Bioenergy and Catalysis Laboratory

Secondary organic aerosol formation from small scale wood stoves

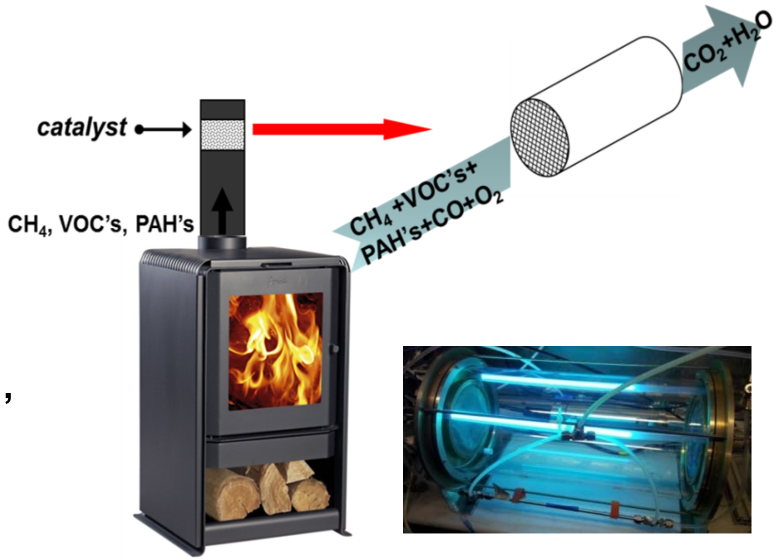
Can it be reduced by application of catalytic VOC converters?

Simone Pieber[1] – *emissions measurements*
Paul Scherrer Institute, Laboratory of Atmospheric Chemistry, Villigen
simone.pieber@psi.ch, 0041 056 310 4467

Anastasios Kampolis[2] – *catalyst development*
Paul Scherrer Institute, Bioenergy and Catalysis Laboratory, Villigen
anastasios.kampolis@psi.ch, 0041 056 310 5321

Emily Bruns[1], Imad El Haddad[1], Dogushan Kilic[1], Davide Ferri[2], Oliver Kröcher[2,3], Urs Baltensperger[1] and André S.H. Prévôt[1]

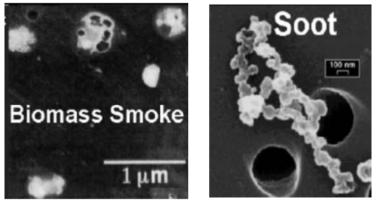
[1] Laboratory of Atmospheric Chemistry, Paul Scherrer Institute
[2] Bioenergy and Catalysis Laboratory, Paul Scherrer Institute
[3] École Polytechnique Fédérale de Lausanne



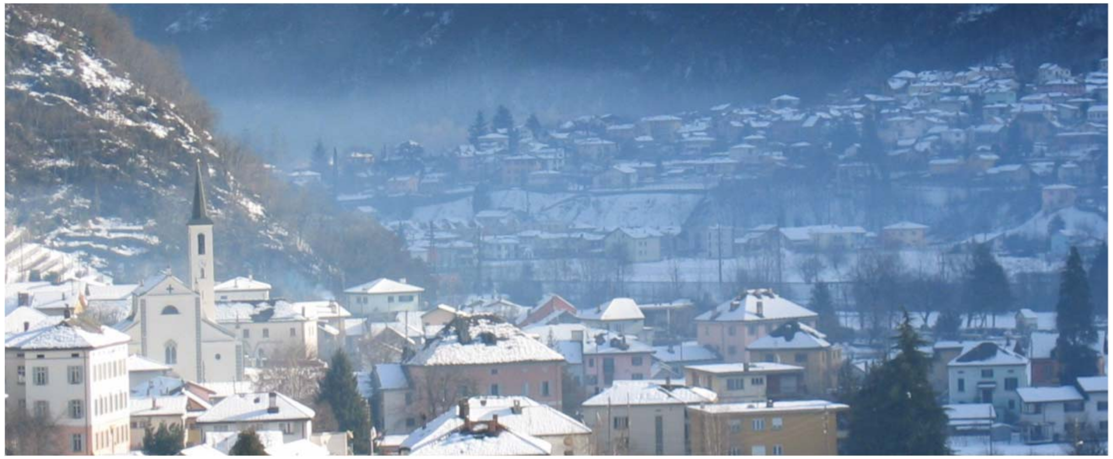
INTRODUCTION

Residential log wood combustion

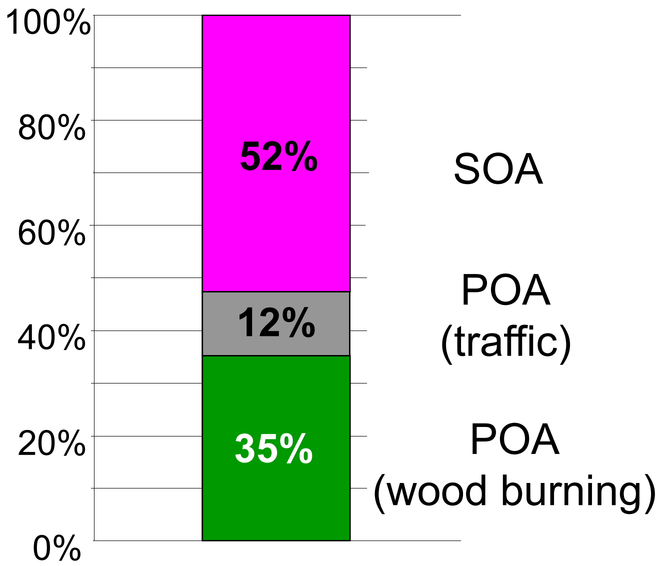
- common heating method
- black carbon, primary organic aerosol (POA)
- gasphase hydrocarbons
- significant formation of secondary organic aerosol (SOA)



(Heintzenberg et al., 2003)



Organic Particulate Mass



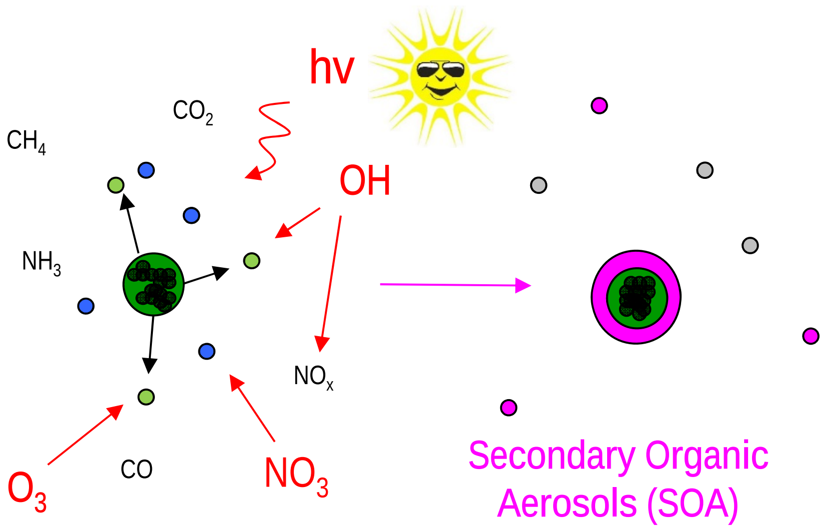
Average organic components in Winter from various sites in central Europe

(Lanz et al., ACP., 2010)

GASPHASE EMISSIONS

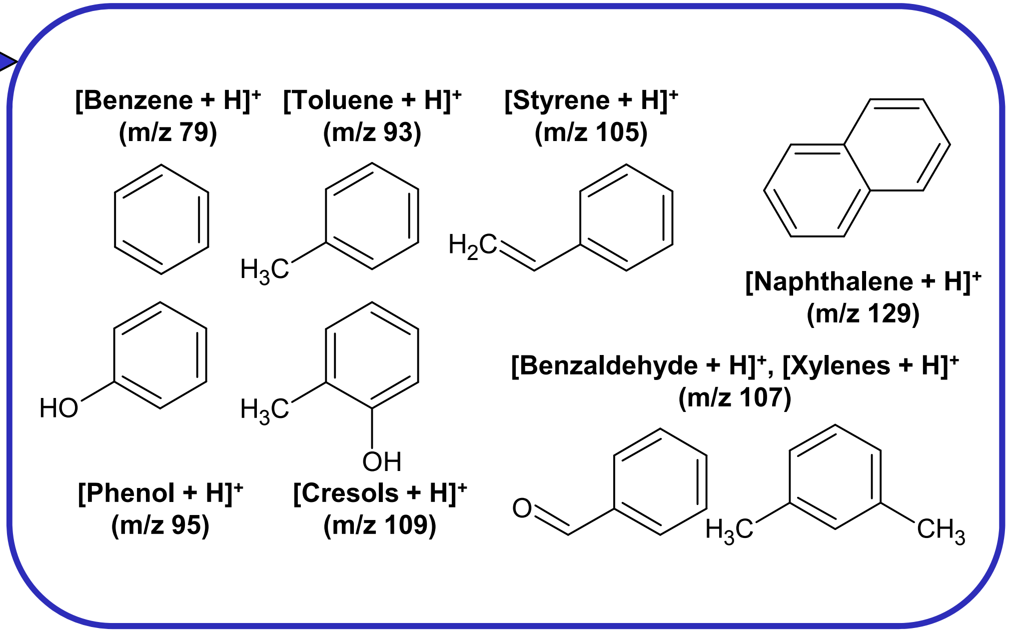
average exhaust composition

CO_2	**up to 10.000 ppm**
CO	**up to 5000 ppm**
CH_4	**up to 500 ppm**
H_2O	**up to 8 vol.%**
NMHC	**up to 1000 ppmC**



NMHC fraction can be dominated by (polycyclic) aromatic hydrocarbons

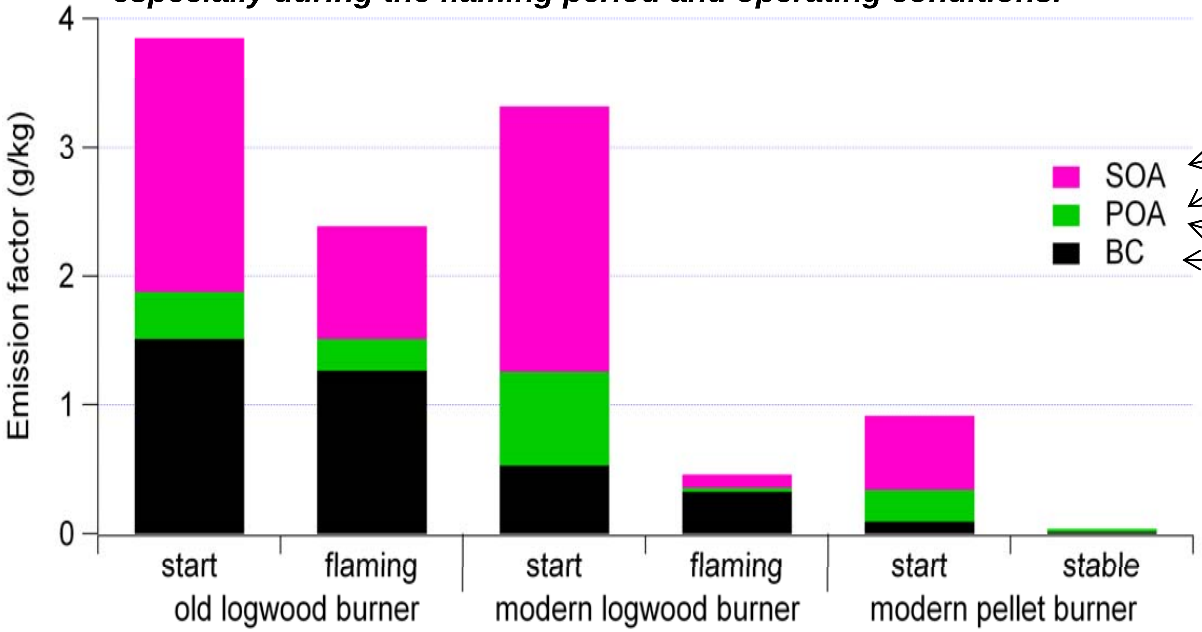
⇒ deleterious health effects
⇒ increased formation of secondary organic aerosol in atmospheric aging



SECONDARY ORGANIC AEROSOL

n = 7 n = 7 n = 3

POA and BC can be reduced by optimization of the oven design, especially during the flaming period and operating conditions.



After-treatment options:

needs (catalytic) reduction of precursors (NMHC)

could be reduced with mechanical methods

(Heringa et al., ACP, 2011)

PROJECT IDEA

Bioenergy and Catalysis
Laboratory, PSI0

- **Efficient catalyst for oxidation of CH_4 and NMHC at low temperature**

- **Pt / Al_2O_3 and Pt / x%CeO_2-Al_2O_3**
  - powder (model gas, H_2O stability)
  - coated monolith
    - ✓ model gas vs. real wood burning exhaust
    - ✓ effect on NMHC &
      secondary organic aerosol

Al_2O_3

- great mechanical properties
- high surface area - porosity
- water resistant

Pt

- high activity for CO and HC
- fair stability against poisoning
- H_2PtCl_6 left overs may prevent poisoning by inorganic compounds

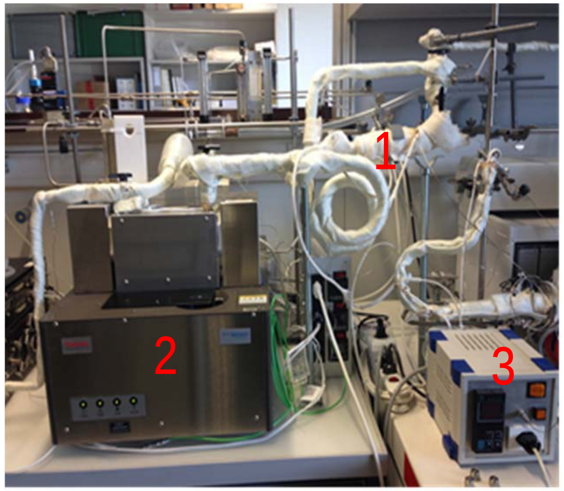
CeO_2

- high oxygen storage capacity (OSC)
- improves dispersion of supported metal:
  smaller metal clusters,
  more active centers in metal-support interface
- enhances catalyst's thermal stability

EXPERIMENTAL SET-UP

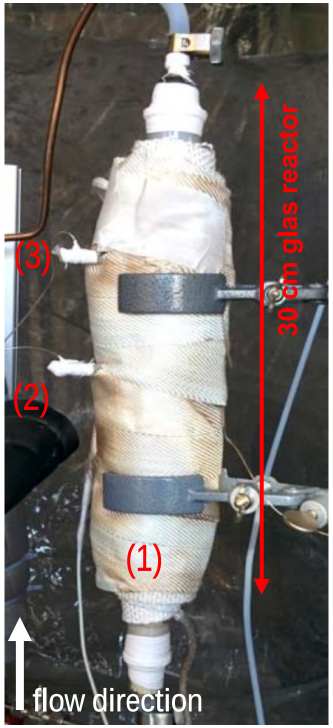
Catalyst in powder form

Bioenergy and Catalysis Laboratory, PSI

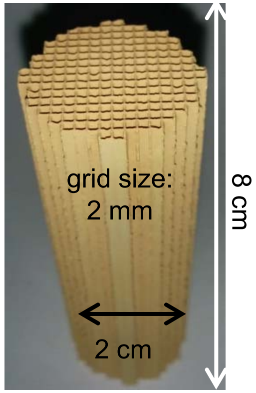


(1) Reactor, (2) FT-IR, (3) Temp. controller

Catalyst coated on monolith



Bioenergy and Catalysis Laboratory, PSI



(1) temperature controlled glass reactor, filled with coated monolith,
(2) temp. sensor inlet,
(3) temp. sensor outlet

fixed-bed reactor

reaction feed: 20% O_2, 1000 ppm CH_4, balance N_2 ,
F = 100 mL min^{-1}, GHSV = 118 L g^{-1} h^{-1}

coating on ceramic monolith

reaction feed:

Lab: 10% O_2, 1000 ppm CH_4,
4.7% H_2O, balance N_2 ,
F = 8 L min^{-1}, GHSV = 180 L g^{-1} h^{-1}

Wood Burning Exhaust, F = 6 L min^{-1}

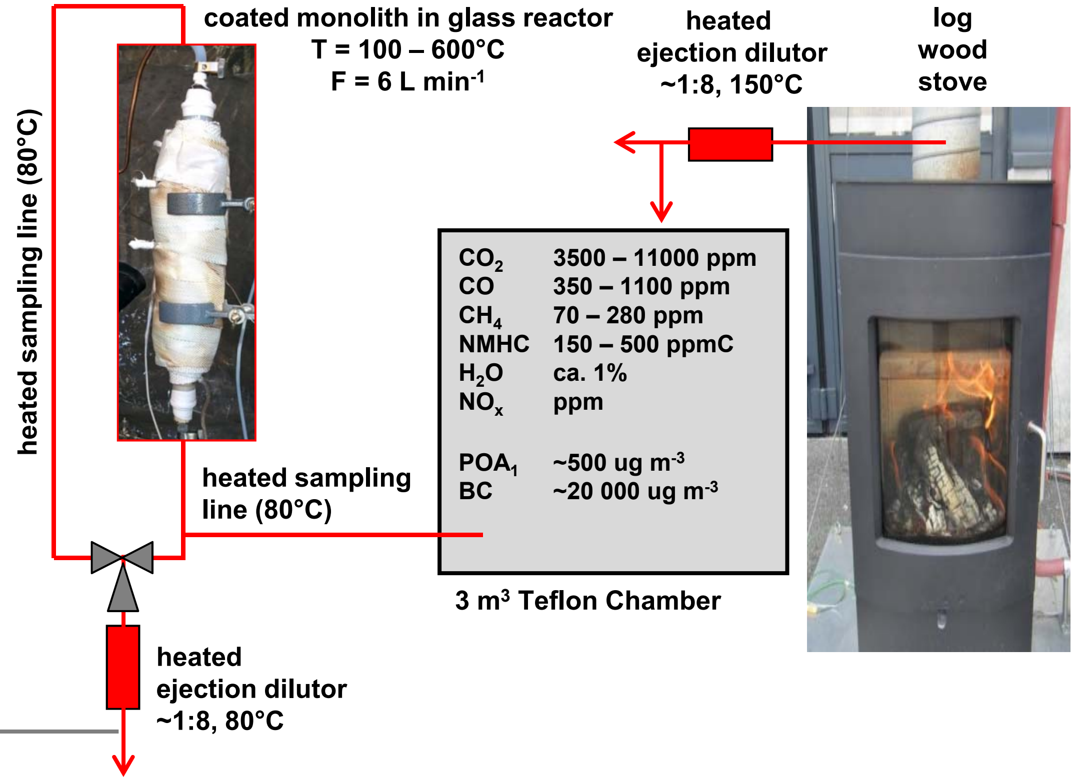
(Kampolis et al., in prep.)

EXPERIMENTAL SET-UP

Catalyst coated on monolith – tested with wood burning emissions

Laboratory of Atmospheric Chemistry, PSI

Proton transfer reaction mass spectrometer (HR-PTR-ToF-MS)	Volatile organic compounds, degree of aging (OH exposure)
Flame Ionisation Detector	CH_4, NMHC, THC
Cavity Ring Down Spectrometer	CO_2, CO, CH_4, H_2O
Aerosol mass spectrometer (HR-ToF-AMS)	Non-refractory PM quantification, chemical composition,
Aethalometers	Black carbon (soot) quantification

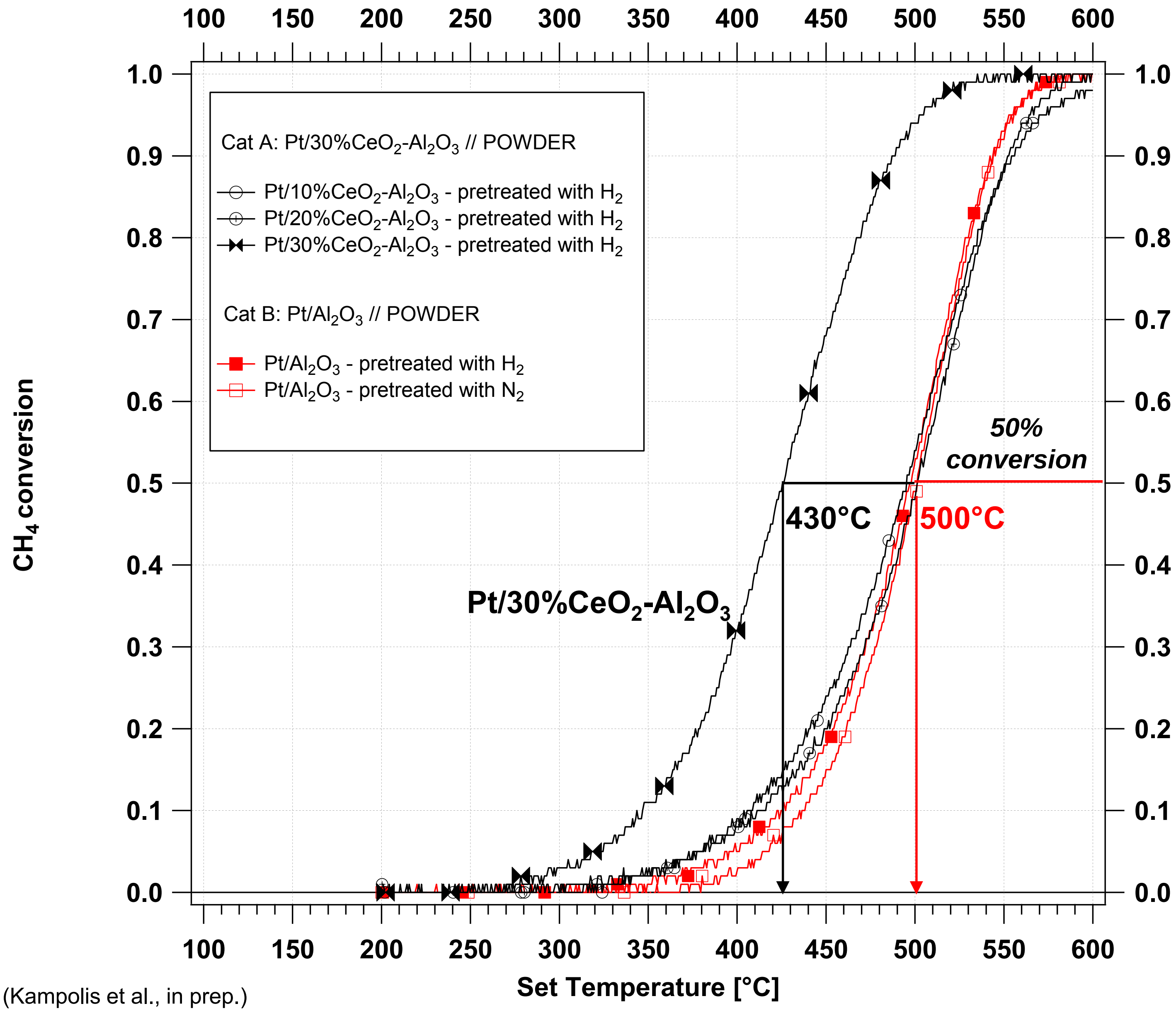


Potential Aerosol Mass (PAM) Chamber to simulate secondary organic aerosol formation

(Kang et al., ACP, 2007 and Lambe et al, AMT, 2010)

RESULTS

CH_4 conversion with powder in lab reactor

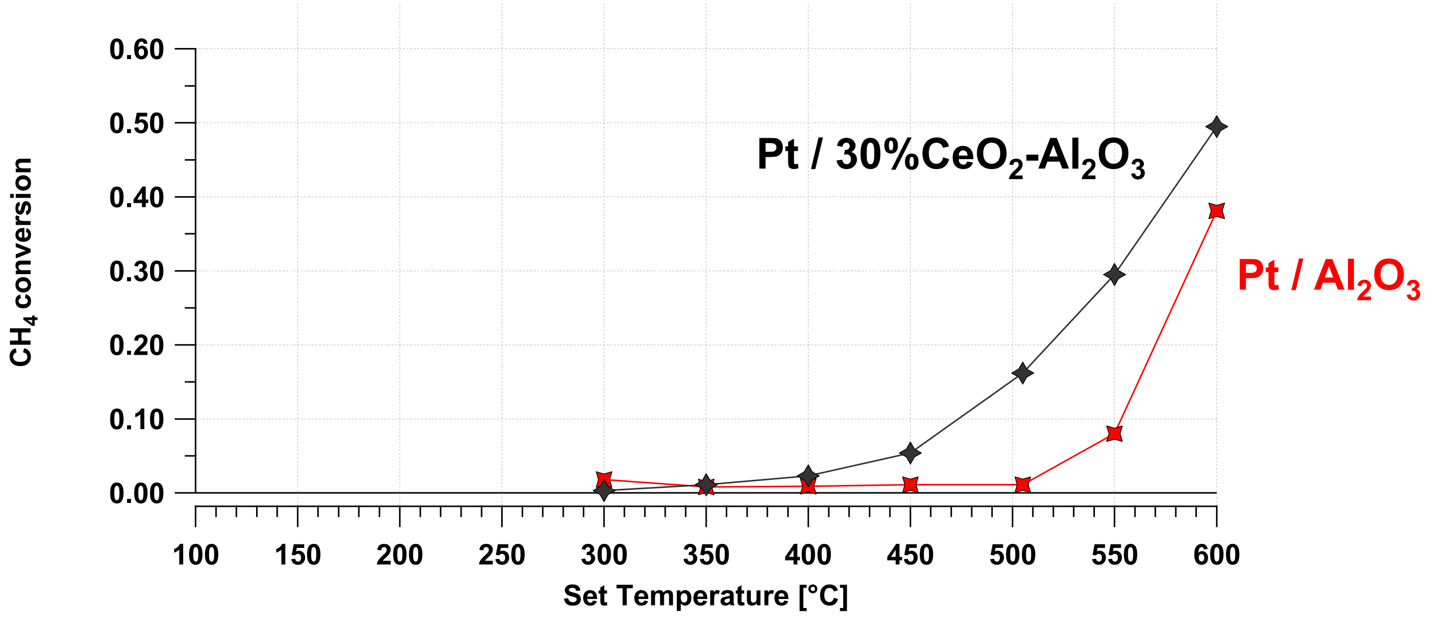


(Kampolis et al., in prep.)

CH_4 conversion with coated monoliths in lab reactor

Bioenergy and Catalysis Laboratory, PSI

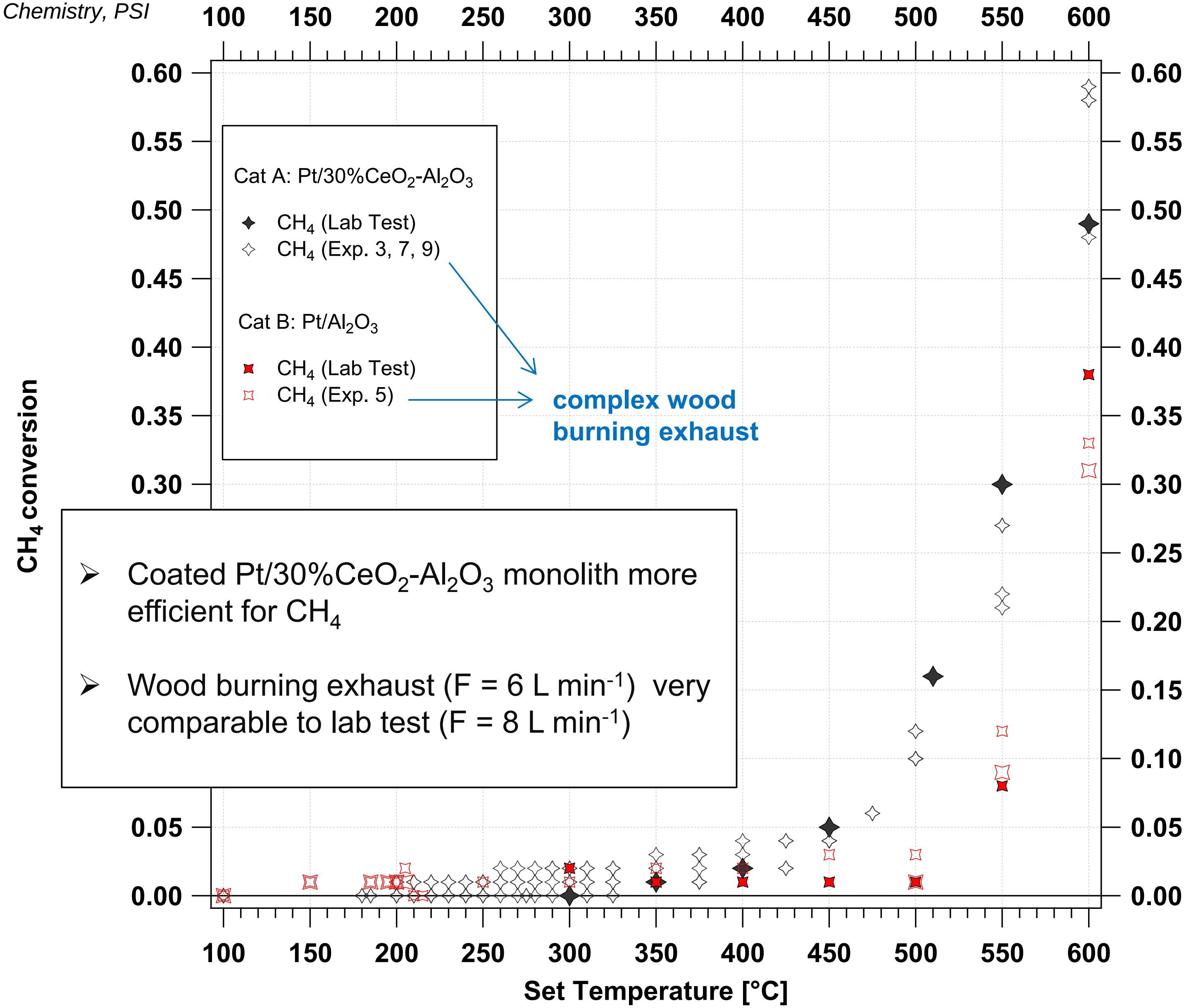
- Coated $Pt/30\%CeO_2\text{-}Al_2O_3$ monolith more efficient for CH_4
- T for 50% CH_4 conv. for monolith is 600°C vs. 430°C for powder



(Kampolis et al., in prep.)

CH_4 conversion with monolith: *lab test vs. WB exhaust*

Laboratory of Atmospheric Chemistry, PSI



- Coated $Pt/30\%CeO_2\text{-}Al_2O_3$ monolith more efficient for CH_4
- Wood burning exhaust ($F = 6\ L\ min^{-1}$) very comparable to lab test ($F = 8\ L\ min^{-1}$)

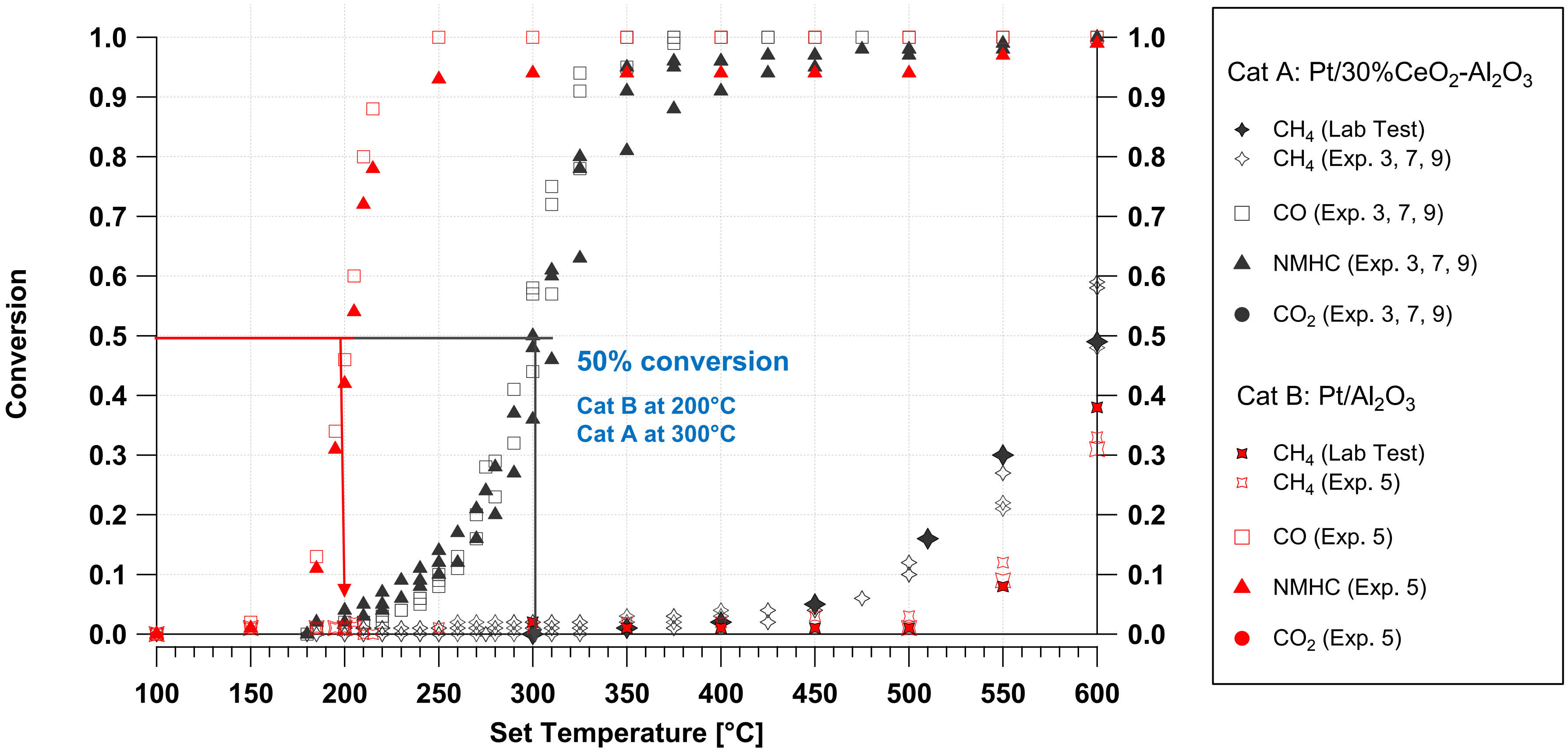
fresh

after exposure to WB

CO and NMHC conversion with monolith: WB exhaust

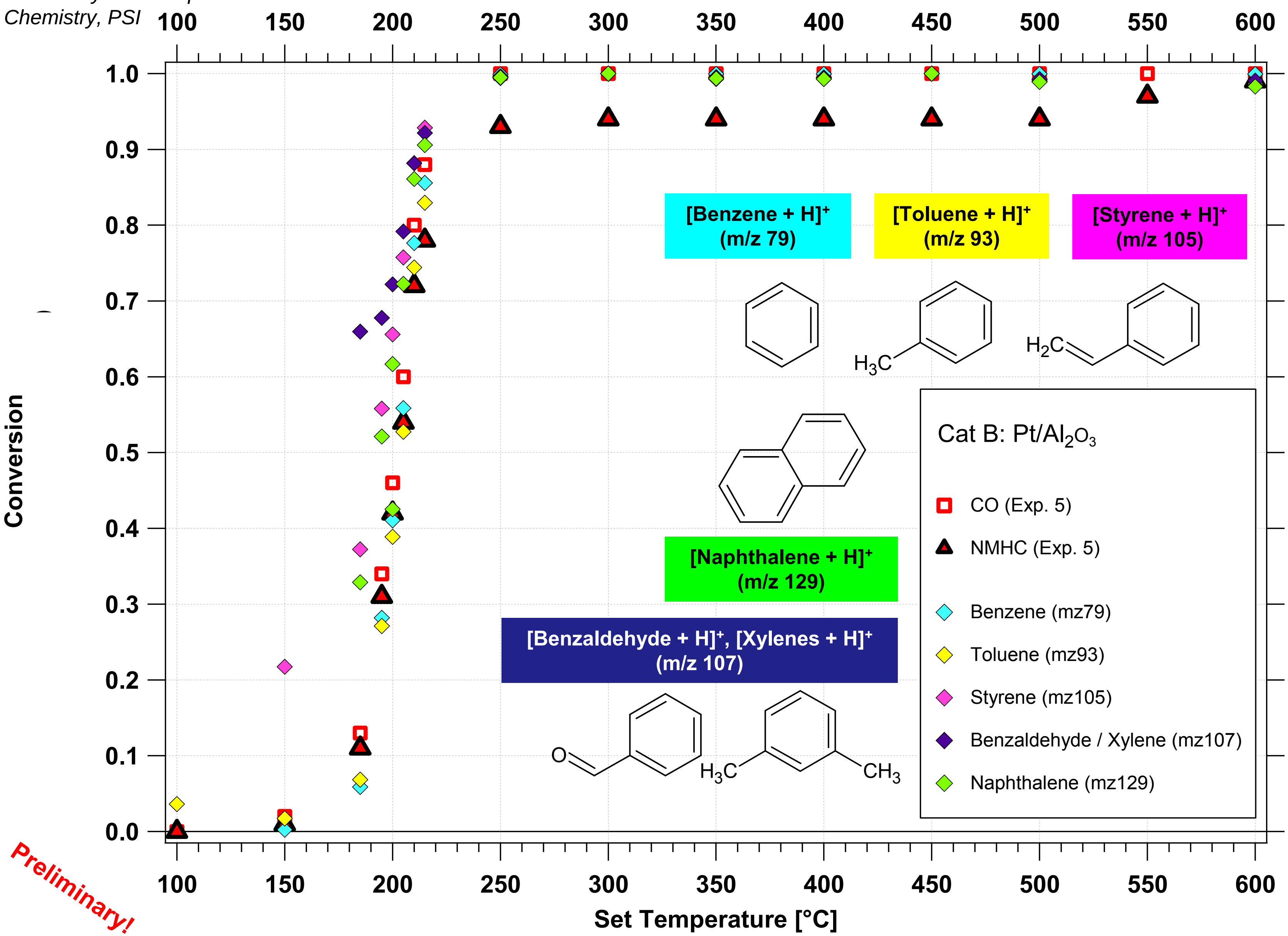
Laboratory of Atmospheric Chemistry, PSI

- for CO and NMHC lower T than for CH_4
- CO and NMHC conv. with 30%CeO_2 needs further investigation



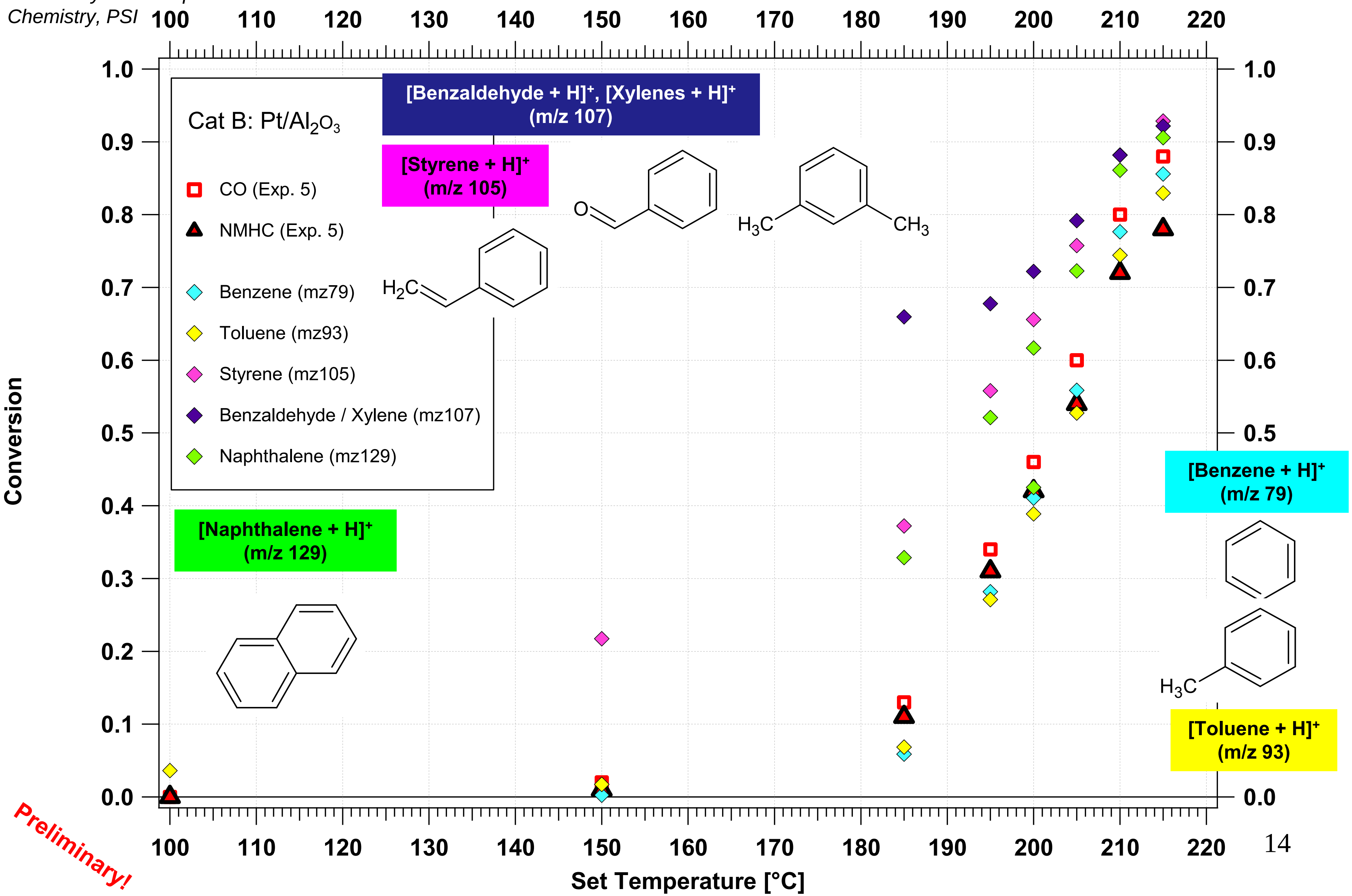
Aromatic HC conversion with monolith: WB exhaust

Laboratory of Atmospheric Chemistry, PSI



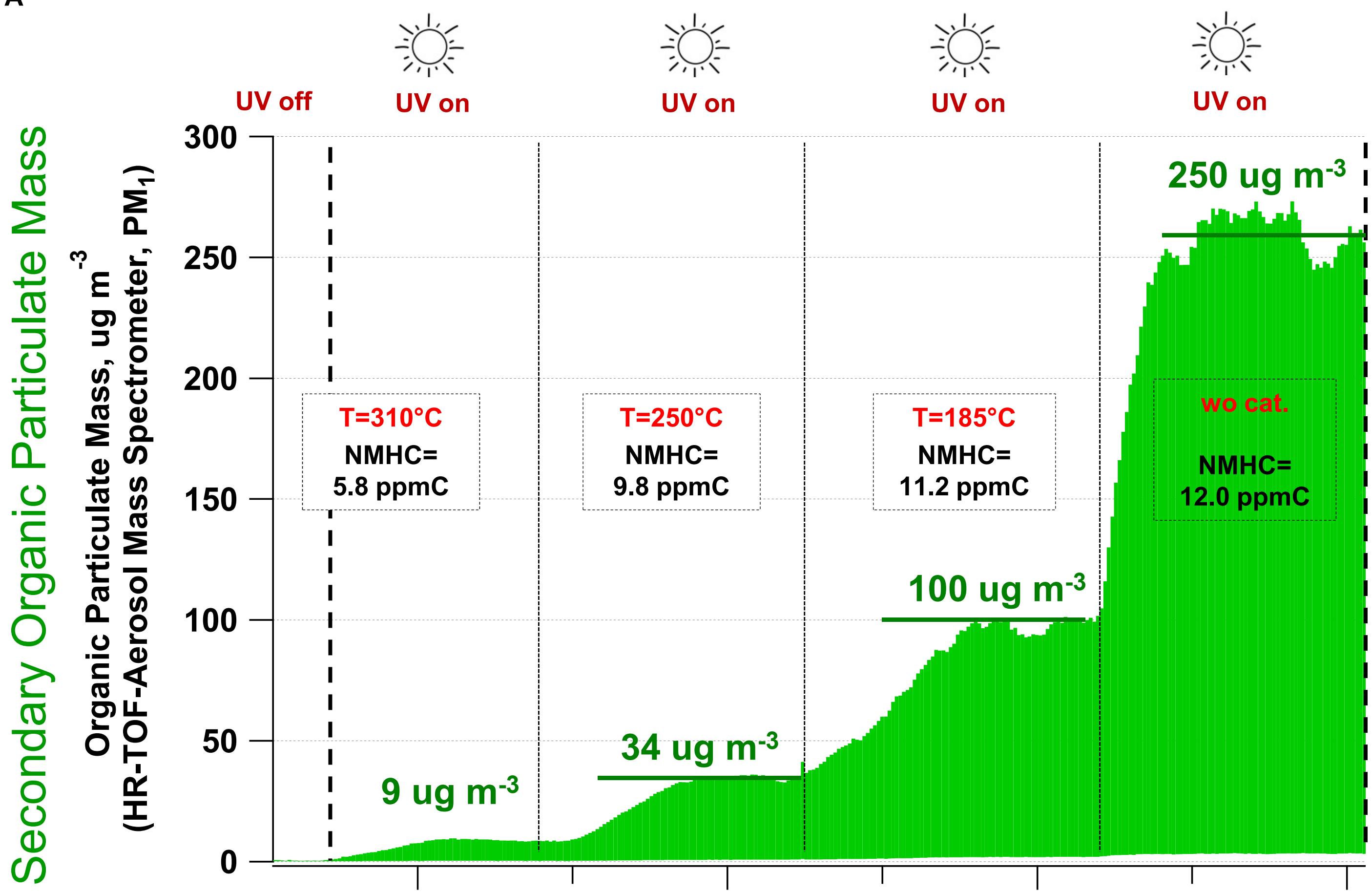
Aromatic HC conversion with monolith: WB exhaust

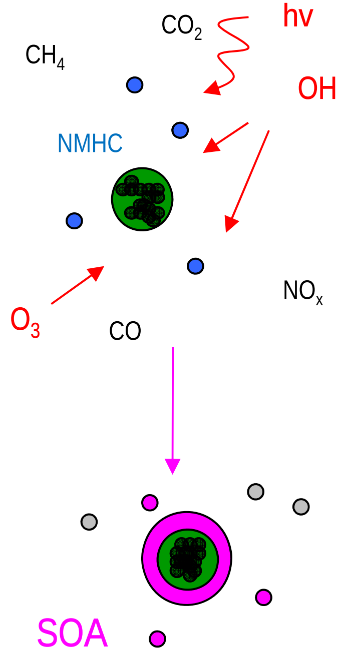
Laboratory of Atmospheric Chemistry, PSI

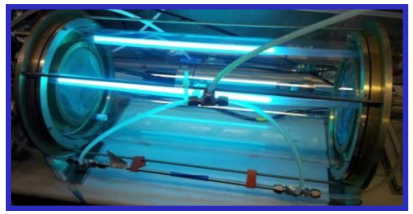


Secondary organic aerosol formation w/wo catalyst

Cat A







Estimated Reduction:	310°C	250°C	185°C
NMHC	-52%	-18%	-7%
SOA	-96%	-86%	-60%

- conversion of aromatics?
- adsorption of high molecular weight compounds to catalyst surface area?

CONCLUSIONS

- Tested catalysts work very well for CH_4 conversion in lab test and with wood burning exhaust, light off temperature should be further reduced.
- Low conversion temperatures for CO and NMHC,
  unclear why CeO_2 did not increase the catalyst efficiency for this conversion.
- Aromatic hydrocarbons (important SOA precursors) removed already at low catalyst temperatures (e.g. burner start up)
- SOA formation can be potentially reduced by a large proportion – requires further analysis of gasphase HC species
- *Open questions:*
  - Stability to H_2O and in long term?
  - Effect on primary PM
  - Stability > 600°C
  - Alternatives to Pt based catalysts, especially for NMHC conversion?

PAUL SCHERRER INSTITUT PSI

LABOR FÜR ATMOSPHÄREN-CHEMIE

Bioenergy and Catalysis Laboratory

cces

THANK YOU FOR YOUR ATTENTION!

Secondary organic aerosol formation from small scale wood stoves

Can it be reduced by application of catalytic VOC converters?

Simone Pieber – *emissions measurements*

Paul Scherrer Institute,
Laboratory of Atmospheric Chemistry, Villigen

simone.pieber@psi.ch , 0041 056 310 4467

Anastasios Kampolis – *catalyst development*

Paul Scherrer Institute,
Bioenergy and Catalysis Laboratory, Villigen

anastasios.kampolis@psi.ch, 0041 056 310 5321

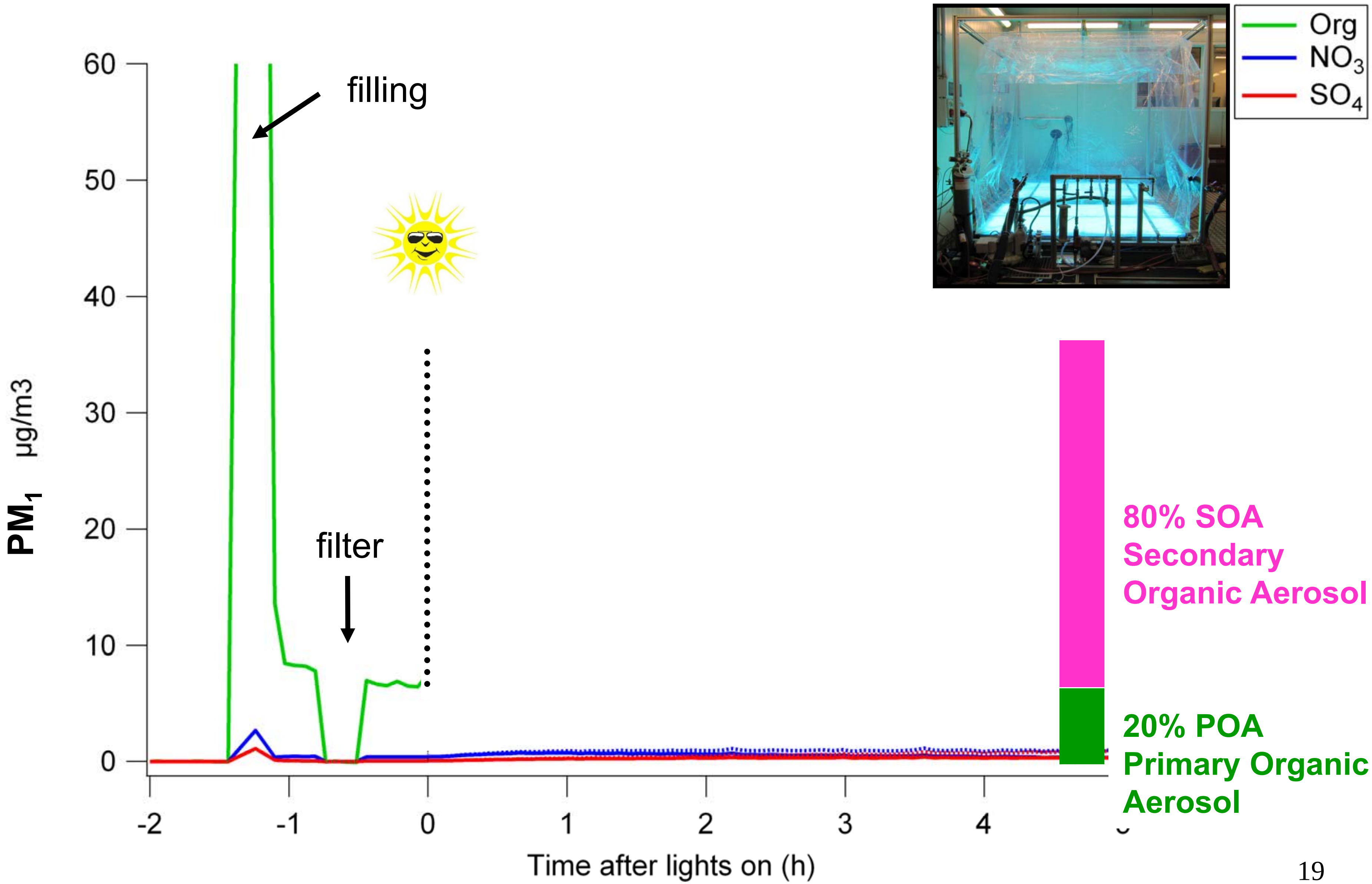
Acknowledgements

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement no. 290605 (PSI-FELLOW), from the Competence Center Environment and Sustainability (OPTIWARES) and from the Swiss National Science Foundation (WOOSHI).

We thank René Richter, Felix Klein and Maarten Heringa for their contribution to the work presented in this presentation.

BACK UP SLIDES

SECONDARY ORGANIC AEROSOL



(Heringa et al., 2011, SOA formation in smog chamber)

CATALYTIC SYSTEMS

Why this material?

Pt/Al_2O_3 ("Cat B") and Pt/x%CeO_2-Al_2O_3 ("Cat A)

Al_2O_3

- widely used in catalysis
- great mechanical properties
- high surface area - porosity
- water resistant

Pt

- high activity for combustion of CO and HC
- fair stability against poisoning

CeO_2

- high oxygen storage capacity (OSC)
- improves dispersion of supported metal:
  smaller metal clusters,
  more active centers in metal-support interface
- enhances catalysts thermal stability

(Kampolis et al., in prep.)

Preparation

Pt/Al_2O_3 ("Cat B") and Pt/x%CeO_2-Al_2O_3 ("Cat A)

Powder

Pt

- wet impregnation (WI) of H_2PtCl_6 on the commercial γ-Al_2O_3 support (200 um), Pt content: 1.3 wt%
- drying at 90 ^oC overnight, calcination at 500 ^oC (50 ^oC/min) for 2h

substrate pretreatment for Pt/x%CeO_2-Al_2O_3

- deposition-precipitation (DP) of $Ce(NO_3)_3 \cdot 6H_2O$ on commercial γ-Al_2O_3, x= 10, 20, 30 wt%
- drying at 90 ^oC overnight, calcination at 500 ^oC (50 ^oC/min) for 2h

Monolith

- ceramic monoliths of appropriate size
- aluminum-based binder (γ-Al_2O_3, 5-10 um)
- calcination at 500 ^oC in air for 2 h, hydrothermal aging at 600 ^oC for 6h, using 10% H_2O/N_2

POTENTIAL AEROSOL MASS (PAM)

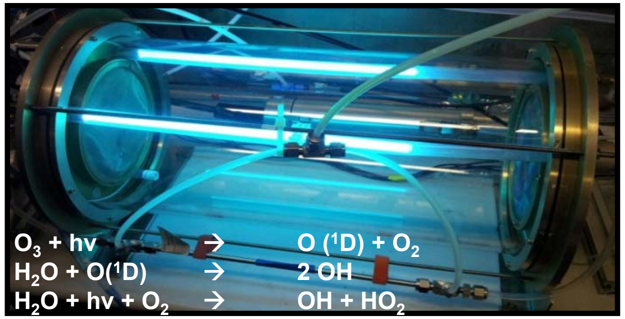
Potential Aerosol Mass (PAM) Chamber (Kang et al., ACP, 2007 and Lambe et al, AMT, 2010)

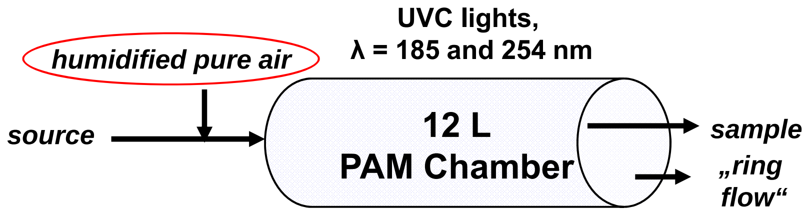
Continuous Flow Reactor, Residence time ca 2 min,

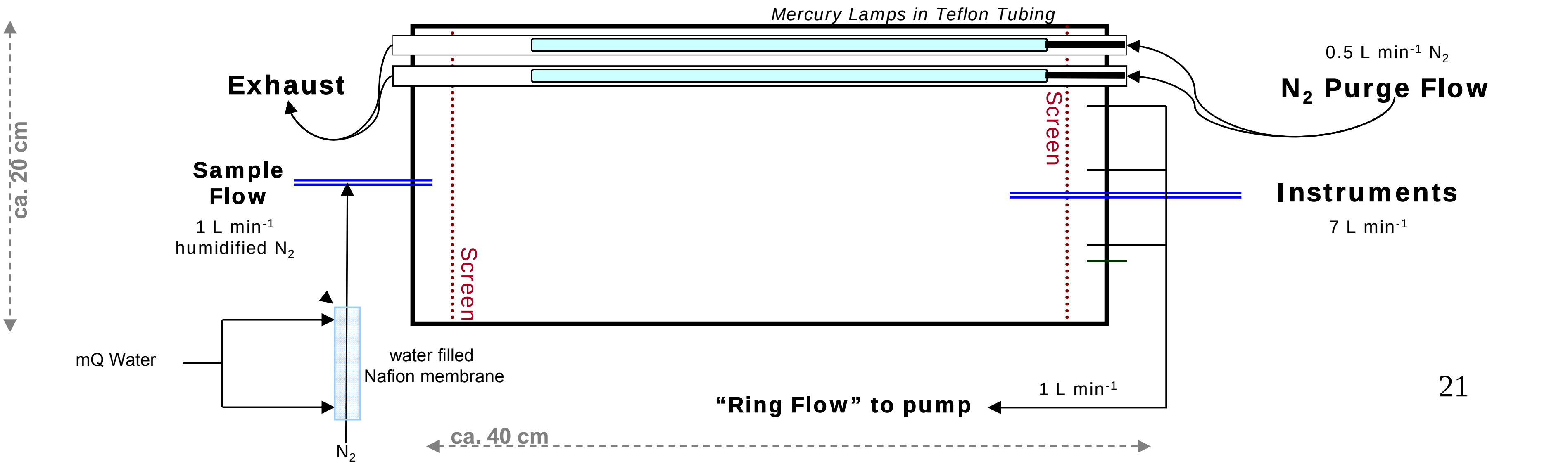
main oxidants O_3, OH, HO_2

O_3 source: - photolysis of O_2
OH source: - photo-dissociation of O_3 , reaction of $O(^1D) + H_2O$;
- photolysis of H_2O

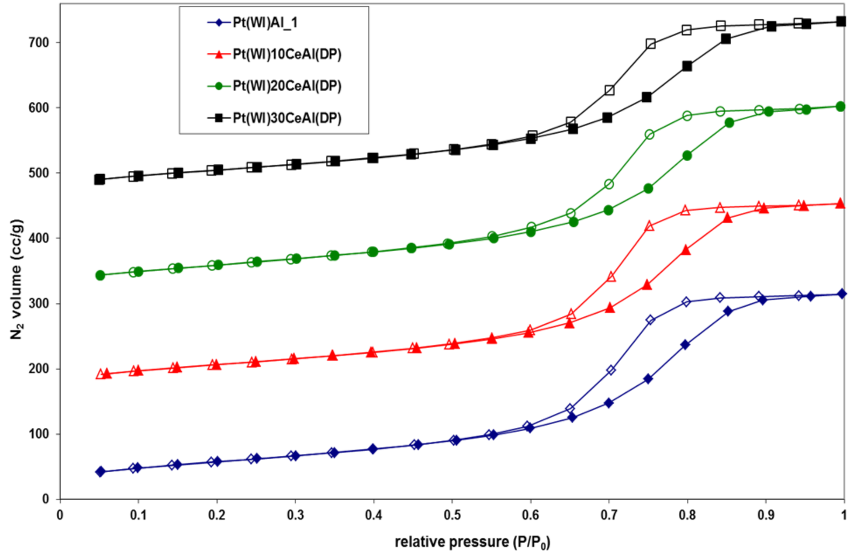
Photochemical age can be varied,
e.g. UV intensity and H_2O (g)
(OH up to 400 ppt_v (~10^{13} molecules / cm^3), O_3 up to 15 ppm_v)

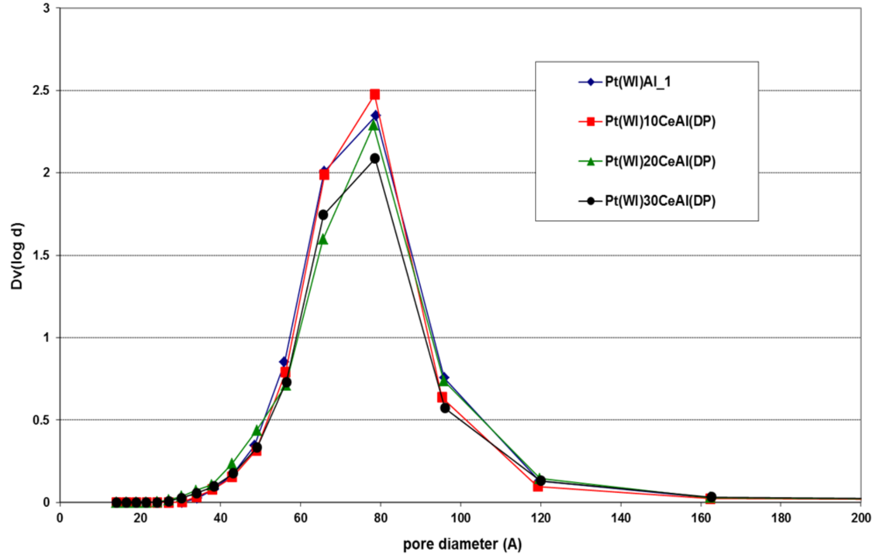






BET and Porosity of Pt/xCeO_2-Al_2O_3 catalysts





- Textural characteristics: unaffected by CeO_2
- Mesoporous structure

Catalyst	BET (m^2/g)	Pore volume (cm^3/g)	Pore size (Å)
Pt(WI)Al	209	0.519	66.0
Pt(WI)10CeAl(DP)	205	0.499	78.6
Pt(WI)20CeAl(DP)	216	0.490	78.3
Pt(WI)30CeAl(DP)	199	0.459	78.7