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Wir schaffen Wissen – heute für morgen

Mitigation of secondary organic aerosol formation from wood burning emissions by catalytic removal of aromatic hydrocarbons

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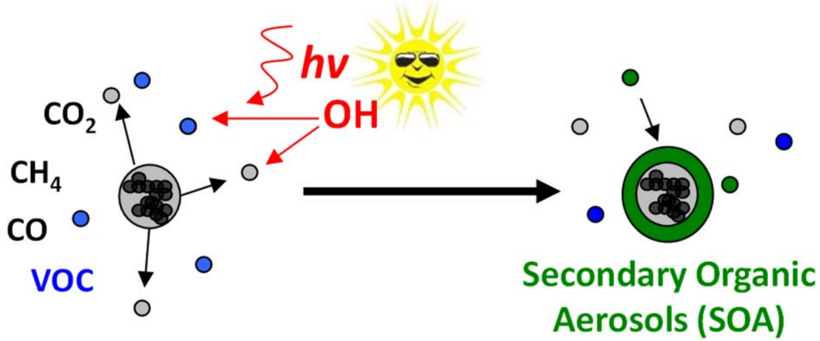
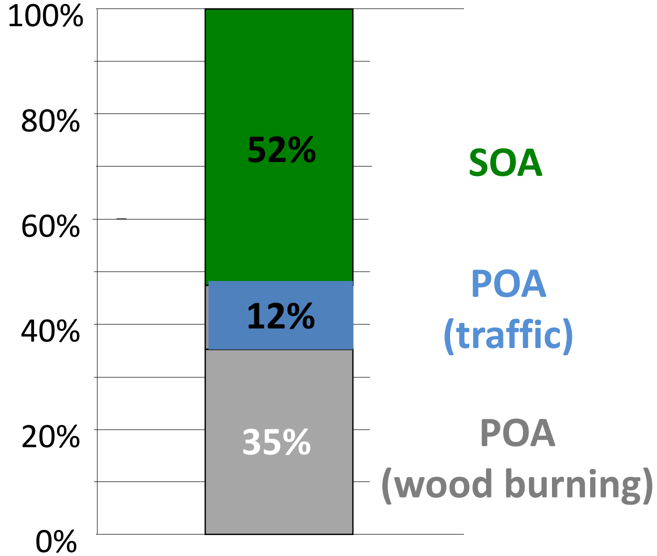


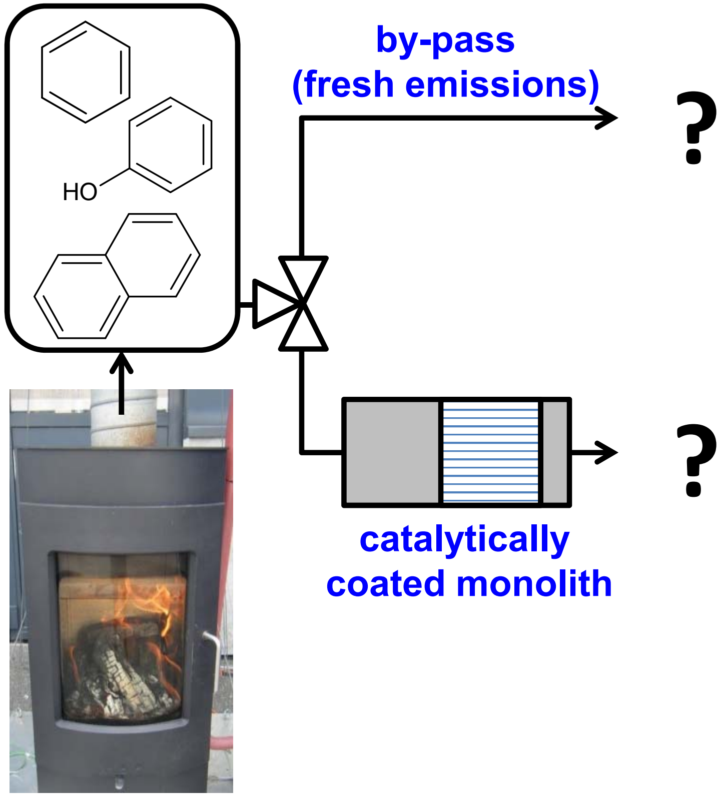
Residential logwood burning emits

- harmful volatile organic compounds (VOC)
- toxic carbon monoxide (CO)
- greenhouse gases (CH_4, CO_2)
- fine particulate matter (PM) with complex, adverse effects
- emissions form secondary organic aerosol (SOA)



Average organic PM components in Winter from various sites in central Europe

(Lanz et al., ACP., 2010)


HO
by-pass
(fresh emissions)
?
catalytically
coated monolith
?

SET-UP (1)

Logwood Appliance

1:8, 150°C

CO_2 3400-10500 ppm
CO 360-1100 ppm
CH_4 65-220 ppm

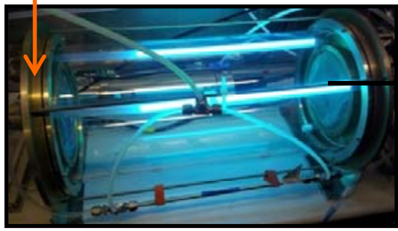
NMHC 75-270 ppmC
ArHC 70-320 ppmC
H_2O 1 vol%

POA 500-1500 µg m^{-3}
BC 5000 µg m^{-3}

3 m^3 Teflon Chamber

SilcoTek steel sampling lines (80°C)

1:8, 80°C



Oxidation Flow Reactor

- ✓ simulates atmospheric photochemistry using hydroxyl (OH) radicals
- ✓ 13 L flow through system
- ✓ UV185 nm and UV254nm
- ✓ OH exposure of days in few minutes

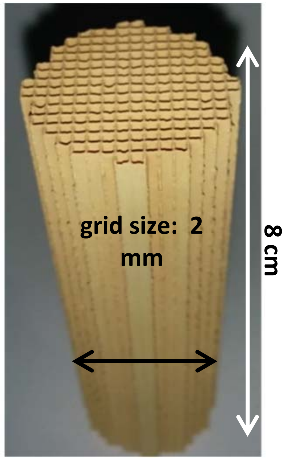
Instruments

- ✓ PTR-ToF-MS
- ✓ FID
- ✓ CRDS
- ✓ HR-ToF-AMS
- ✓ AE33
- ✓ CPC
- ✓ SMPS

Coated monolith in quartz glass reactor:

1) **Pt/Al_2O_3**
2) **Pt/CeO_2-Al_2O_3**

SET-UP (2)



Coated monolith

Al_2O_3

- ✓ good mechanical properties
- ✓ high surface area - porosity
- ✓ water resistant

Pt

- ✓ high activity for CO and NMHC oxidation
- ✓ fair stability against poisoning
- ✓ H_2PtCl_6 left overs may prevent poisoning by inorganics

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

SET-UP (3)

$$R + H_3O^+ \rightarrow RH^+ + H_2O$$

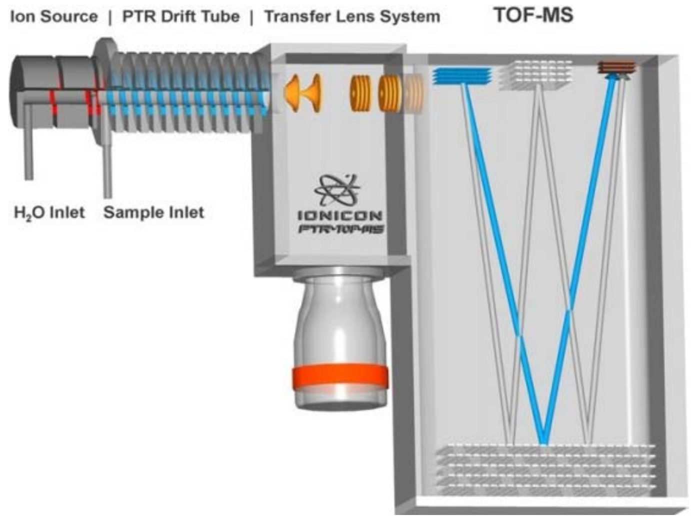
Proton Transfer Reaction Mass Spectrometry (PTR-MS)

Jordan et al., 2011

Gas phase organic compounds

Proton affinitiy higher than water
(**good for aromatics, limited for alkanes**)

Soft ionization, molecular information retained



Aerosol Mass Spectrometry (AMS)

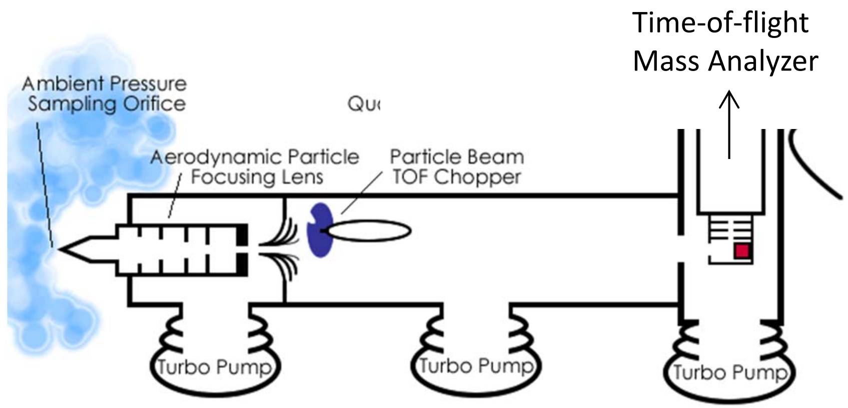
Canagaratna et al., 2007

Particulate, sub-mircon, non-refractory PM

Total mass information

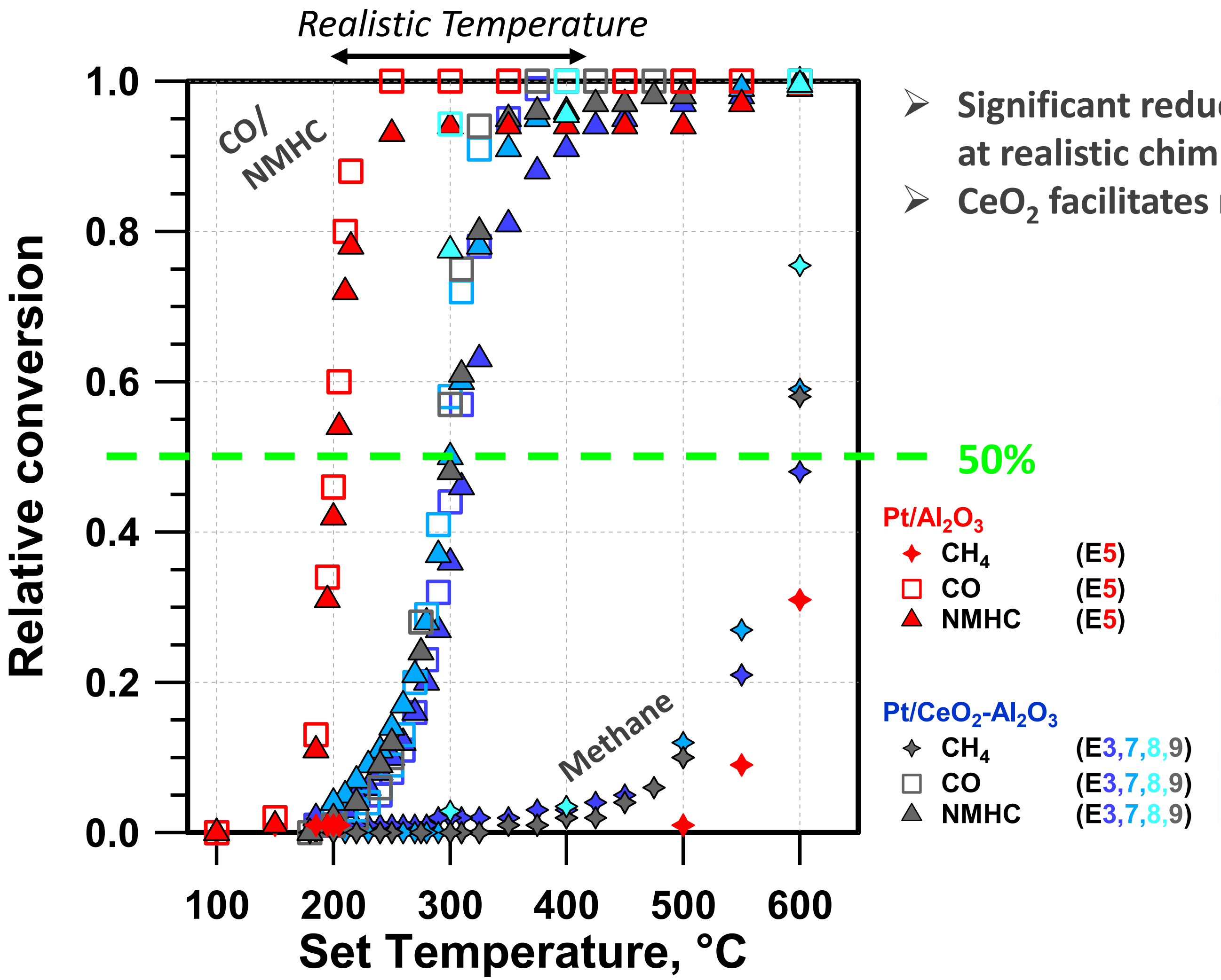
Speciation: NO_3, NH_4, SO_4, Chl, **OA**

Bulk properties of
OA O:C, H:C, etc., mass spectra

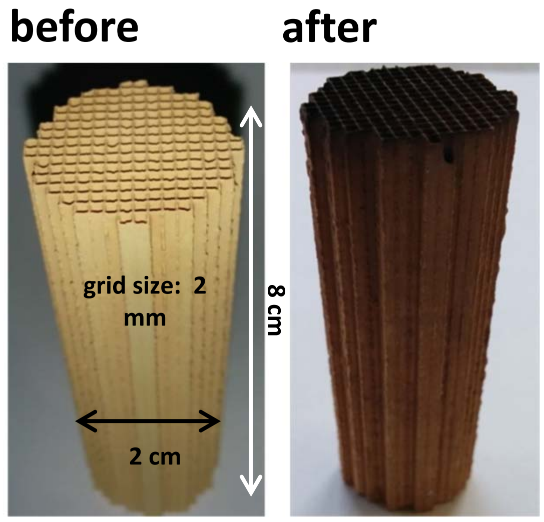



RESULTS

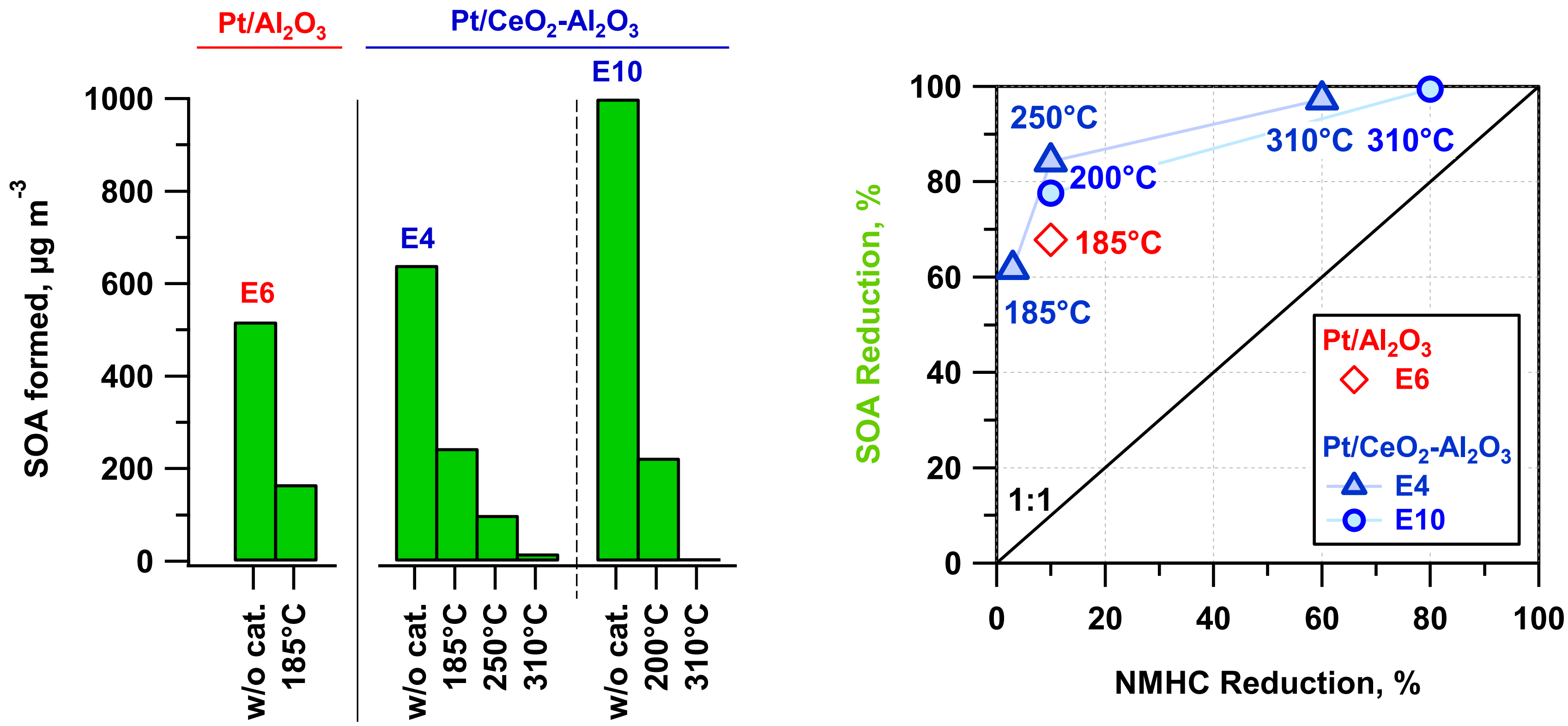
CO, NMHC & METHANE



- Significant reduction of CO and NMHC at realistic chimney temperatures (200-400°C)
- CeO_2 facilitates methane conversion

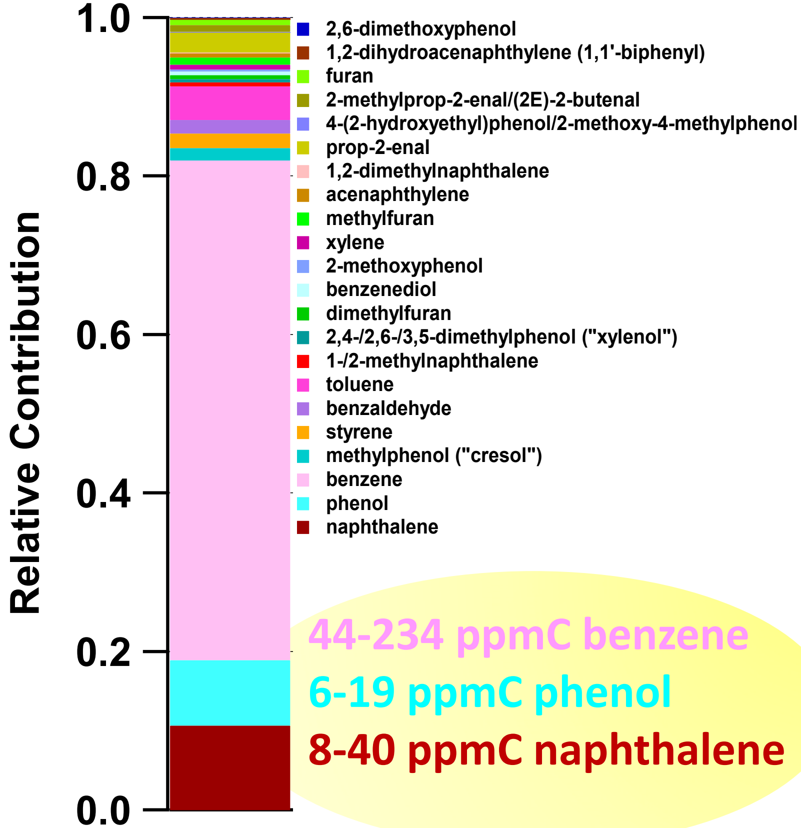


SOA REDUCTION *VS.* NMHC



- Significant reduction of SOA at realistic chimney temperatures (185-310°C)
- SOA reduction exceeds «FID-based NMHC» reduction by far

VOC SPECIATION

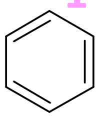


44-234 ppmC benzene
6-19 ppmC phenol
8-40 ppmC naphthalene

structural assignment[2, 3]	class	*m/z*	protonated ion	k_{H3O^+} see [a)]	k_{OH} see [b)]	feed composition (mean±1SD), ppmC				
						E5 (*E6**) n=2	E3 (*E4**) n=2	E7 n=4	E8 n=2	E9 (*E10**) n=2
benzene	mono-c.	79	$[C_6H_6+H]^+$	1.93	1.22	56 ±1	109 ±2	178 ±5	44 ±7	234 ±9
naphthalene	PAH	129	$[C_{10}H_8+H]^+$	2.45	23	11 ±0	21 ±1	29 ±4	8.1 ±1.0	40 ±4
phenol	phOH	95	$[C_6H_6O+H]^+$	2.13	28	9.1 ±0.6	13 ±0	17 ±1	6.4 ±0.7	19 ±1
toluene	mono-c.	93	$[C_7H_8+H]^+$	2.08	5.63	4.2 ±0.4	7.6 ±0.2	11 ±1	3.0 ±0.4	10 ±0
styrene	vinylic	105	$[C_8H_8+H]^+$	2.27	28	1.9 ±0.2	3.5 ±0.1	4.9 ±0.4	1.4 ±0.2	3.6 ±0.4
prop-2-enal	non-ArHC	57	$[C_3H_4O+H]^+$	3.43	20	2.7 ±0.2	3.2 ±0.1	4.0 ±0.2	1.2 ±0.1	3.5 ±0.1
benzaldehyde	ox. ArHC	107	$[C_7H_6O+H]^+$	3.63	40	1.9 ±0.2	3.6 ±0.1	3.4 ±0.2	1.0 ±0.1	4.1 ±0.1
methylphenol (*o-/m-/p*-cresol)	phOH	109	$[C_7H_8O+H]^+$	2.27	34-48	2.0 ±0.3	2.5 ±0.1	2.9 ±0.2	1.3 ±0.2	2.5 ±0.2
2-/3-methylfuran	furan	83	$[C_5H_6O+H]^+$	2	62-73	1.1 ±0.1	0.9 ±0.0	1.6 ±0.1	0.5 ±0.1	0.8 ±0.1
acenaphthylene	PAH	153	$[C_{12}H_8+H]^+$	2.86	100-120	0.7 ±0.3	1.0 ±0.3	1.4 ±0.5	0.6 ±0.2	1.1 ±0.6
2-methylprop-2-enal/ (2E)-2-butenal	non-ArHC	71	$[C_4H_6O+H]^+$	3.43	33-40	1.0 ±0.1	1.0 ±0.0	1.3 ±0.1	0.4 ±0.0	0.8 ±0.1
o-/m-/p-xylene, ethylbenzene	mono-c.	107	$[C_8H_{10}+H]^+$	2.26	7-23	1.0 ±0.1	1.5 ±0.1	1.0 ±0.1	0.3 ±0.0	0.7 ±0.0
1-/2-methyl-naphthalene	PAH	143	$[C_{11}H_{10}+H]^+$	2.71	52	0.7 ±0.1	1.1 ±0.1	1.2 ±0.3	0.4 ±0.0	0.9 ±0.3
furan	furan	69	$[C_4H_4O+H]^+$	1.69	40	0.8 ±0.1	0.7 ±0.0	1.2 ±0.2	0.4 ±0.0	0.6 ±0.1
2,4-/2,5-dimethyl-furan	furan	97	$[C_6H_8O+H]^+$	2	87-130	0.9 ±0.1	0.6 ±0.0	0.8 ±0.1	0.3 ±0.0	0.4 ±0.0
2,4-/2,6-/3,5-dimethylphenol (xylenol)	phOH	123	$[C_8H_{10}O+H]^+$	2	80-91	0.6 ±0.1	0.6 ±0.1	0.6 ±0.1	0.3 ±0.1	0.4 ±0.1
benzenediol	phOH	111	$[C_6H_6O_2+H]^+$	2	104	0.6 ±0.1	0.5 ±0.0	0.6 ±0.1	0.3 ±0.0	0.4 ±0.1
1,2-dihydroacenaphthylene (1,1'-biphenyl)	PAH	155	$[C_{12}H_{10}+H]^+$	2.81	7-8	0.4 ±0.1	0.5 ±0.0	0.6 ±0.2	0.2 ±0.1	0.5 ±0.3
2-methoxyphenol	phOH	125	$[C_7H_8O_2+H]^+$	2	54-78	0.3 ±0.1	0.2 ±0.0	0.4 ±0.1	0.2 ±0.0	0.2 ±0.0
1,2-dimethyl-naphthalene	PAH	157	$[C_{12}H_{12}+H]^+$	2	77	0.2 ±0.1	0.2 ±0.0	0.1 ±0.0	0.0 ±0.0	0.1 ±0.0
4-(2-hydroxyethyl)phenol/ 2-methoxy-4-methylphenol	phOH	139	$[C_8H_{10}O_2+H]^+$	2	75	0.1 ±0.0	0.1 ±0.0	0.2 ±0.0	0.1 ±0.0	0.1 ±0.0
2,6-dimethoxy-phenol	phOH	155	$[C_8H_{10}O_3+H]^+$	2	75-81	0.1 ±0.0	0.1 ±0.0	0.1 ±0.1	0.1 ±0.0	0.0 ±0.0
Total SOA-22				-	-	***97±5***	***173±1***	***261±4***	***71±10***	***324±1***
°NMOC (PTR-ToF-MS)				-	-	***179±15***	***265±1***	***381±28***	***110±14***	***404±7***
NMHC (FID)				-	-	***95***	***160***	***270***	***100***	***260***
CO (Picarro)				-	0.15	***450***	***700***	***1000***	***400***	***1100***
CH_4 (FID)				-	0.00635	***85***	***130***	***190***	***75***	***220***

SOA CONTRIBUTION

1



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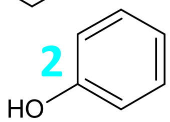
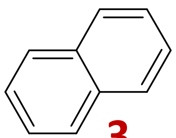
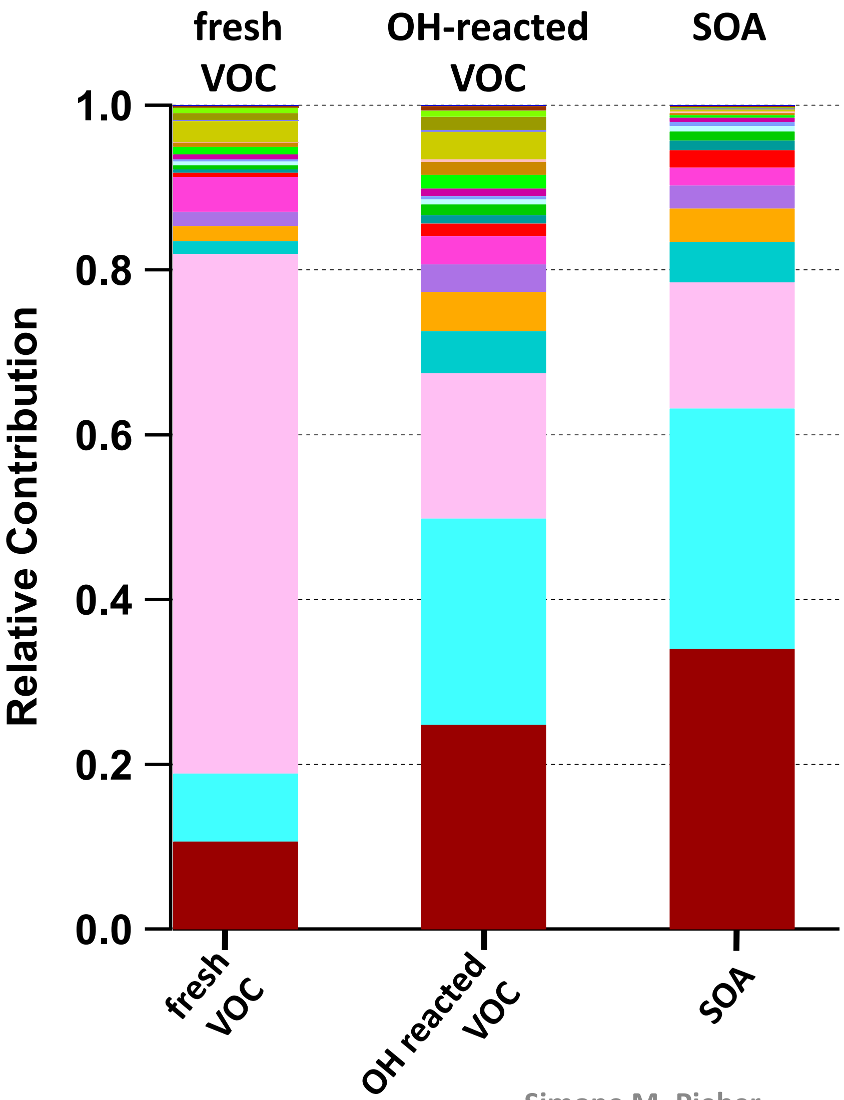




3

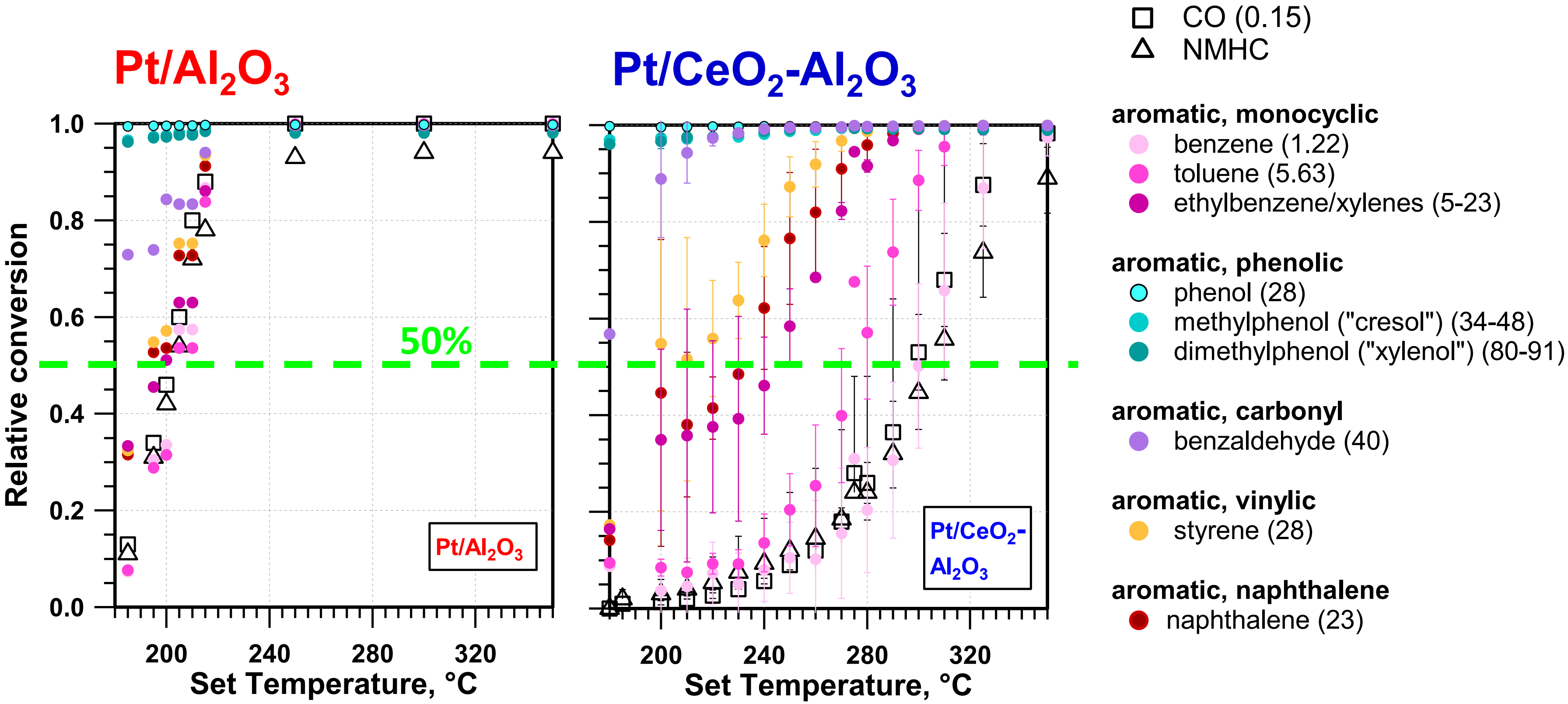


5-25% ppmC benzene SOA

25-33% ppmC phenol SOA

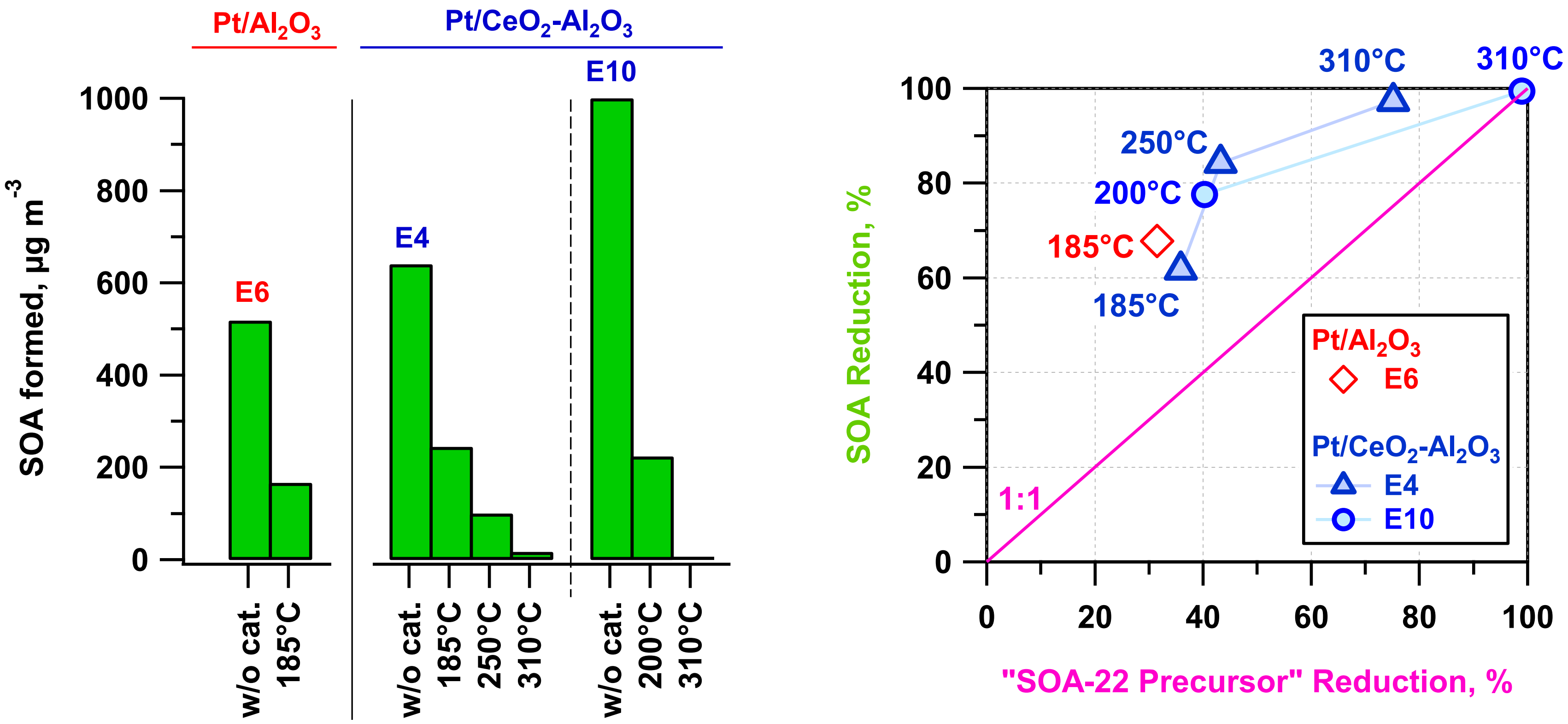
30-38% naphthalene SOA

AROMATIC HC (SOA-PRECURSORS)



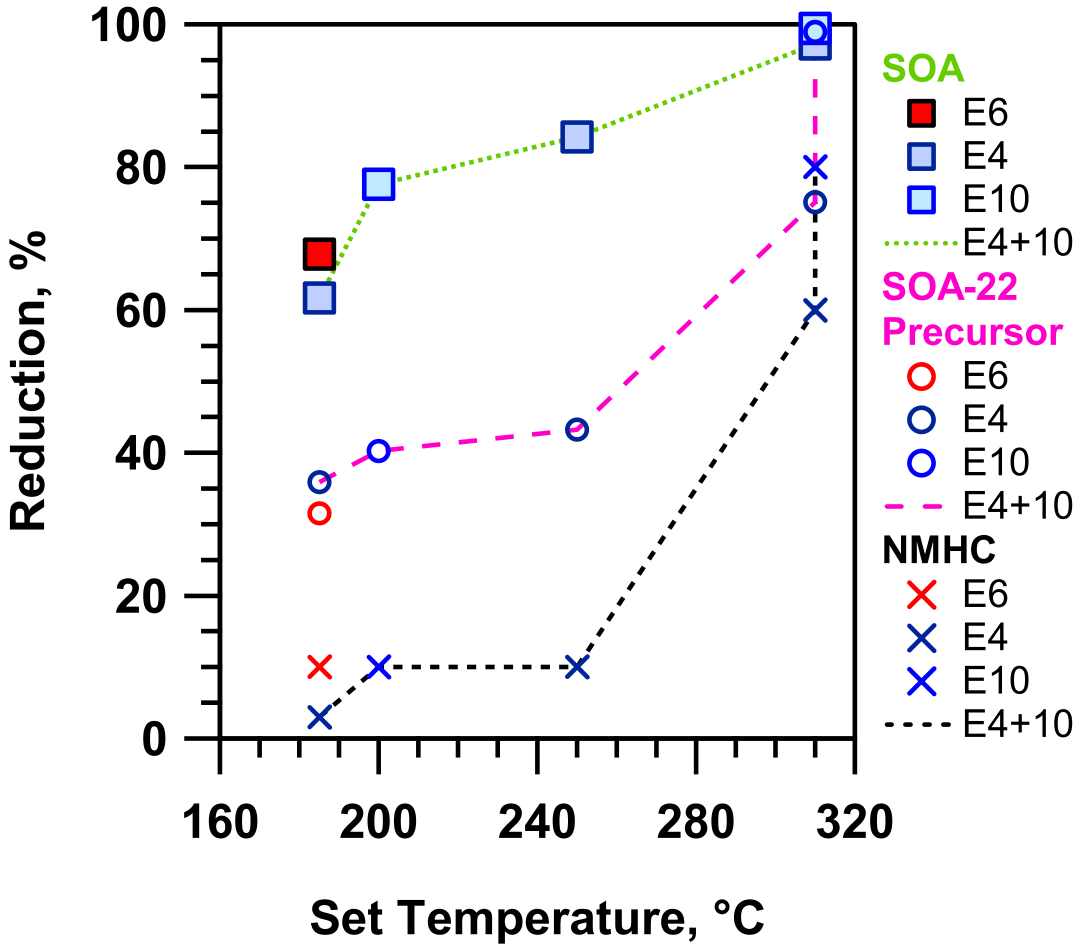
- **Significant reduction of harmful aromatic hydrocarbons**
- **Discrimination between species dependent on their reactivity as measured by their k_{OH} (in cm^3 $molecule^{-1}$ s^{-1})**

SOA REDUCTION *VS.* SOA-PRECURSOR (22)

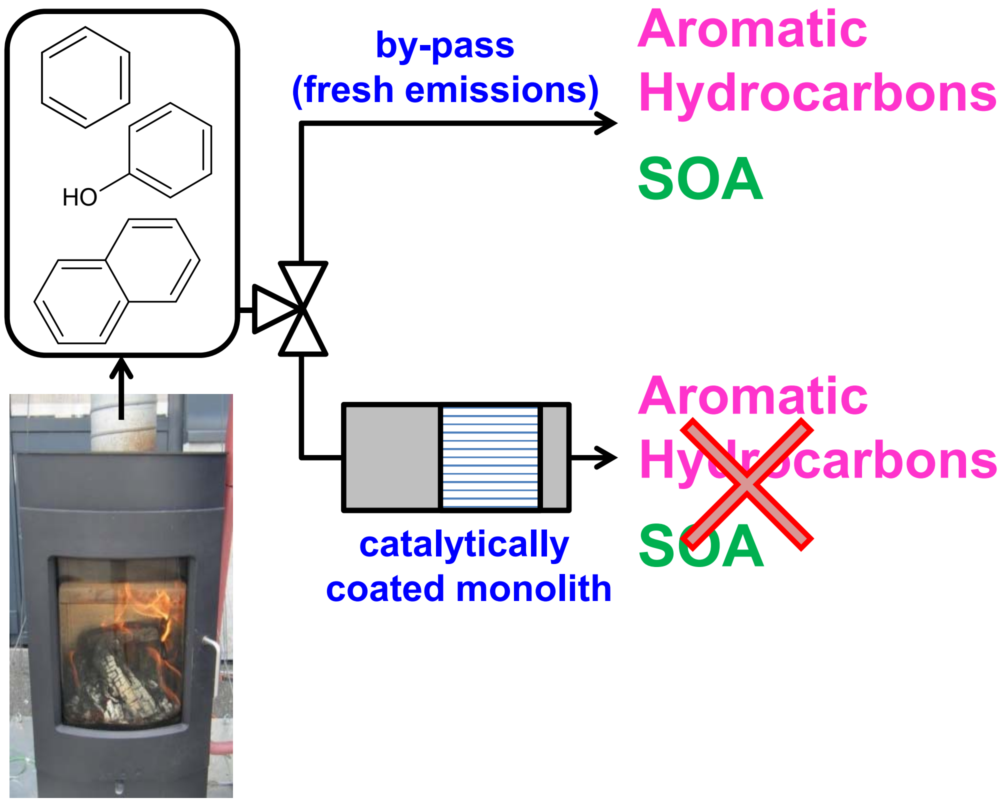


- Significant reduction of SOA at realistic chimney temperatures (185-310°C)
- SOA reduction follows «SOA-22» precursor reduction

NMHC, SOA-22 AND SOA REDUCTION



Conclusions



1) Removal of toxic CO & harmful aromatics at relatively low temperatures
2) SOA formation significantly reduced, following the SOA-22 precursors
3) Reduction of methane at high temperatures; CeO_2 is effective
4) Low cost/impact-materials should be studied, as phenolic / naphthalenes appear easily convertable

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QUESTIONS?

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http://www.ccem.ch/optiwares
https://www.psi.ch/lac/ccesccem-optiwares