Secondary organic aerosol formation from small scale wood stoves

Can it be reduced by application of catalytic VOC converters?

Simone Pieber¹ – emissions measurements
Paul Scherrer Institute, Laboratory of Atmospheric Chemistry, Villigen
simone.pieber@psi.ch, 0041 056 310 4467

Anastasios Kampolis² – catalyst development
Paul Scherrer Institute, Bioenergy and Catalysis Laboratory, Villigen
anastasios.kampolis@psi.ch, 0041 056 310 5321

Emily Bruns¹, Imad El Haddad¹, Dogushan Kilic¹, Davide Ferri², Oliver Kröcher²,³, Urs Baltensperger¹ and André S.H. Prévôt¹

¹ Laboratory of Atmospheric Chemistry, Paul Scherrer Institute
² Bioenergy and Catalysis Laboratory, Paul Scherrer Institute
³ École Polytechnique Fédérale de Lausanne
Residential log wood combustion

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

Average organic components in Winter from various sites in central Europe

(Heintzenberg et al., 2003)

(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\(_2\)O 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

![Chemical structures and reactions](attachment:image.png)
SECONDARY ORGANIC AEROSOL

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)
Efficient catalyst for oxidation of CH₄ and NMHC at low temperature

Pt / Al₂O₃ and Pt / x%CeO₂-Al₂O₃

- powder (model gas, H₂O stability)
- coated monolith
  - model gas vs. real wood burning exhaust
  - effect on NMHC & secondary organic aerosol

Al₂O₃
- great mechanical properties
- high surface area - porosity
- water resistant

Pt
- high activity for CO and HC
- fair stability against poisoning
- H₂PtCl₆ left overs may prevent poisoning by inorganic compounds

CeO₂
- 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*

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**Catalyst coated on monolith**

*Bioenergy and Catalysis Laboratory, PSI*

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**fixed-bed reactor**

**reaction feed:** 20% O₂, 1000 ppm CH₄, balance N₂,
F = 100 mL min⁻¹, GHSV = 118 L g⁻¹ h⁻¹

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**coating on ceramic monolith**

**reaction feed:**

**Lab:** 10% O₂, 1000 ppm CH₄,
4.7% H₂O, balance N₂,
F = 8 L min⁻¹, GHSV = 180 L g⁻¹ h⁻¹

**Wood Burning Exhaust**, F = 6 L min⁻¹

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(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**
  - CH₄, NMHC, THC
- **Cavity Ring Down Spectrometer**
  - CO₂, CO, CH₄, H₂O
- **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)

**CO₂**: 3500 – 11000 ppm
**CO**: 350 – 1100 ppm
**CH₄**: 70 – 280 ppm
**NMHC**: 150 – 500 ppm
**H₂O**: ca. 1%
**NOₓ**: ppm
**POA₁**: ~500 ug m⁻³
**BC**: ~20 000 ug m⁻³

- **Catalyst coated in glass reactor**
  - T = 100 – 600°C
  - F = 6 L min⁻¹

- **Heated Ejection Dilutor** ~1:8, 150°C

- **3 m³ Teflon Chamber**
RESULTS
**CH₄ conversion with powder in lab reactor**

Cat A: Pt/30%CeO₂-Al₂O₃ // POWDER
- Pt/10%CeO₂-Al₂O₃ - pretreated with H₂
- Pt/20%CeO₂-Al₂O₃ - pretreated with H₂
- Pt/30%CeO₂-Al₂O₃ - pretreated with H₂

Cat B: Pt/Al₂O₃ // POWDER
- Pt/Al₂O₃ - pretreated with H₂
- Pt/Al₂O₃ - pretreated with N₂

50% conversion

430°C

500°C

Pt/30%CeO₂-Al₂O₃

(Kampolis et al., in prep.)
CH$_4$ conversion with coated monoliths in lab reactor

Bioenergy and Catalysis
Laboratory, PSI

- Coated Pt/30%CeO$_2$-Al$_2$O$_3$ monolith more efficient for CH$_4$
- T for 50% CH$_4$ conv. for monolith is 600°C vs. 430°C for powder
**CH₄ conversion with monolith: lab test vs. WB exhaust**

Laboratory of Atmospheric Chemistry, PSI

- Cat A: Pt/30%CeO₂-Al₂O₃
  - CH₄ (Lab Test)
  - CH₄ (Exp. 3, 7, 9)

- Cat B: Pt/Al₂O₃
  - CH₄ (Lab Test)
  - CH₄ (Exp. 5)

- Coated Pt/30%CeO₂-Al₂O₃ monolith more efficient for CH₄

- Wood burning exhaust (F = 6 L min⁻¹) very comparable to lab test (F = 8 L min⁻¹)

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**Graph Details:**
- X-axis: Set Temperature [°C]
- Y-axis: CH₄ conversion
- Data points for lab test and WB exhaust at different temperatures.
CO and NMHC conversion with monolith: WB exhaust

Laboratory of Atmospheric Chemistry, PSI

- for CO and NMHC lower T than for CH₄
- CO and NMHC conv. with 30%CeO₂ needs further investigation

Cat A: Pt/30%CeO₂-Al₂O₃
- CH₄ (Lab Test)
- CH₄ (Exp. 3, 7, 9)
- CO (Exp. 3, 7, 9)
- NMHC (Exp. 3, 7, 9)
- CO₂ (Exp. 3, 7, 9)

Cat B: Pt/Al₂O₃
- CH₄ (Lab Test)
- CH₄ (Exp. 5)
- CO (Exp. 5)
- NMHC (Exp. 5)
- CO₂ (Exp. 5)
Aromatic HC conversion with monolith: WB exhaust

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Conversion vs. Set Temperature [°C]

- [Benzene + H]^+ (m/z 79)
- [Toluene + H]^+ (m/z 93)
- [Styrene + H]^+ (m/z 105)
- [Naphthalene + H]^+ (m/z 129)
- [Benzaldehyde + H]^+, [Xylenes + H]^+ (m/z 107)

Cat B: Pt/Al₂O₃

CO (Exp. 5)
NMHC (Exp. 5)
Benzene (mz79)
Toluene (mz93)
Styrene (mz105)
Benzaldehyde / Xylene (mz107)
Naphthalene (mz129)

Preliminary!
Aromatic HC conversion with monolith: WB exhaust

Cat B: Pt/Al₂O₃

- CO (Exp. 5)
- NMHC (Exp. 5)
- Benzene (m/z 79)
- Toluene (m/z 93)
- Styrene (m/z 105)
- Benzaldehyde / Xylene (m/z 107)
- Naphthalene (m/z 129)

Conversion from start value

Set Temperature [°C]

- [Benzaldehyde + H]^+ (m/z 107)
- [Styrene + H]^+ (m/z 105)
- [Benzene + H]^+ (m/z 79)
- [Toluene + H]^+ (m/z 93)
- [Naphthalene + H]^+ (m/z 129)
Secondary organic aerosol formation w/wo catalyst

Estimated Reduction:

<table>
<thead>
<tr>
<th>Temperature</th>
<th>NMHC</th>
<th>SOA</th>
</tr>
</thead>
<tbody>
<tr>
<td>310°C</td>
<td>-52%</td>
<td>-96%</td>
</tr>
<tr>
<td>250°C</td>
<td>-18%</td>
<td>-86%</td>
</tr>
<tr>
<td>185°C</td>
<td>-7%</td>
<td>-60%</td>
</tr>
</tbody>
</table>

- 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$_2$O and in long term?
  - Effect on primary PM
  - Stability > 600°C
  - Alternatives to Pt based catalysts, especially for NMHC conversion?
THANK YOU FOR YOUR ATTENTION!

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BACK UP SLIDES
SECONDARY ORGANIC AEROSOL

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

Why this material?
Pt/Al$_2$O$_3$ ("Cat B") and Pt/x%CeO$_2$-Al$_2$O$_3$ ("Cat A")

Al$_2$O$_3$
- 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

Preparation
Pt/Al$_2$O$_3$ ("Cat B") and Pt/x%CeO$_2$-Al$_2$O$_3$ ("Cat A")

Powder
Pt
- wet impregnation (WI) of H$_2$PtCl$_6$ on the commercial $\gamma$-Al$_2$O$_3$ support (200 um), Pt content: 1.3 wt%
- drying at 90 °C overnight, calcination at 500 °C (50 °C/min) for 2h

substrate pretreatment for Pt/x%CeO$_2$-Al$_2$O$_3$
- deposition-precipitation (DP) of Ce(NO$_3$)$_3$·6H$_2$O on commercial $\gamma$-Al$_2$O$_3$, x= 10, 20, 30 wt%
- drying at 90 °C overnight, calcination at 500 °C (50 °C/min) for 2h

Monolith
- ceramic monoliths of appropriate size
- aluminum-based binder ($\gamma$-Al$_2$O$_3$, 5-10 um)
- calcination at 500 °C in air for 2 h, hydrothermal aging at 600 °C for 6h, using 10% H$_2$O/N$_2$
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 O₃, OH, HO₂

O₃ source: - photolysis of O₂
OH source: - photo-dissociation of O₃, reaction of O(¹D) + H₂O;
- photolysis of H₂O

*Photochemical age* can be varied,
e.g. UV intensity and H₂O (g)
(OH up to 400 pptv (~10¹³ molecules / cm³), O₃ up to 15 ppmv)

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![Diagram of PAM Chamber](image)

**Mercury Lamps in Teflon Tubing**
**Screen**
**Instruments**

- **Sample Flow**: 1 L min⁻¹ humidified N₂
- **Exhaust**: ca. 20 cm
- **N₂ Purge Flow**: 0.5 L min⁻¹ N₂
- **“Ring Flow” to pump**: 1 L min⁻¹
- **“Ring Flow”**: ca. 40 cm
- **Water**: mQ Water
- **Screen**: Nafion membrane

**UVC lights, λ = 185 and 254 nm**

**12 L PAM Chamber**

BET and Porosity of Pt/xCeO$_2$-Al$_2$O$_3$ catalysts

- Textural characteristics: unaffected by CeO$_2$
- Mesoporous structure

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET (m$^2$/g)</th>
<th>Pore volume (cm$^3$/g)</th>
<th>Pore size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(W)Al</td>
<td>209</td>
<td>0.519</td>
<td>66.0</td>
</tr>
<tr>
<td>Pt(W)10CeAl(DP)</td>
<td>205</td>
<td>0.499</td>
<td>78.6</td>
</tr>
<tr>
<td>Pt(W)20CeAl(DP)</td>
<td>216</td>
<td>0.490</td>
<td>78.3</td>
</tr>
<tr>
<td>Pt(W)30CeAl(DP)</td>
<td>199</td>
<td>0.459</td>
<td>78.7</td>
</tr>
</tbody>
</table>