Multi-site Modeling for Urea/NH_3-SCR over Fe-Zeolites

Stavros SKARLIS

CLEERS Workshop 2012

VECOM
Vehicle Concept Modeling

Technical advisors team
André NICOLLE (Supervisor, IFP E.N.)
David BERTHOUT (Supervisor, IFP E.N.)
Christophe DUJARDIN (Academic Supervisor, Univ. Lille 1)
Pascal GRANGER (Thesis Director, Univ. Lille 1)

UCCS – Université Lille 1

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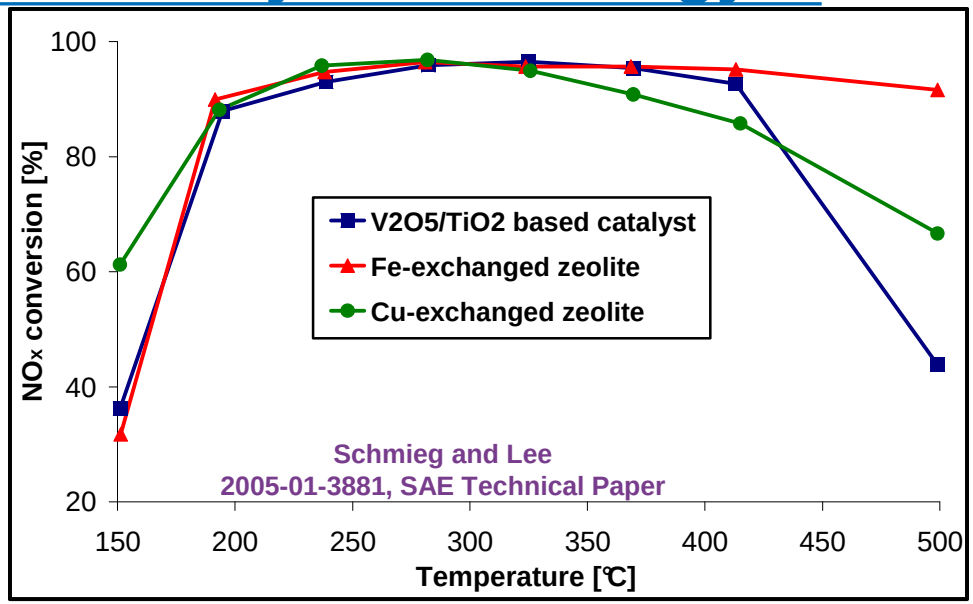
- **Fe-zeolite Urea-SCR catalyst technology**
- A multi-site kinetic model
- NH_3 storage on Fe-ZSM5
- Multi-site model development
- Conclusions and perspectives

Fe-zeolite based Urea-SCR catalyst technology

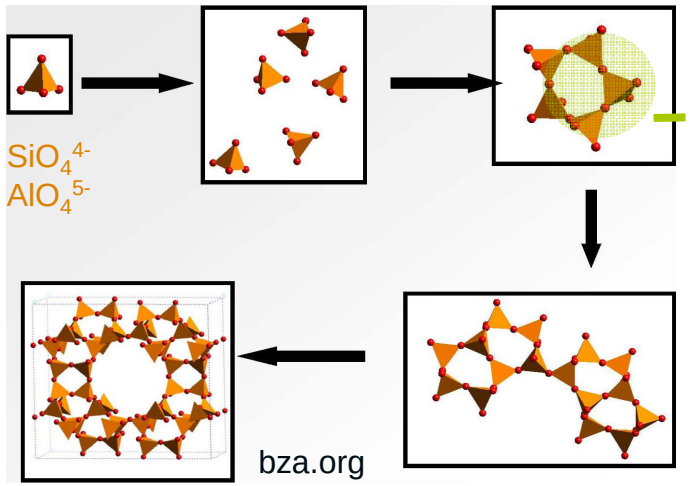
Fe-Zeolites as SCR catalysts

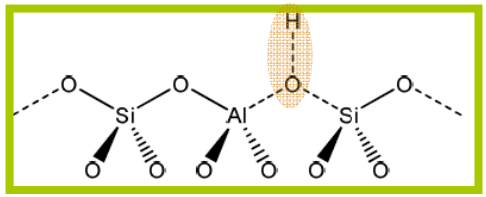
- High deNO_x efficiency over a broad range of temperatures: 150 – 500 °C

- Resistance to hydrothermal ageing



Alumina (Al_2O_3) – Silica (SiO_2) natural or synthetic materials



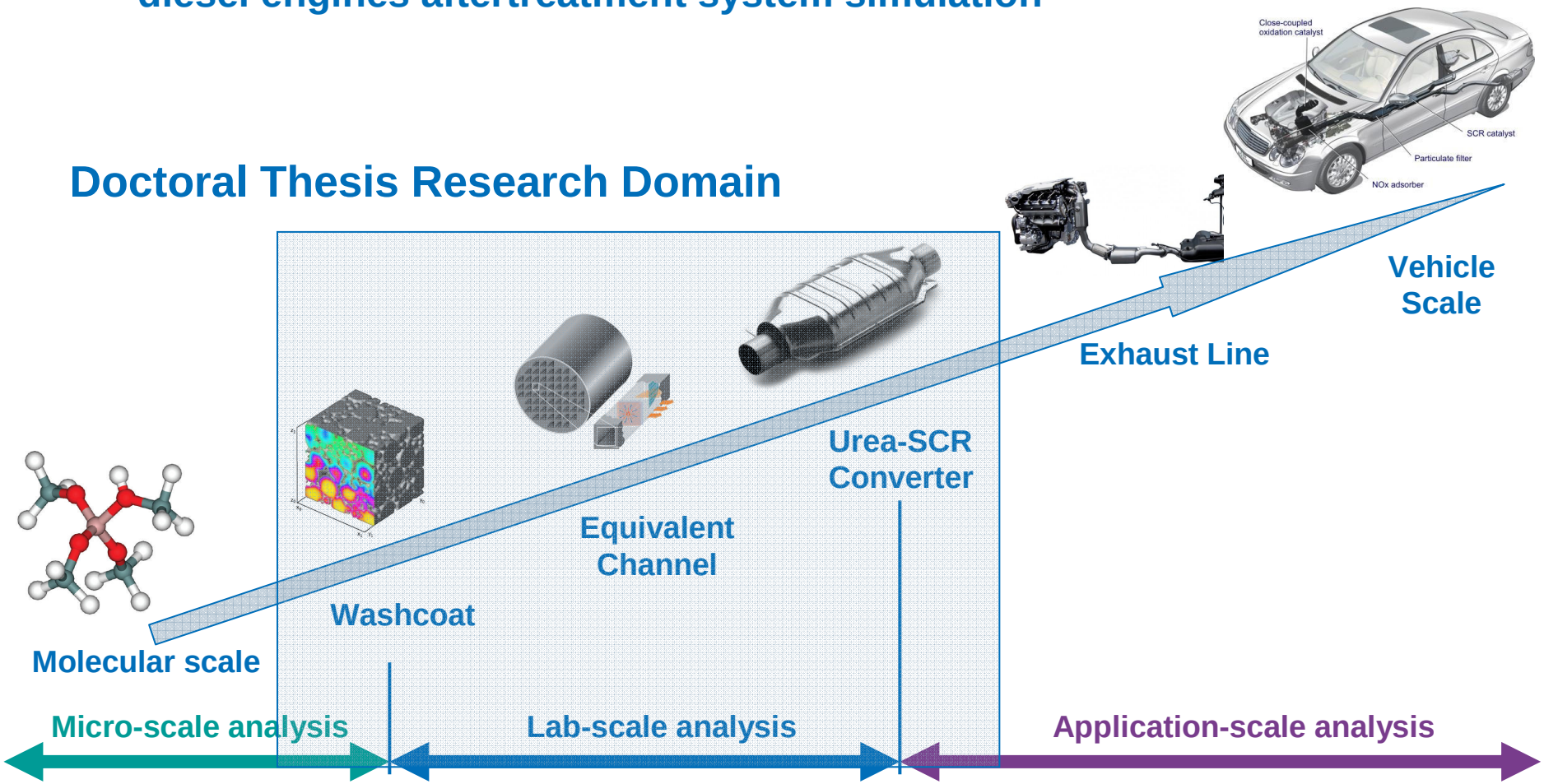


- H proton: **acidic properties**
- Exchanging the proton with transition metals (Fe, Cu, ...): **redox properties**

Doctoral Thesis Scope

- **Macro-kinetic modeling of a Fe-zeolite based Urea-SCR catalyst for diesel engines aftertreatment system simulation**

Doctoral Thesis Research Domain



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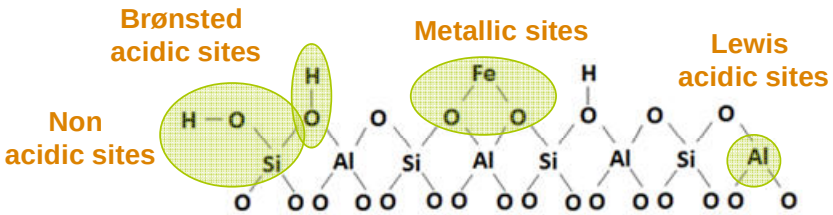
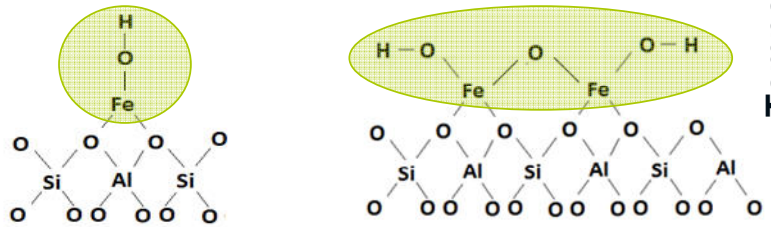
A multi-site kinetic model (1/3)

NH_3 storage on different sites



Metallic Sites



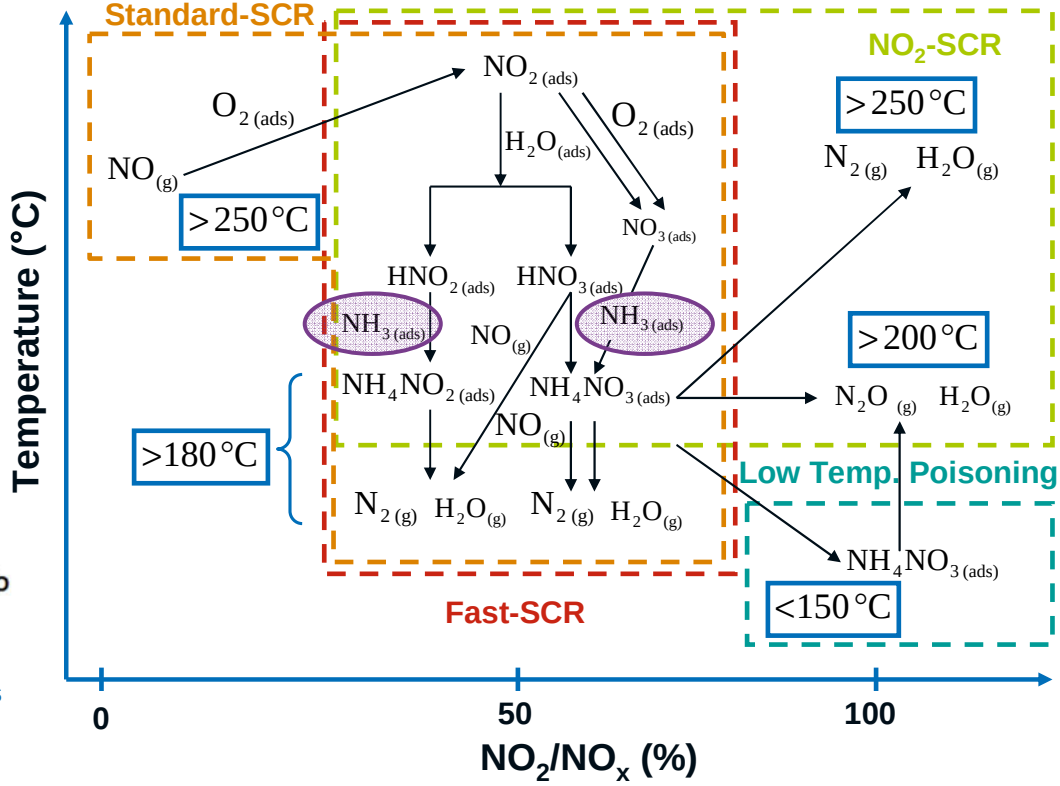
Fe(OH)

Monomeric species

$Fe_2O(OH)_2$

Dimeric (oligomeric) species

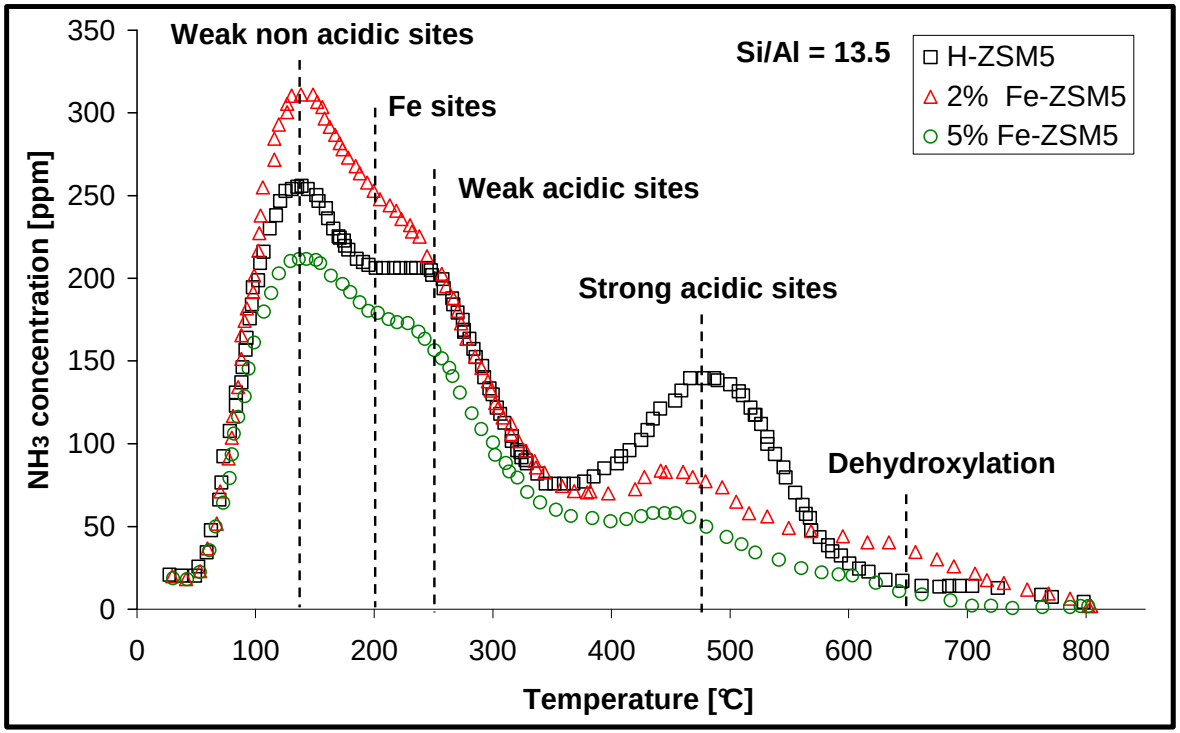
Crucial role of NH_3 storage on $deNO_x$ efficiency



Data extracted from Iwasaki et al. (A. Cat. A Gen., (2010), 390, 71-77)

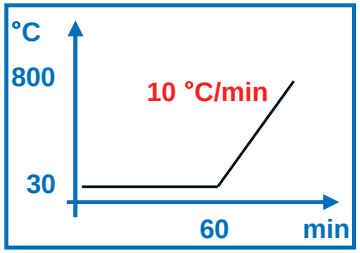
Development of a multi-site kinetic model based on NH_3 adsorption/desorption

A multi-site kinetic model (2/3)



Exp. results by Brandenberger et al. (J. Cat., (2009), 268, 297-306)

Pre-adsorption of 1% NH_3 at 30 °C



Types of surface sites included in the model:

- **S1: NON acidic sites for weak adsorption or physisorption**
- **S2: Weak acidic sites**
- **S3: Strong acidic sites**
- **S4: Metallic sites**
- **S5: Sites accounting for dehydroxylation effects at high temperatures**

Skeleton of a multi-site kinetic model

A multi-site kinetic model (3/3)

Kinetic model

Reaction rate expressions

Adsorption

$$R_{NH_3\_ads} = k_{ads}(T_s) \cdot C_{NH_3} \cdot (1-\theta_j)$$

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

Desorption

$$R_{NH_3\_des} = k_{des}(T_s, \theta_j) \cdot \theta_j$$

$$k_{des} = A_{des} \cdot \exp\left(-\frac{E(\theta_j)_{des}}{R \cdot T_s}\right)$$

$$E(\theta_j)_{des} = E_0 \cdot (1-\alpha \cdot \theta_j)$$

Species Conservation

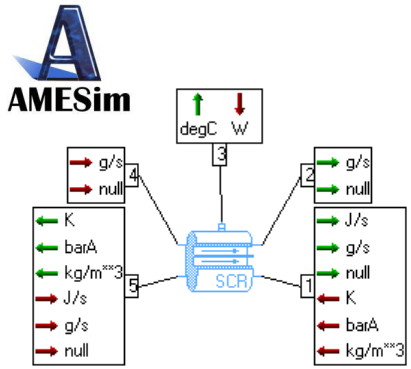
$$\dot{\omega}_{NH_3} = \left(\sum_{j=1}^{5} \nu_j R_j\right) \cdot m_{zeolite}$$

$$N_j \cdot \frac{\partial \theta_j}{\partial t} = \sum_{j=1}^{5} \nu_j \cdot R_j$$

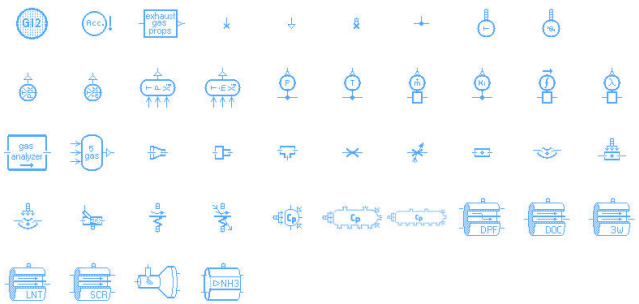
$$j = S1, S2, S3, S4, S5$$

The IFP-Exhaust Library

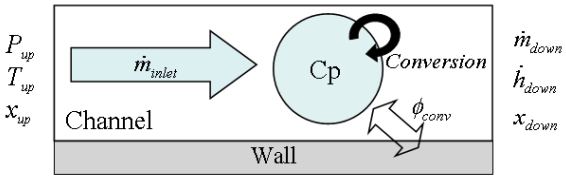
LMS.Imagine.Lab AMESim
0D SCR Catalyst modeling



IFP Exhaust Library



Modeling the exhaust line using components



Equivalent channel approach

0D solid energy balance

$$\rho_s \cdot Cp_s \cdot V_s \cdot \frac{dT_s}{dt} = h_s \cdot S_{geom.} \cdot (T_g - T_s) + S$$

$$S = Q_{conv.} + Q_{reac.} + Q_{rad.}$$

External/Internal species diffusion through Thiele modulus approach

$$k_{m,i} \cdot s \cdot \left(c_{g,i} - c_{s,i}\right) = \frac{\eta_i \cdot \dot{\omega}_i}{V_{wash}}$$

$$\eta_i = \frac{\tanh(\phi)}{\phi \cdot \left[1 + \frac{\phi \cdot \tanh(\phi)}{Bi_m}\right]}$$

Equivalent channel: gas balances Momentum/Energy/Species

$$P_{in} - P_{out} = \frac{d_w \cdot \rho_g \cdot A_{open}}{32 \cdot \dot{m}_g \cdot \mu \cdot L_{mono}}$$

$$m_g \cdot C_v \cdot \frac{dT_g}{dt} = \sum_i m_i \cdot h_i + \frac{dQ_{conv.}}{dt} - P_g \cdot \frac{dV_{mixt.}}{dt} - m_g \cdot \sum_i \frac{dx_i}{dt} \cdot u_i - \frac{dm_g}{dt} \cdot \int C_v dT$$

$$\frac{dc_{g,i}}{dt} = (\dot{c}_{g,i\_in} - \dot{c}_{g,i\_out}) + \phi_{film} \qquad \dot{\omega} = \sum_i v_i \cdot R_i$$

Catalytic reactor modeling based on the bond graph theory

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NH_3 storage on Fe-ZSM5 (1/5)

A) Model Calibration

Calibration based on data reported in literature

Kinetic parameters calibration

Type of site	A_{ads} [$m^3/s \cdot kg_{zeolite}$]	E_{ads} [kJ/mol]	A_{des} [$mol/s \cdot kg_{zeolite}$]	E_{des} [kJ/mol]	α [-]
S1 (weak non acidic sites)	1200	0	10^{13}	95.0	0.39
S2 (weak acidic sites)	700	0	10^{13}	134.5	0.155
S3 (strong acidic sites)	950	0	10^{13}	195.0	0.130
S4 (metallic sites)	500	0	10^{13}	125.0	0.10
S5 (dehydroxylation effects)	800	0	10^{14}	255.0	0.00

Reference Database

Non activated process

Immobile molecules

Homogeneous acidic strength

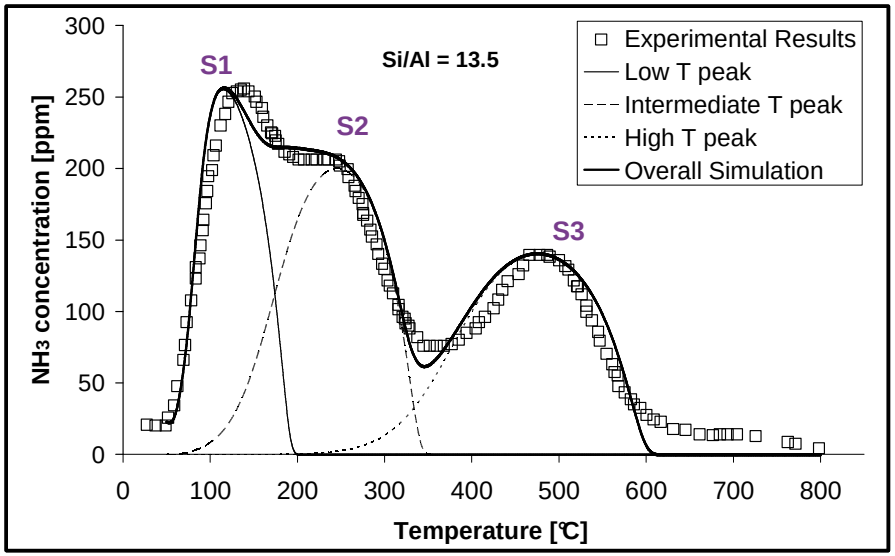
Data from thermogravometric, calorimetric measurements..

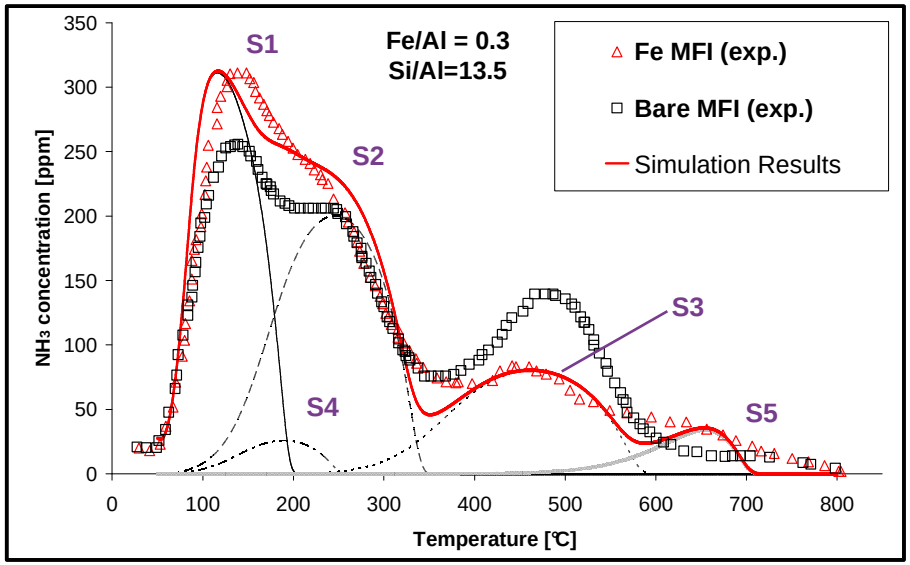
NH_3 storage capacity estimation

- Estimation of NH_3 storage capacity **over each surface site**
- Estimation based on **zeolite structural properties**:
  - **Si/Al**
  - **Fe/Al**

NH_3 storage on Fe-ZSM5 (2/5)

Kinetic parameters manual calibration





Exp. results by Brandenberger et al. (J. Cat., 2009, 268, 297-306)

Type of site	A_{ads} [$m^3/s \cdot kg_{zeolite}$]	E_{ads} [kJ/mol]	A_{des} [$mol/s \cdot kg_{zeolite}$]	E_{des} [kJ/mol]	α [-]
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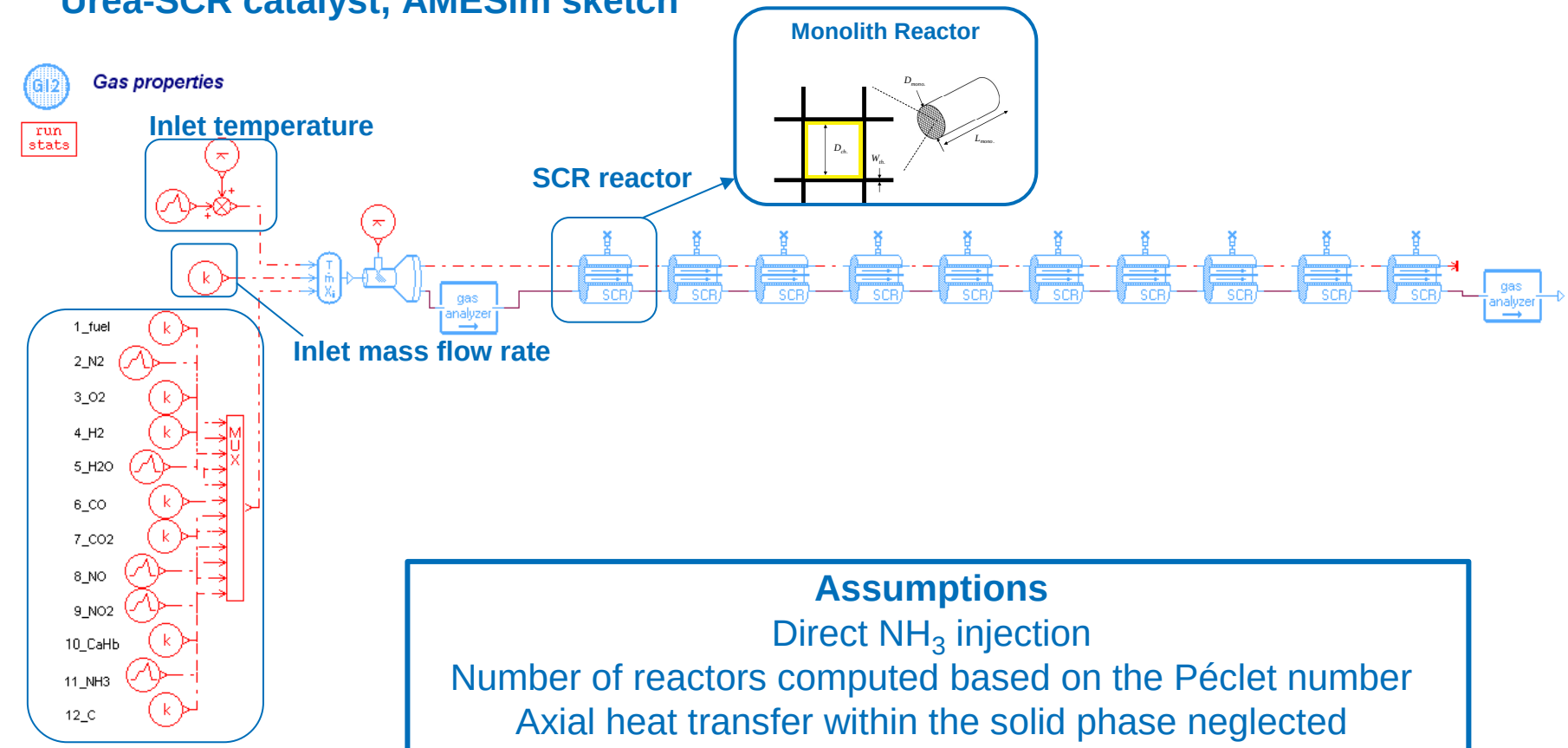
Manual calibration

NH_3 storage on Fe-ZSM5 (3/5)

Urea-SCR catalyst, AMESim sketch



Assumptions

Direct NH_3 injection

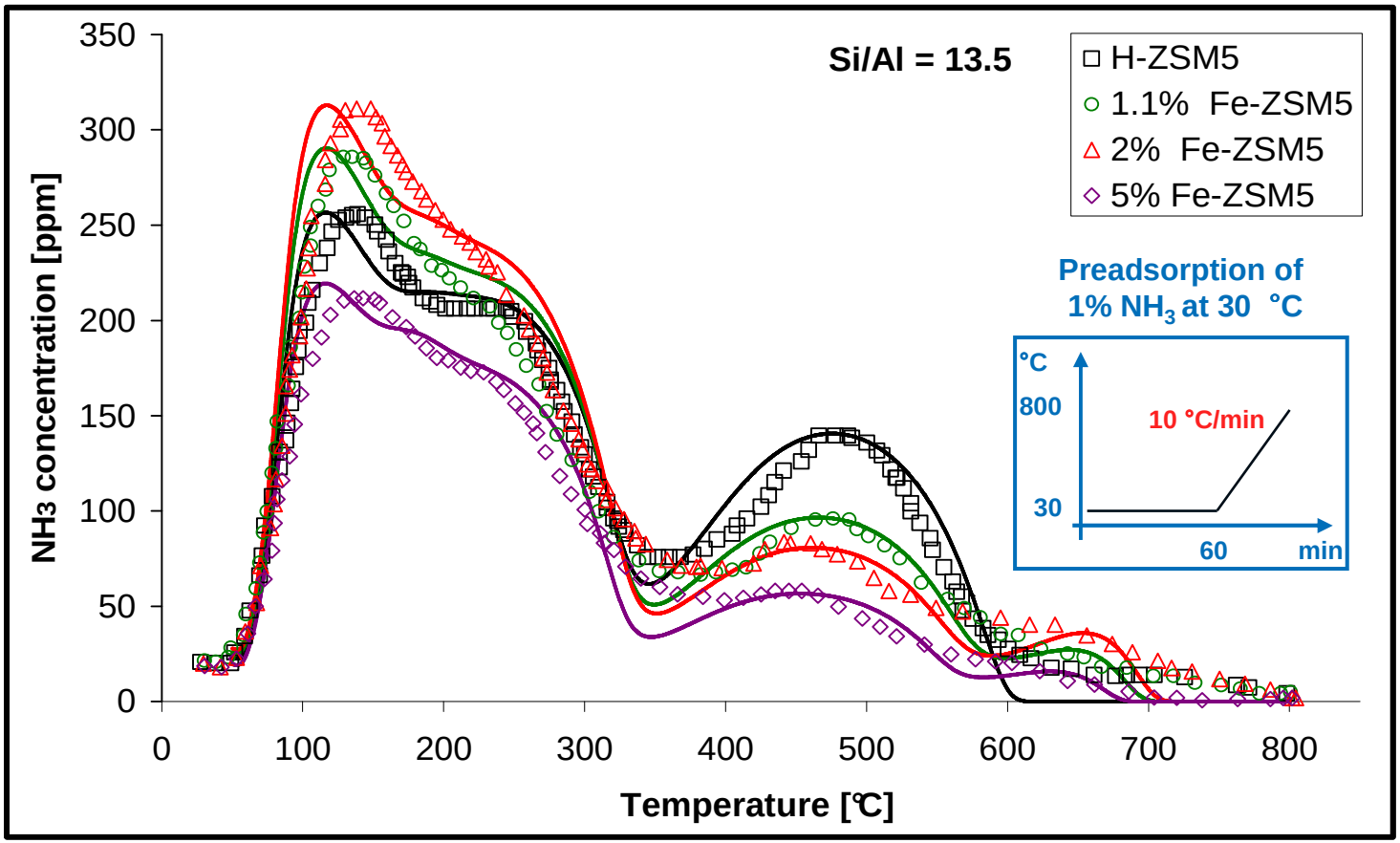
Number of reactors computed based on the Péclet number

Axial heat transfer within the solid phase neglected

Heat loses to ambient neglected

NH_3 storage on Fe-ZSM5 (4/5)

B) Model Validation: Fe-ZSM5 with different Fe loading



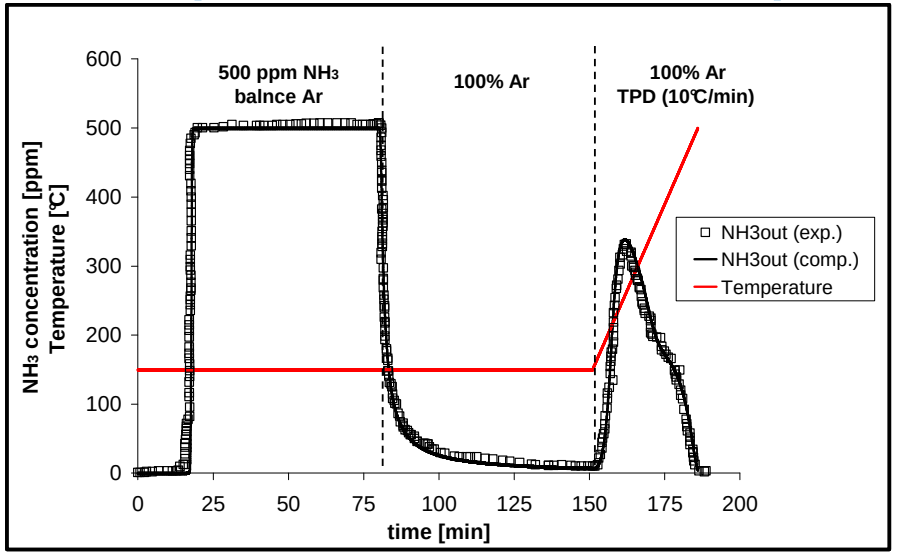
Exp. results by Brandenberger et al. (J. Cat., (2009), 268, 297-306)

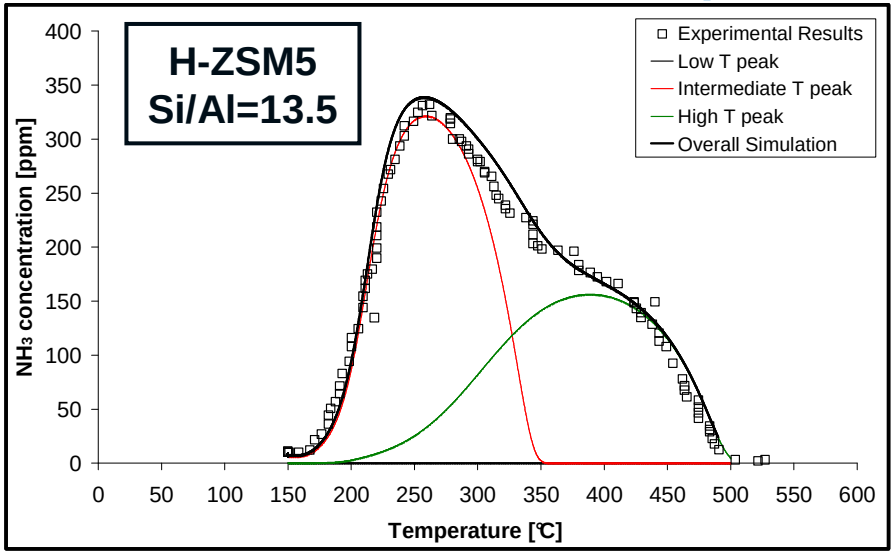
Points: Experimental Data **Lines: Simulation Results**

Skarlis et al. J. Phys. Chem. C 2012 116 (15), pp 8437–8448

NH_3 storage on Fe-ZSM5 (5/5)

C) Model Robustness: Experiment on a different H-ZSM5 sample





Exp. results by Sjövall et al. (J. Phys. Chem. C, (2009), 113, 1393-1405)

Recalibration of kinetic parameters

data reported in literature

recalibrated values

Type of site	A_{ads} [$m^3/s \cdot kg_{zeolite}$]	E_{ads} [kJ/mol]	A_{des} [$mol/s \cdot kg_{zeolite}$]	E_{des} [kJ/mol]	α [-]
S1 (weak non acidic sites)	1200	0	10^{13}	95 **92.7**	0.39
S2 (weak acidic sites)	700	0	10^{13}	134.5 **132**	0.155
S3 (strong acidic sites)	950	0	10^{13}	195 **170**	0.130

Different characteristics of parent zeolite with respect to the state of its structure (eg. history of the sample) (Rodriguez-Gonzalez et al., A. Cat. A: Gen. (2007) 328, 174-182)

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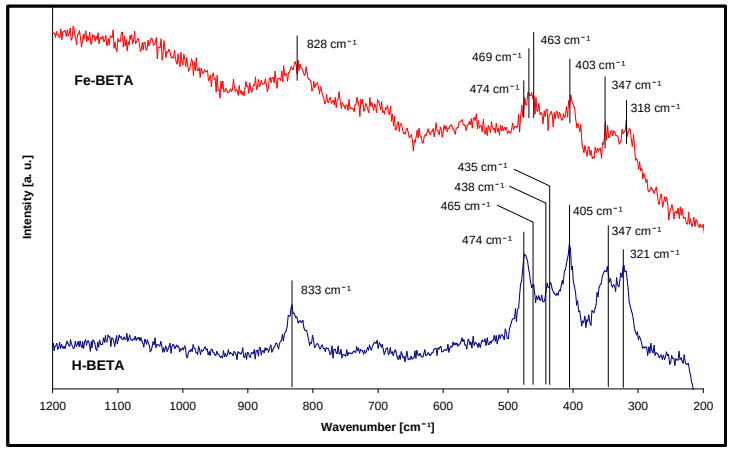
Model capitalization (1/2)

A. Lab-scale experiments

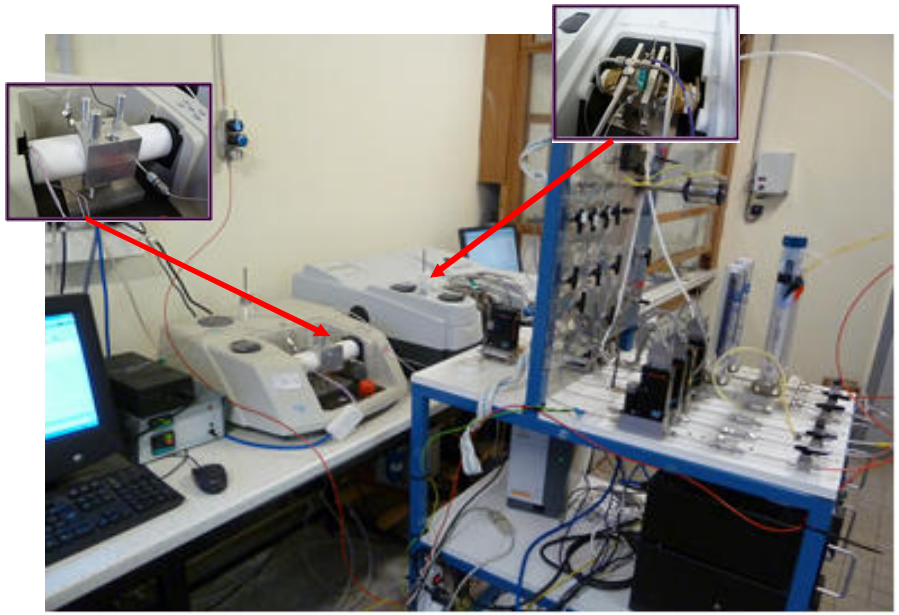
Catalysts preparation/characterization

1.75 %wt Fe-BETA



1.75 %wt Fe-BETA and H-BETA characterization through **RAMAN spectroscopy**

SCR experiments coupling IR spectroscopy

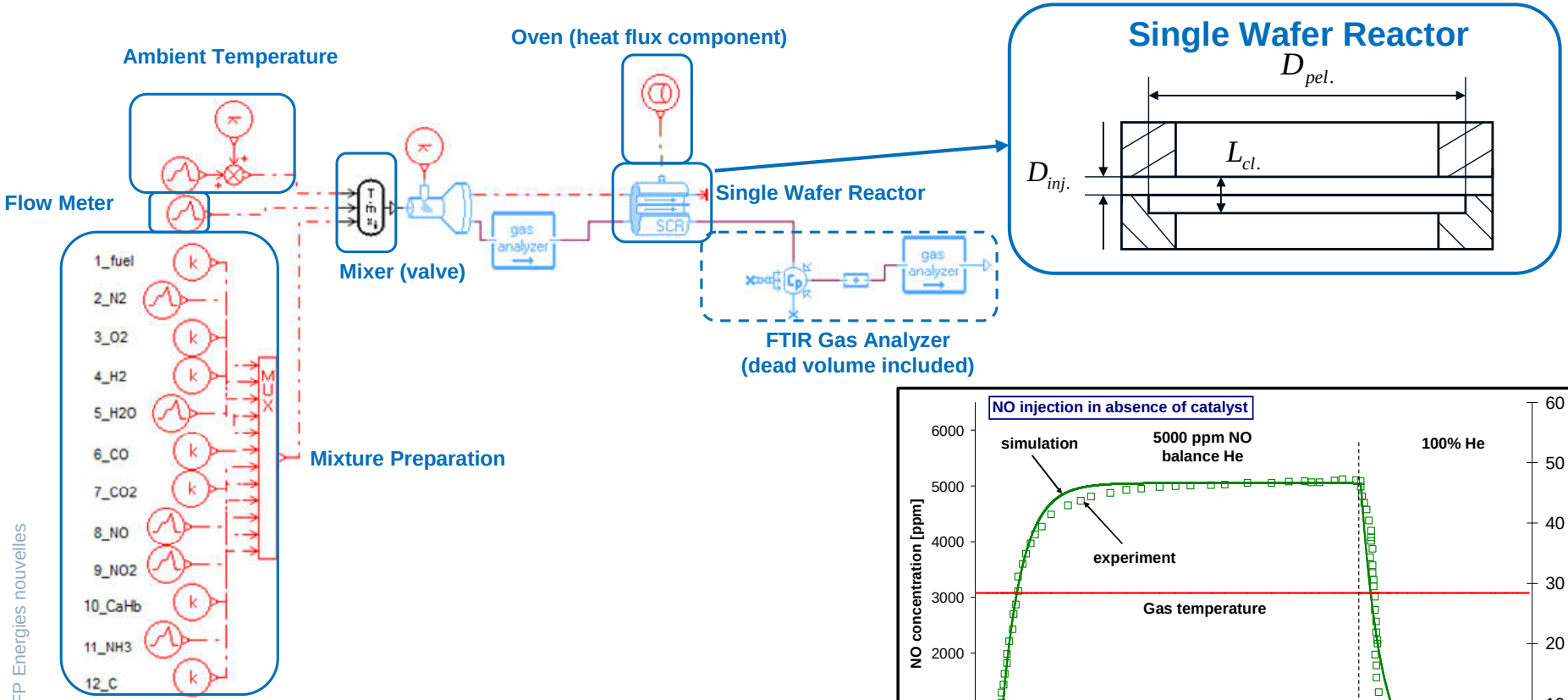


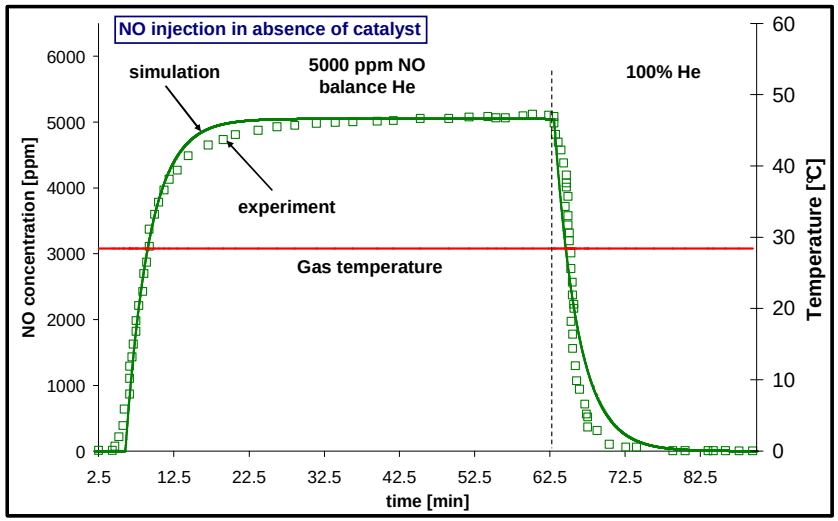
Experimental set-up of UCCS laboratory of University of Lille

Model capitalization (2/2)

B. Modeling and Simulation using IFP-Exhaust Library

Reproduction of experimental set-up





Reactor Model Calibration

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Conclusions and perspectives

- **Development of a multi-site kinetic model for NH_3 adsorption and desorption over Fe-ZSM5.**
  - **Validation and calibration** by simulation of experiments applying **different operating conditions**
  - Skeleton of a multi-site kinetic model for SCR reactions over different Fe-zeolites

- **Multi-site model capitalization: Experimental investigation** and **modeling and simulation**.

- **Work underway**
  - **Correlation between model sites and natural surface sites** (Brønsted, Lewis etc.):
    - NH_3 adsorption and TPD experiments on 1.75% wt. Fe-BETA
    - publication under development.

  - Multi-site model development through **experiments over 1.75% Fe-BETA**:
    - **NO_x storage and disproportionation**
    - **Focus on NH_4NO_3 formation and decomposition**

Thank you for your kind attention

Stavros A. Skarlis kindly acknowledges the EU FP7 Marie Curie Initial Training Network (ITN) VECOM

Study of NH_3 storage on Fe-ZSM5 performed under supervision of:

David Berthout[a], André Nicolle[a], Christophe Dujardin[b], Pascal Granger[b]

[a]IFP Energies Nouvelles, France
[b]Unité de Catalyse et de Chimie du Solide - Université de Lille 1, France

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