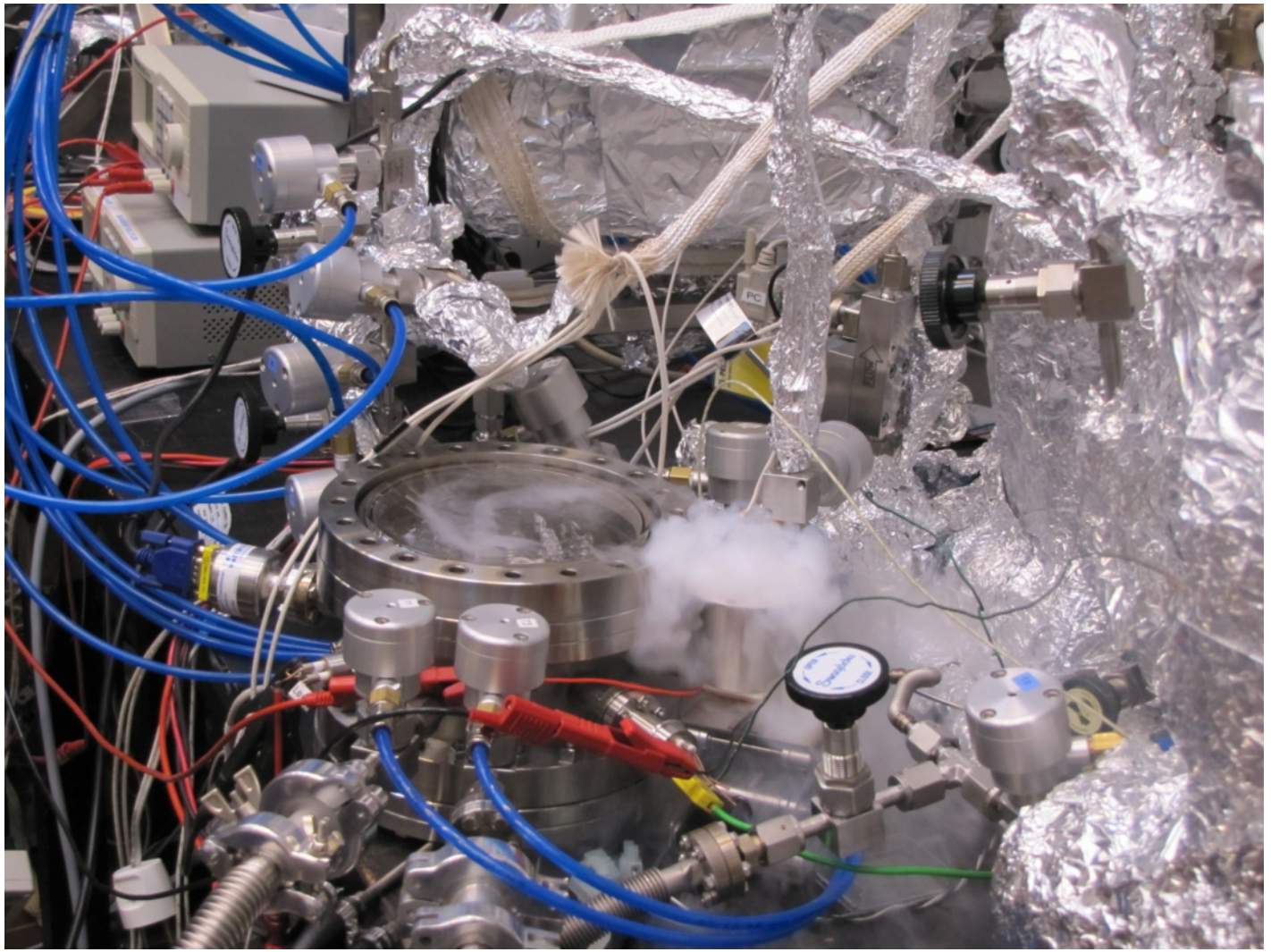
μ-reactors for Heterogeneous Catalysis



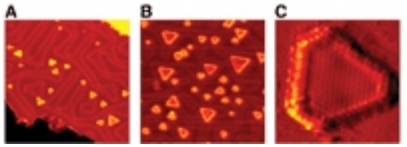
Outline

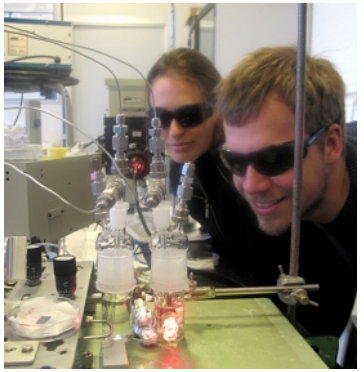
- Motivation & Introduction
- Heating
- The Grand Master Plan
- Area Measurements
- Oscillating CO oxidation
- Sensitivity Measurements
- Time-Of-Flight Mass Spectrometry
- Summary

Introduction & Motivation

Heterogeneous catalysis is important in many parts of modern life:

- Fertilizers
- Crude oil cleaning
- Chemical industry
- Car exhaust cleaning
- …





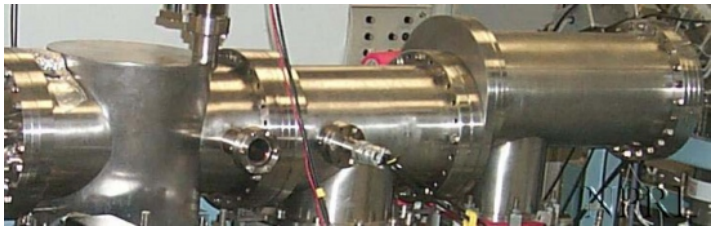
- Harvesting of solar energy
- Chemical processes utilizing excess energy from renewable sources
- Energy storage

Introduction & Motivation

Many kinds of experimental catalysts needs to be tested in an early state of development

Often the amount of material will be extremely limited due to factors such as

- Material costs
- Fabrication constraints
- Toxicity



Introduction & Motivation

The μ-reactor provides an excellent platform for testing of experimental catalysts.

Advantages includes:

- High sensitivity
- Low gas consumption
- High safety level
- Low thermal mass

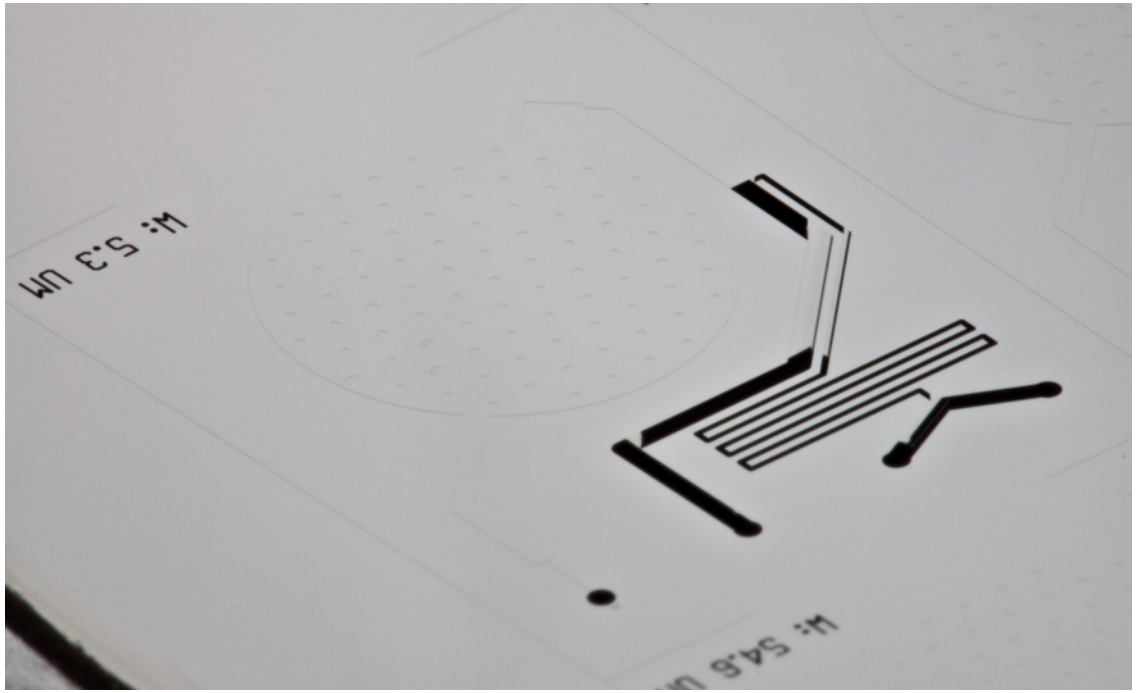
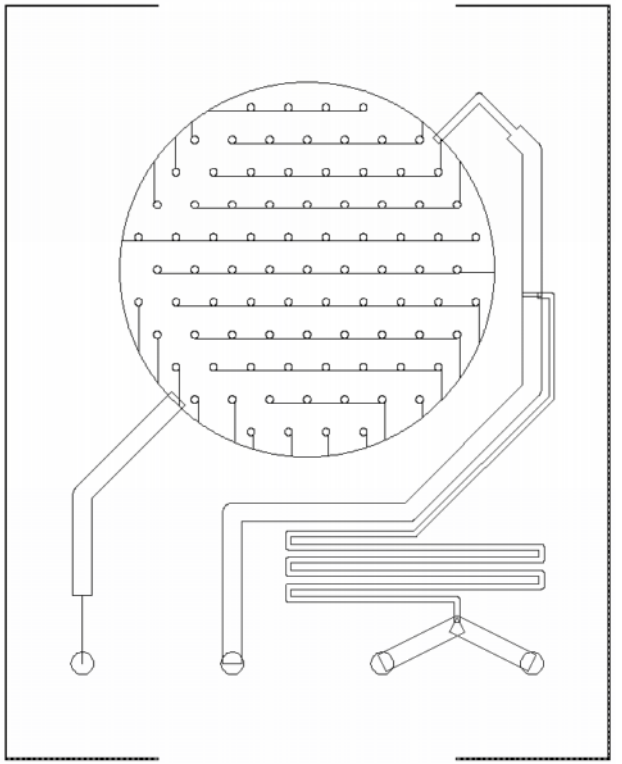


Photo: Thomas Pedersen



CAD-drawing: Thomas Pedersen

Experimental Setup

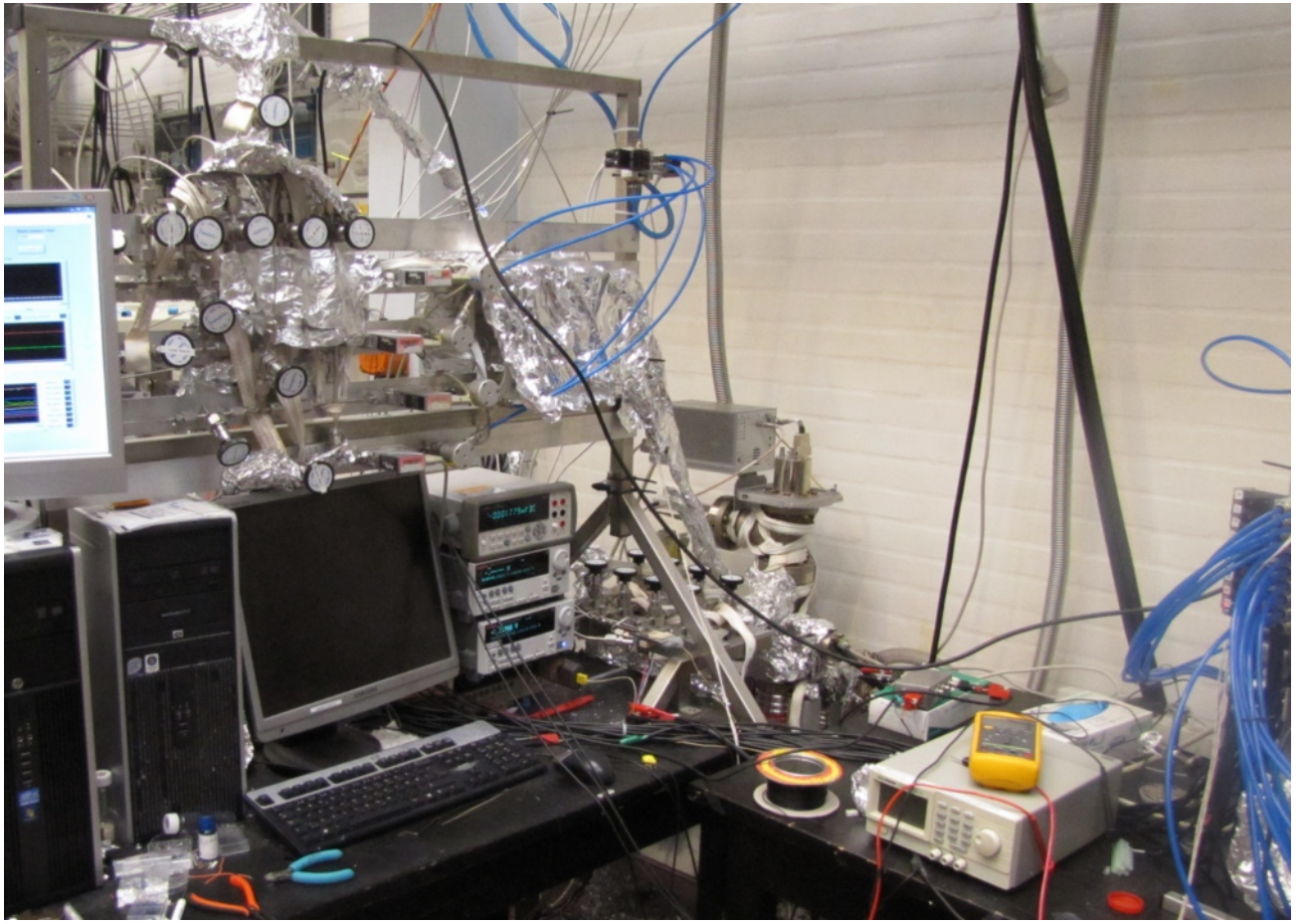


Photo: Mathias Kjærgaard Christensen

Experimental Setup

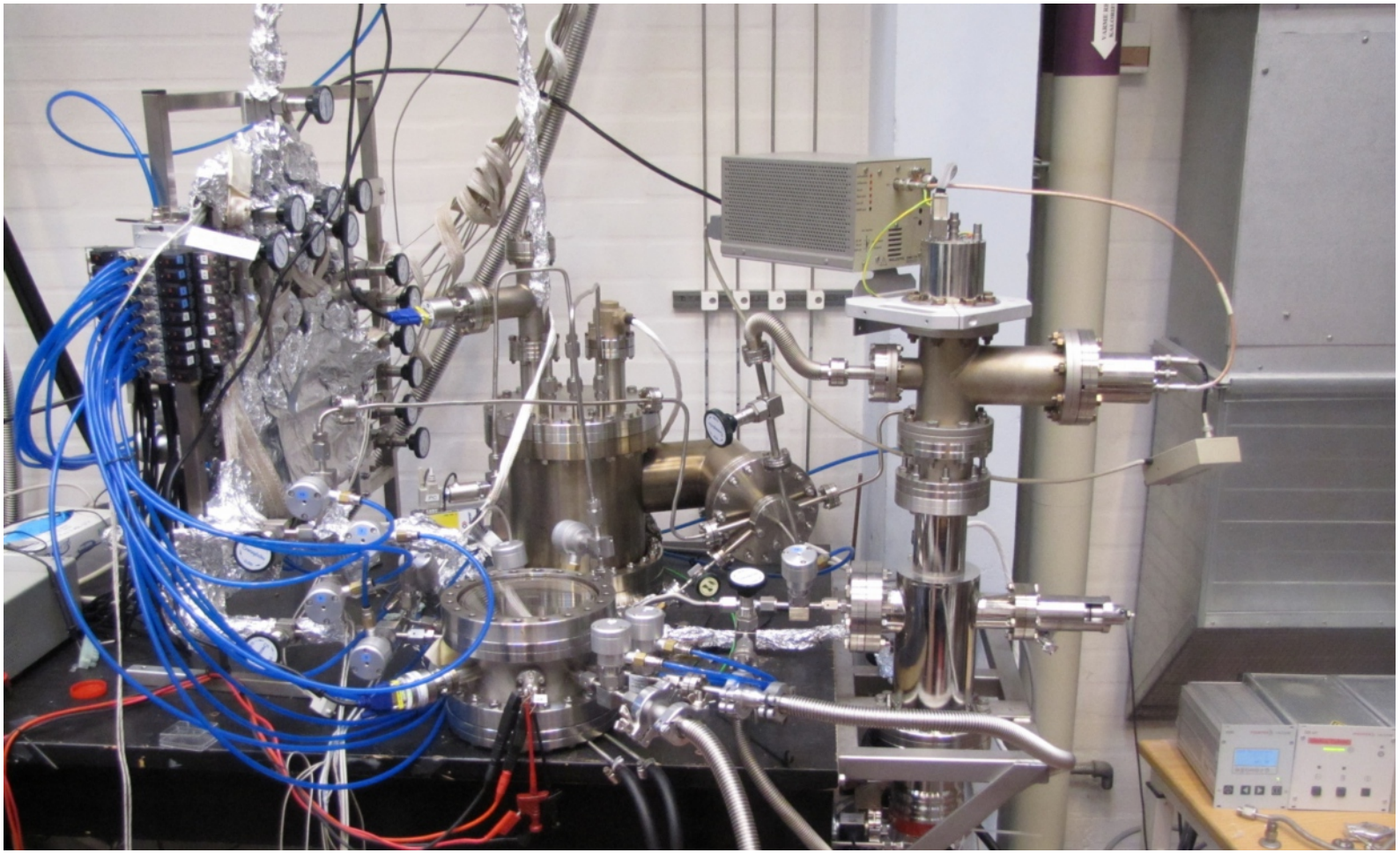
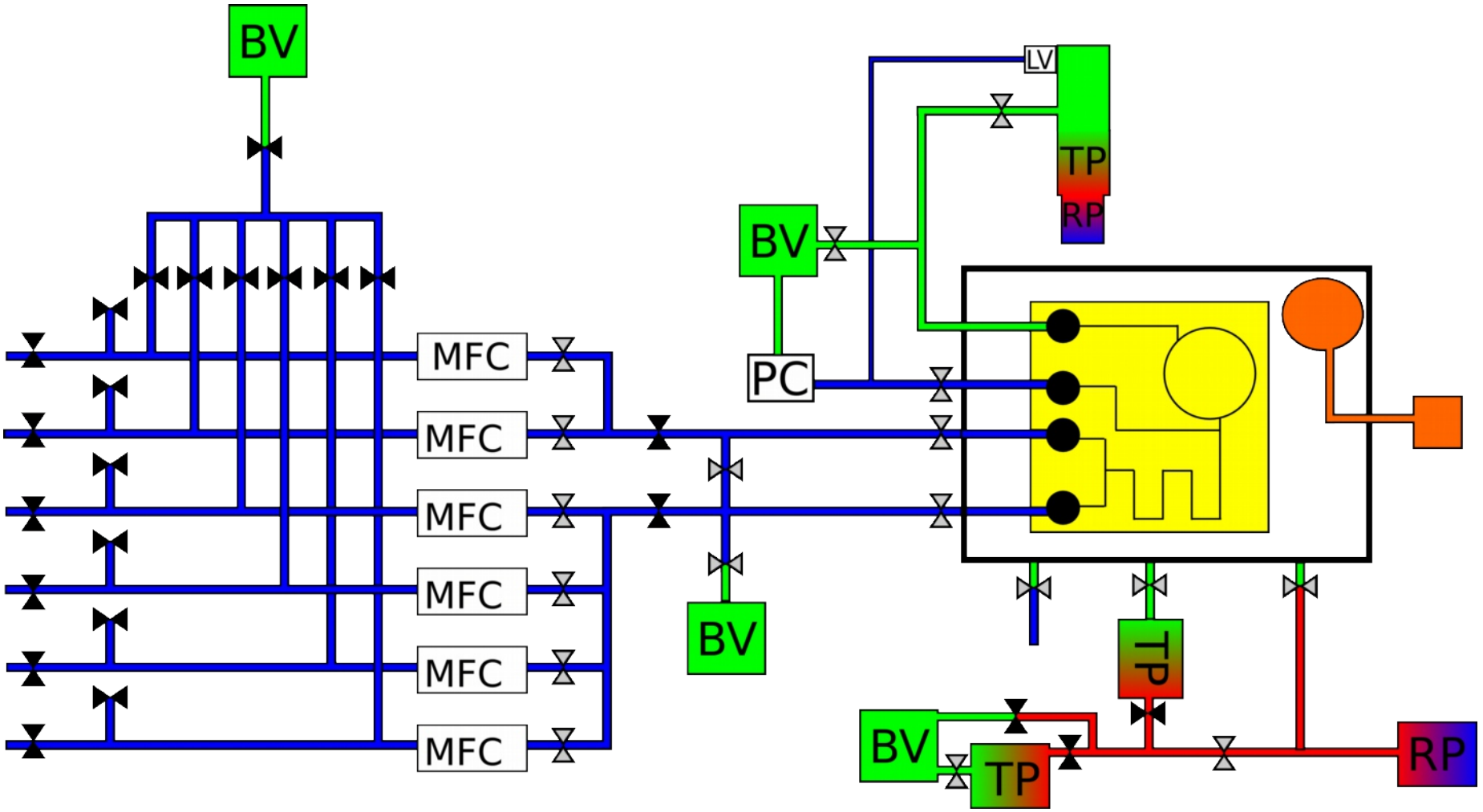


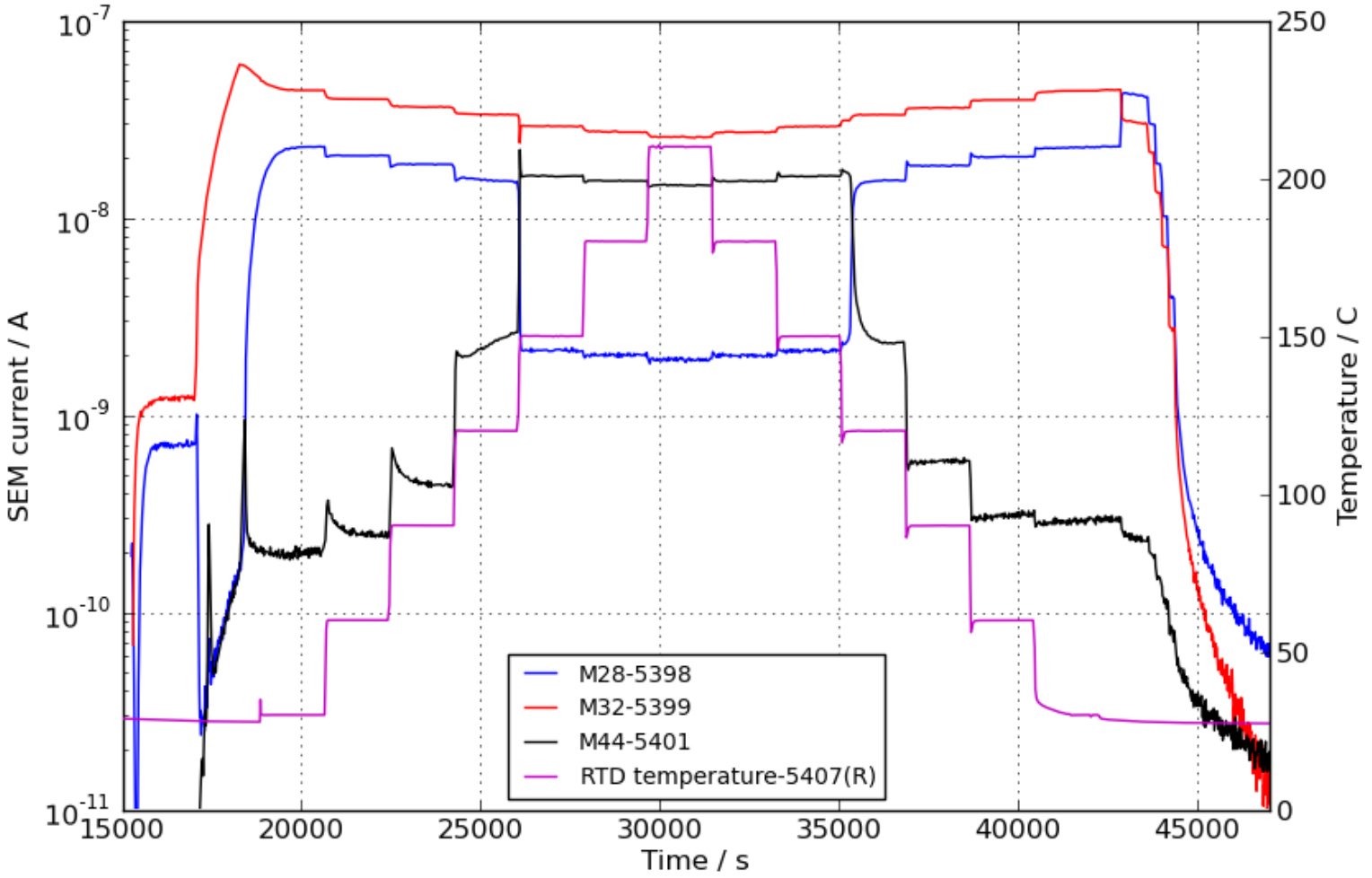
Photo: Mathias Kjærgaard Christensen

Experimental Setup



A Typical Measurement

CO oxidation on Pd thin film

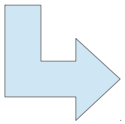


General Measurement Strategy

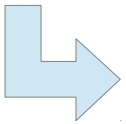
General Measurement Strategy

The Grand Master Plan:

Thin-film measurements



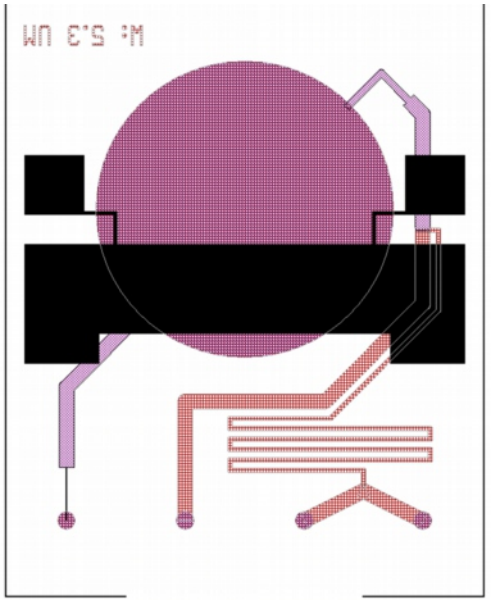
Nanoparticle measurements

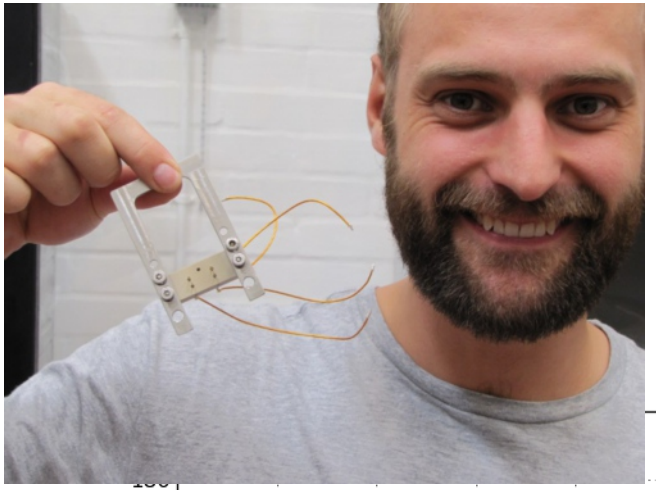


Publish

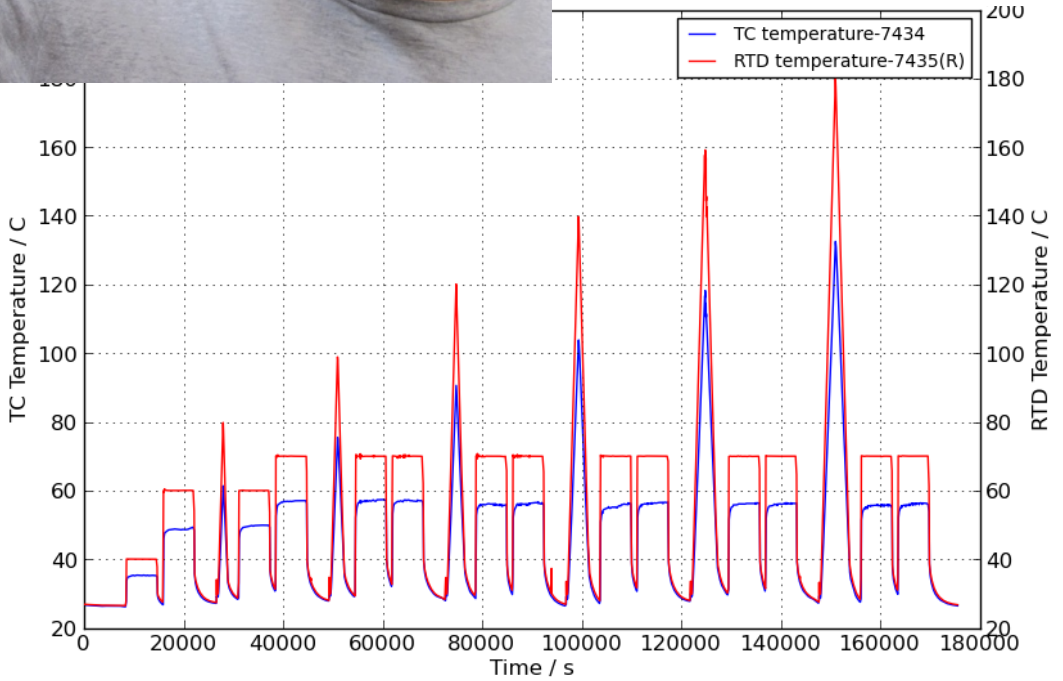
Heating

Heating

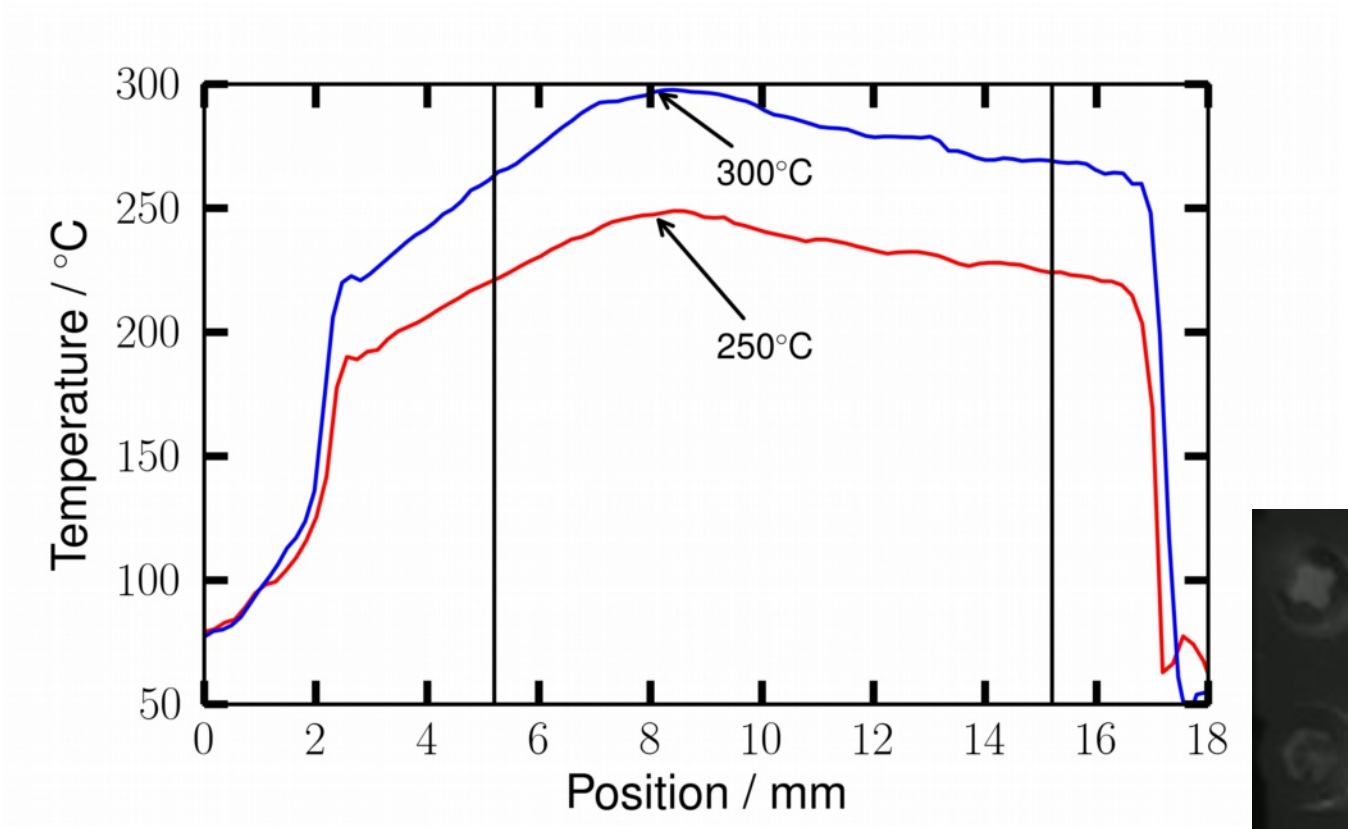


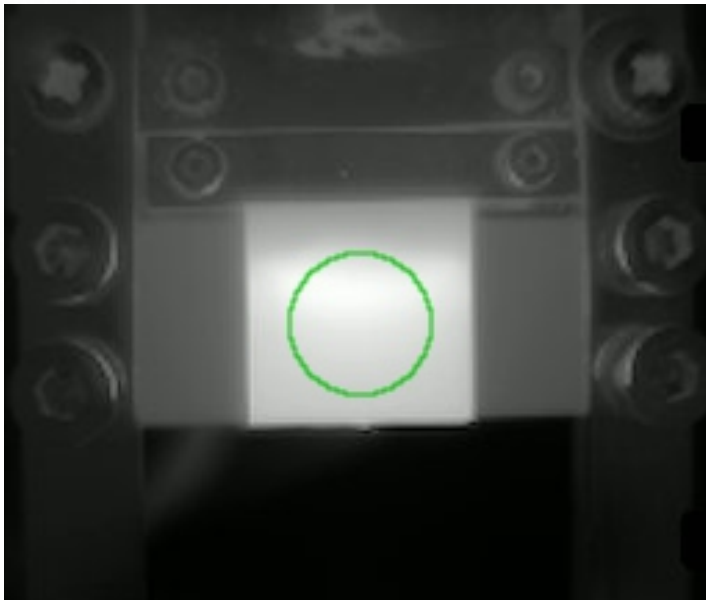



+200.003 V

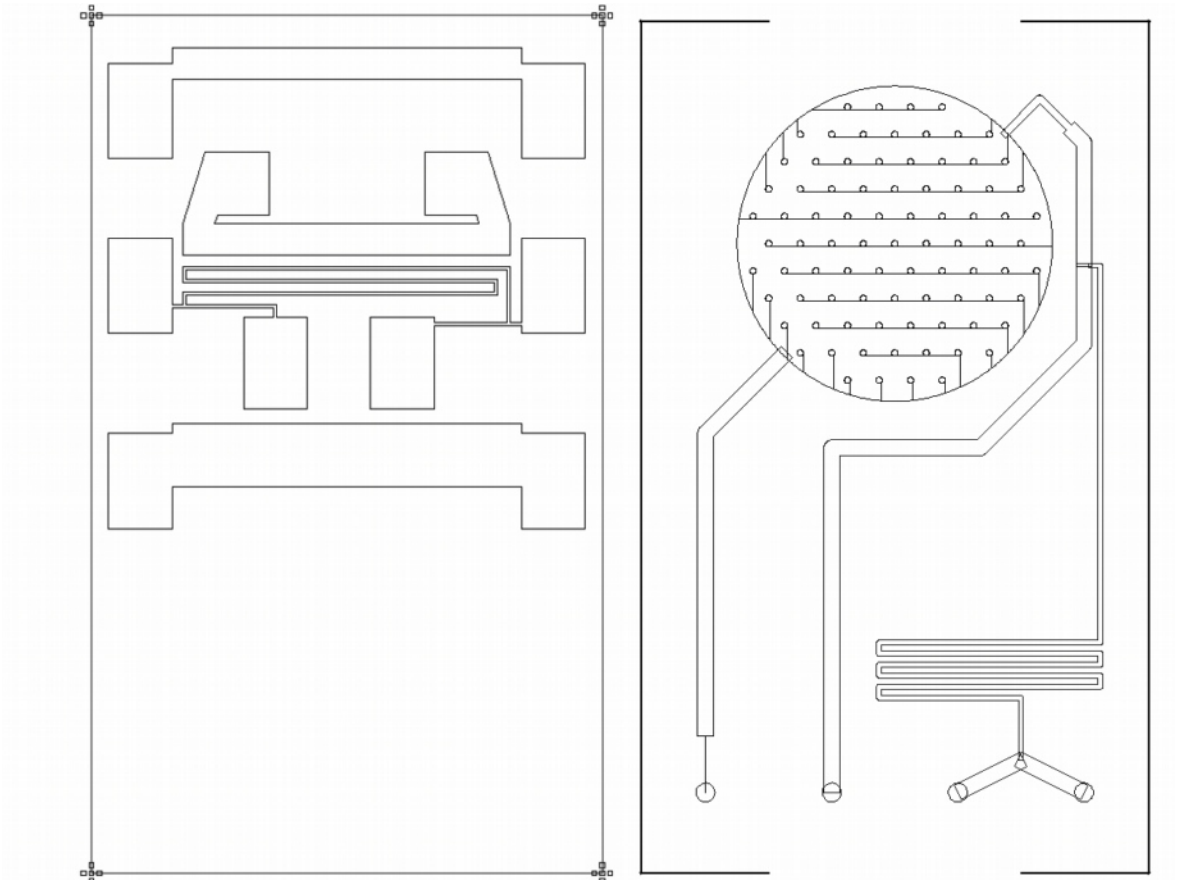

TC temperature-7434
RTD temperature-7435(R)
TC Temperature / C
RTD Temperature / C
Time / s
0
20000
40000
60000
80000
100000
120000
140000
160000
180000
20
40
60
80
100
120
140
160
180
200

Temperature profiles

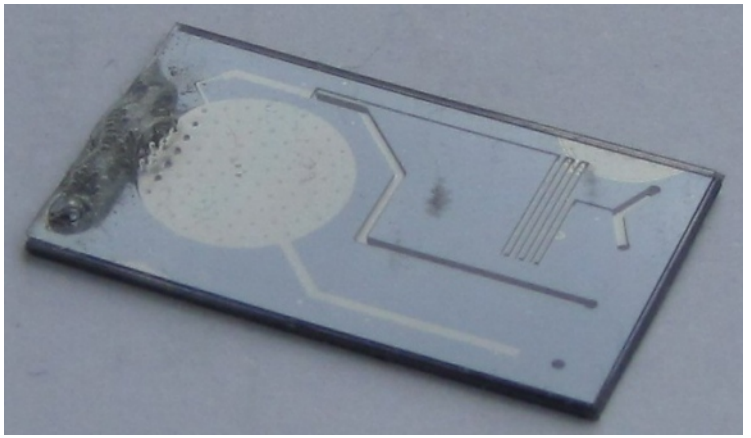




Heating V2.0



CAD Drawing: Thomas Pedersen



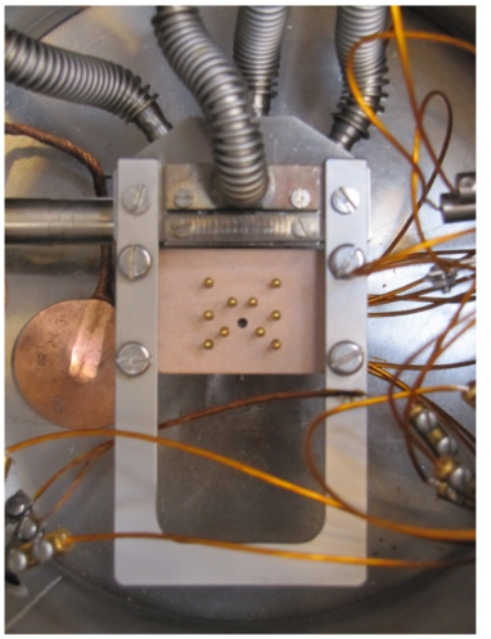
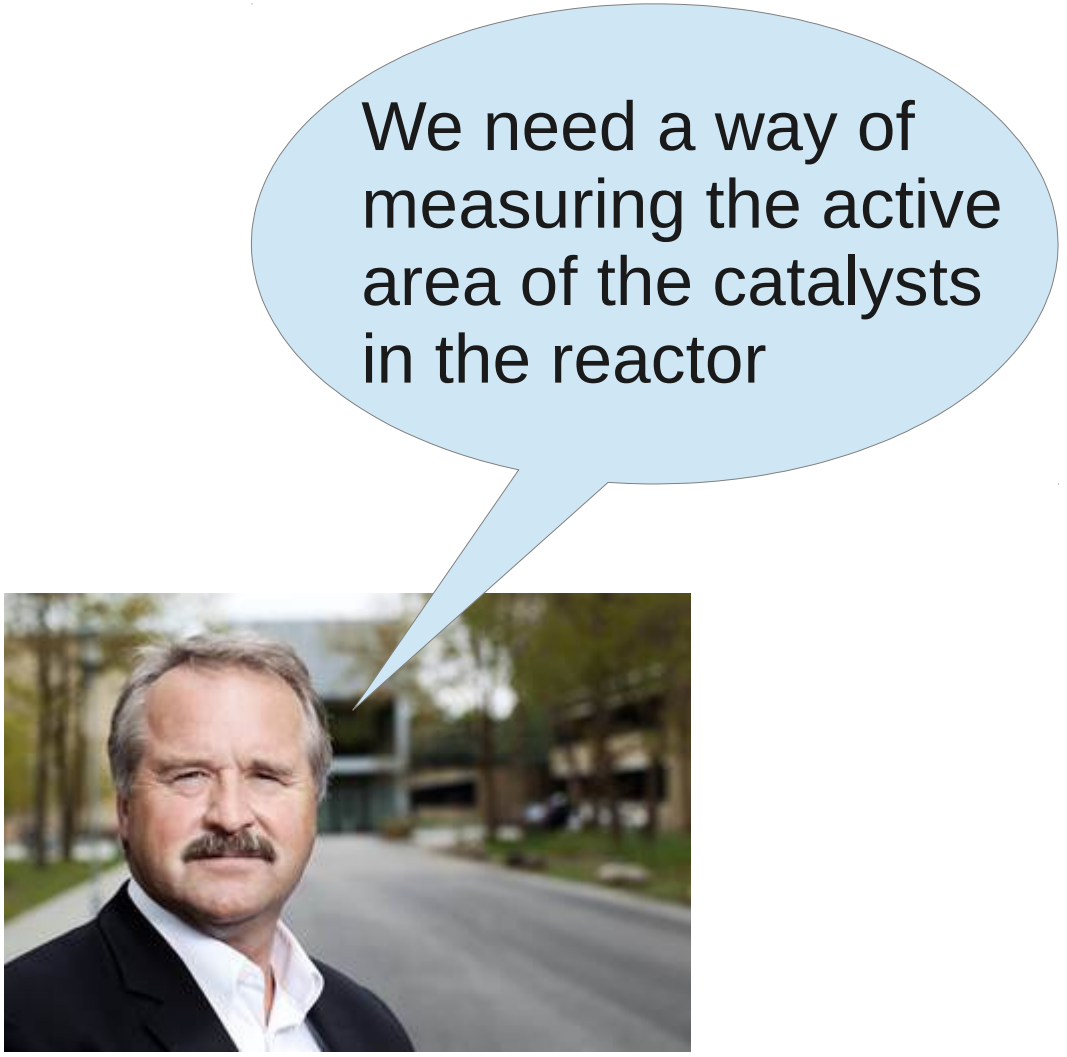


Photo: Mathias Kjærgaard Christensen

Measuring surface area

Measuring surface area



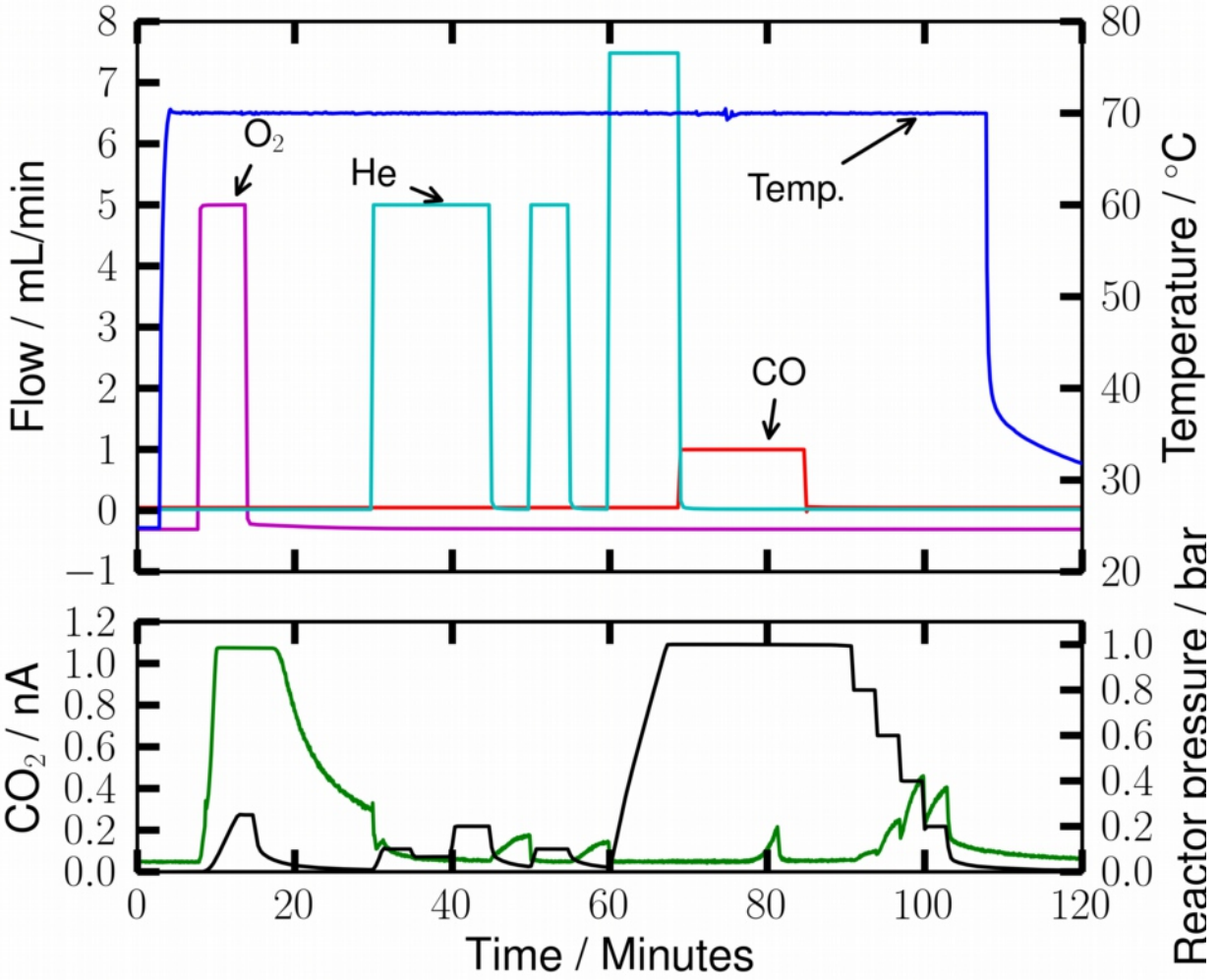
Area Measurements

Measurement principle: CO-titration

- Dose oxygen
- Evacuate reactor
- Dose CO
- Watch for CO_2

Limitations

- Works only for Pt
- Not very sensitive

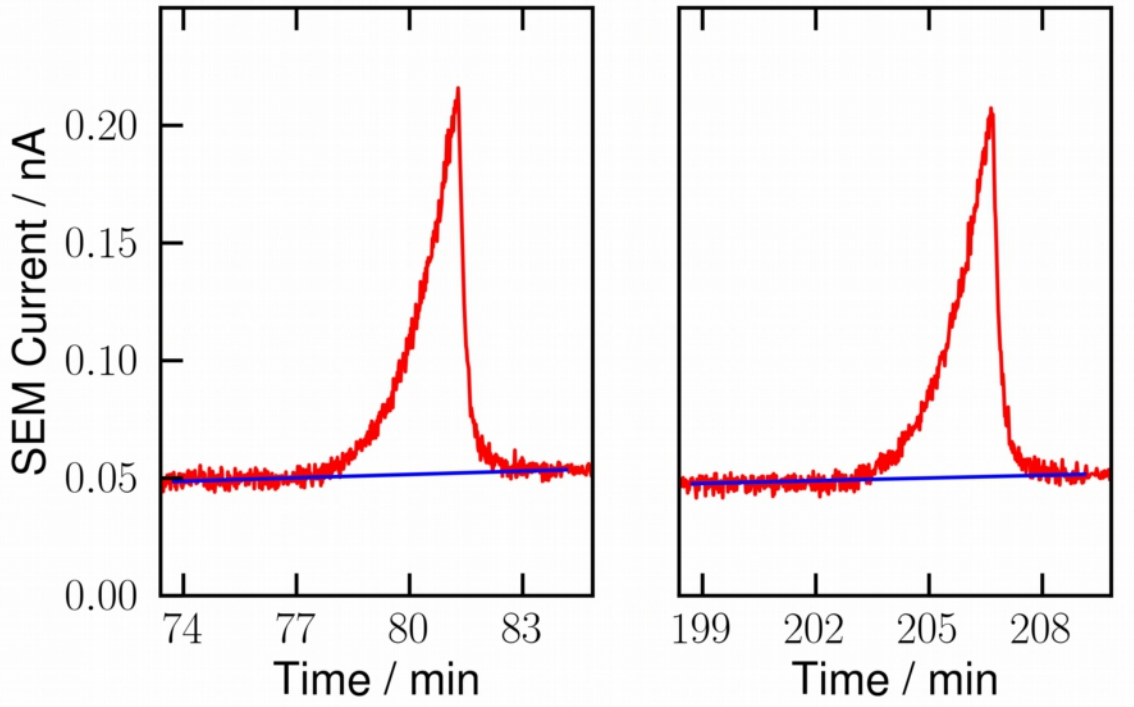


Area Measurements

Calibration experiments performed on thin films

- Easy cleaning
- Known surface area
- Stable system allows for lots of experimentation

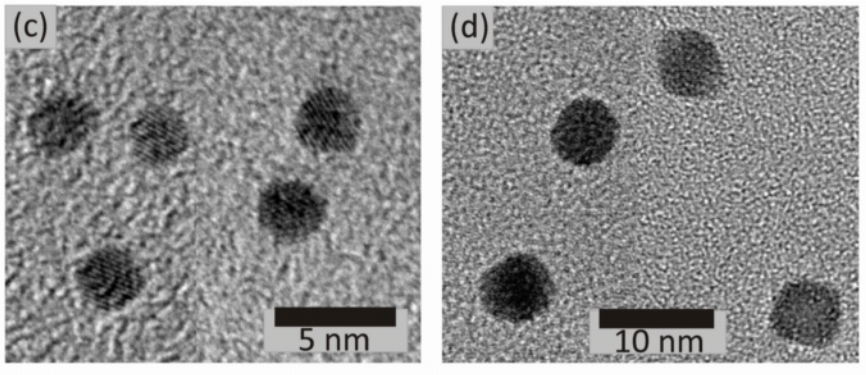
Sensitivity....
Reproducebility....



Area Measurements

According to the Grand Master Plan, we should now measure on nanoparticles.

The chosen sample has a nominal coverage of 10% of 5nm particles.

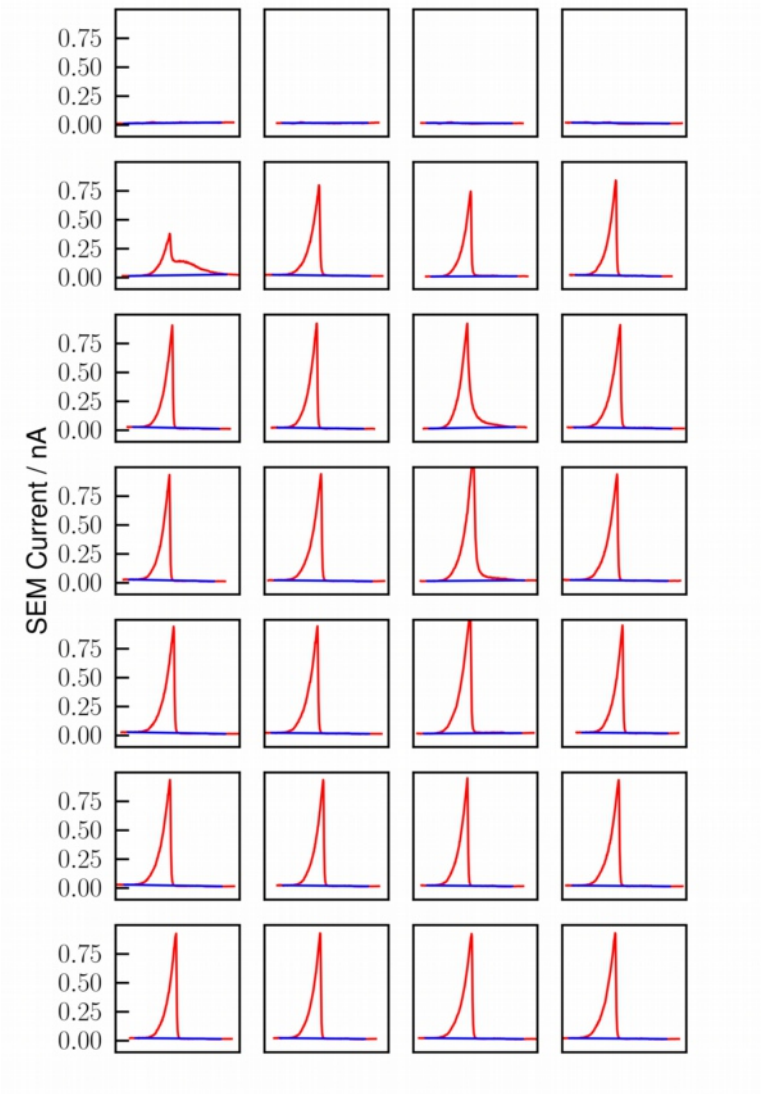


Structural modification of Pt model systems under high pressure CO annealing
D.N. McCarthy, et. al C.E. Strebel, T.P. Johansson, A. den Dunnen, A. Nierhoff, J.H.Nielsen, and Ib Chorkendorff, 2012

Measurement program:

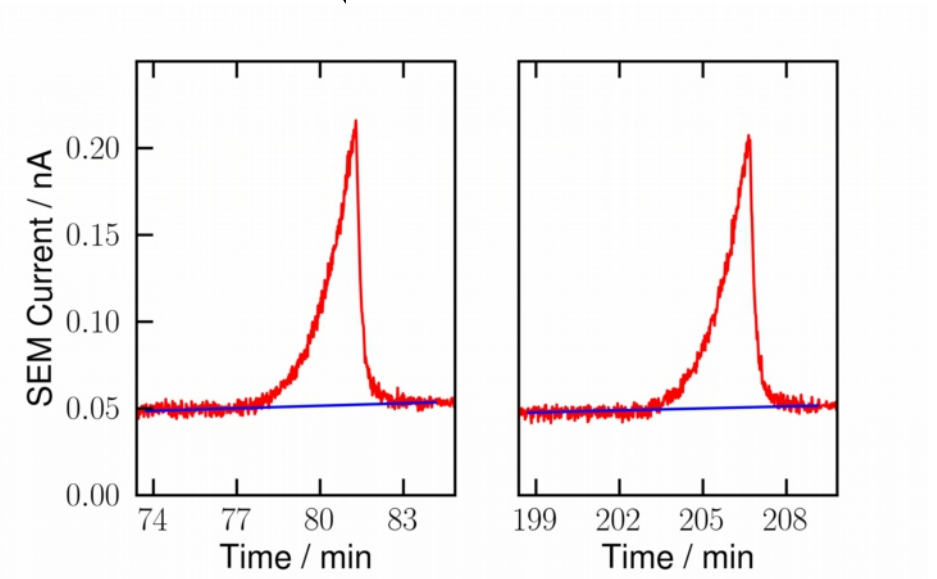
- Heating to 420° C in 1.0 bar O_2
- Heating to 300° C in 1.0 bar He
- Heating to 300◦ C in 0.5 bar CO
- Heating to 350◦ C in 1.0 bar O_2
- Heating to 300◦ C in 0.5 bar CO
- Heating to 250◦ C in 1.0 bar O_2
- Heating to 300◦ C in 0.5 bar CO
- Heating to 150◦ C in 1.0 bar O_2
- Heating to 300◦ C in 0.5 bar CO

Area Measurements

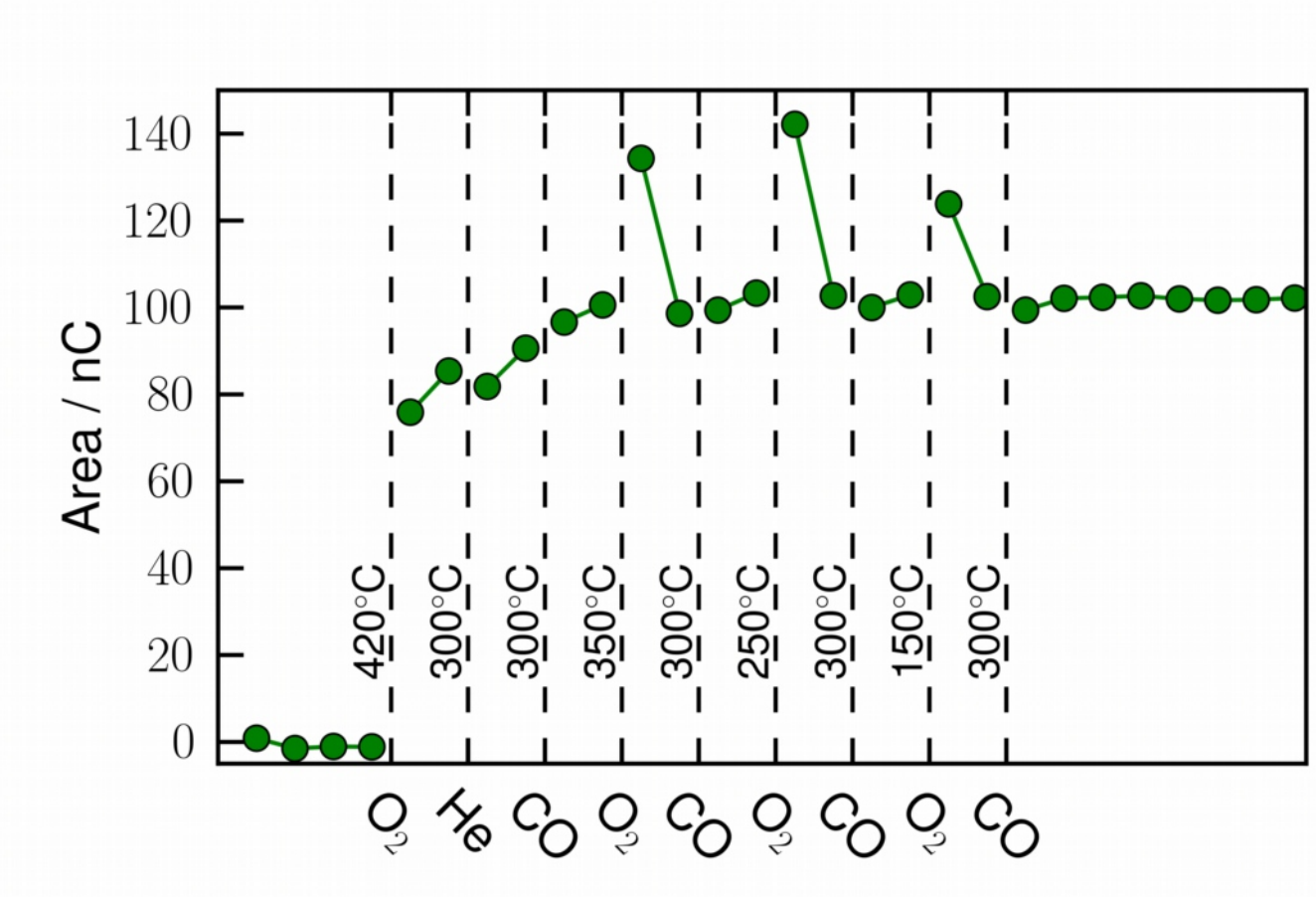


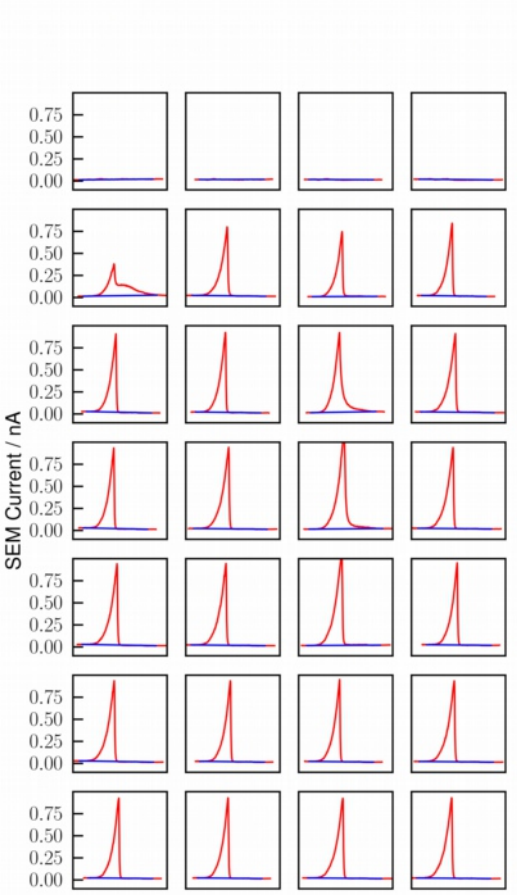
Nanoparticle sample

Thin-film sample



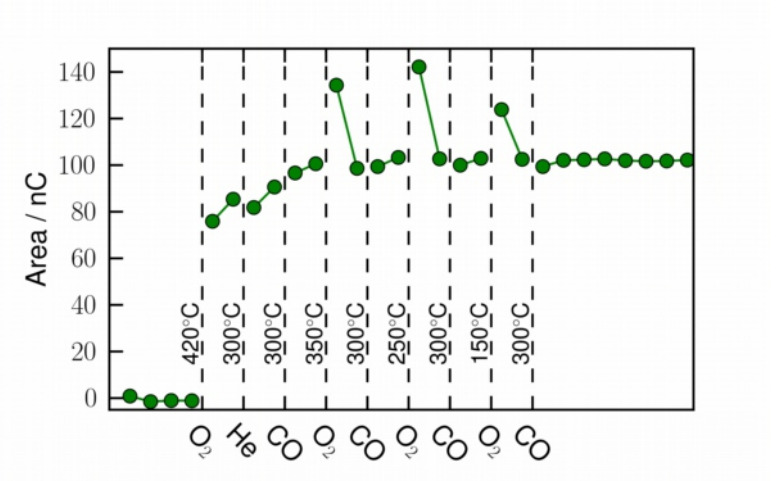
Area Measurements





Area Measurements

The Grand Master Plan:



Thin-film measurements

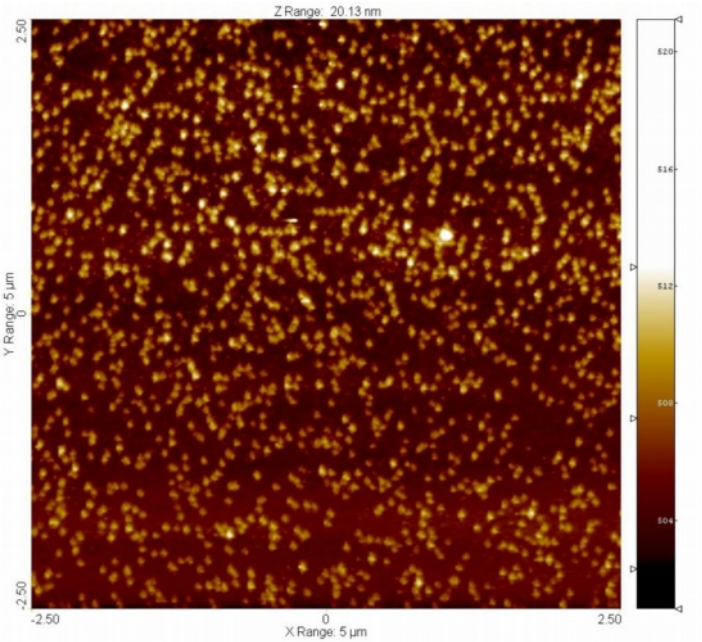
→ **Nanoparticle measurements**

→ ~~**Publish**~~
Establish new characterization tool for the reactors

Oscillating Reactions

Oscillating Reactions

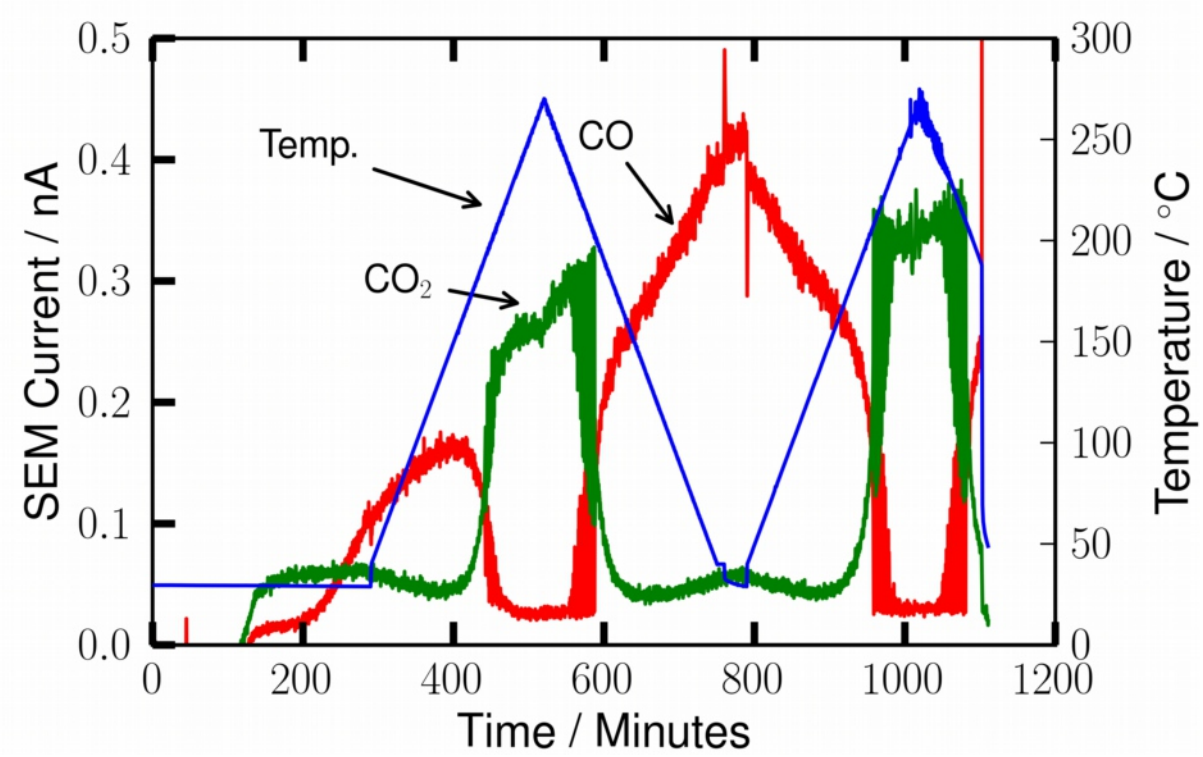
- The story starts a dark and stormy saturday evening....
- Experiments for a bachelors thesis[1] a was done and the setup was idling for the rest of the weekend
- An idling sample of size-selected nano-clusters is the perfect time for random experiments!
- Tried to run a classic CO oxidation light-off experiment in extremely high oxygen concentration



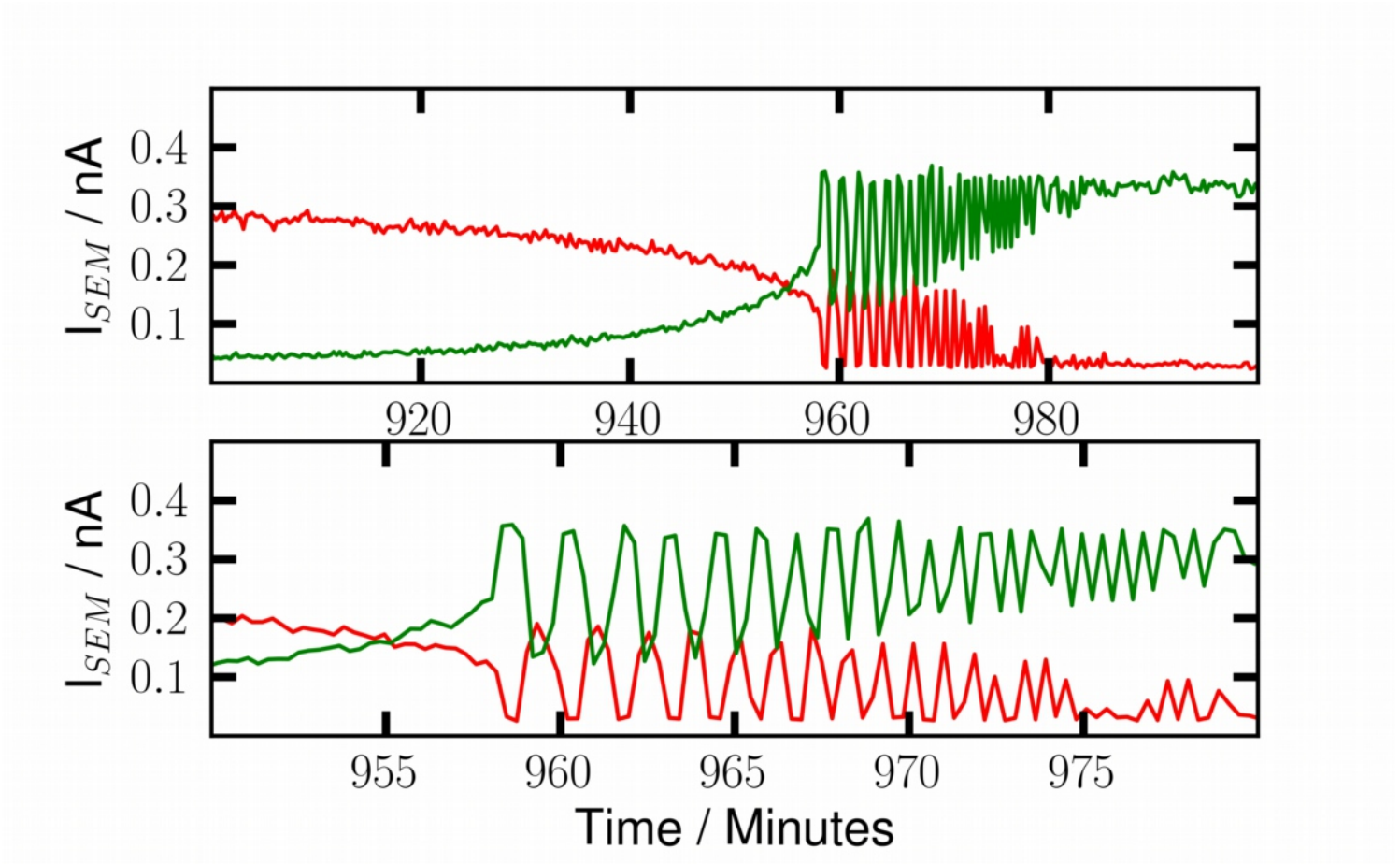
[1] Mikkel Rykær Kraglund: Reactivity of mass selected nanoparticles measured in microreactors, 2011

Oscillating Reactions

Data with unusually low quality called for an explanation



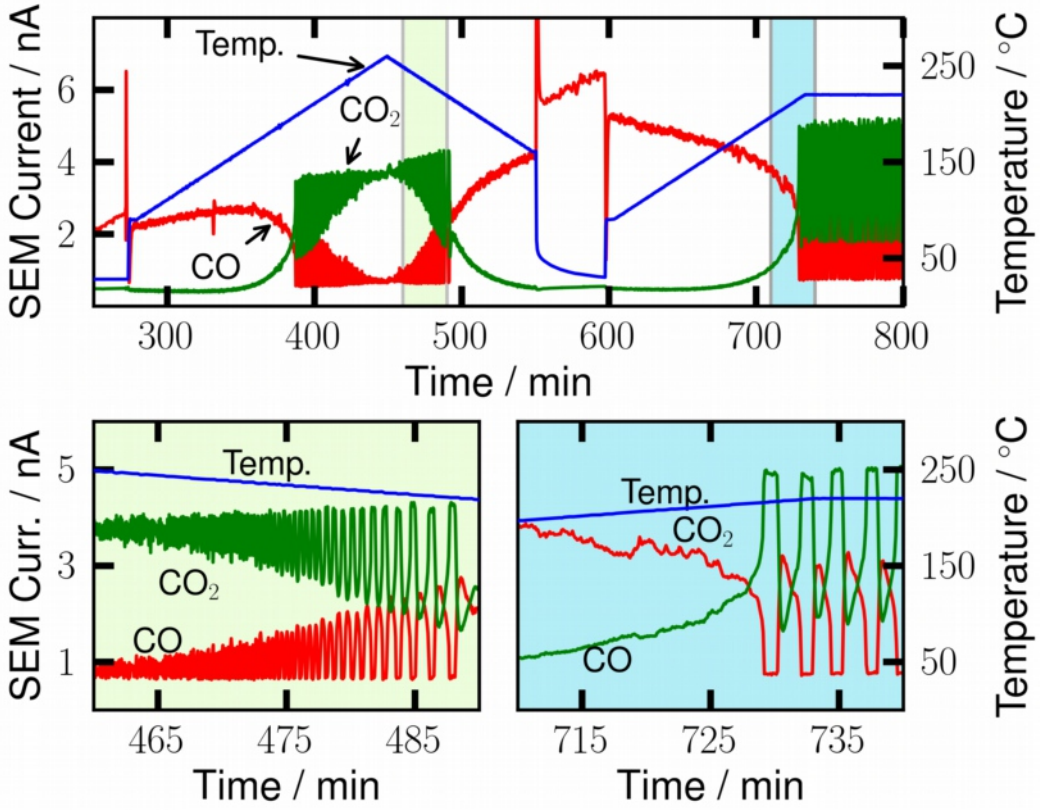
Oscillating Reactions



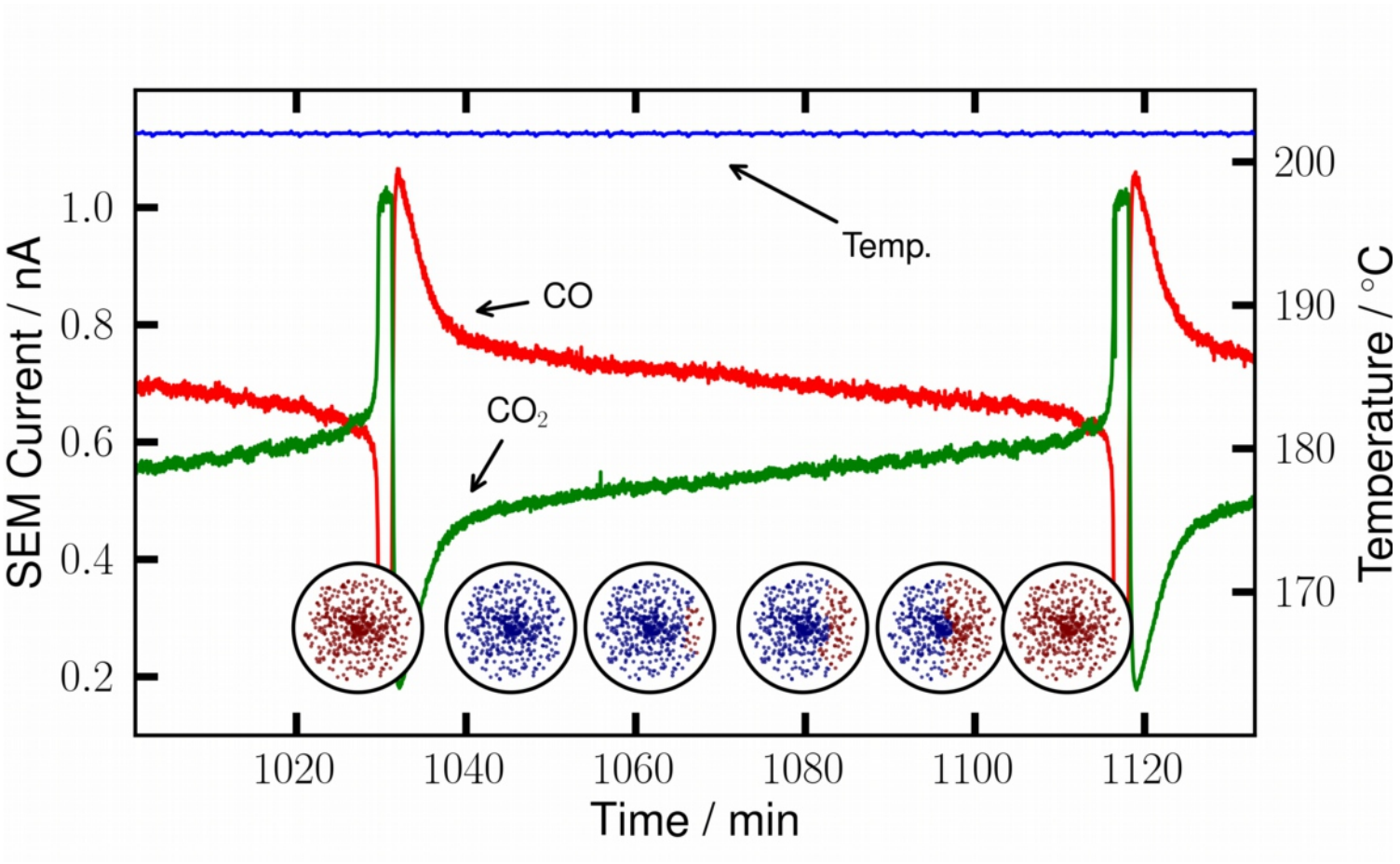
Oscillating Reactions

A more systematic study was initialized

A large set of nanoparticle samples was tested for oscillatory behavior



Oscillating Reactions

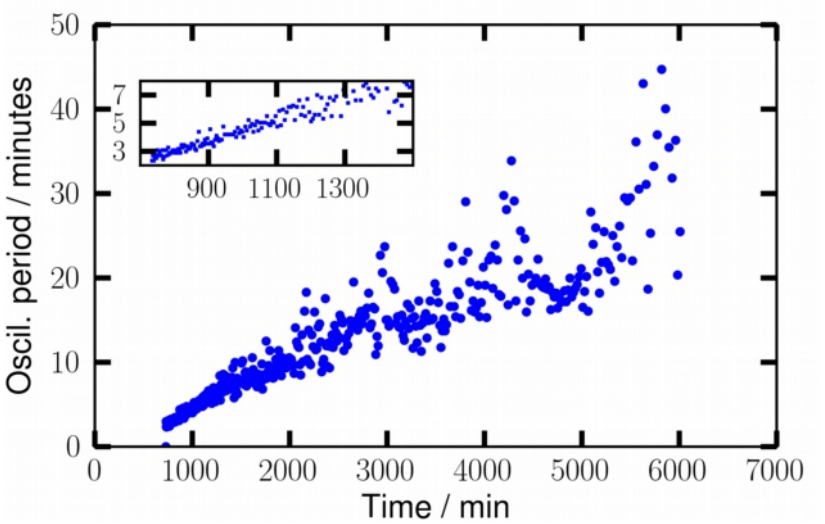


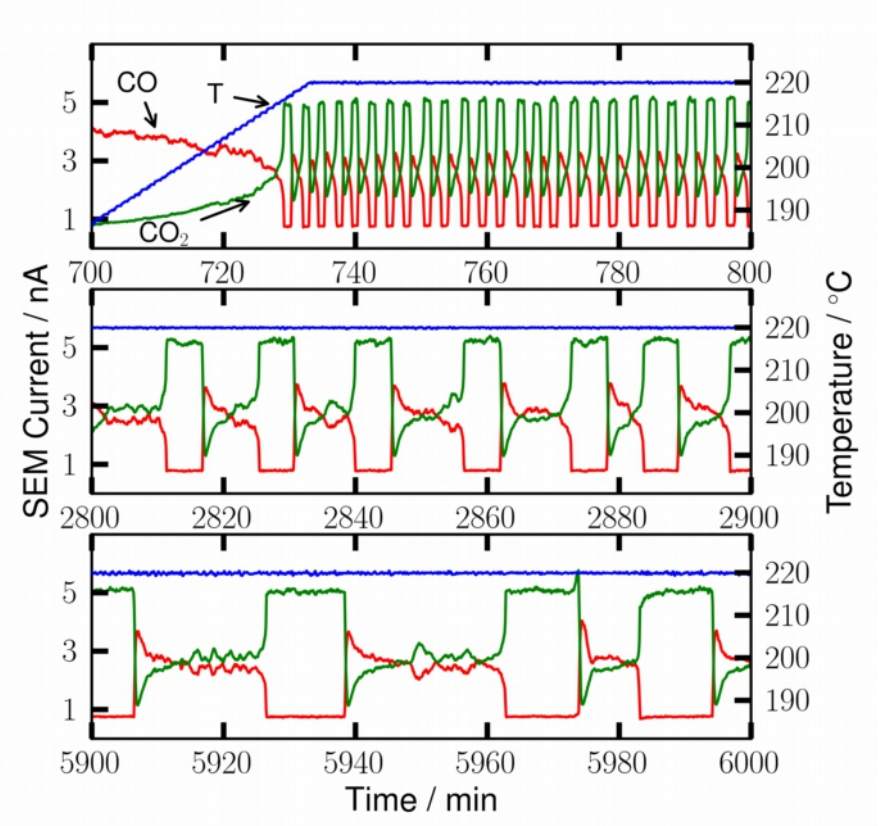
Model based on work from:

B. L. M. Hendriksen, M. D. Ackermann, R. van Rijn, D. Stoltz, I. Popa, O. Balmes, A. Resta, D. Wermeille, R. Felici, S. Ferrer, and J. W. M. Frenken. The role of steps in surface catalysis and reaction oscillations. Nature Chemistry, 2(9):730–734, September 2010.

Oscillating Reactions

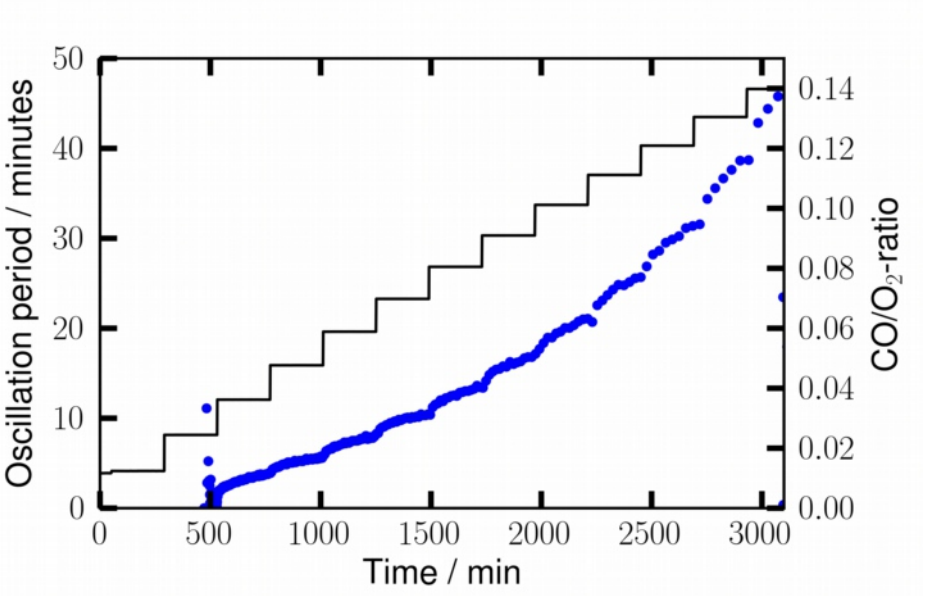
Oscillations self sustained for several days, with steadily increasing period.

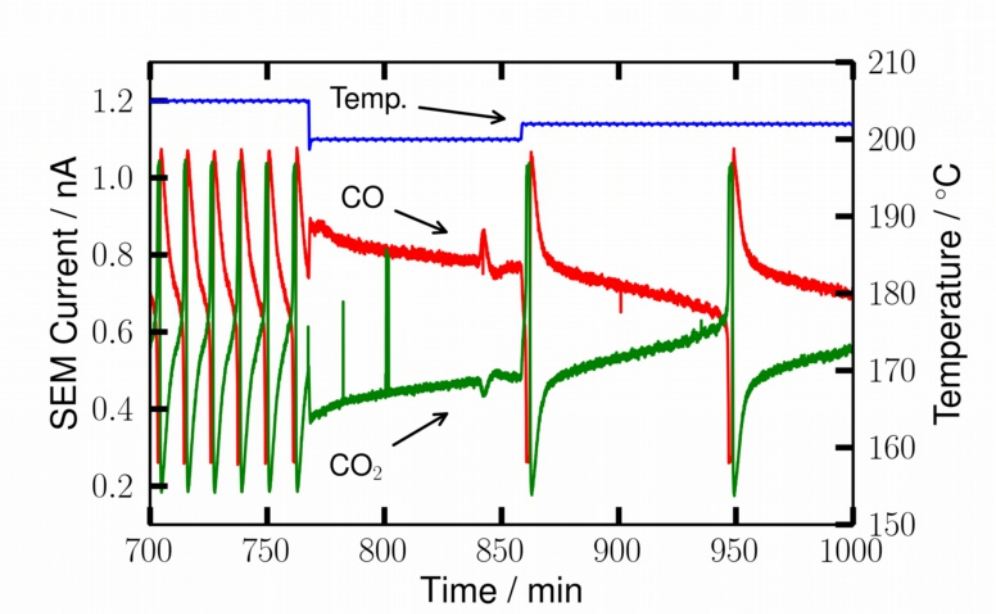




Oscillating Reactions

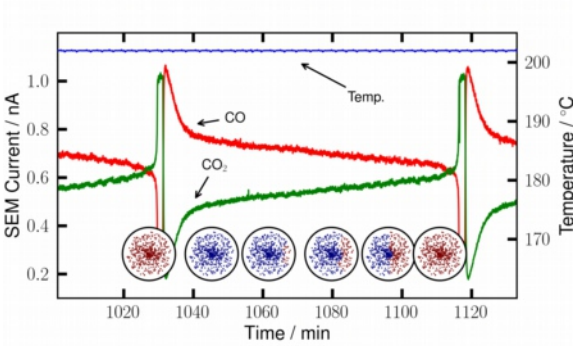
Oscillations are heavily dependent on temperature and mildly dependent on gas composition.





Oscillating Reactions

The Grand Master Plan:



Thin film measurements

↳ **Nanoparticle measurements**

↳ ~~**Publish**~~ **Submit**

Sensitivity Measurements

Observation. The sample loading for the oscillation experiments was very low.

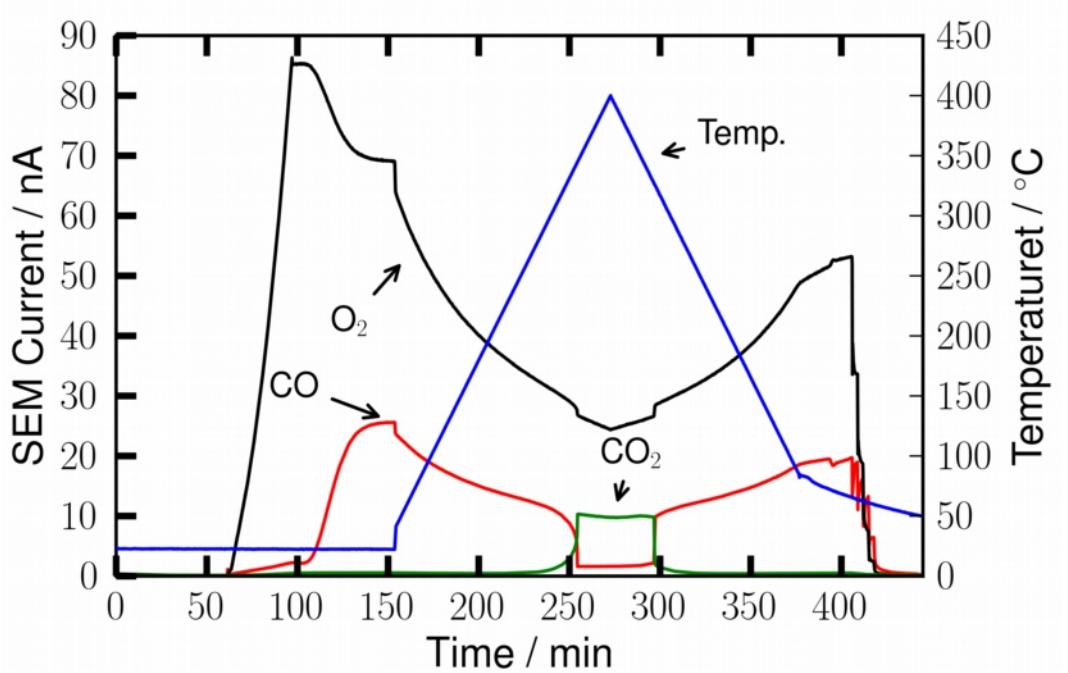
Question. How small amounts of catalyst can be measured in the μ-reactor setup?

Sensitivity Measurements

Thomas Pedersen produced a wafer with Pt spots of different sizes. Six of these have so far been successfully measured.

#	Radius / μm	Area / μm^2	Reactor coverage
N5	3.5	38.5	4.9×10^{-7}
N8	15	707	9.0×10^{-6}
N9	25	1960	2.5×10^{-5}
N10	50	7850	1.0×10^{-4}
N11	250	196000	2.5×10^{-3}

Sensitivity Measurements



#	Radius / µm	Area / µm^2	Reactor coverage
N5	3.5	38.5	4.9 x 10^{-7}
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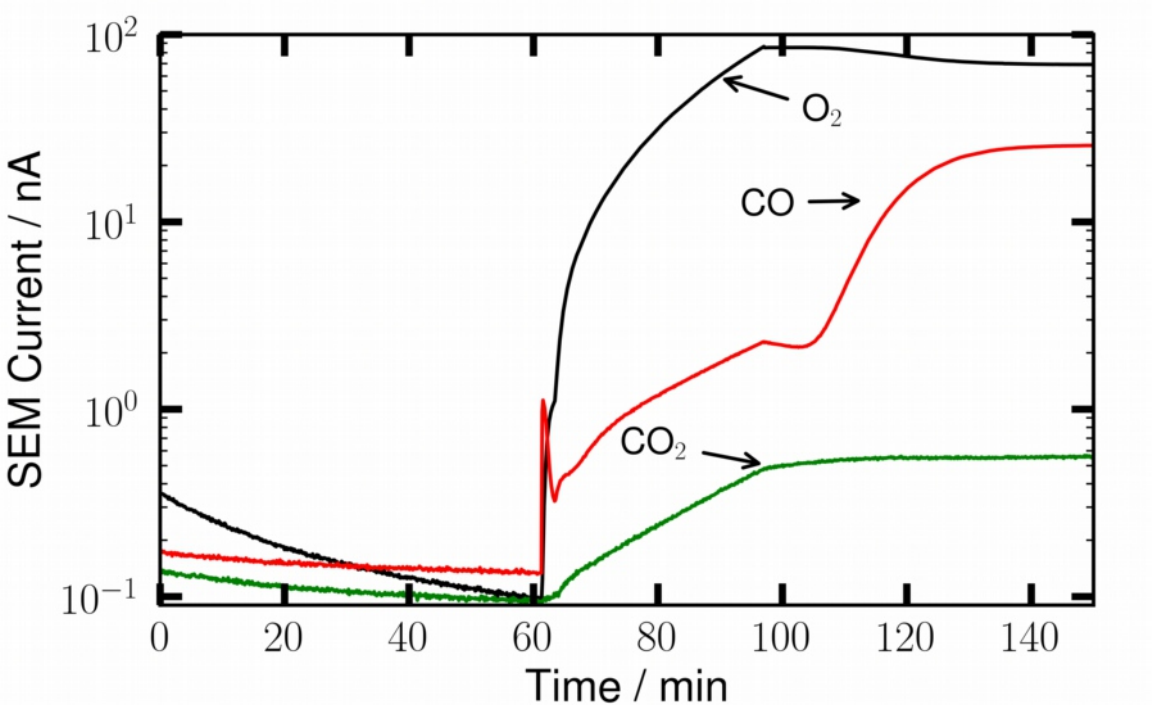
N9	25	1960	2.5 x 10^{-5}
N10	50	7850	1.0 x 10^{-4}
N11	250	196000	2.5 x 10^{-3}

Sensitivity Measurements

Background correction

To do quantitative analysis, it is necessary to subtract the CO_2 background.



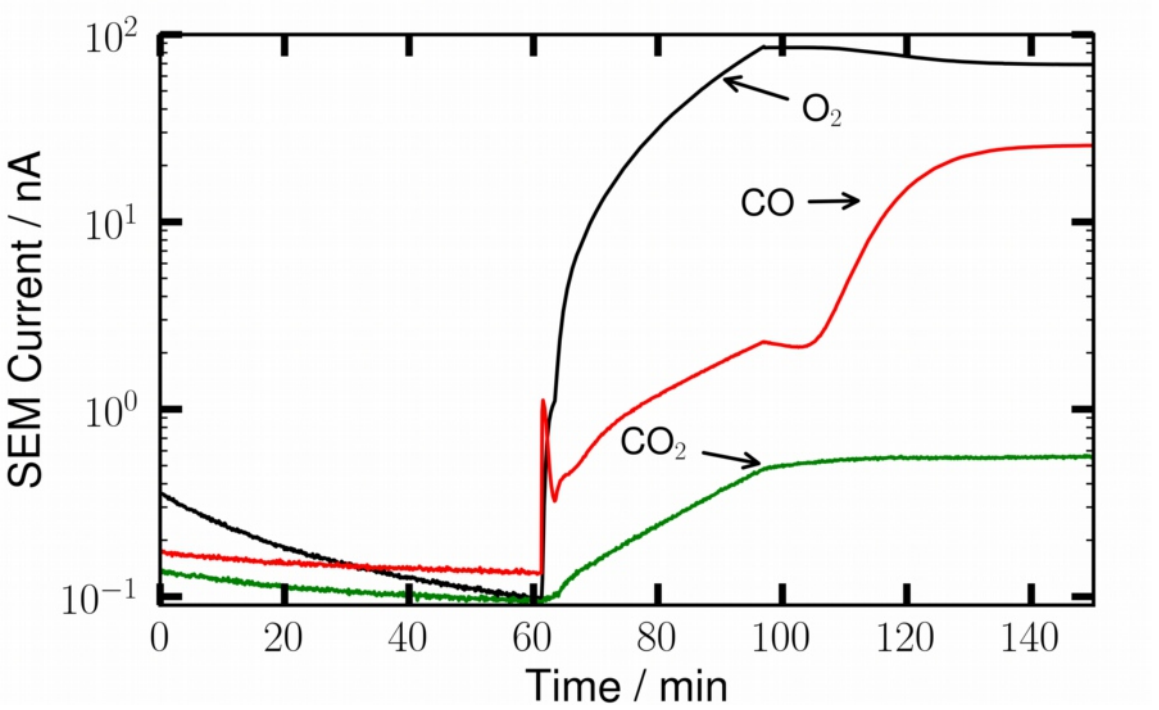
Sensitivity Measurements

Background correction

To do quantitative analysis, it is necessary to subtract the CO_2 background.

Background turns out to be dominated by oxygen:

$I_{CO_2} \sim 0.0082 \times I_{O_2}$

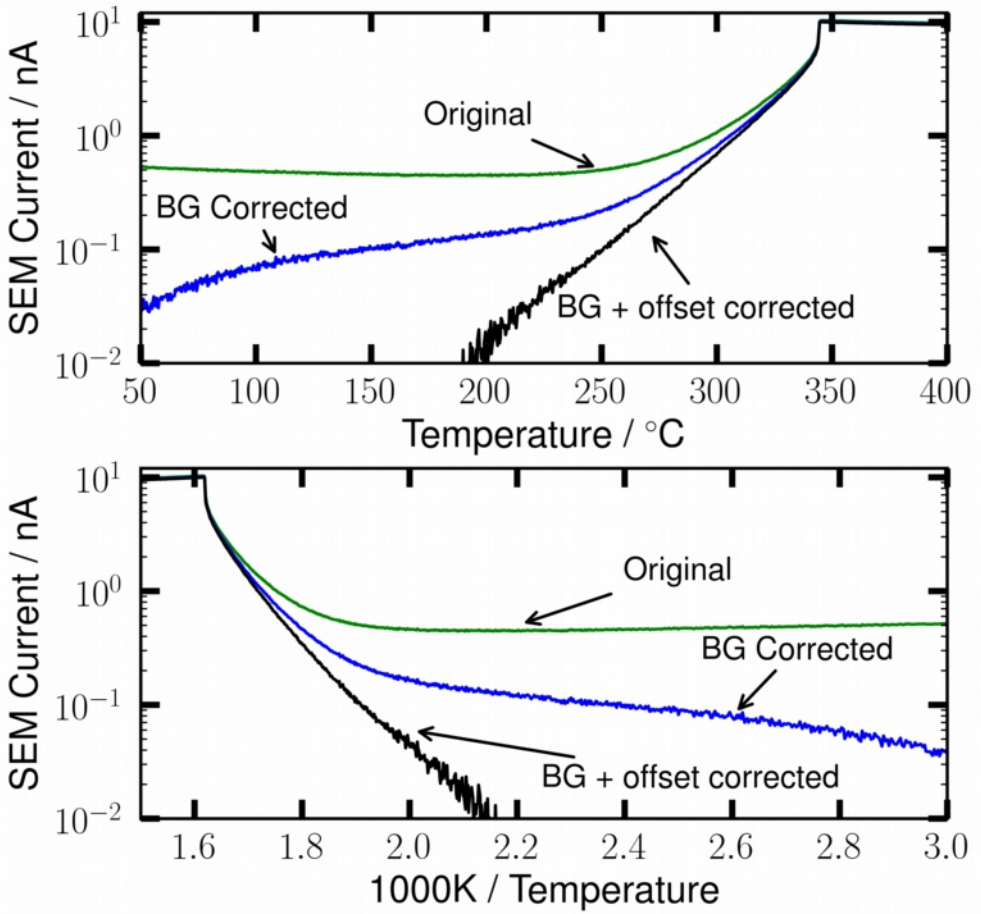


Sensitivity Measurements

Background correction

Using the background correction the linear region can be significantly extended.

$$k = Ae^{-E_a/k_bT}$$

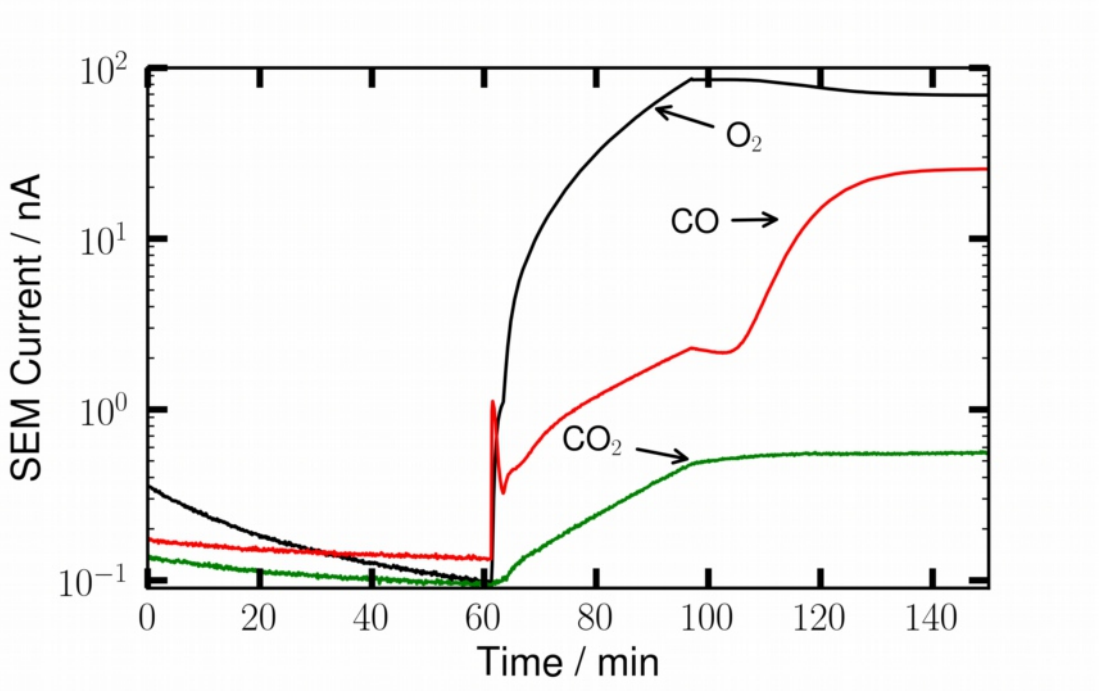


Sensitivity Measurements

Mass Spec Calibration

How do we get from MS-output to actual turn over frequency?

Use the approximately known total flow and calculate from the total SEM current.

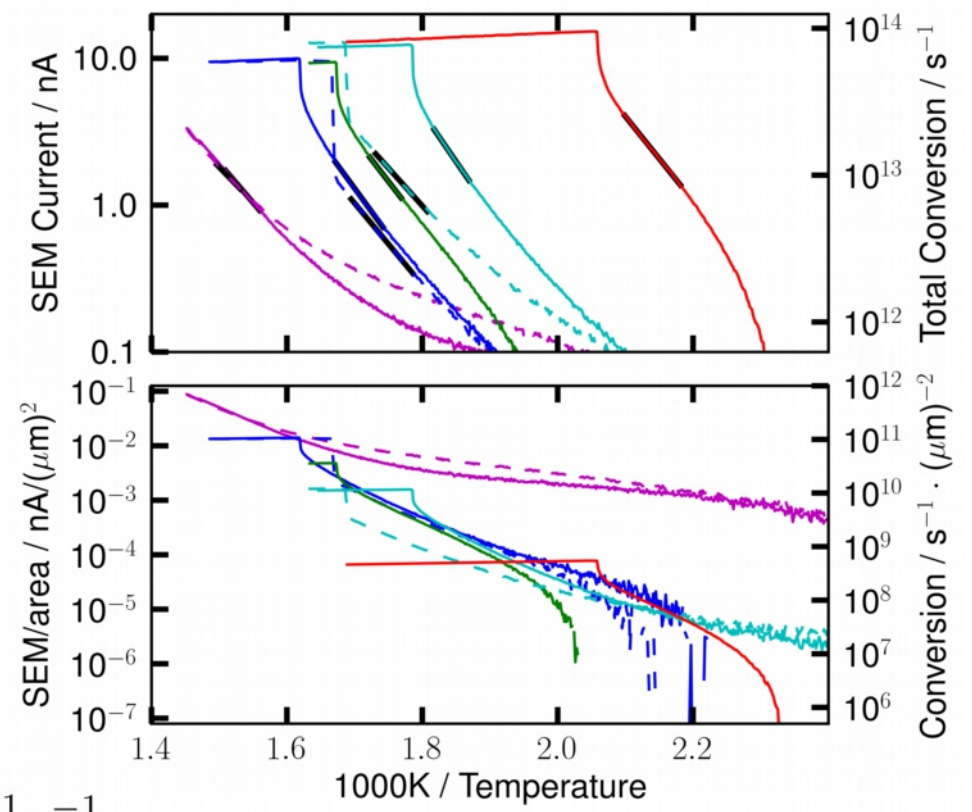


$$S \approx \frac{(69.4 + 25.5)\ \mathrm{nA}}{6 \times 10^{14}\ \mathrm{molecules/s}} = \frac{1.6 \times 10^{-13}\ \mathrm{nA}}{\mathrm{molecule/s}} = \frac{1.6 \times 10^{-22}\ \mathrm{C}}{\mathrm{molecule}}$$

Sensitivity Measurements

From the known sensitivity absolute turnover can be calculated.

Area normalization shows that all samples falls on approximately the same line.



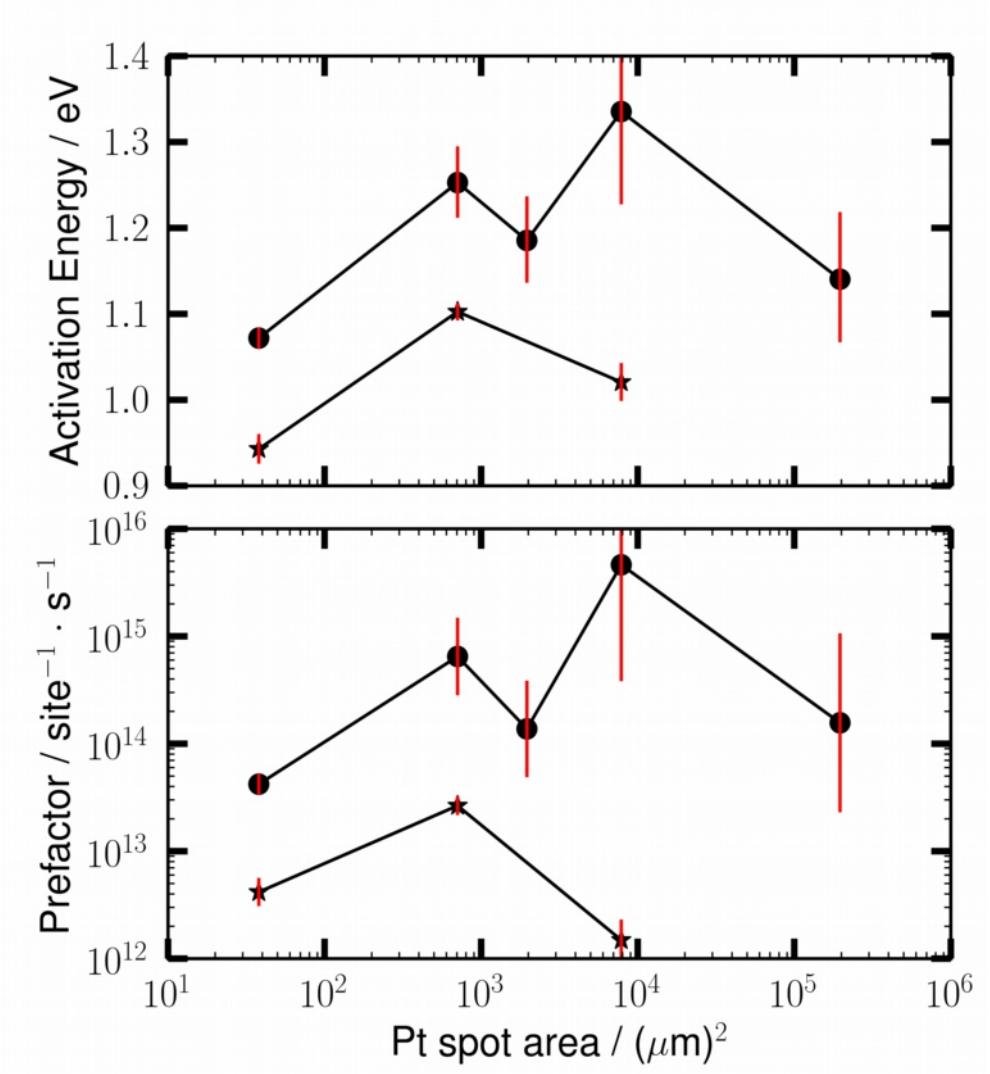
Number of sites on Pt: ~6.5x10^6 µm^{-2}

$$TOF_{Max} = \frac{7 \times 10^{11} \mathrm{s}^{-1} \mu\mathrm{m}^{-2}}{6.5 \times 10^{6} \mathrm{site} \times \mu\mathrm{m}^{-2}} \approx 10^{5}\,\mathrm{site}^{-1}\,\mathrm{s}^{-1}$$

Sensitivity Measurements

Finally, we are able to calculate absolute numbers for activation energy and prefactor.

Errorbars expresses fitting uncertainty and thus under estimates the real error.



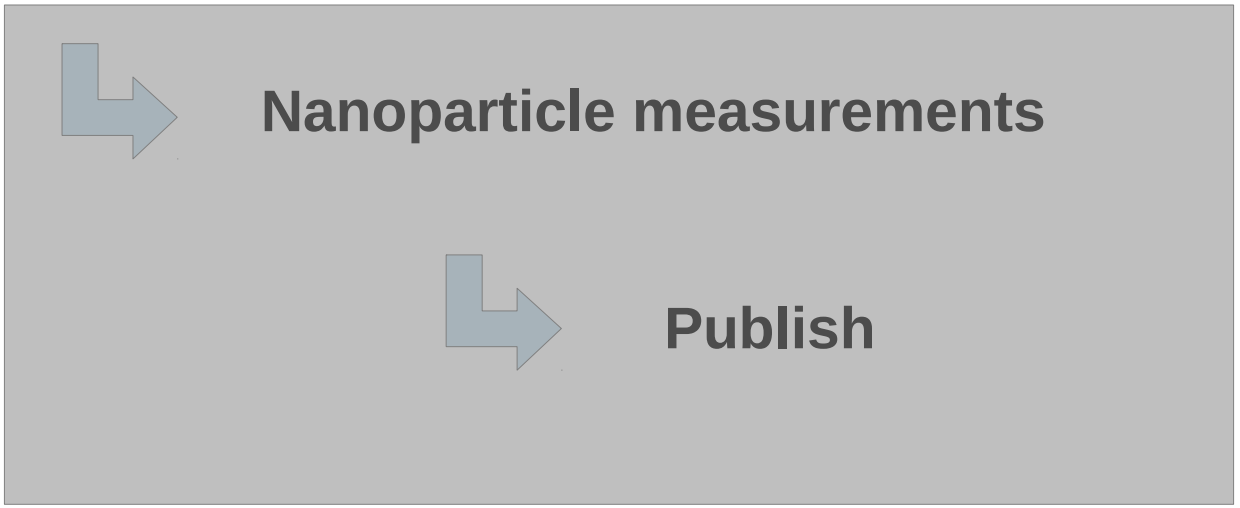
Sensitivity Measurements

Take home messages regarding sensitivity:

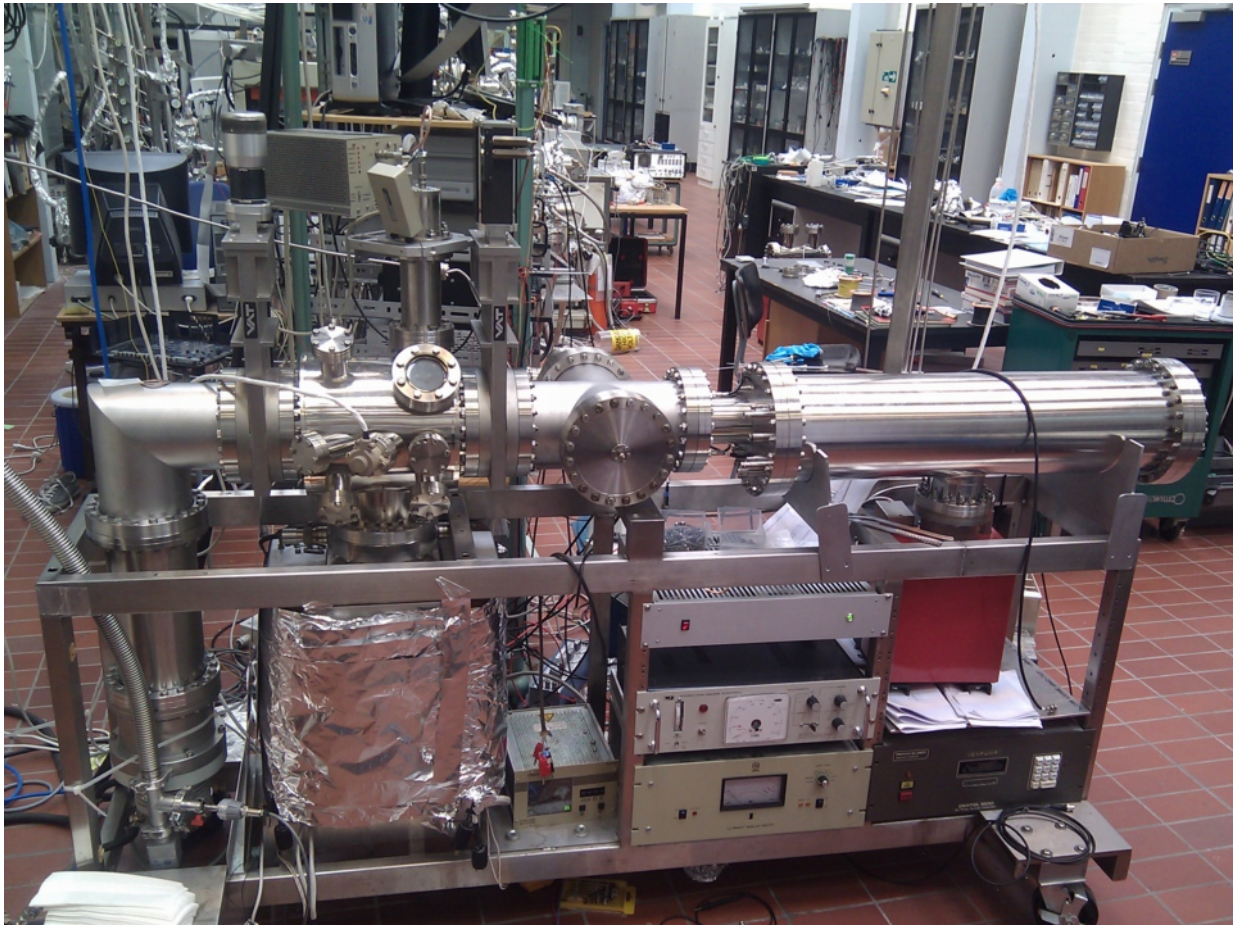
- CO oxidation can be extremely efficient on Pt
- Even minute amounts of metal (espcially Pt) contamination must be avoided in the µ-reactors

The Grand Master Plan:

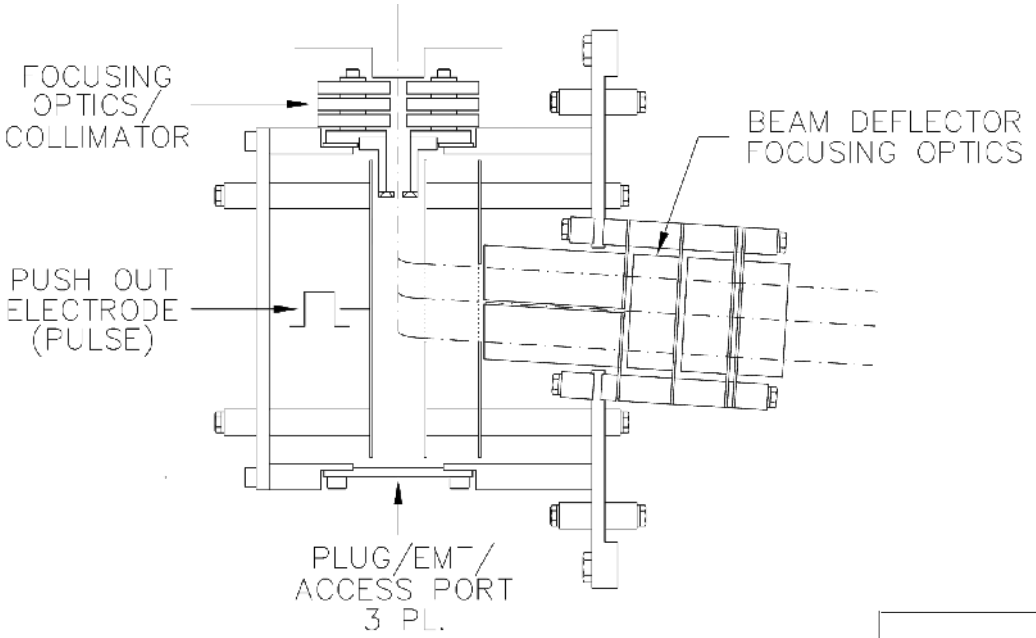
Thin film measurements



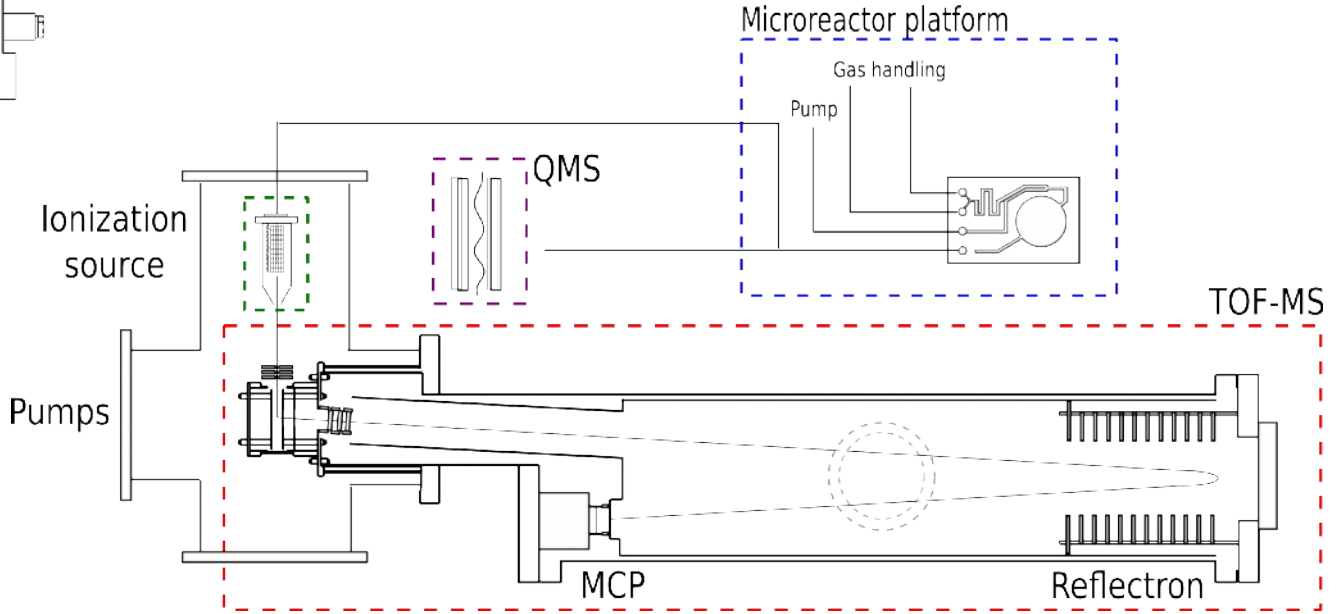
Time-Of-Flight Mass Spectrometry



Time-Of-Flight Mass Spectrometry

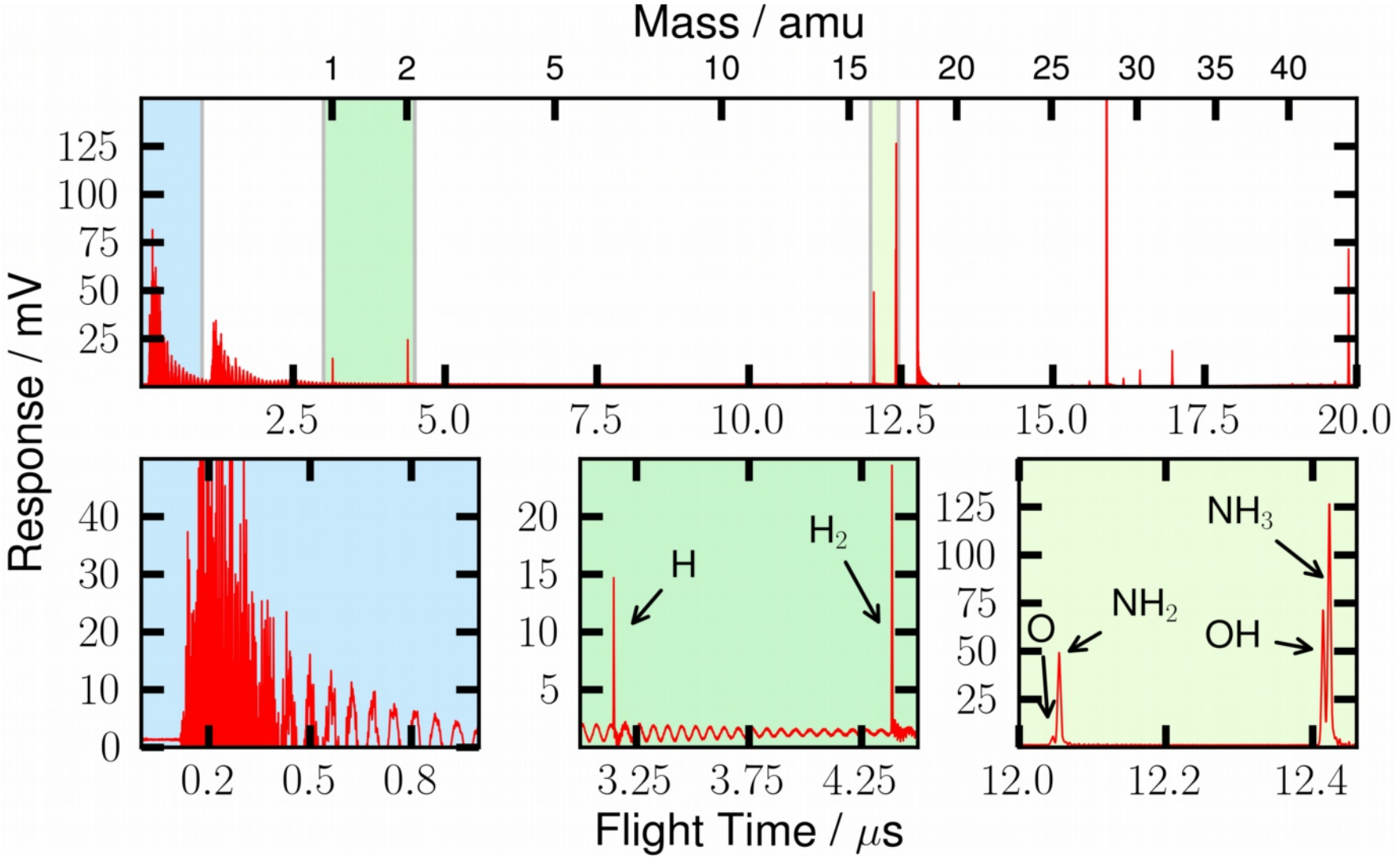


Drawing:
Jordan TOF Products, Inc



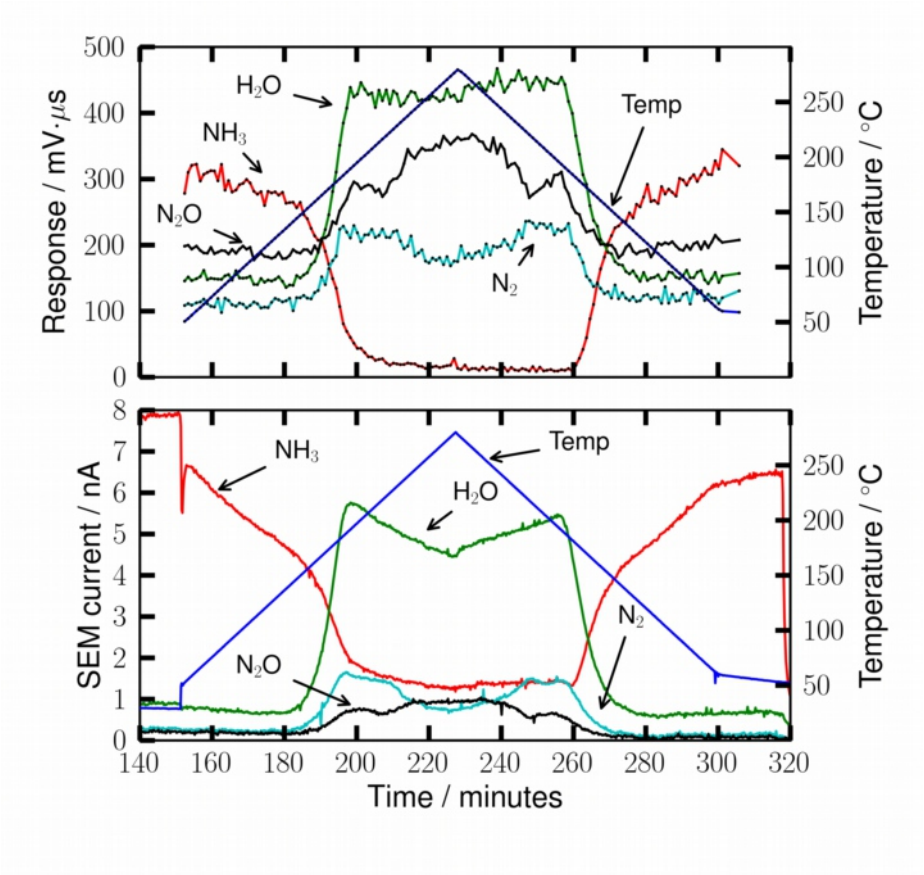
Drawing: Thomas Andersen

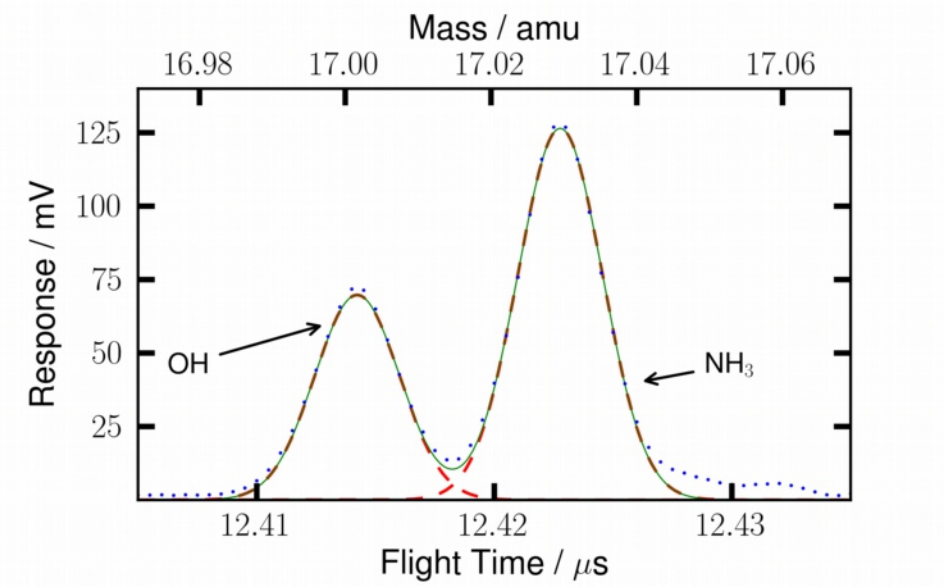
Time-Of-Flight Mass Spectrometry



Time-Of-Flight Mass Spectrometry

Mass resolution much superior to a QMS allows for separation of OH and NH3





Time-Of-Flight Mass Spectrometry

The Grand Master Plan:

Thin film measurements

- **Nanoparticle measurements**
  - **Thin film measurements**
    - **Publish**

Conclusions

- The many advantages of the μ-reactor platform has been demonstrated
- A new and improved heating scheme has been implemented
- A method to determine the amount of actual active catalyst surface area has been developed (at least for Platinum...)
- Oscillating CO oxidation reactions has been demonstrated
- The very high sensitivity of the platform has been shown and turn over frequencies of almost 10^5 has been achived
- The successful application of Time-Of-Flight Mass Spectrometry to the platform has been shown

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