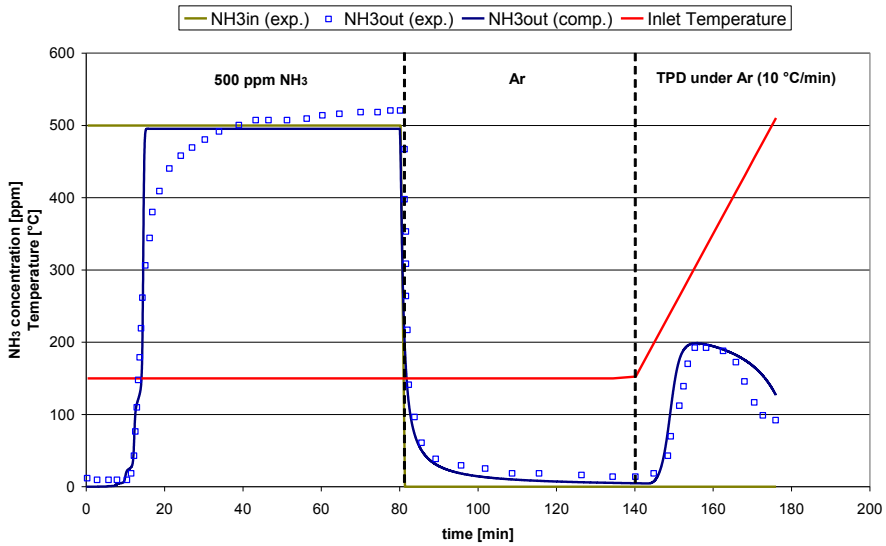
Arrhenius equation

$$R_{des,NH_3} = k_{des,NH_3} \cdot \theta_{NH_3}$$

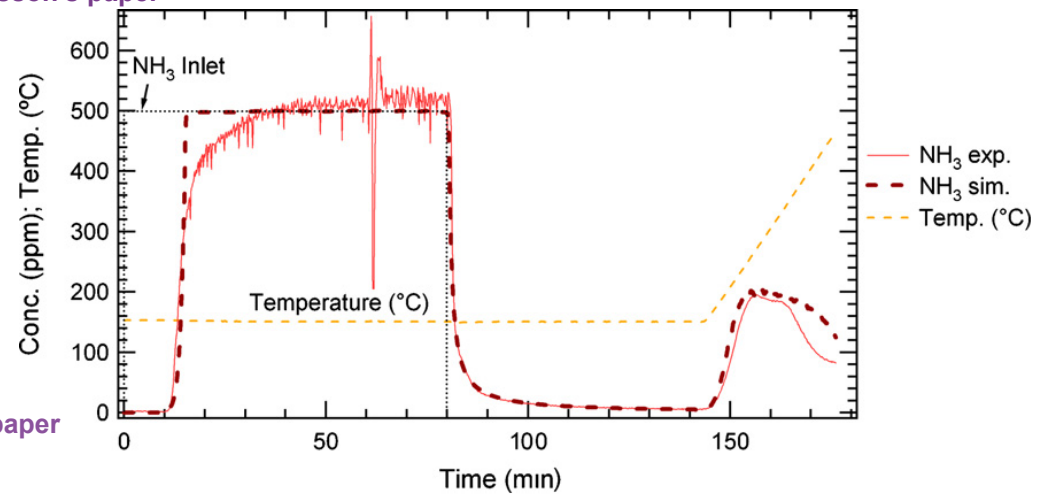
$$k_{des,NH_3} = A_{des,NH_3} \cdot \exp\left(-\frac{E_{des,NH_3} \cdot (1 - a_{NH_3} \cdot \theta_{NH_3})}{R \cdot T_s}\right)$$

Hybrid expression, including coverage dependent activation energy for desorption (Temkin)

The single site approach (2/2)



Reproduction of the adsorption and TPD test reported in Olsson's paper



Original results from Olsson's paper

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The four sites approach (1/3)

- Source: J. Phys. Chem. C 2009, 113,1393-1405, H. Sjövall.
- Description of the ads/desorption of NH_3 over a **Cu-zeolite** catalyst.
- Reaction rate expressions:

$$R_{ads,NH_3,Si} = k_{ads,NH_3,Si} \cdot C_{NH_3} \cdot (1 - \theta_{NH_3,Si})$$

$$k_{ads,NH_3,Si} = A_{ads,NH_3,Si} \cdot \exp\left(-\frac{E_{ads,NH_3,Si}}{R \cdot T_s}\right)$$

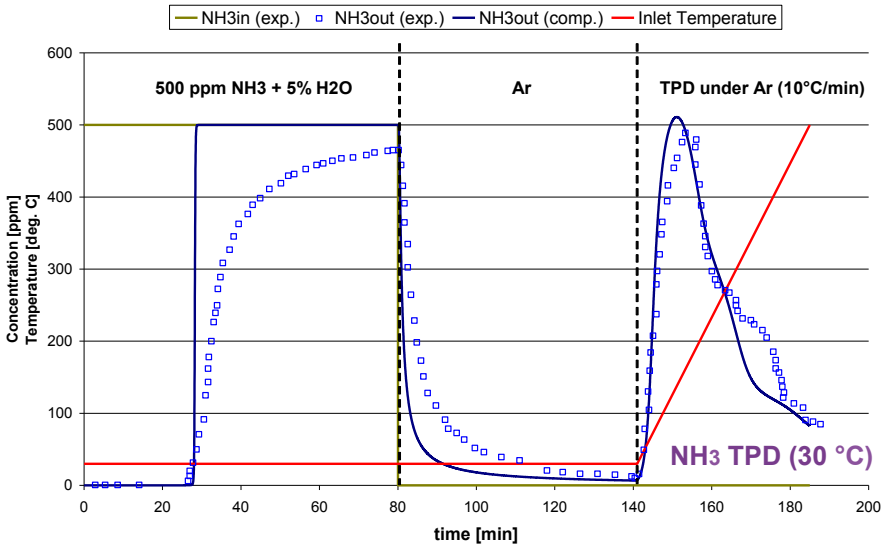
$$R_{des,NH_3,Si} = k_{des,NH_3,Si} \cdot \theta_{NH_3,Si}$$

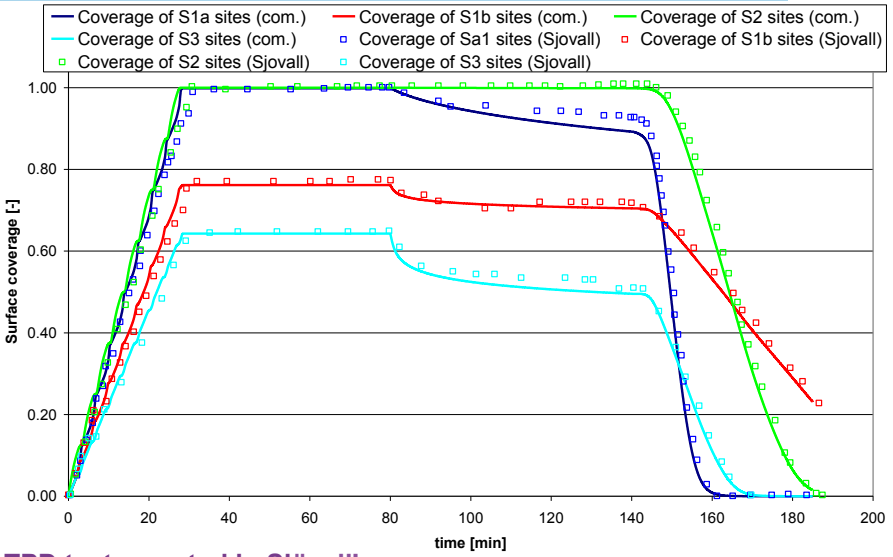
$$k_{des,NH_3,Si} = A_{des,NH_3,Si} \cdot \exp\left(-\frac{E_{des,NH_3,Si} \cdot (1 - a_{NH_3,Si} \cdot \theta_{NH_3,Si})}{R \cdot T_s}\right)$$

Types of sites:

- **S1a: Cu – metal sites**
- **S1b: Cu – metal sites**
- **S2: acid sites**
- **S3: sites for weak physisorption**

The four sites approach (2/3)





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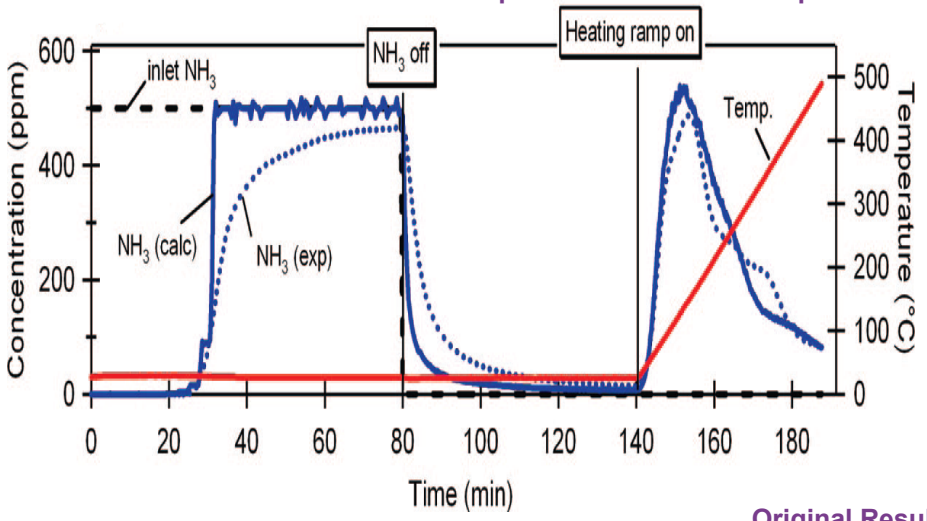
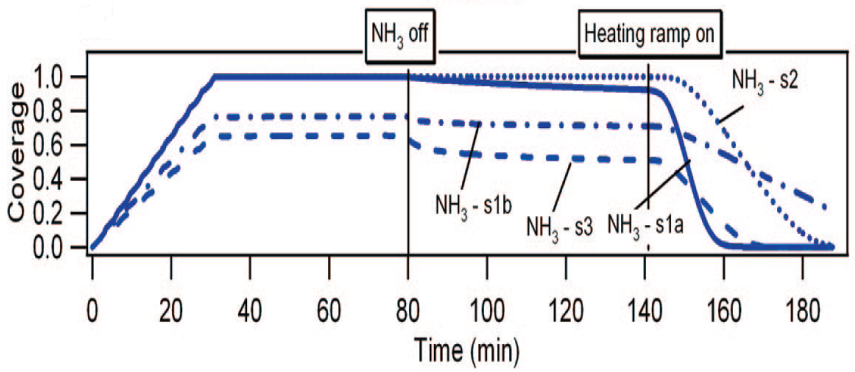
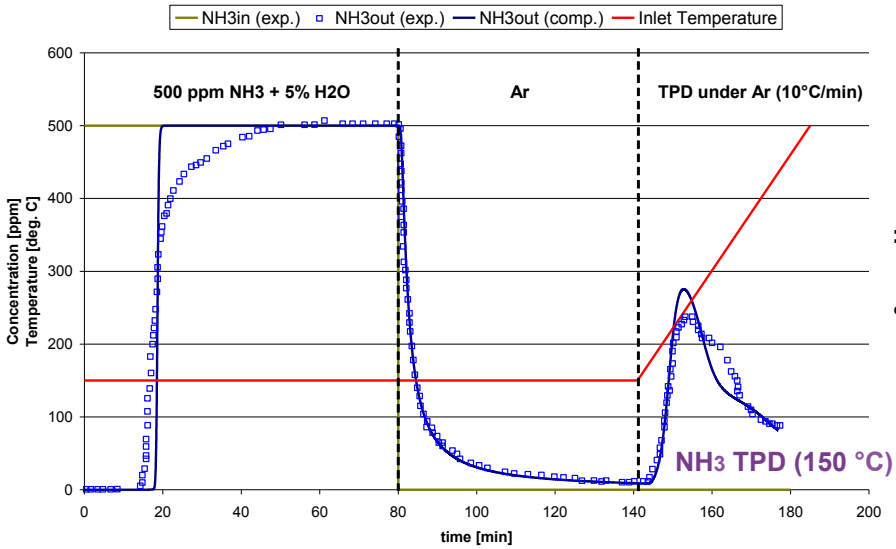
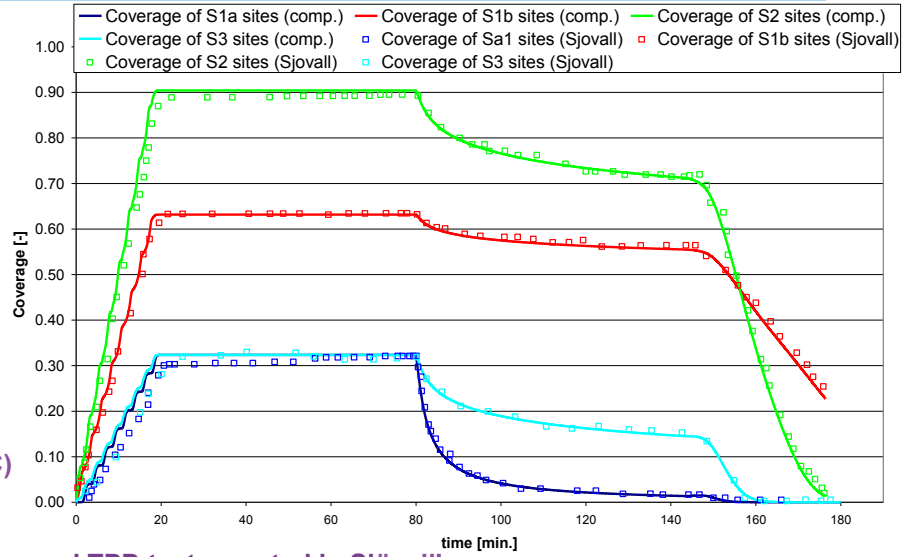




Original Results from Sjövall's paper

The four sites approach (3/3)





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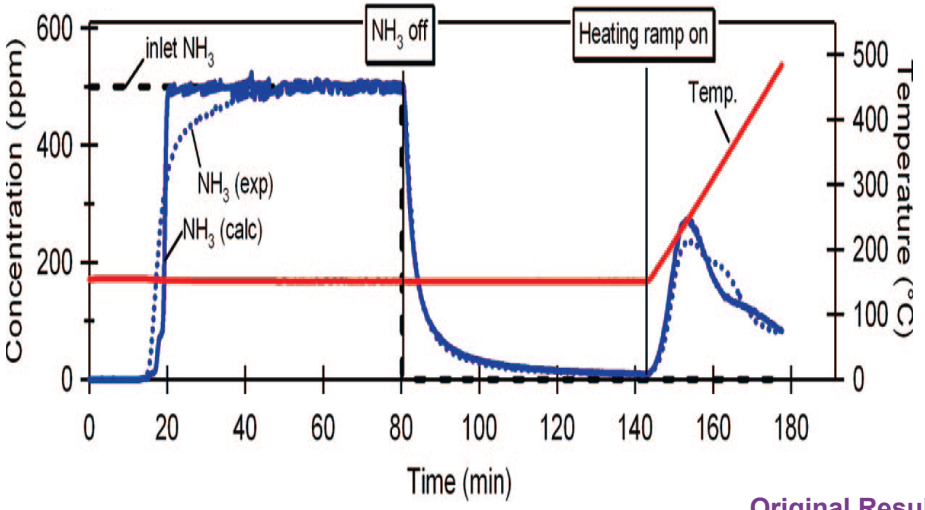

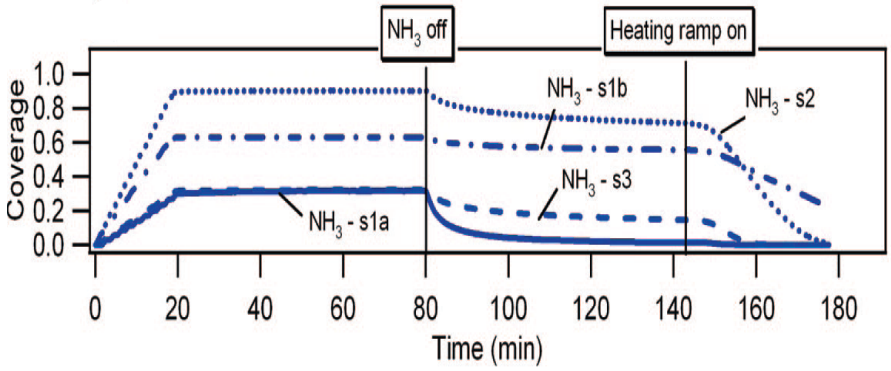

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Competitive storage between NH_3 and H_2O (1/2)

- **Source:** A. Cat. B: Env., 81 (2008) 203-217, L. Olsson

- Description of the NH_3 and H_2O competitive storage over **Cu-based** catalysts.

Adsorption of NH_3

$$R_{ads,j,Si} = k_{ads,j,Si} \cdot C_j \cdot (1 - \theta_{NH_3,Si} - \theta_{j,Si})$$

$$k_{ads,NH_3,Si} = A_{ads,NH_3,Si} \cdot \exp\left(-\frac{E_{ads,NH_3,Si}}{R \cdot T_s}\right)$$

Adsorption of j - species

$$R_{ads,NH_3,Si} = k_{ads,NH_3,Si} \cdot C_{NH_3} \cdot (1 - \theta_{NH_3,Si} - \theta_{j,Si})$$

$$k_{ads,j,Si} = A_{ads,j,Si} \cdot \exp\left(-\frac{E_{ads,j,Si}}{R \cdot T_s}\right)$$

Desorption of NH_3

$$R_{des,NH_3,Si} = k_{des,NH_3,Si} \cdot \theta_{NH_3,Si}$$

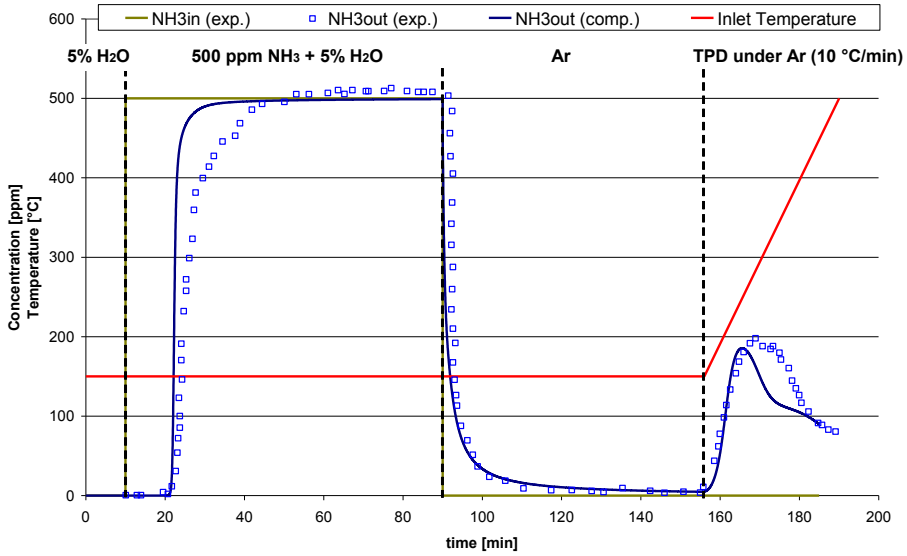
$$k_{des,NH_3,Si} = A_{des,NH_3,Si} \cdot \exp\left(-\frac{E_{des,NH_3,Si} \cdot (1 - a_{NH_3,Si} \cdot \theta_{NH_3,Si})}{R \cdot T_s}\right)$$

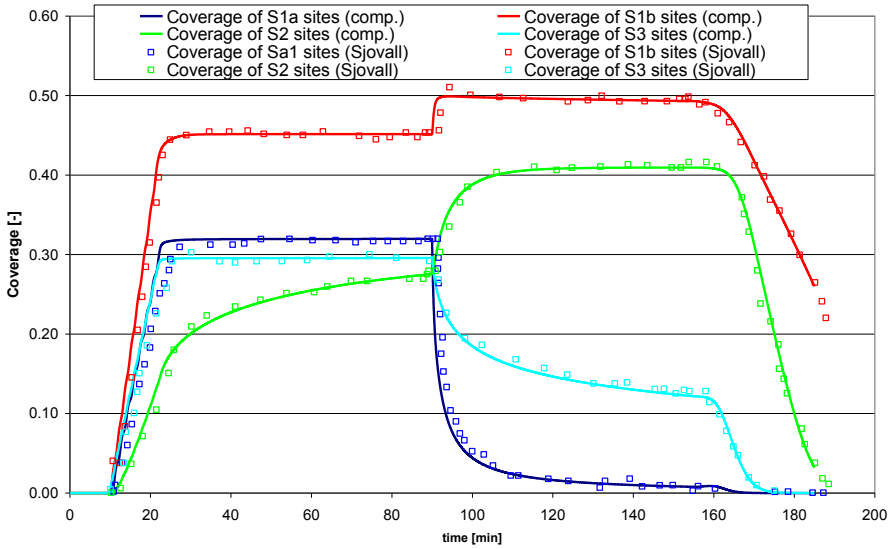
Desorption of j - species

$$R_{des,j,Si} = k_{des,j,Si} \cdot \theta_{j,Si}$$

$$k_{des,j,Si} = A_{des,j,Si} \cdot \exp\left(-\frac{E_{des,j,Si} \cdot (1 - a_{j,Si} \cdot \theta_{j,Si})}{R \cdot T_s}\right)$$

Competitive storage between NH_3 and H_2O (2/2)





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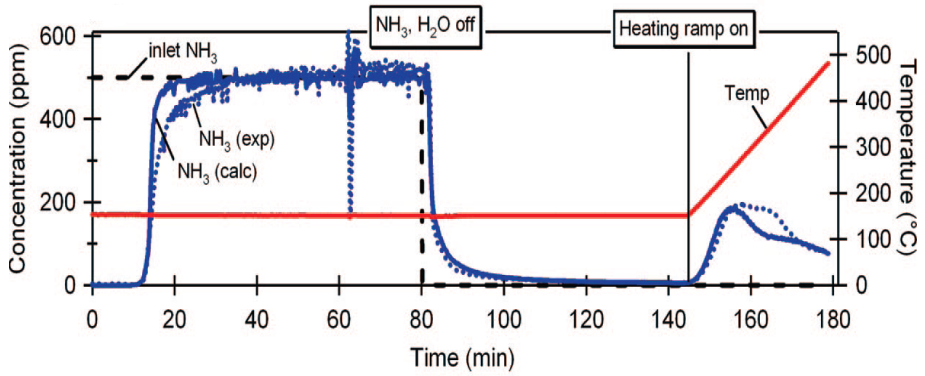

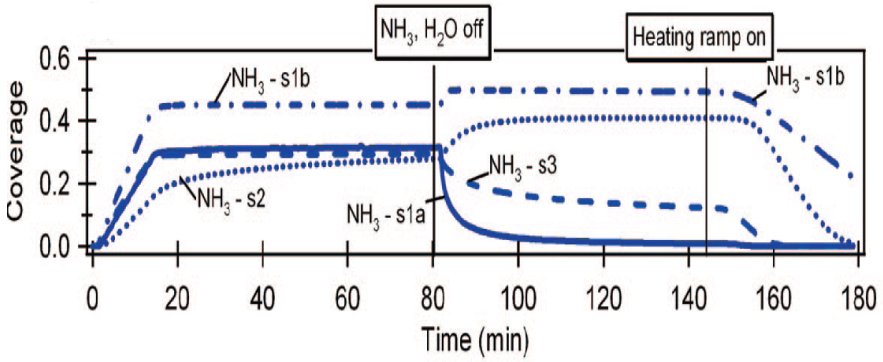

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Evaluation of the methodologies and conclusions

- **The single site approach:** Approximate but sufficient modeling approach.
- **The four sites approach:**
  - Semi-detailed modeling approach
  - Enables the connection between surface sites and reaction mechanisms
  - Demand for experimental data for the determination of the nature of surface sites.

- **Our intention:**
  - Use of a **multi-site approach** for the development of the **semi detailed kinetic model**.
  - **Extend** this approach to **Fe-zeolite** based, urea-SCR catalysts.
  - **Globalization** of the semi-detailed model.

THANK YOU FOR YOUR ATTENTION

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