IR-spectroscopy based multi-site kinetic modeling for NH_3-SCR on Fe-BEA

Stavros SKARLIS

CLEERS Workshop 2013

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UCCS – Université Lille 1

Outline

- Fe-zeolite based Urea-SCR catalysts
- A multi-site kinetic modeling approach
- IR spectroscopy based multi-site kinetic modeling
  - Fe-BEA synthesis and characterization
  - NH_3 adsorption: IR spectroscopic measurements
  - Modeling and simulation
- Conclusions and perspectives

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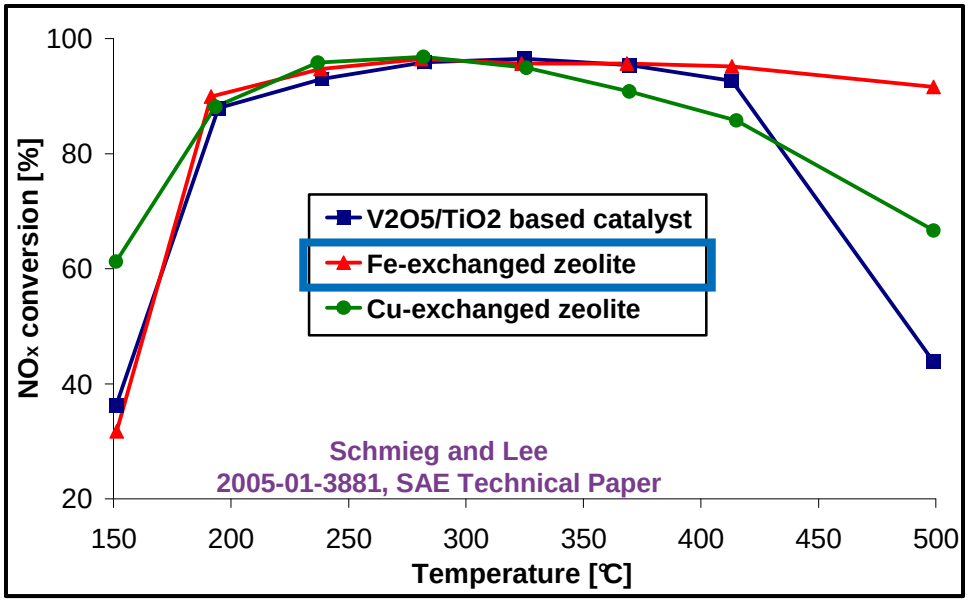
Fe-zeolite based Urea-SCR catalysts (1/2)

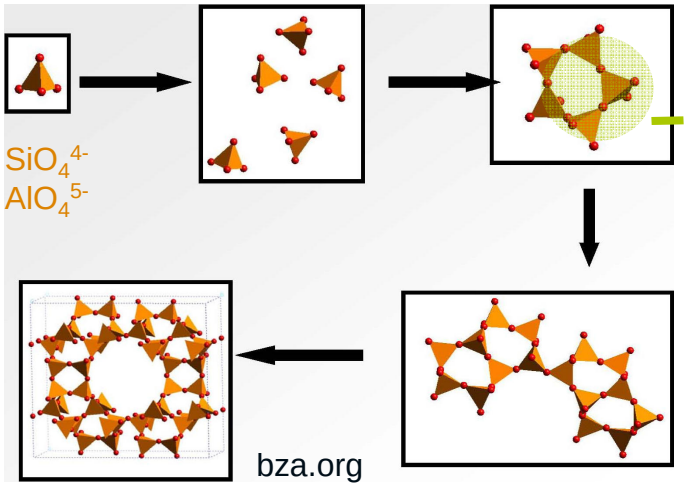
Fe-zeolites as SCR catalysts

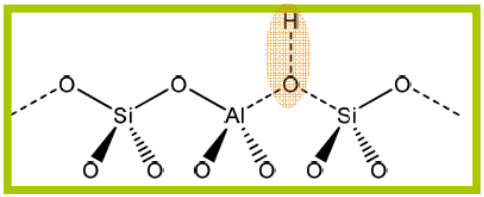
- High deNO$_x$ efficiency over a broad range of temperatures: 200 – 550 °C

- Resistance to hydrothermal ageing



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

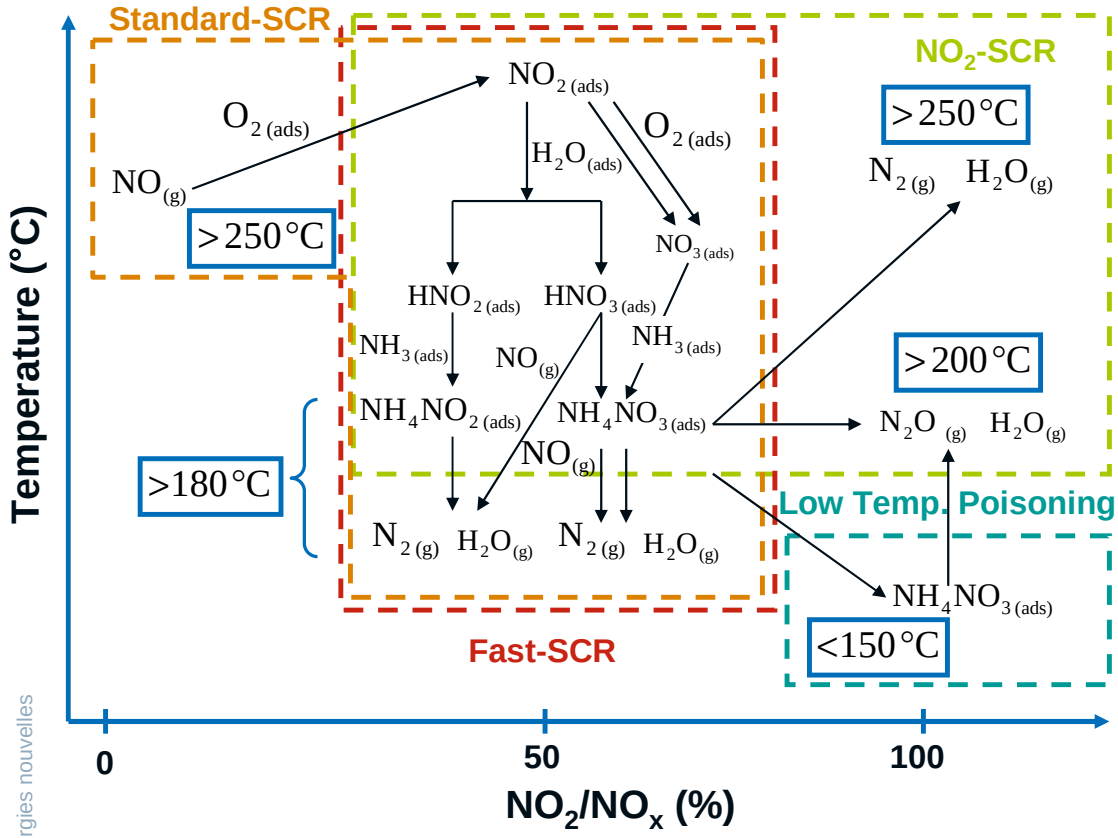


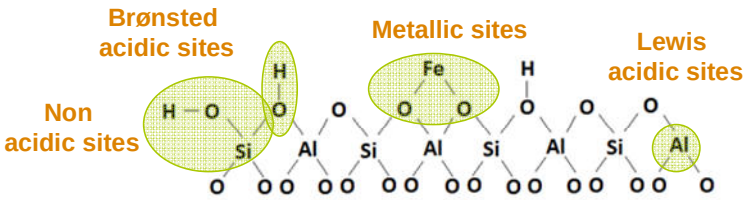


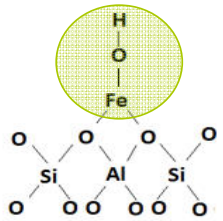
- H proton: **acidic properties**
- Exchanging the proton with transition metals (Fe, Cu, ...): **redox properties**

Fe-zeolite based Urea-SCR catalysts (2/2)

NH_3-SCR chemistry over Fe-zeolites

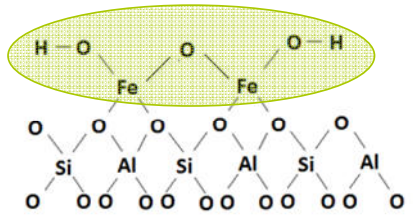






Fe(OH)

Monomeric species



$Fe_2O(OH)_2$

Dimeric (oligomeric) species

Iwasaki et al. A. Cat. A Gen. (2010), 390, 71-77
Brandenberger et al. J. Catal. (2009) 268, 297-306
Grossale et al. Catal. Lett. (2009) 130, 525-531
Granger et al. Chem. Rev. (2011) 111, 3155-3207
Brandenberger et al. A. Cat. A Gen. (2010) 373, 168-175

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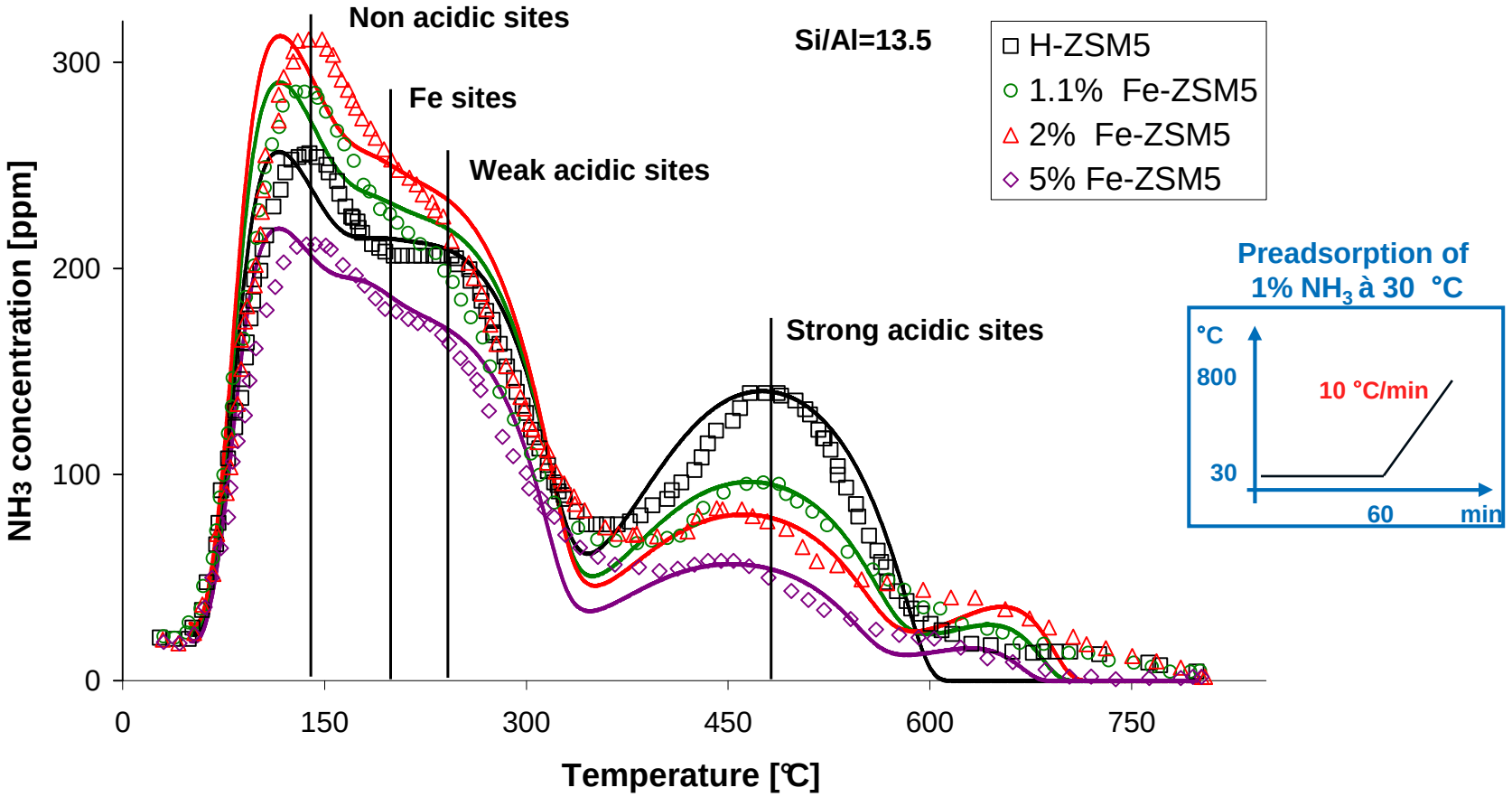
A multi-site kinetic modeling approach (1/2)

Multi-site kinetic modeling of NH_3 adsorption and desorption on Fe-ZSM5

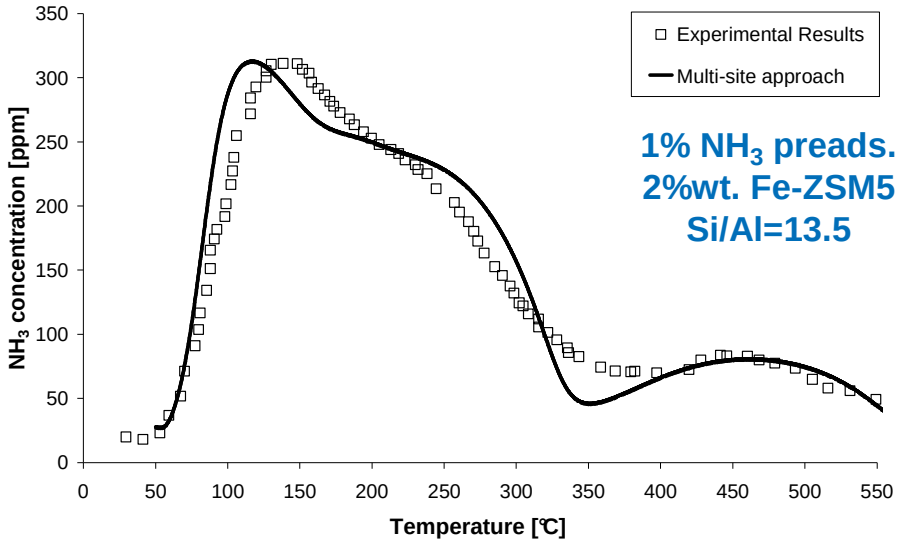


Exp. results by Brandenberger et al. (J. Catal., (2009), 268, 297-306)

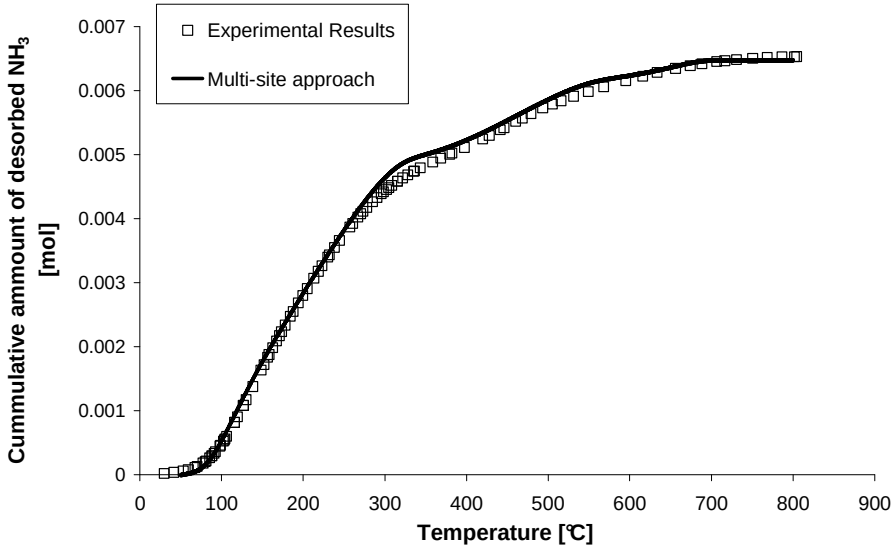
Symbols: Experimental results Lines: Simulation results

SKARLIS et al. J. Phys. Chem. C (2012) 116, 8437-8448

A multi-site kinetic modeling approach (2/2)



1% NH_3 preads.
2%wt. Fe-ZSM5
Si/Al=13.5



SKARLIS et al. TRA Europe 2012

Multi-site kinetic modeling approach evaluation

✓	✗
Phenomenological approach	**Experimental results required for model development**
Precision	**Kinetics calibration complexity**

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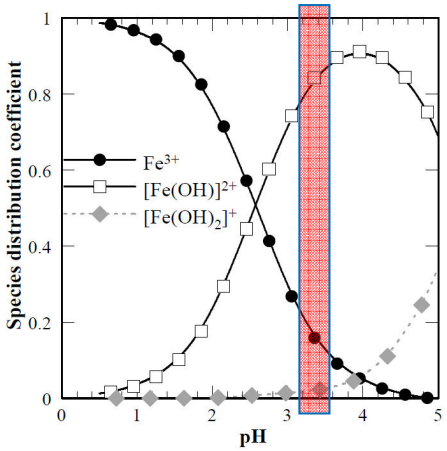
Fe-BEA synthesis and characterization (1/2)

Fe-BEA synthesis



Parent zeolite: **H-BEA (Si/Al=11.8)** [IFP EN]

Synthesis method: **Wet ion exchange**

Fe precursor: **$Fe(NO_3)_3$ aqueous solution**

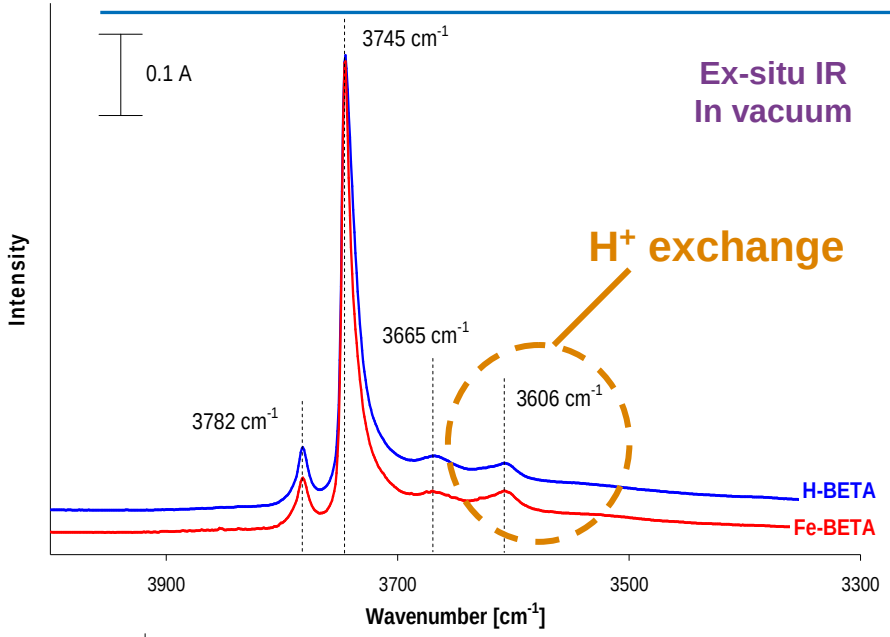
Protocol: **G. Delahay et al.**

(A. Cat. B: Environ., 55, 149-155)

ICP-AES results

Element	Composition (wt.%)	Molar amount ($mol/kg_{cat.}$)
Fe	1.75	0.31
Al	2.98	1.11
Si	36.93	13.15

Fe-BEA synthesis and characterization (2/2)



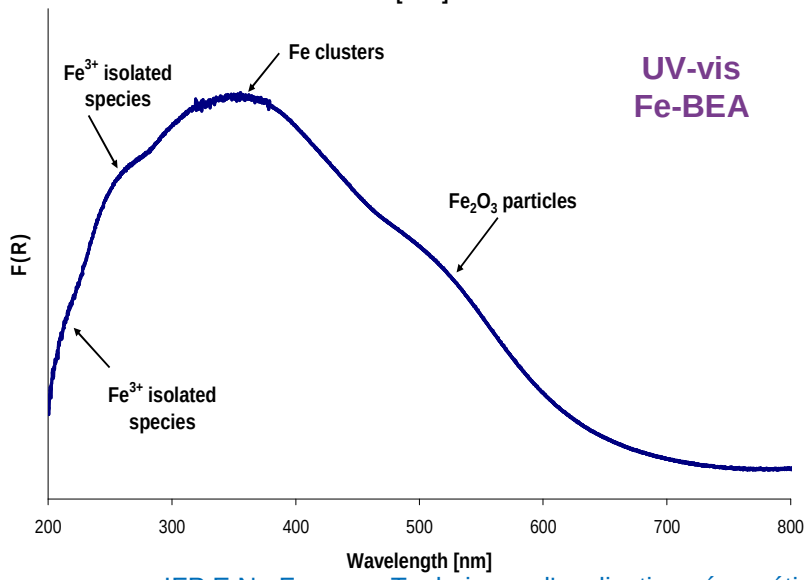
Surface sites characterization

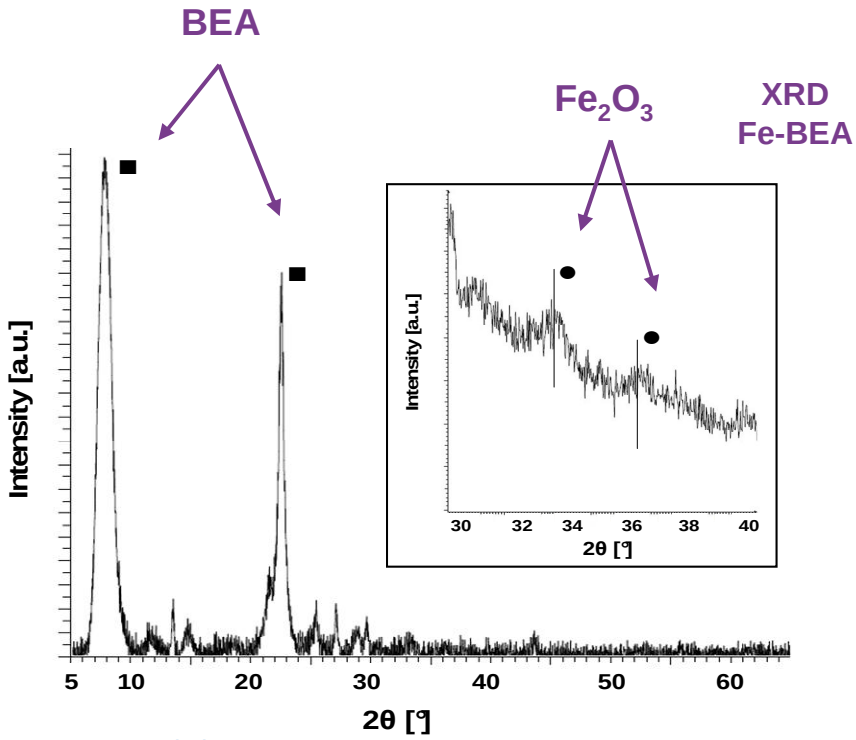
3782 cm^{-1}: Framework Al (FAl)

3745 cm^{-1}: Terminal silanol

3665 cm^{-1}: Extra-framework Al (EfAl)

3606 cm^{-1}: OH^+ Brønsted acidic sites





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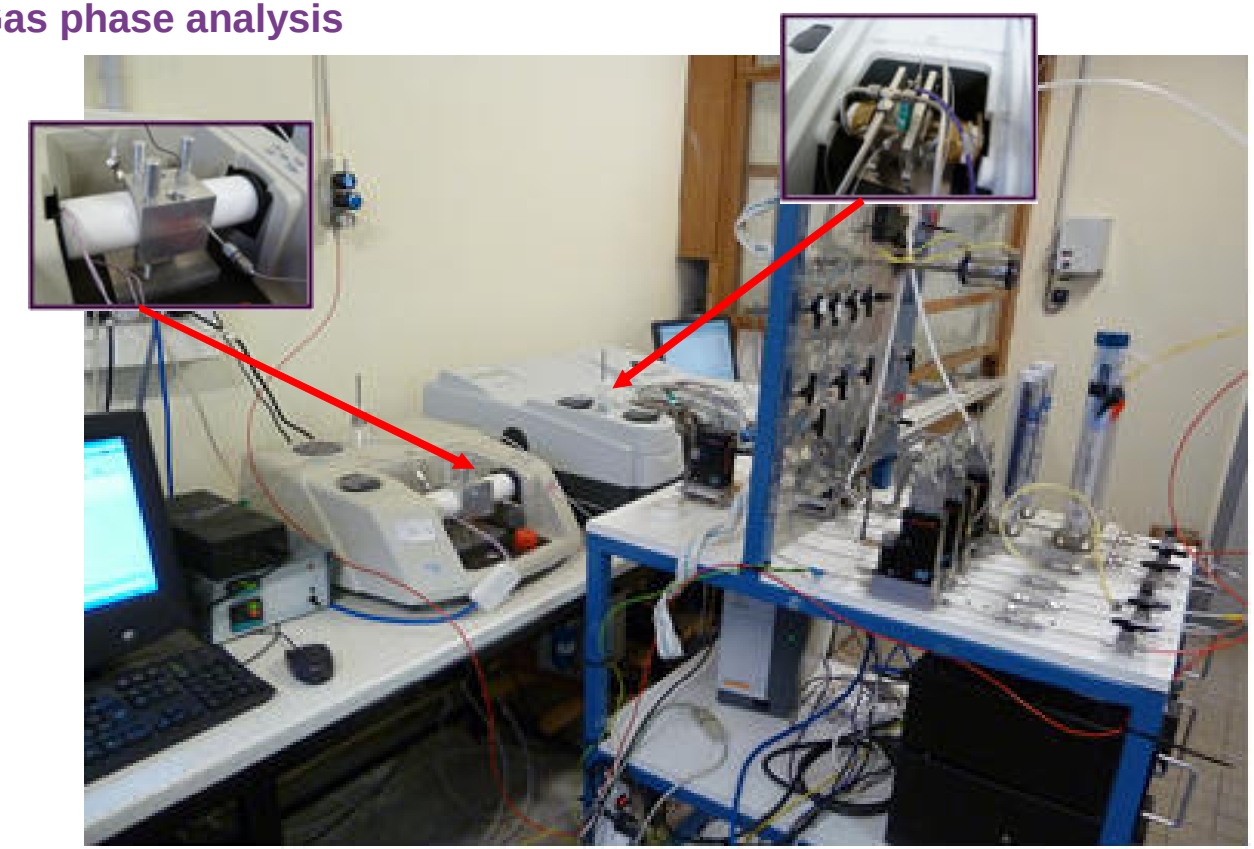
NH_3 adsorption: IR spectroscopic measurements (1/4)

Experimental set-up

Solid phase analysis

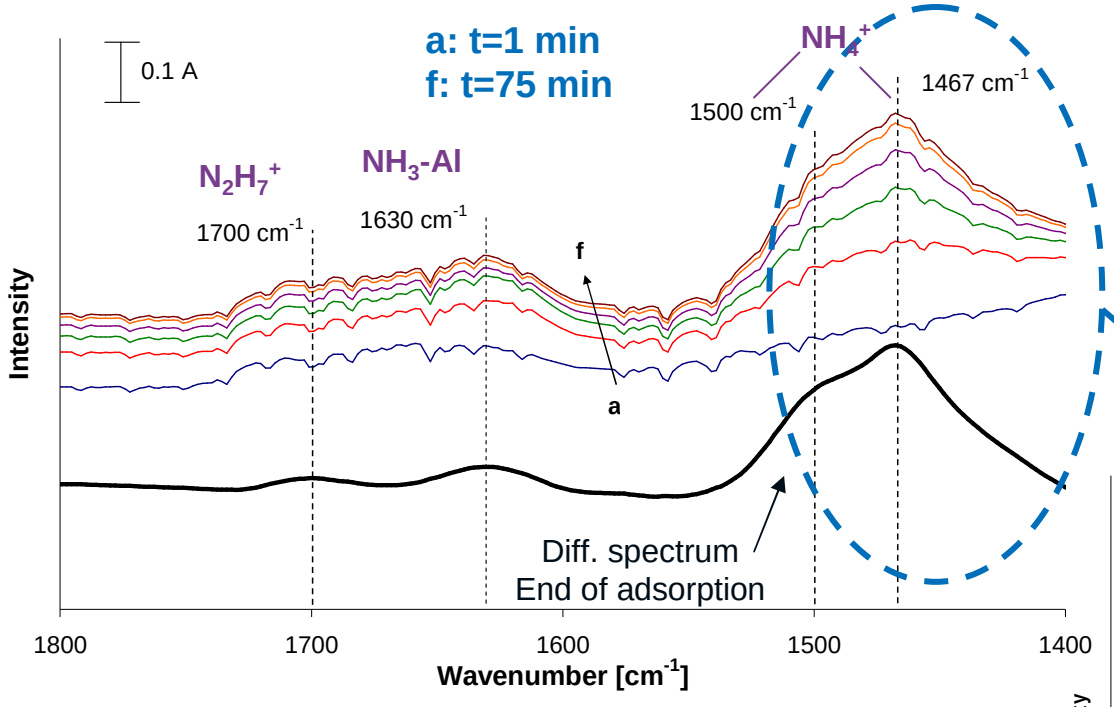
Gas phase analysis



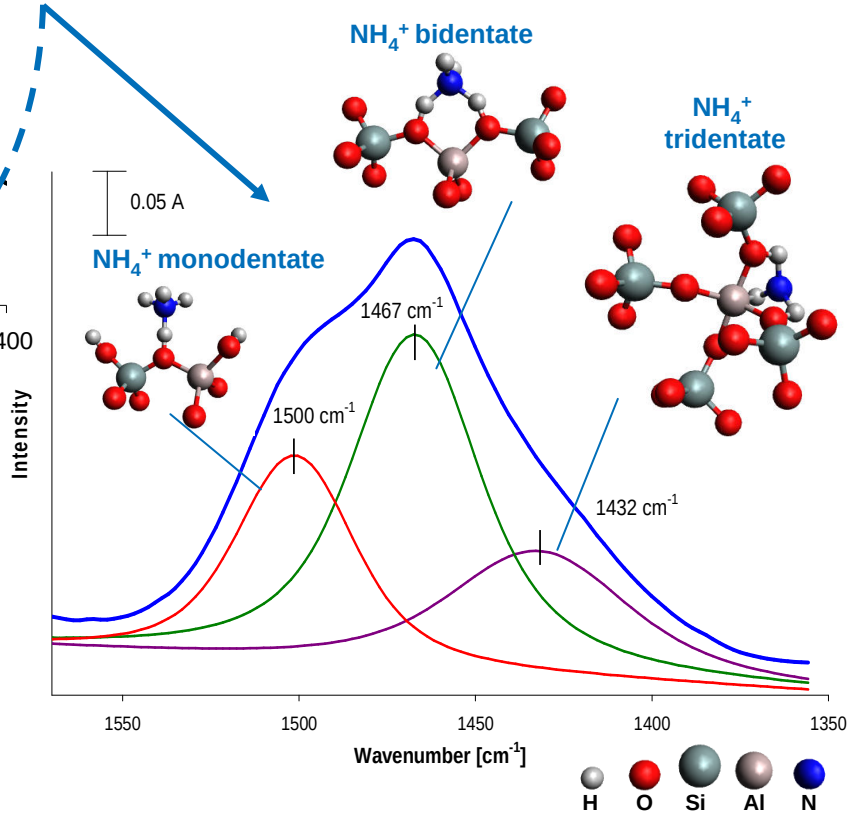
10 mg H- & Fe-BEA
Crushed in pellet
$P = P_{atm.}$

NH_3 adsorption: IR spectroscopic measurements (2/4)

Measurements on H-BEA



Experimental conditions
500 ppm NH_3
balance He
$T_{ads.}$ = 30 °C
$\Delta t_{ads.}$ = 75 min

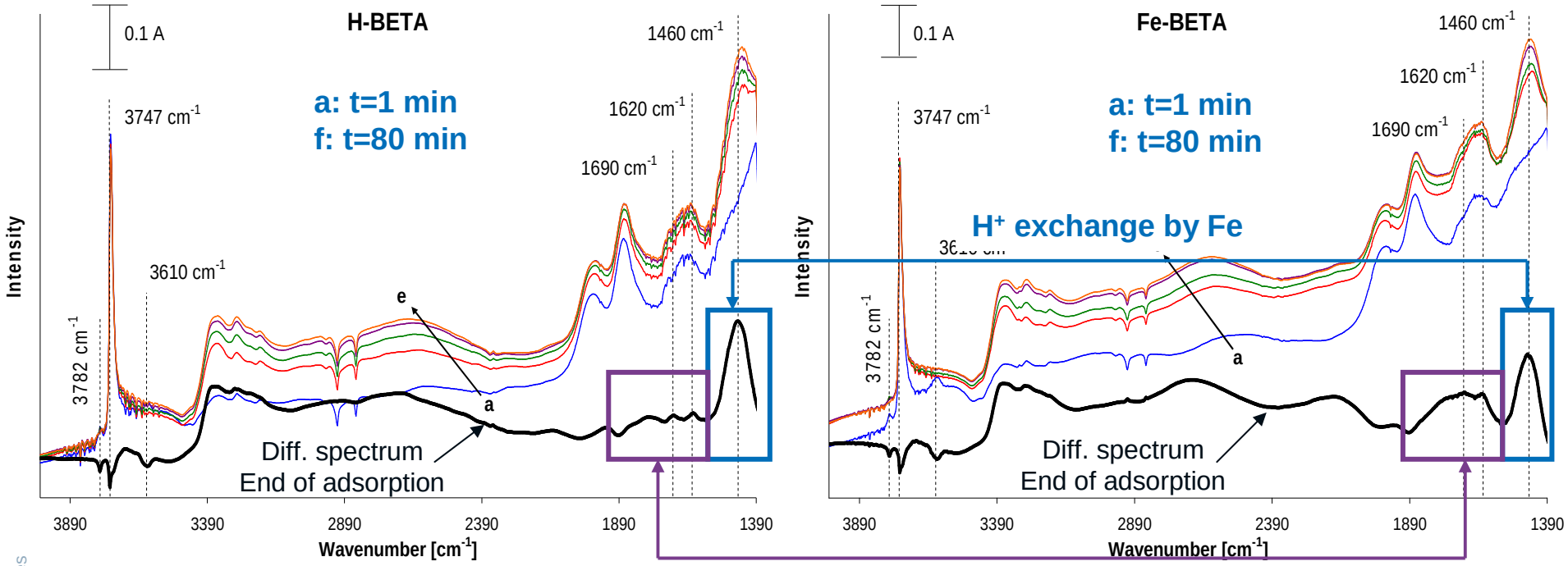


Adspecies characterization

1500 cm^{-1}: weakly H-bonded NH_3
1630 cm^{-1}: NH_3 on Al (Lewis acidic sites)
1467 cm^{-1}: NH_4^+ on Brønsted acidic sites
1700 cm^{-1}: $N_2H_7^+$ - Multi-layer adsorption

NH_3 adsorption: IR spectroscopic measurements (3/4)

Measurements on Fe-BEA

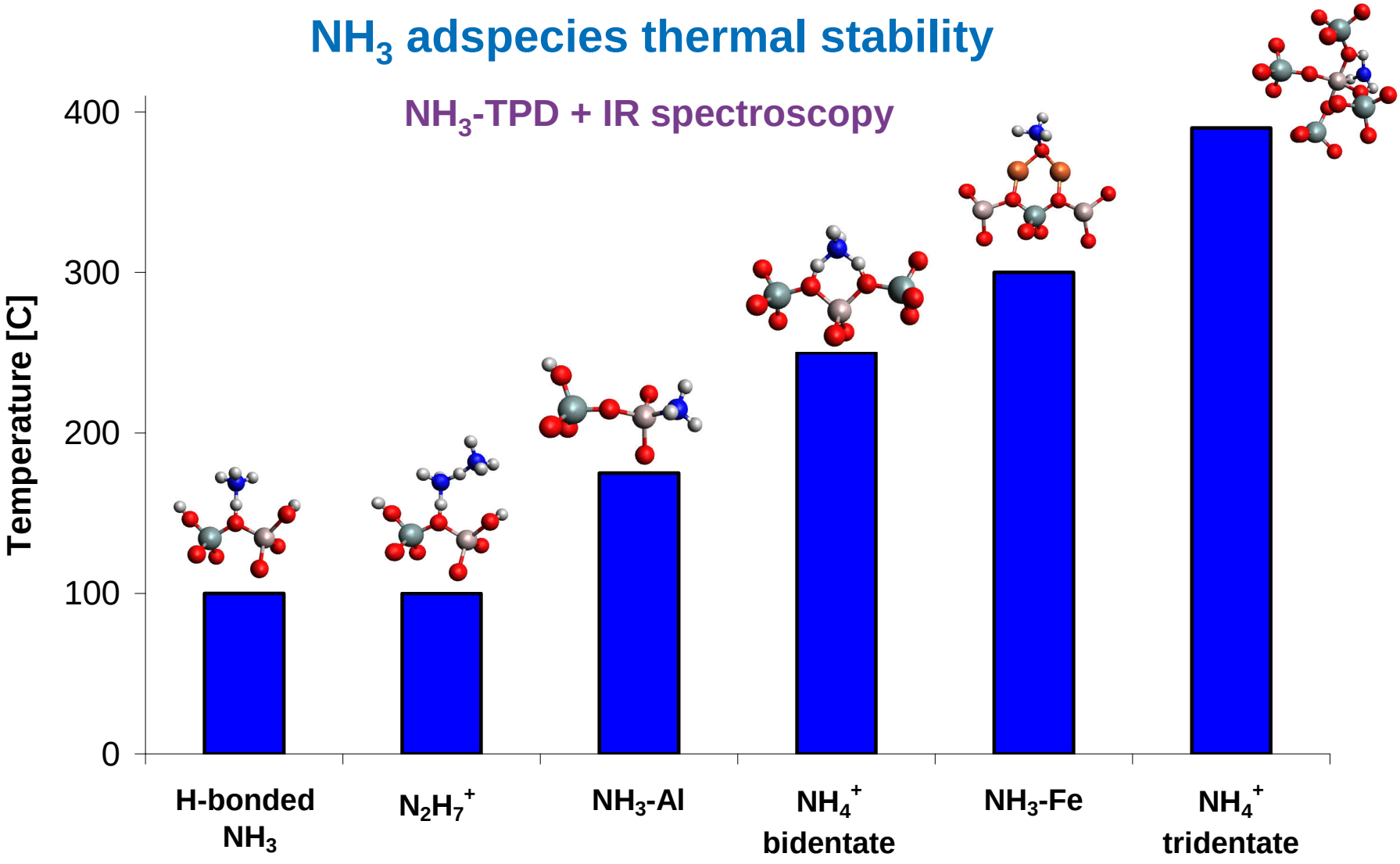


Formation of Lewis type Fe sites

Experimental conditions
500 ppm NH_3
balance He
$T_{ads.}$ = 150 °C
$\Delta t_{ads.}$ = 80 min

NH_3 adsorption: IR spectroscopic measurements (4/4)

NH_3 adspecies thermal stability



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Modeling and simulation (1/5)

Kinetic model

S1a site for weak adsorption and physisorption	$NH_{3(g)} + S1a \rightleftharpoons NH_3 - S1a$
S1b weak Brønsted and Lewis sites	$NH_{3(g)} + S1b \rightleftharpoons NH_3 - S1b$
NH_3 multi-layer formation on S1a and S1b sites	$2NH_{3(g)} + NH_3 - S_j \rightleftharpoons NH_3 - NH_3 - NH_3 - S_j$
S2 intermediate Brønsted acidic sites	$NH_{3(g)} + S2 \rightleftharpoons NH_3 - S2$
S3 strong Brønsted acidic sites	$NH_{3(g)} + S3 \rightleftharpoons NH_3 - S3$
S4 monomeric and/or binuclear Fe	$NH_{3(g)} + S4 \rightleftharpoons NH_3 - S4$

Reaction rate expressions

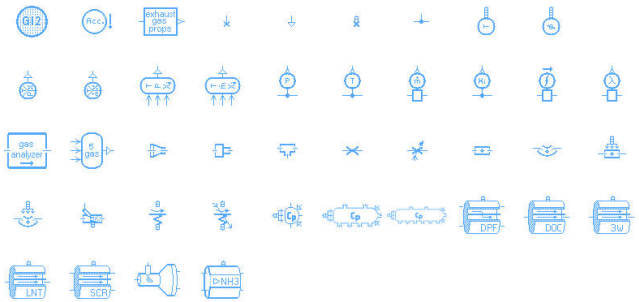
$$R_{j\_NH_3\_ads} = A_{j\_NH_3\_ads} \cdot \exp\left(-\frac{E_{j\_NH_3\_ads}}{R \cdot T_s}\right) \cdot C_{NH_3} \cdot \left(1 - \vartheta_j\right)$$

$$R_{j\_NH_3\_des} = A_{j\_NH_3\_des} \cdot \exp\left(-\frac{E_{j\_NH_3\_des} \cdot \left(1 - a_j \cdot \vartheta_j\right)}{R \cdot T_s}\right) \cdot \vartheta_j$$

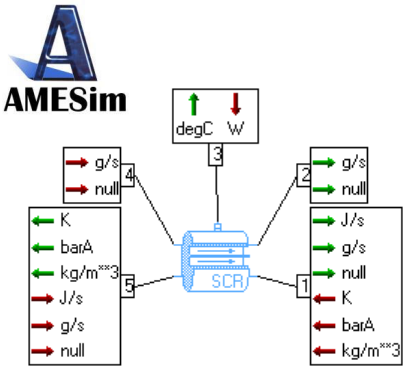
The IFP-Exhaust Library

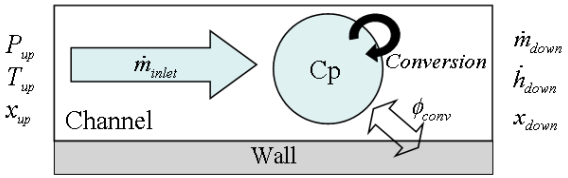
LMS.Imagine.Lab AMESim 0D SCR Catalyst modeling

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

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

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

Equivalent channel: gas balances Momentum/Energy/Species

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

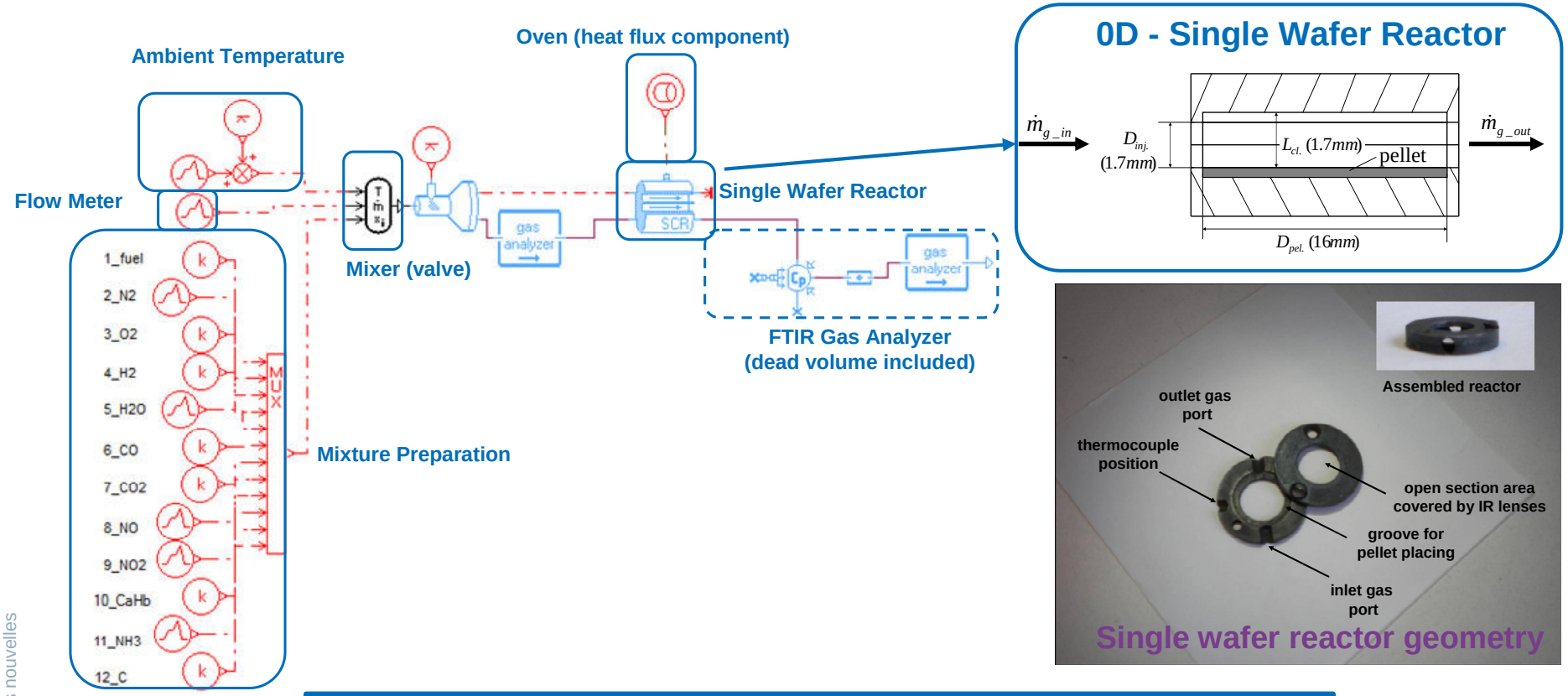
$$m_g \cdot C_v \cdot \frac{dT_g}{dt} = \sum_i m_i \cdot h_i + \frac{dQ_{conv.}}{dt} - P_g \cdot \frac{dV_{mixt.}}{dt} - m_g \cdot \sum_i \frac{dx_i}{dt} \cdot u_i - \frac{dm_g}{dt} \cdot \int C_v dT$$

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

Catalytic reactor modeling based on the bond graph theory

Modeling and simulation (2/5)

Reproduction of experimental set-up



Assumptions

Number of reactors computed based on the Péclet number
Oven modeled through imposed external heat conduction
Dead volume included

Modeling and simulation (3/5)

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 [-]
S1a (sites for physisorption and weak adsprption)	700	0	$1.8 \cdot 10^{12}$	80.80	0.11
S1b (weak acidic sites)	1200	0	10^{13}	97.79	0.11
Multi-layer formation on S1a, S1b sites	$6.6 \cdot 10^{8}$	0	$9.6 \cdot 10^{13}$	40.00	0.00
S2 (intermediate Brønsted sites)	900	0	10^{13}	119.50	0.11
S3 (strong Brønsted sites)	900	0	10^{13}	148.80	0.11
S4 (metallic sites)	500	0	10^{13}	145.00	0.15

Entropy change

Non activated process

Immobile molecules

Data from thermo-gravimetric measurements

Homogeneous acidity strength

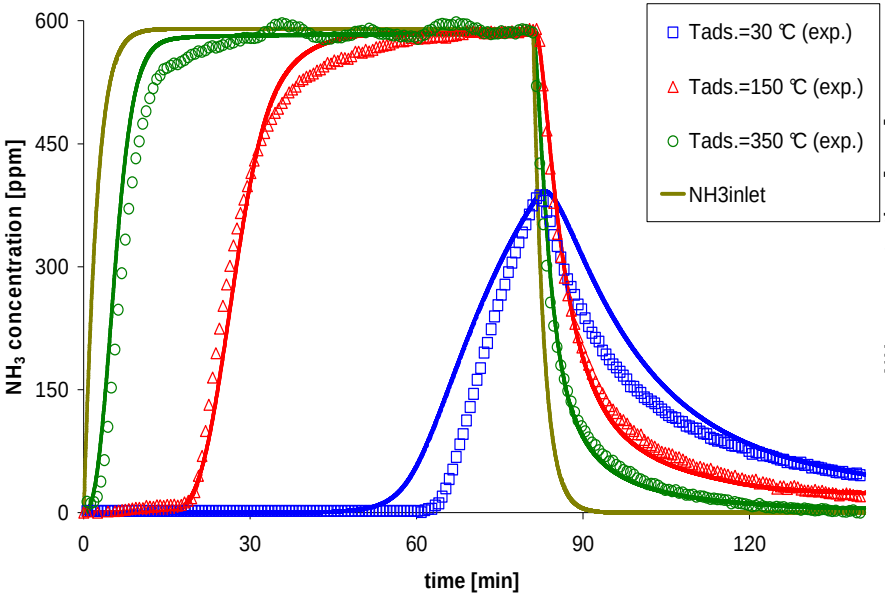
NH_3 storage capacity estimation over each site based on

- **Fe-BEA structural properties**: Si/Al and Fe/Al
- Data obtained from **catalyst characterization**: Ex-situ IR
- **NH_3-TPD profiles** obtained over the H- and Fe-BEA studied samples

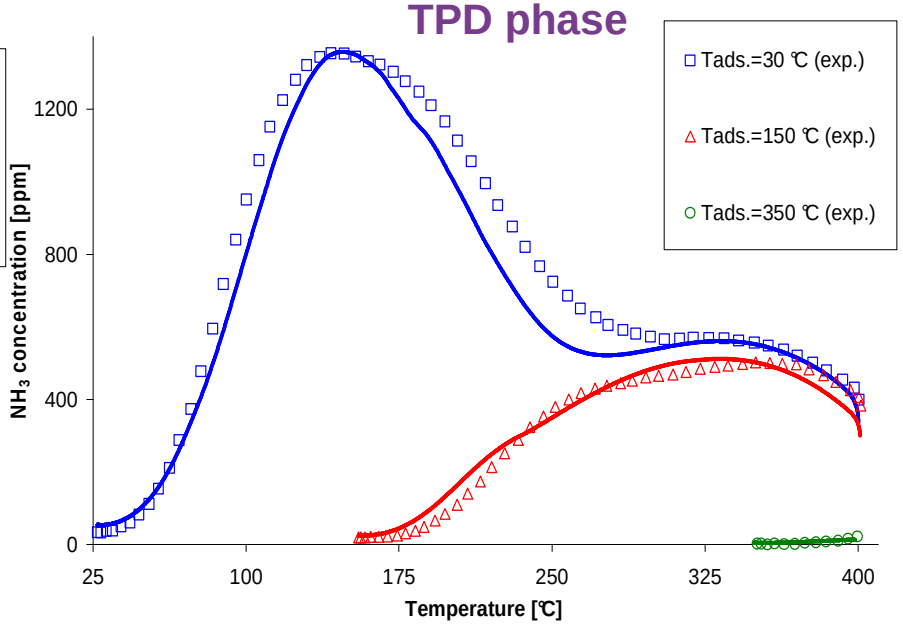
SKARLIS et al. J. Phys. Chem. C 2013 117, 7154–7169

Modeling and simulation (4/5)

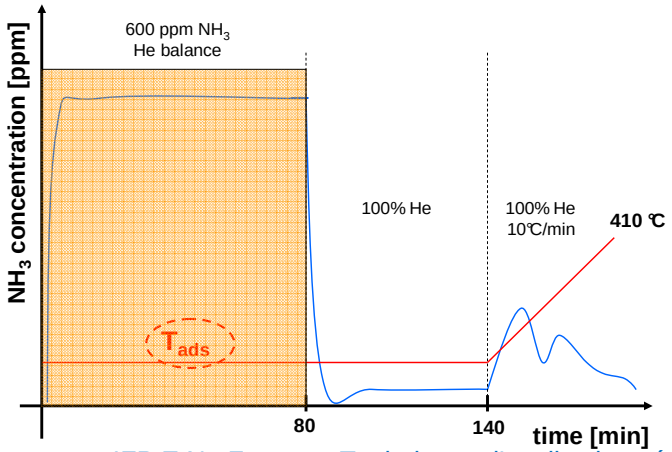
Adsorption phase

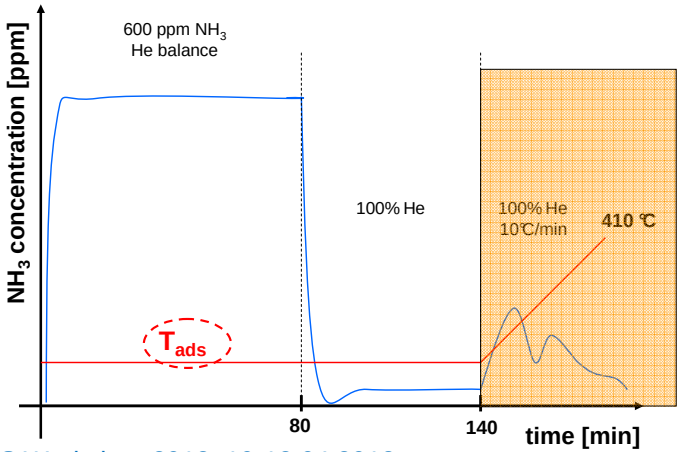


TPD phase



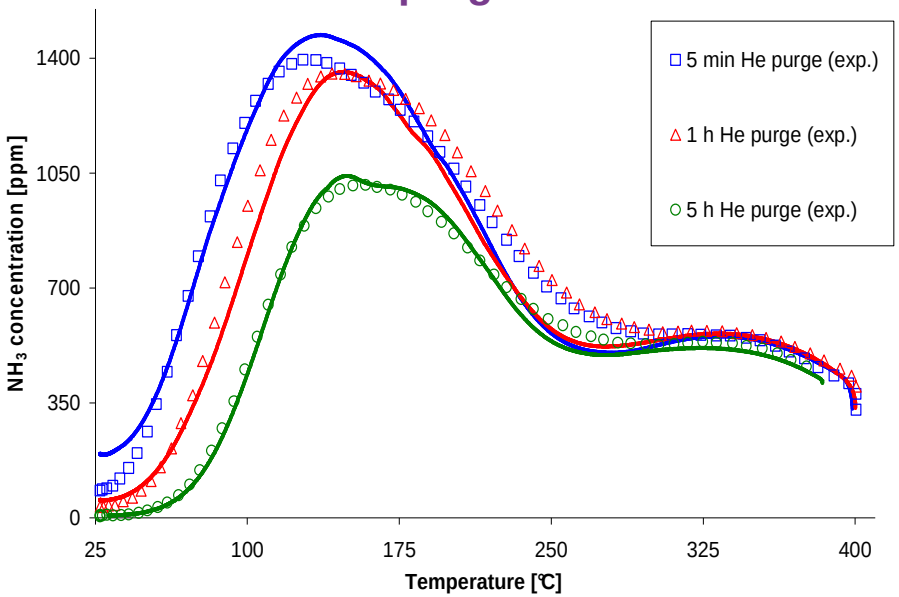
Symbols: Experimental results **Lines: Simulation results**



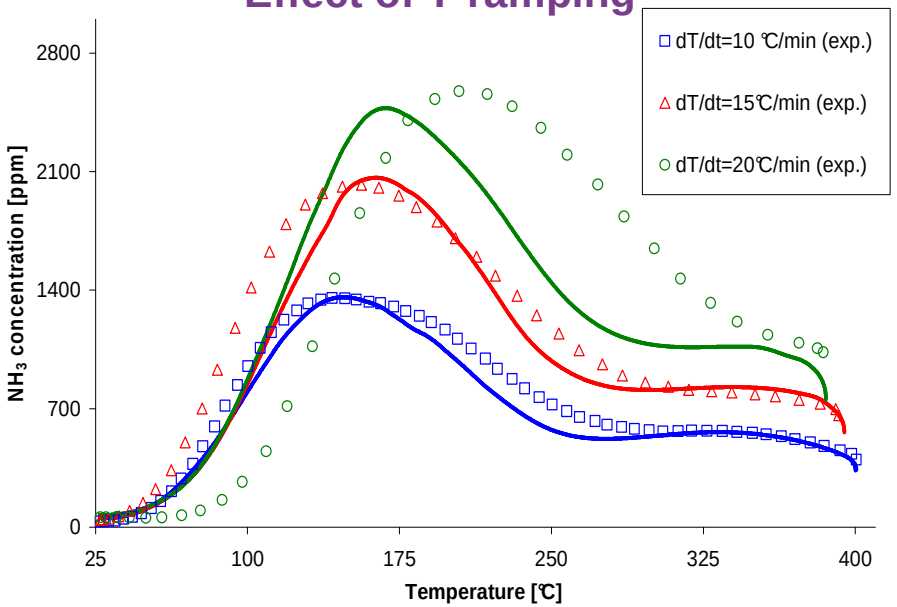


Modeling and simulation (5/5)

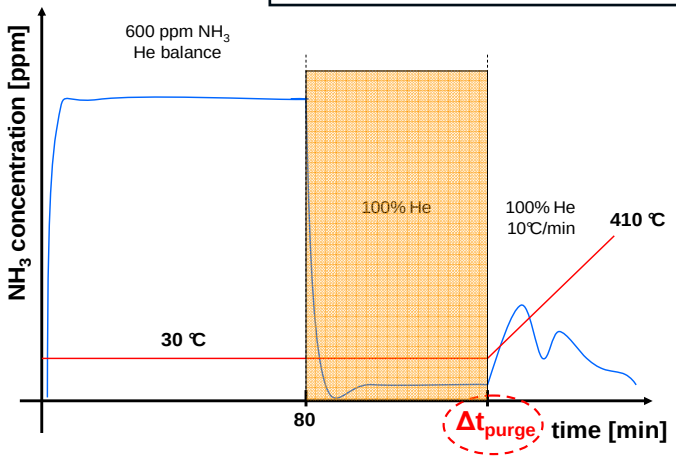
Effect of He purge duration

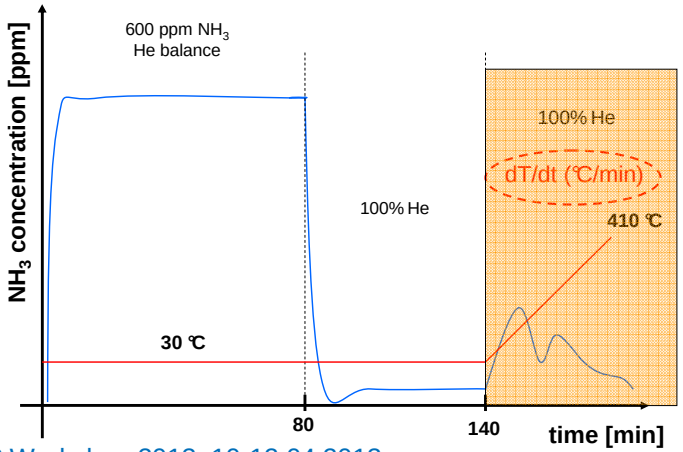


Effect of T-ramping



Symbols: Experimental results **Lines: Simulation results**





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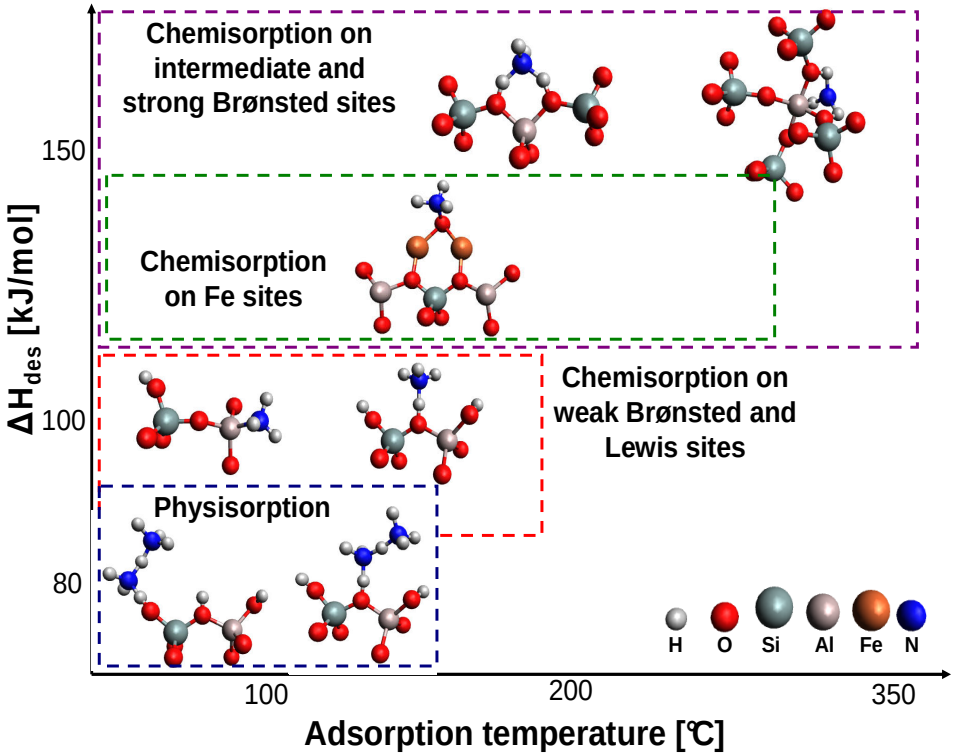
Conclusions and perspectives

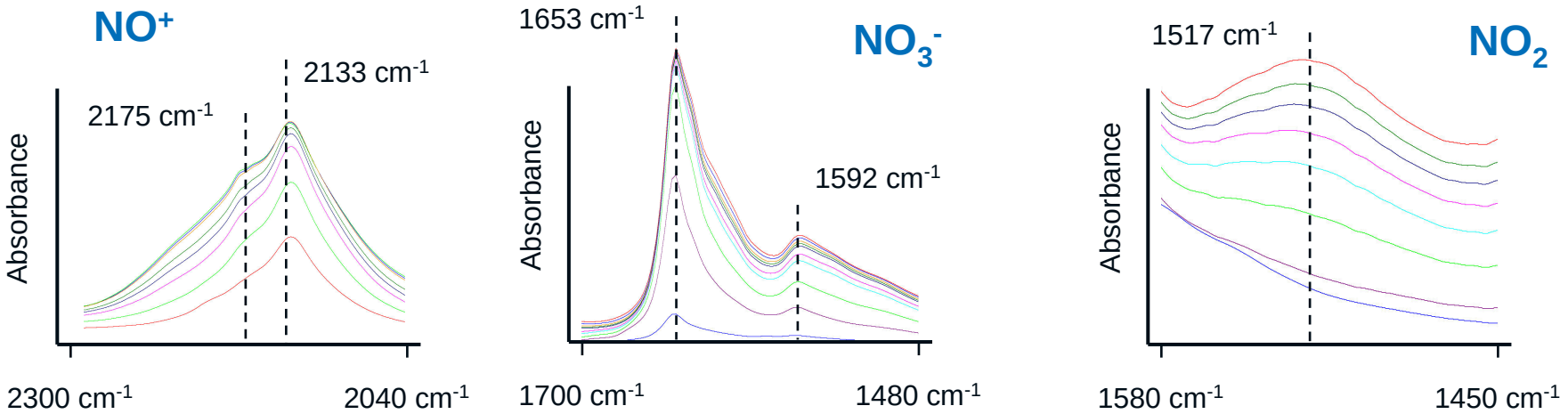
- Multi-site kinetic model for NH_3 adsorption and desorption over Fe-BEA
- Model development based on IR spectroscopic measurements
- Kinetics calibration according to theoretical and experimental studies



Further extension of the multi-site kinetic model to include additional reactions is underway

Model extension to NO_x adsorption

Operando IR spectroscopic measurements over the 1.75% Fe-BEA



Multi-site kinetic modeling

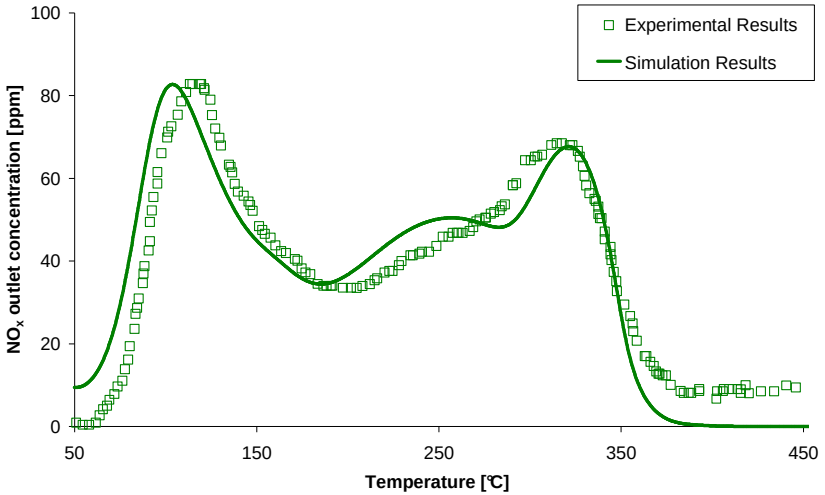
$$NO_2 + S \leftrightarrow NO_2 - S$$

$$O_2 + 2S \leftrightarrow 2O - S$$

$$3NO_2 - S + O - S \leftrightarrow 2NO_3 - S + NO_{(g)}$$

$$NO + O - S \leftrightarrow NO_2 - S$$

NO_2-TPD over a commercial Fe-zeolite



Exp. results by Grossale et al. Cat. Today 136 (2008) 18–27

Thank you for your kind attention

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