



Bioenergy and Catalysis Laboratory



Secondary organic aerosol formation from small scale wood stoves

Can it be reduced by application of catalytic VOC converters?

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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



SECONDARY ORGANIC AEROSOL



(Heringa et al., ACP, 2011)

PROJECT IDEA

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

\succ 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

AI_2O_3

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

Pt

- high activity for CO and HC •
- fair stability against poisoning ٠
- 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

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

fixed-bed reactor

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

Catalyst coated on monolith



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

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

EXPERIMENTAL SET-UP



RESULTS

CH₄ conversion with <u>powder</u> in lab reactor



CH₄ conversion

CH₄ conversion with <u>coated monoliths</u> in lab reactor



CH₄ conversion with monolith: lab test vs. WB exhaust



CO and NMHC conversion with monolith: WB exhaust

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Aromatic HC conversion with monolith: WB exhaust



Aromatic HC conversion with monolith: WB exhaust



Secondary organic aerosol formation w/wo catalyst



CONCLUSIONS

- Tested catalysts work very well for CH₄ 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 CeO₂ 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?





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THANK YOU FOR YOUR ATTENTION!

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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%CeO₂-Al₂O₃ ("Cat A)

AI_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

CeO₂

- 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/Al₂O₃ ("Cat B") and Pt/x%CeO₂-Al₂O₃ ("Cat A)

Powder

Pt

- wet impregnation (WI) of H₂PtCl₆ on the commercial γ-Al₂O₃ 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%CeO₂-Al₂O₃

- deposition-precipitation (DP) of Ce(NO₃)₃·6H₂O on commercial γ-Al₂O₃, 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 (γ-Al₂O₃, 5-10 um)
- calcination at 500 °C in air for 2 h, hydrothermal aging at 600 °C for 6h, using 10% ${\rm H_2O/N_2}$

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 O₃, OH, HO₂

 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 (~10¹³ molecules / cm³), O₃ up to 15 ppm_v)







BET and Porosity of Pt/xCeO₂-Al₂O₃ catalysts





- Textural characteristics: unaffected by CeO₂
- Mesoporous structure

Catalyst	BET (m²/g)	Pore volume (cm ³ /g)	Pore size (Å)
Pt(WI)AI	209	0.519	66.0
Pt(WI)10CeAI(DP)	205	0.499	78.6
Pt(WI)20CeAI(DP)	216	0.490	78.3
Pt(WI)30CeAI(DP)	199	0.459	78.7 22



