SCR-Catalyst Materials for Exhaust Gas Detection

D. Schönauer-Kamin, R. Moos

2012

EUNETAIR
European Network on New Sensing Technologies
for Air-Pollution Control and Environmental Sustainability

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EUROPEAN COOPERATION
IN SCIENCE AND TECHNOLOGY

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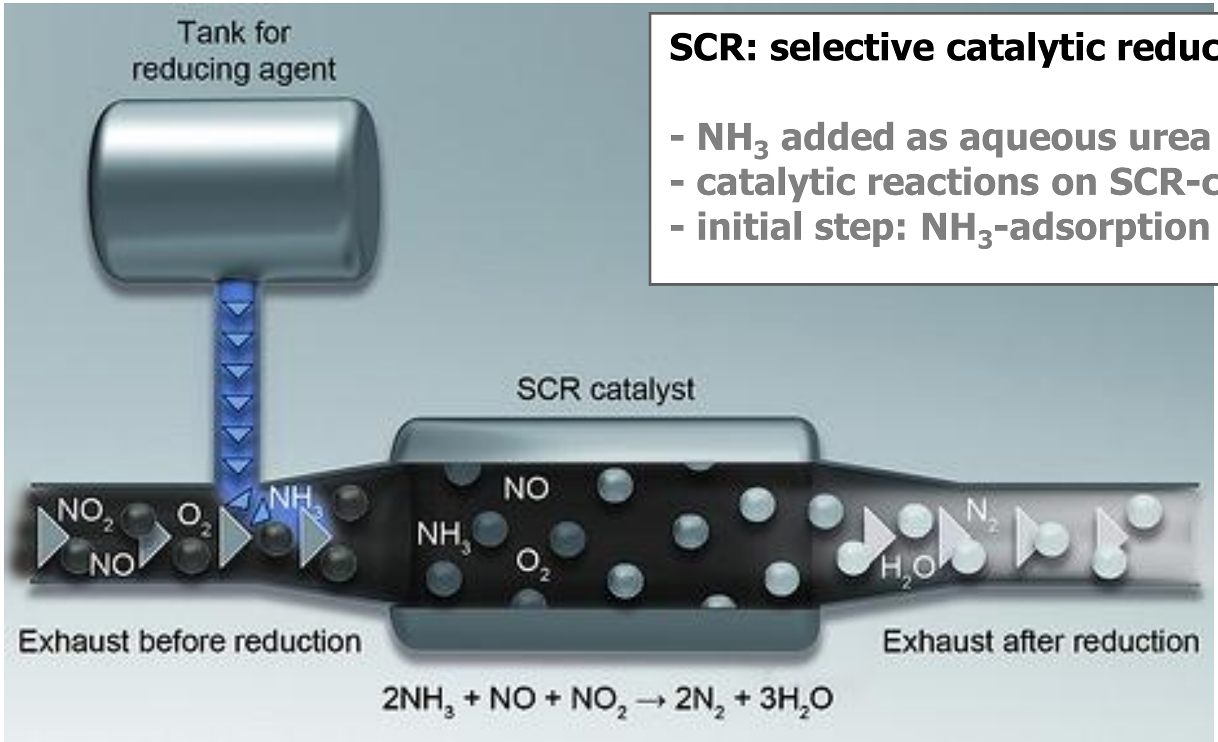
Motivation



SCR: selective catalytic reduction of NO_x by NH_3

- NH_3 added as aqueous urea solution
- catalytic reactions on SCR-catalyst
- initial step: NH_3-adsorption and -storage on the catalyst

SCR-active materials: V_2O_5-WO_3-TiO_2 and Fe-ZSM5

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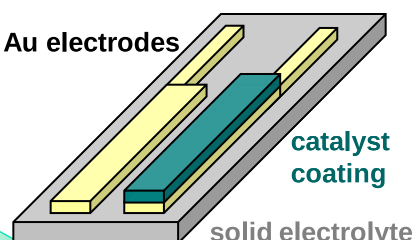
Motivation

SCR-catalyst materials: VWT and Fe-zeolites
NH_3-storage and catalytic reactions

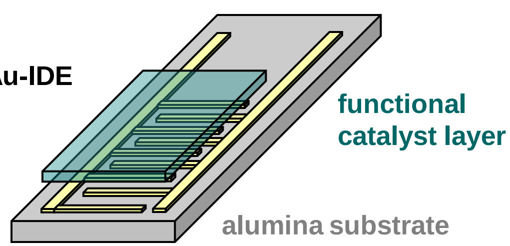
catalyst materials as sensors

- ☺ known catalytic behavior
- ☺ given selectivity
- ☺ proven long term stability
- ☺ stable in harsh environments
- ⇨ detection of c_{gas}
- ⇨ detect the status of the catalyst layer

potentiometric sensors



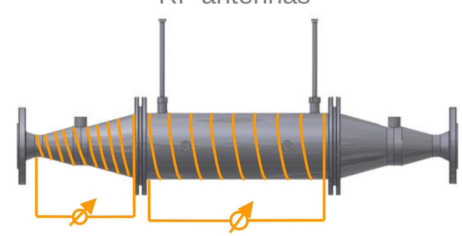
resistive / impedimetric sensors



determination of NH_3-loading

- ⇨ diagnosis of catalyst itself
- ⇨ determination of the amount of stored NH_3 in situ
  - ⇨ radio-frequency technology
  - ⇨ contactless determination of the stored NH_3-amount during operation

RF method



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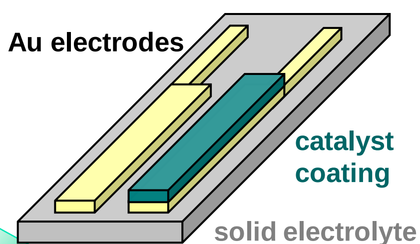

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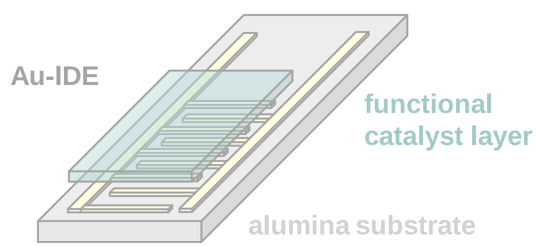

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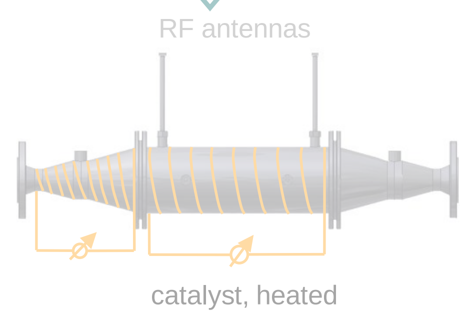
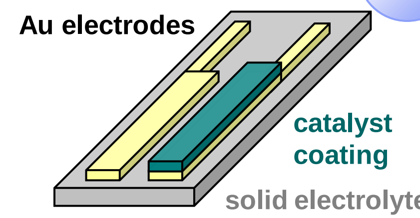
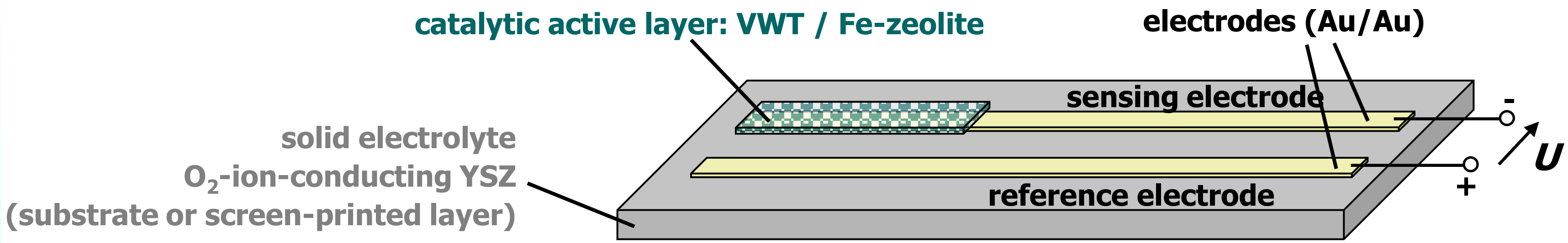


FM FUNCTIONALMATERIALS

Mixed potential NH_3 gas sensor





- two ***equal*** noble metal **electrodes**:
  electric conductivity → potential measurement
- **porous catalytic active coating** of ***one*** **electrode**:
  catalytic activity and NH_3-selectivity
  long-term stability

function of SCR-catalyst layer:
catalytic properties /
adsorption / selectivity

test conditions:

synthetic exhaust gas test bench

base gas: 10% O_2, 6.5% CO_2, 2.5% H_2O, N_2

addition of test gas NH_3 (10 – 300 ppm)

sensor temperature ~ 550 °C
(adjusted by external furnace or platinum heater structure)

source: Schönauer, D., Sens. Act.: Chem. 140 (2009) 585-590

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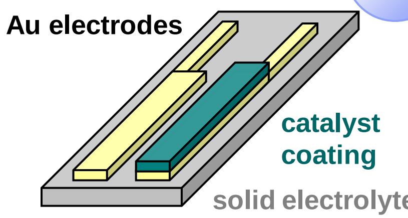
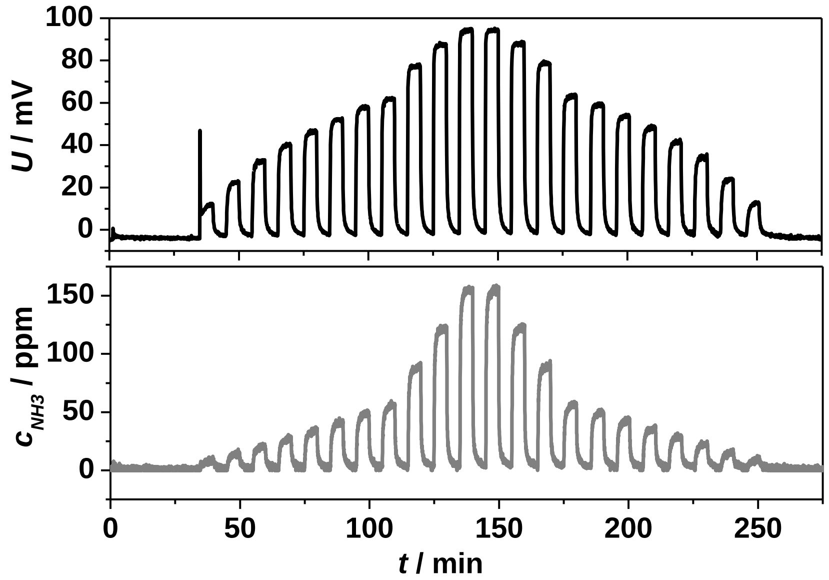
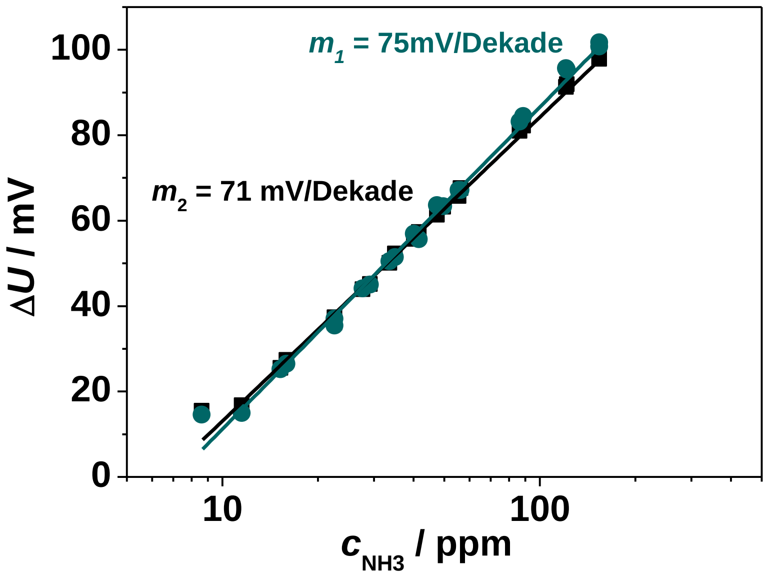
Mixed potential NH_3 gas sensor

VWT, Au|YSZ|Au



self-heated @ 550°C
base gas: 10% O_2, 6.5% CO_2, 7% H_2O, N_2



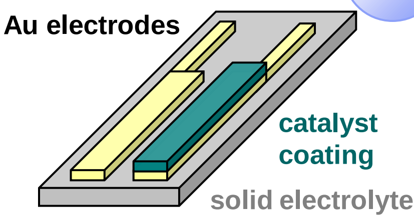


- semi-logarithmic characteristic curve
- sensitivity: 71 – 75 mV / decade NH_3
- sensor does not show hysteresis (NH_3 up & down)
- reproducible sensor behavior

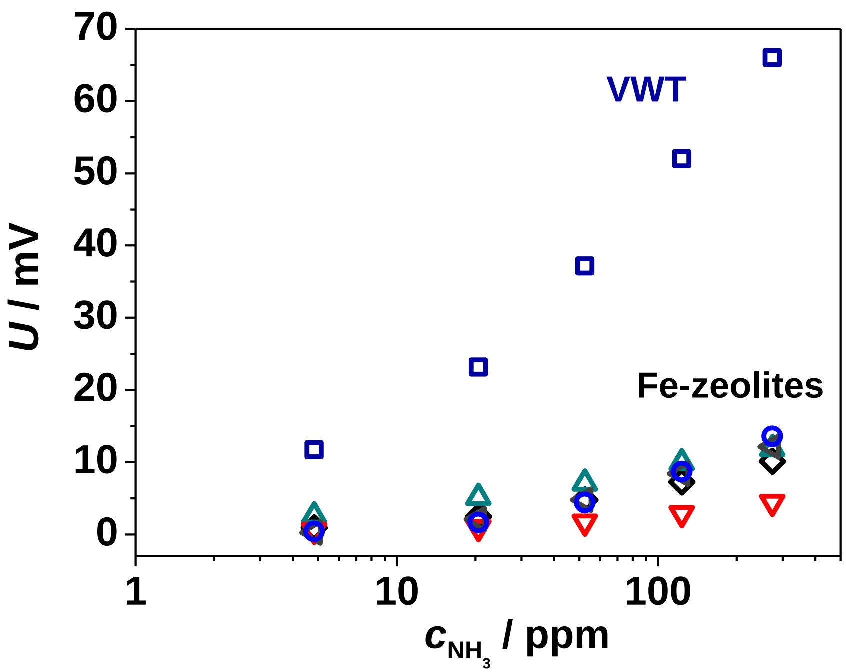
source: Schönauer, D., Sens. Act.: Chem. 140 (2009) 585-590

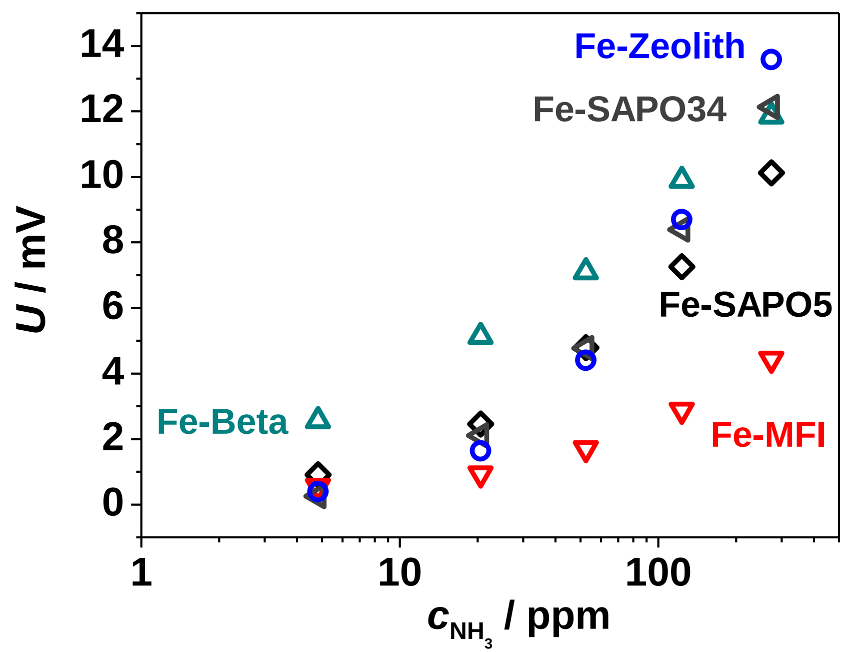
Mixed potential NH_3 gas sensor

Fe-zeolites, Au | YSZ | Au



external-heated @ 550°C
base gas: 10% O_2, 6.5% CO_2, 2.5% H_2O, N_2





- low NH_3-sensitivity of Fe-zeolites
- VWT: highest NH_3-sensitivity

⇨ **VWT: best sensing characteristics**

various Fe-zeolites tested:
Fe-zeolite catalyst
Fe-ZSM5; Fe-Beta; Fe-SAPO-5; Fe-SAPO-34
⇨ **Fe-zeolites: poor sensitivity**

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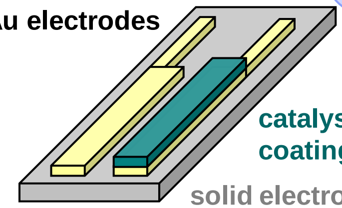
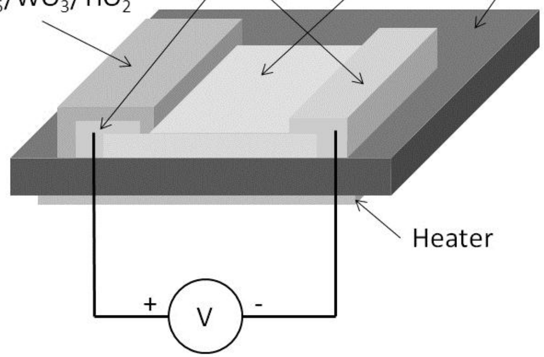
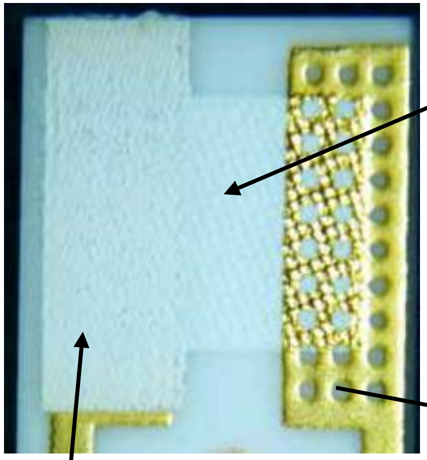


Potentiometric SO_2 gas sensor

VWT, Au | NASICON | Au





function of catalyst layer:
catalytic properties /
adsorption / selectivity

test conditions:

synthetic exhaust gas test bench

base gas: compressed air

addition of test gas SO_2

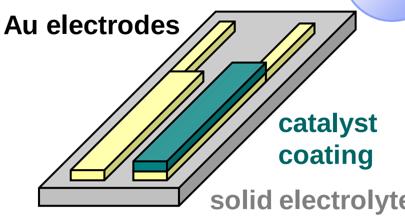
sensor temperature 500 - 600 °C
(adjusted by platinum heater structure)

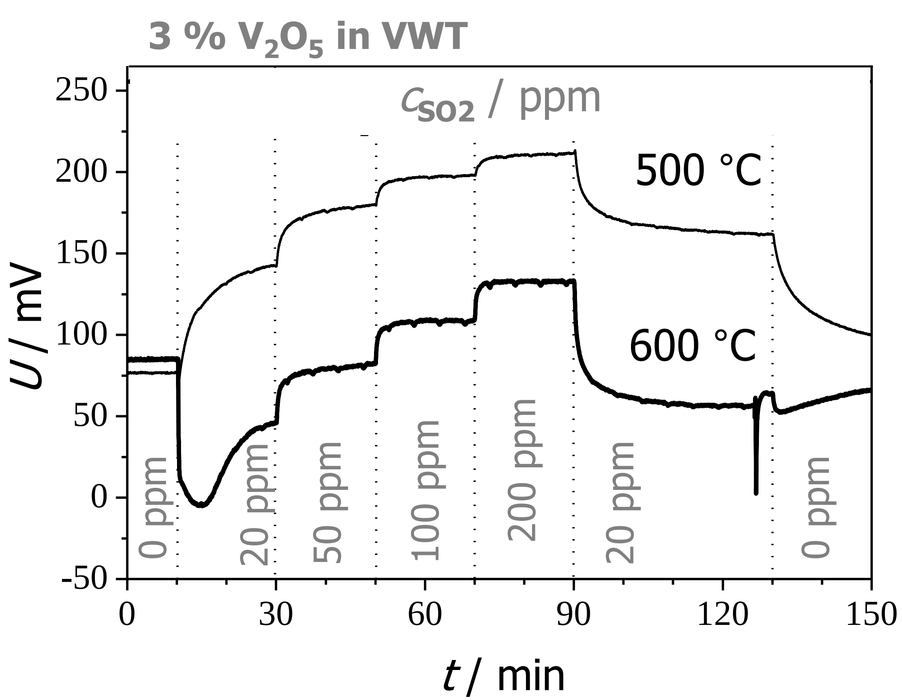
source: Izu, N., J. Ceram. Soc. Jpn. 119 (2011) 687-691

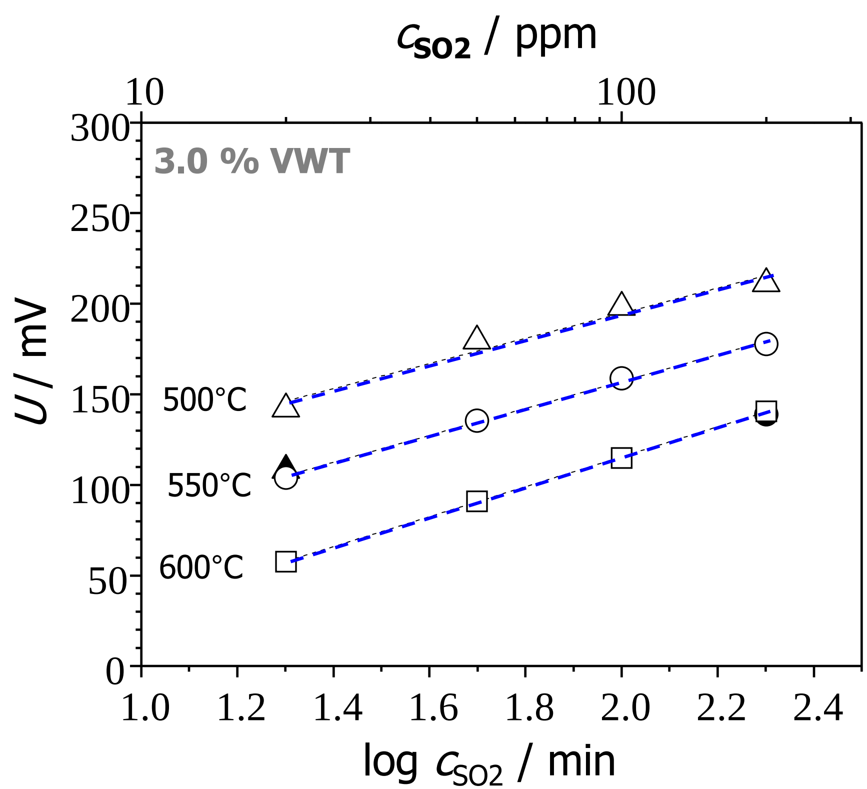
FUNCTIONALMATERIALS

Potentiometric SO_2 gas sensor

VWT, Au|NASICON|Au







- potential difference increases with increasing c_{SO2}
- stable signals @ 500 and 600 °C

- sensitivity @ 600°C: 75 – 85 mV / decade SO_2
- sensitivity increases with increasing temperature

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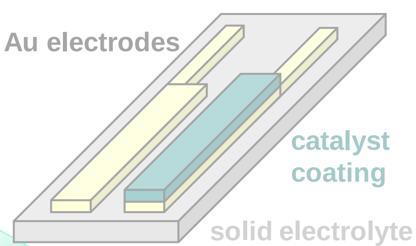
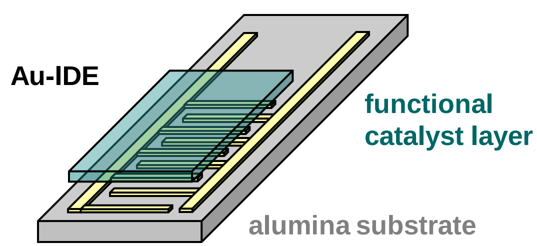


resistive / impedimetric sensors



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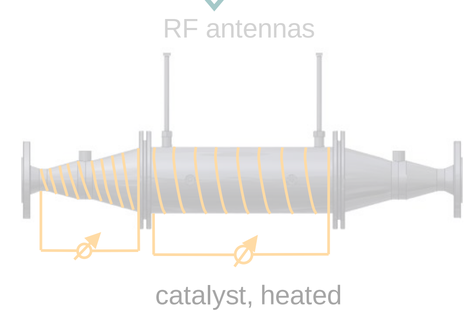
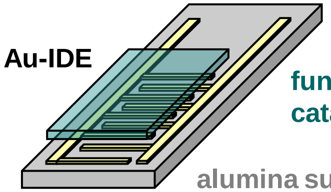
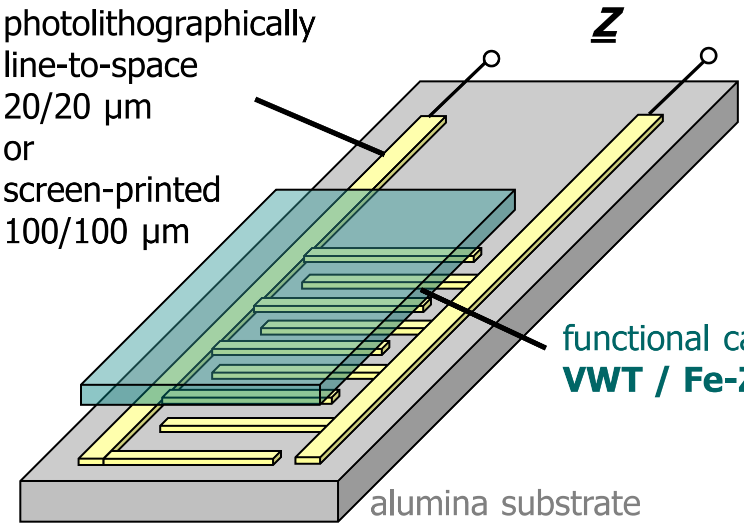


FUNCTIONALMATERIALS

Impedimetric NH_3 gas sensor





impedance measurement of electrical properties:

impedance analyzer

f = 10 MHz – 1 Hz

U_{eff} = 1 V

function of catalyst layer:
sensitive film
electrical properties
measurement of c_{gas}

test conditions:

synthetic exhaust gas test bench

lean base gas: 10% O_2, 6.5% CO_2, 2.5% H_2O, N_2

addition of test gases (NH_3, NO)

sensor temperature ~ 300 - 500 °C
(adjusted by external furnace or platinum heater structure)

source: Schönauer, D., Sens. Act.: Chem. 155 (2010) 199-205

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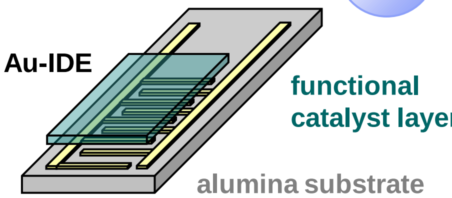
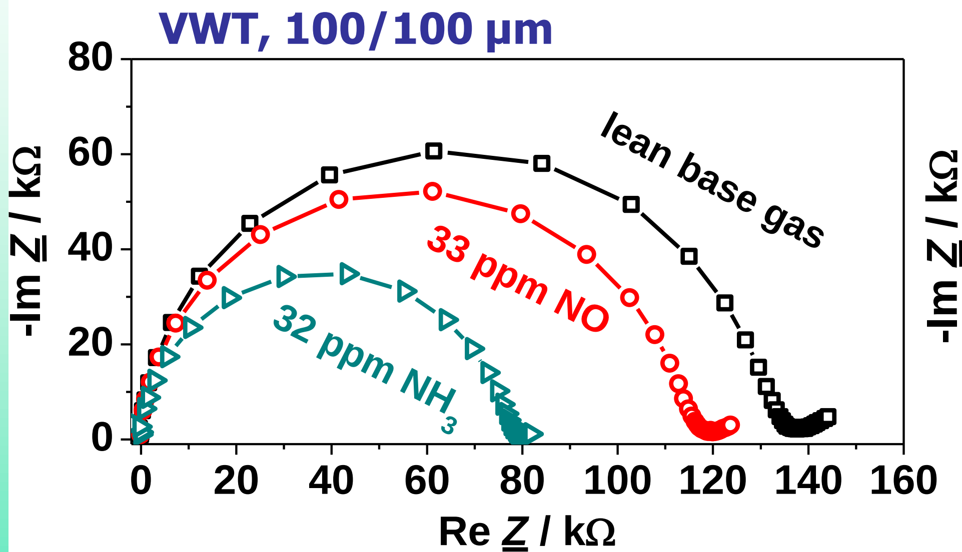
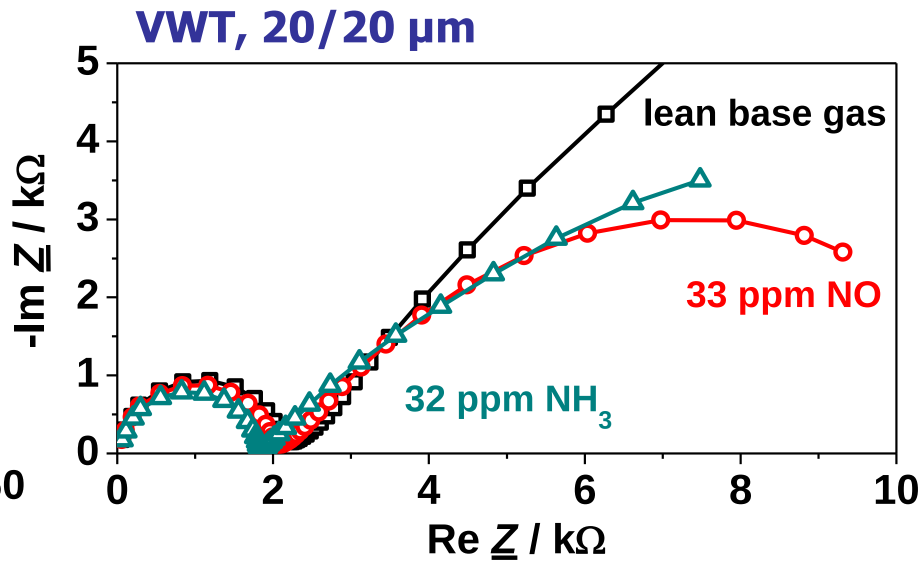
Impedimetric NH_3 gas sensor



Initial Nyquist-Plots at 500 °C





VWT 100/100:

very small tail at low frequencies – marginal electrode effects

Diameter of semi-circle represents resistance of VWT:

- small decrease with c_{NO} addition
- strong decrease with increasing c_{NH3}

VWT 20/20:

huge semicircle at low frequencies

⇨ strong effects at the electrode interface

material properties characterized by semicircle

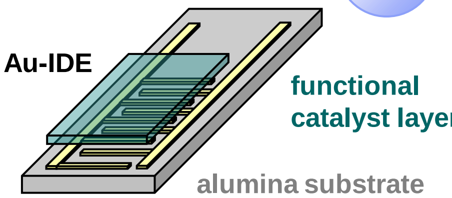
R: decreases with increasing c_{NH3}

almost independent on c_{NO}

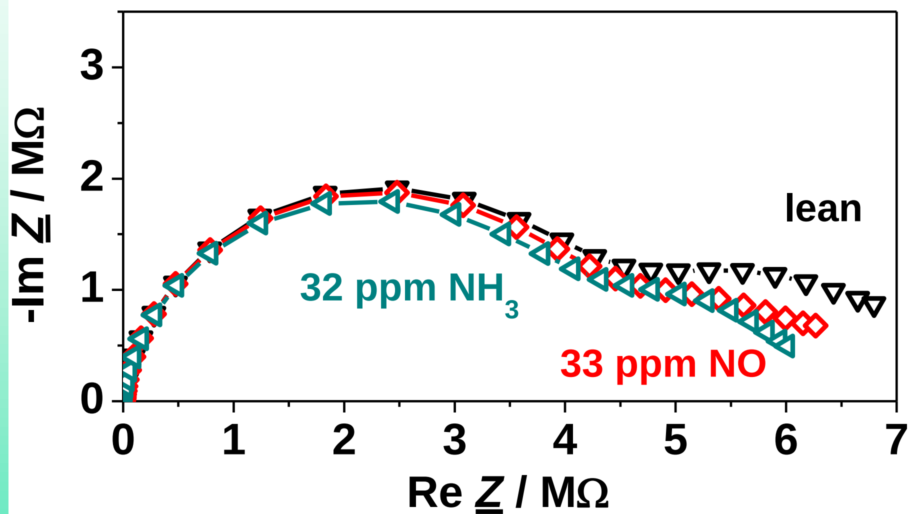
source: Schönauer, D., Sens. Act.: Chem. 155 (2010) 199-205

Impedimetric NH_3 gas sensor

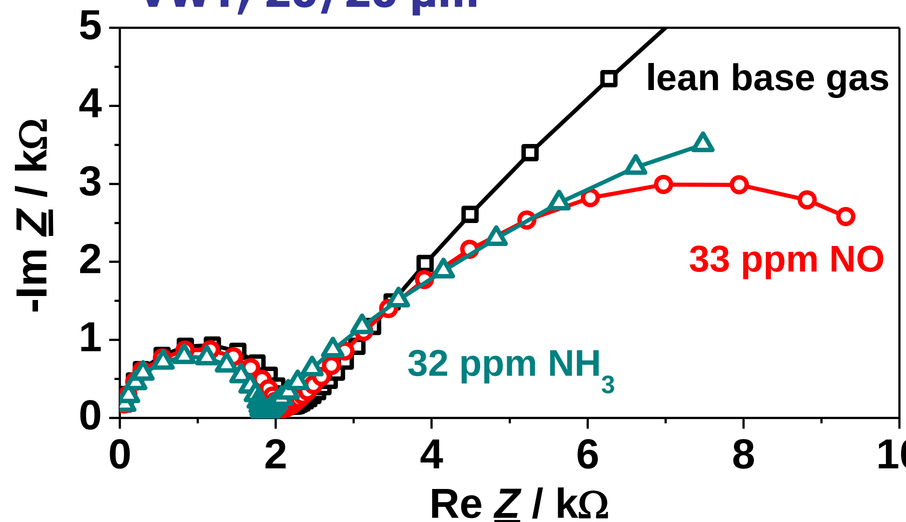
VWT ↔ Fe-ZSM5 @ 500°C



Fe-ZSM5, 20/20 µm



VWT, 20/20 µm



Fe-ZSM5:

small tail at low frequencies:

effects at the electrode interface

diameter represents resistance of Fe-ZSM5

- almost independent on c_{NO}
- decreases with increasing c_{NH3}

VWT 20/20:

huge semicircle at low frequencies

⇨ strong effects at the electrode interface

material properties characterized by semicircle

$|Z|$: decreases with increasing c_{NH3}

almost independent on c_{NO}

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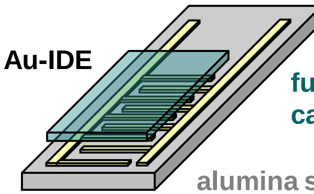
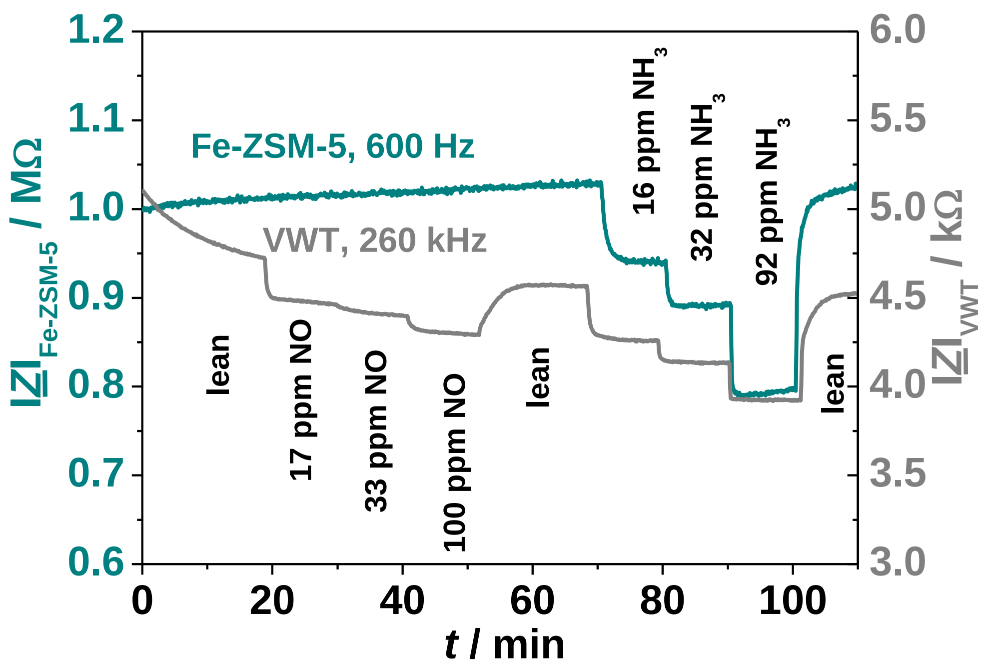
FM FUNCTIONALMATERIALS

Impedimetric NH_3 gas sensor



Time dependent impedance records at 500 °C



f in high-frequency semicircle
⇨ material properties

Fe-ZSM5, 600 Hz:
- no response towards NO
- strong NH_3 effect
⇨ $|\underline{Z}|$ decreases only with increasing c_{NH3}

VWT, 260 kHz:
- small NO response
- NH_3 effect is more pronounced
⇨ $|\underline{Z}|$ decreases with increasing c_{NH3} and c_{NO}

NH_3 sensing effect:
- conductivity change due to changes of bulk properties
- NH_3 adsorption on catalyst surface

VWT: NH_3 reacts with adsorbed oxygen species ⇨ n-type semi-conducting behavior
Fe-ZSM5: NH_3 adsorbs on acidic sites ⇨ proton conductivity increases

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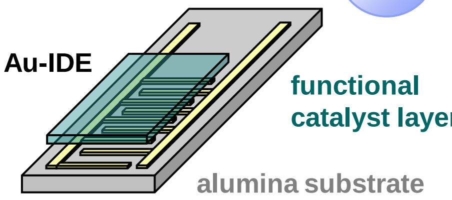
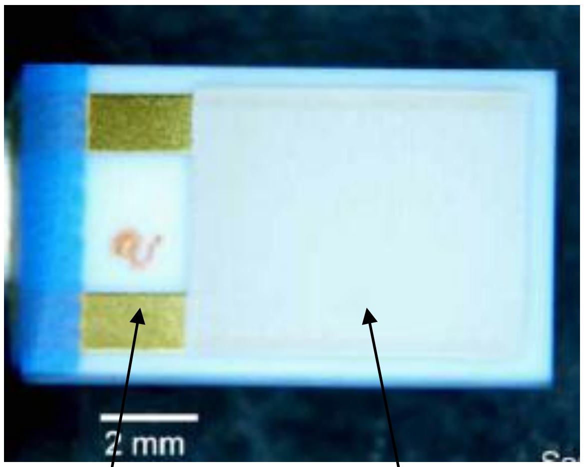
Resistive type SO_2 sensor





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sensitive film
electrical properties
measurement of c_{gas}

test conditions:

synthetic exhaust gas test bench

base gas: compressed air

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source: Izu, N., Sensors 11 (2011) 2982-2991

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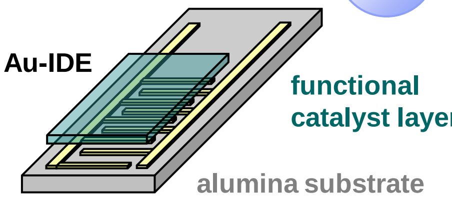
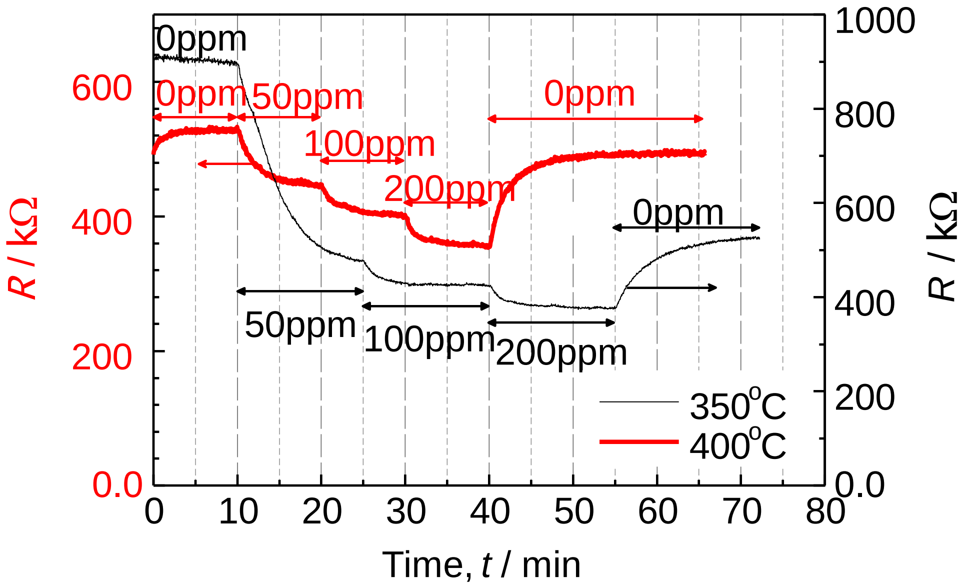
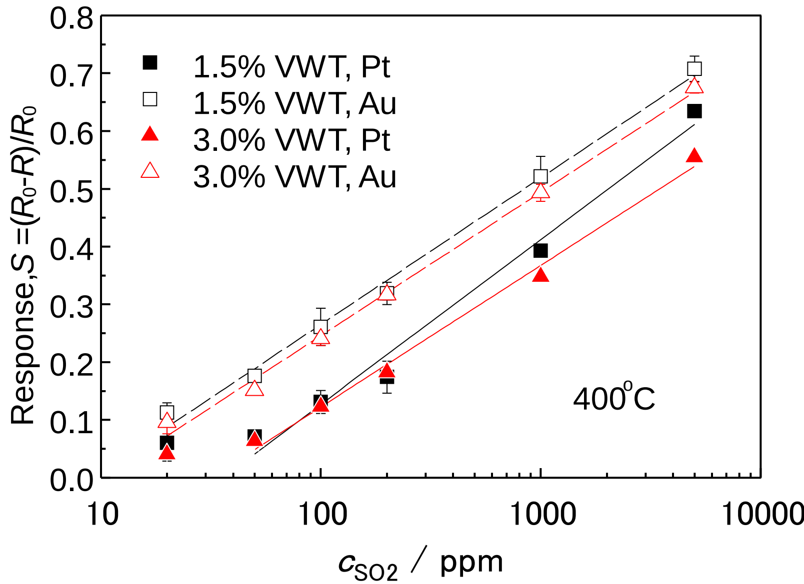


3 % V_2O_5 in VWT





- R decreases strongly with increasing SO_2 concentration
- semi-logarithmic dependence of S and c_{SO2}
- SO_2 detection is possible with Au- and Pt-IDE

source: Izu, N., Sensors 11 (2011) 2982-2991

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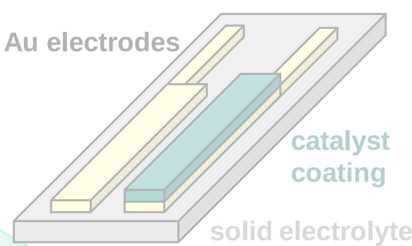

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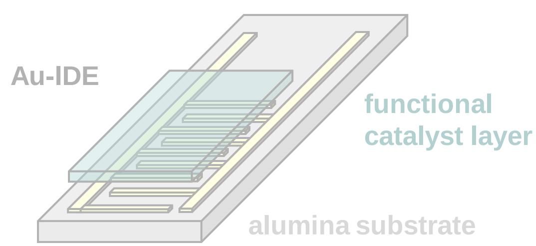

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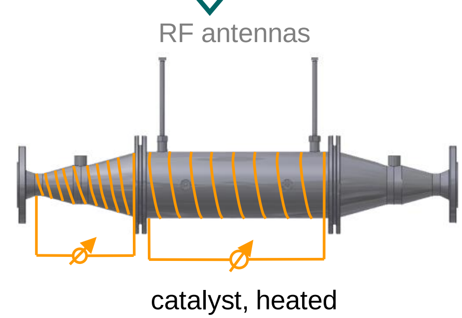
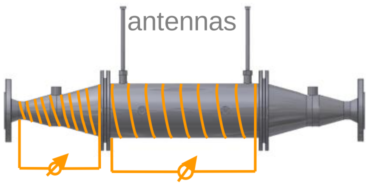
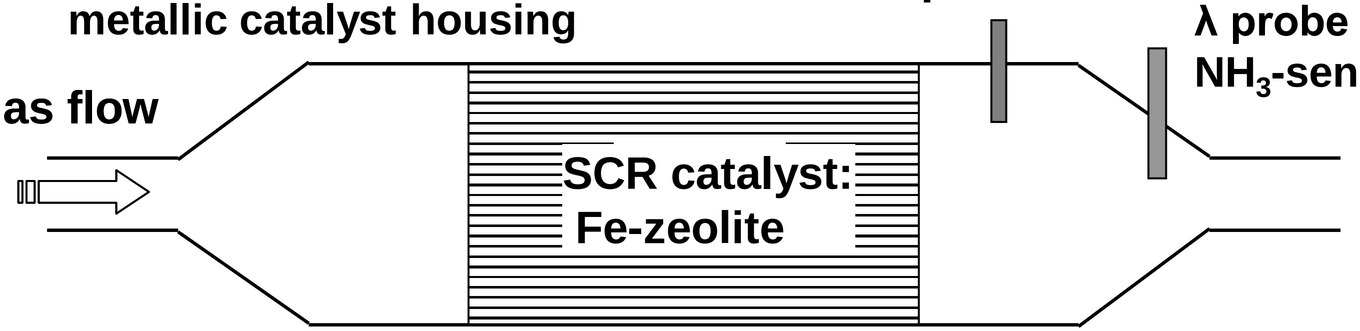


Radio frequency characterization



...material characterization in a cylindrical waveguide



microwave cavity perturbation method
scattering parameters measured
by vector network analyzer
e.g.
reflection coefficient $|S_{11}|$
resonance frequency f_{res} (at minimum of $|S_{11}|$)

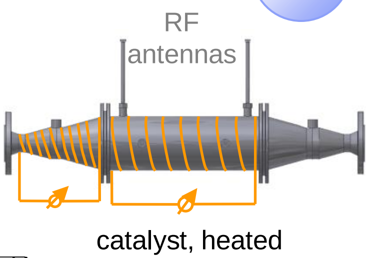
function of catalyst:
catalyst itself is measured
in-situ diagnosis of catalyst properties

e.g. NH_3 loading degree

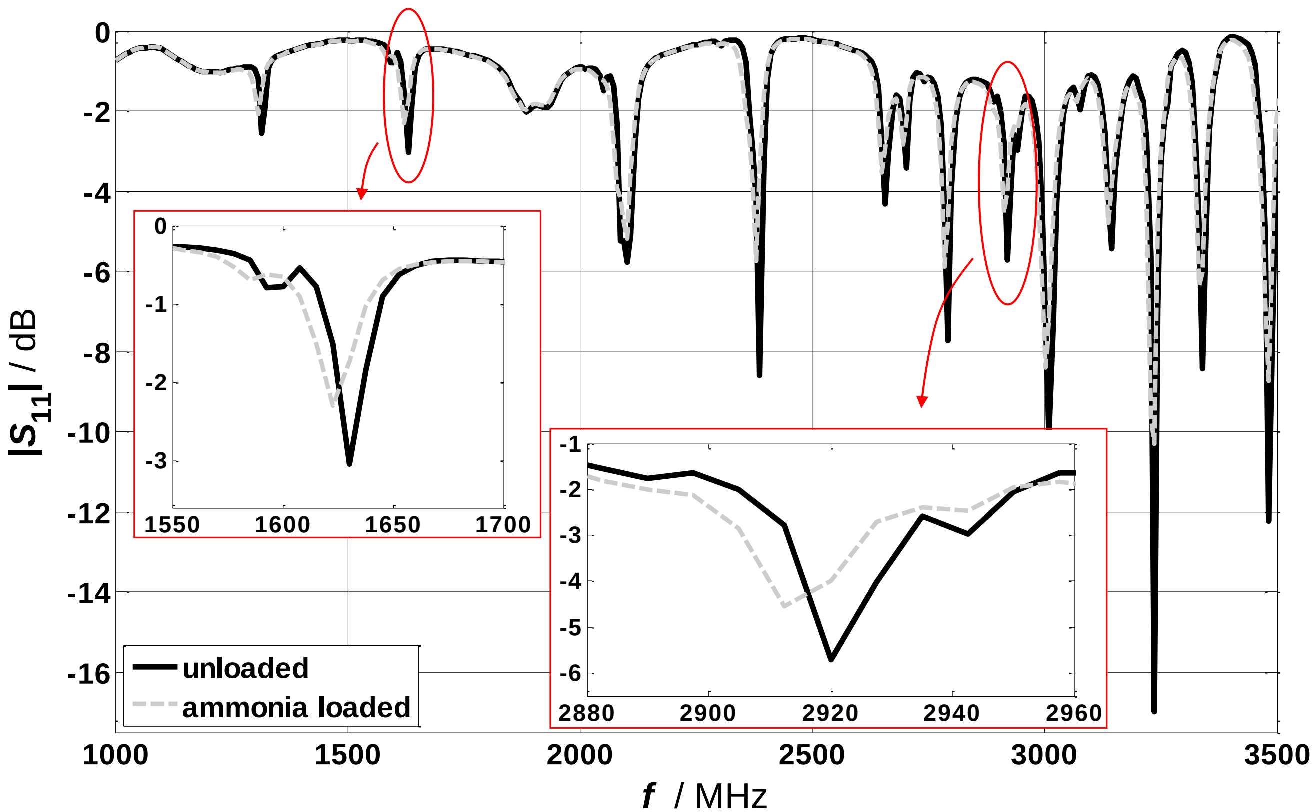
source: Reiß, S., Chem. Eng. Technol. 34 (2011) 791-796

Radio frequency characterization

NH_3 loading of Fe-zeolite catalyst



$T \approx 300$ °C
5 % H_2O in N_2,
+ 500 ppm NH_3



frequency dependent amplitude of reflection coefficient $|S_{11}|$

ammonia loading ⇨ resonance frequencies are reduced

⇨ increased damping ⇨ electrical losses increase

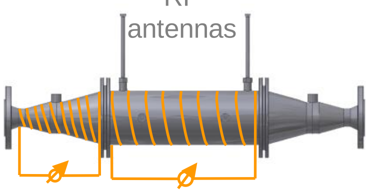
⇨ ionic conductivity of Fe-zeolite increases due to adsorbed ammonia

source: Reiß, S., Chem. Eng. Technol. 34 (2011) 791-796

FunctionalMaterials

Radio frequency characterization

NH_3 loading and desorption



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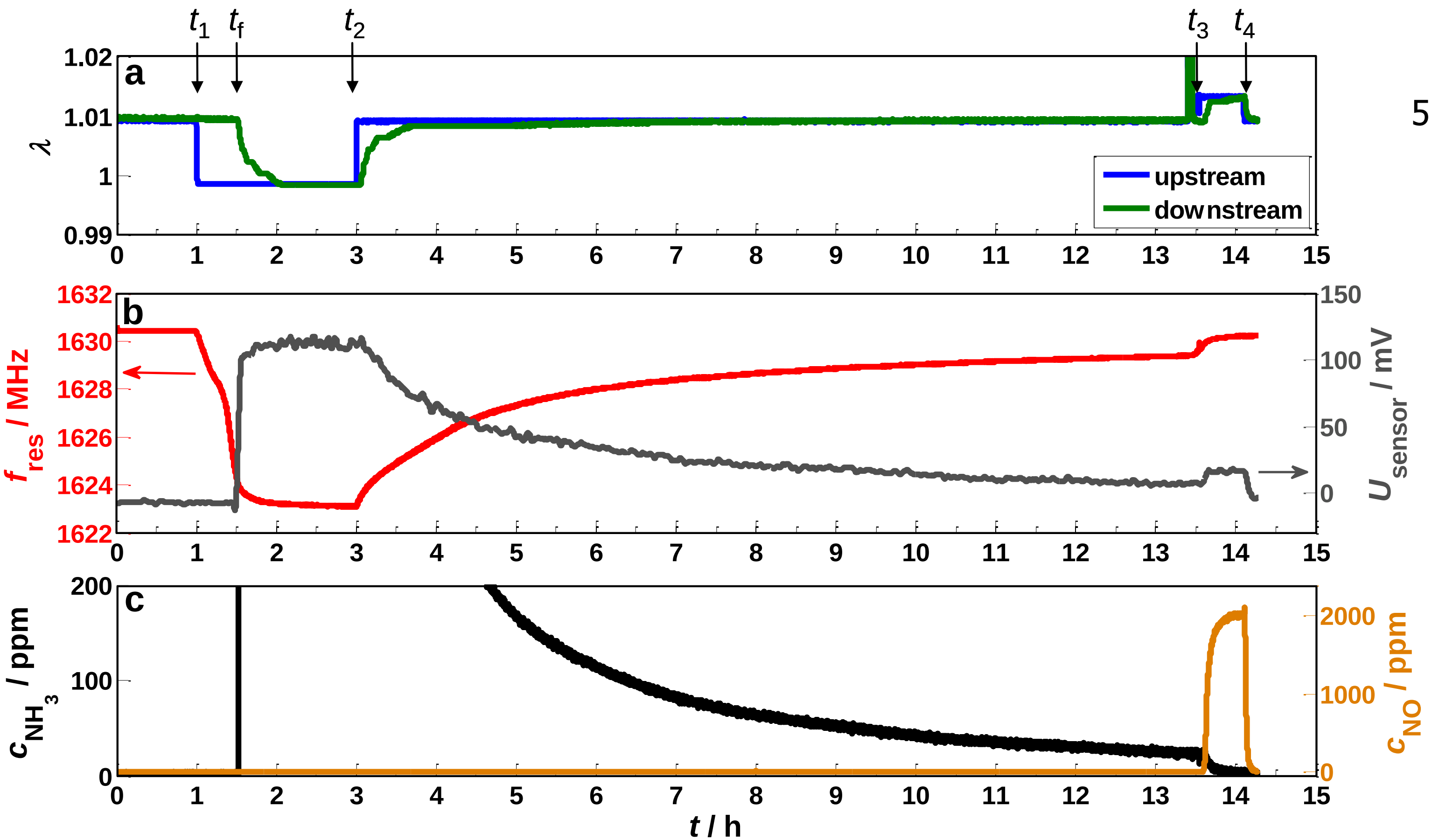

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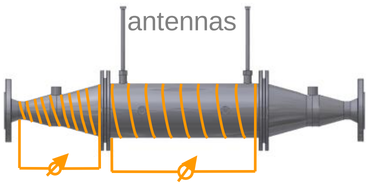
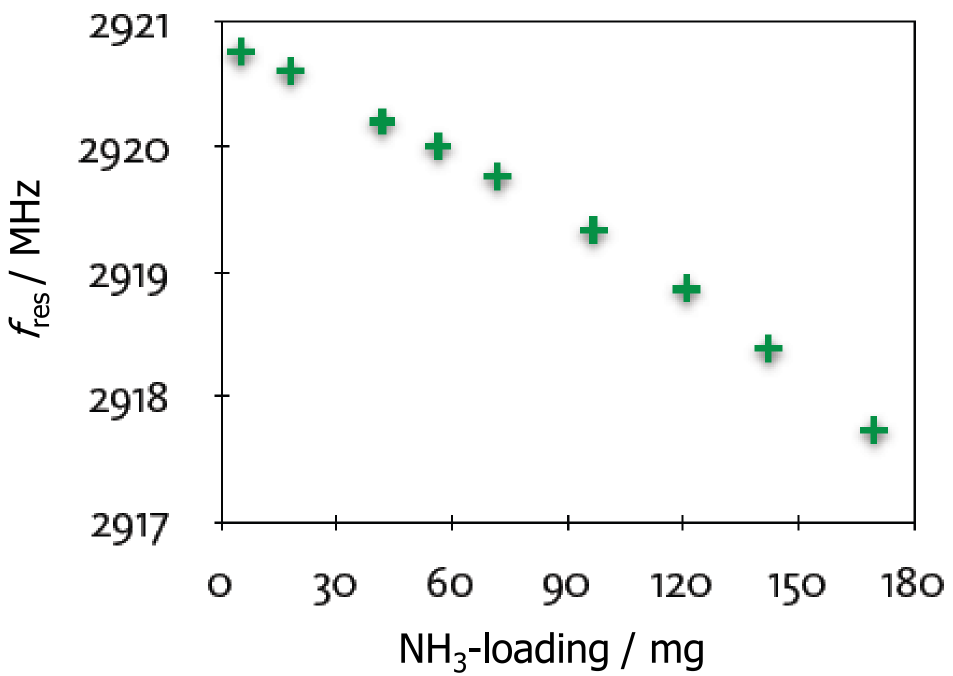
Radio frequency characterization

characteristic curve





- resonance frequency depends almost linearly on NH_3 loading degree
- changes of electrical properties when NH_3 is adsorbed / stored
  ⇨ in accordance to impedimetric Fe-ZSM5 analysis
- possibility to determine NH_3 loading of the catalyst itself during operation

source: Reiß, S., Chem. Eng. Technol. 34 (2011) 791-796

Conclusions

- **SCR-catalysts can be applied for gas sensing application**
- **Potentiometric devices for NH_3 and SO_2 detection**
- **Conductometric sensors for NH_3 and SO_2 detection**
- **Direct electrical characterization of catalyst material**

  ⇨ **SCR active materials can be applied as robust and stable functional sensor films**

  ⇨ **electrical properties change due to adsorption phenomena, e.g. NH_3 adsorption**

  ⇨ **catalytic properties are relevant**

- **RF technique applicable to SCR-catalyst**

  ⇨ **NH_3-loading of the catalyst can be determined in-situ and contactless**

SCR-Catalyst Materials for Exhaust Gas Detection

2012

THANK YOU FOR YOUR ATTENTION!

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