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Title: Multifunctional Reactors for Diesel Nanoparticle Emission Control

Abstract: (min. 300 - max 500 words)

The abstracts for papers and posters should contain unpublished information on the research subject, the investigation methods and results obtained so far. Graphs and references are very welcome. During your presentation at the conference you may expand on this with additional data and results. General information on products which are already commercially available are not the focus of the presentations but are very welcome at the exhibition.

Monolithic reactors such as wall-flow Diesel Particulate Filters (DPFs) continue to be important components of diesel emission control systems, and are increasingly incorporating different functionalities such as gas species oxidation (such as CO, hydrocarbons and NO) storage phenomena (such as NOx and NH3 storage) in addition to soot nanoparticle filtration and oxidation. In the current work, novel catalytic coatings with a variety of methods based on conventional and novel synthesis routes are developed based on mixed oxides of base metals. The developed catalytic composition exhibits significant direct soot oxidation as evaluated by reacting mixtures of diesel soot and catalyst powders. The catalyst compositions were further deposited on porous filter structures that were evaluated on an engine bench with respect to their filtration efficiency, pressure drop behavior and direct soot oxidation activity under realistic conditions. Special emphasis was placed on investigating the effect of the catalyst amount on the filtration efficiency. Indirect soot oxidation through NO2 induced oxidation was optimized by noble metal addition to the base metal catalyst formulation via different techniques. In depth understanding of the coupled transport – reaction phenomena occurring inside the microstructure of the coated walls of DPFs is highly aided by employing computational approaches based on realistic representations of all “actors” involved: nano and microstructured porous substrates/filters, catalyst coatings and dispersions and soot nanoparticle aggregates.

Short CV:

Athanasios G. Konstandopoulos, Descartes Laureate (2006) and SAE fellow has a hybrid background in Mechanical [Dipl. ME - Aristotle University of Thessaloniki, MScME - Michigan Tech]) and Chemical Engineering [MScChE, MPhil, PhD - Yale University]. He is Director of CPERI/CERTH where he founded and heads the Aerosol & Particle Technology Laboratory (APTL) since 1996 and a member of the faculty of Chemical Engineering at the Aristotle University of Thessaloniki, since 2007. He has many years of research and engineering consulting experience in combustion generated aerosols and particulate processes, and he is the author of numerous scientific and technical papers in the field.

Multifunctional Reactors for Diesel Nanoparticle Emission Control

Athanasios G. Konstandopoulos

Aerosol & Particle Technology Laboratory, CPERI/CERTH
and
Dept. Chem. Eng., Aristotle University of Thessaloniki

Characteristics of Structured Reactors

- Large surface/volume ratio (compactness)
- Low pressure drop compared to alternatives
- Can be easily be functionalized (e.g. coated)
- Can combine more than one function (e.g. separation/reaction)

Applications pursued at APT Lab

- **Diesel Emission Control** (Soot nanoparticles, CO/HC/NOx)
- Solar Thermochemical Reactors for H_2/solar fuels production
- Bio-diagnostics & Bio-reactors for high value products

Our Approach

- Materials synthesis with novel routes
- Functionalization (deposition/coating) technologies
- Experimental setups with small and full scale samples
- Coupled transport/separation/reaction phenomena framework
- Multi-scale simulations

Trends in OEM DPF Functionalities

2000 First DPF series introduction. **Uncoated DPF**. Soot oxidation assisted by ceria/iron based fuel borne catalyst.

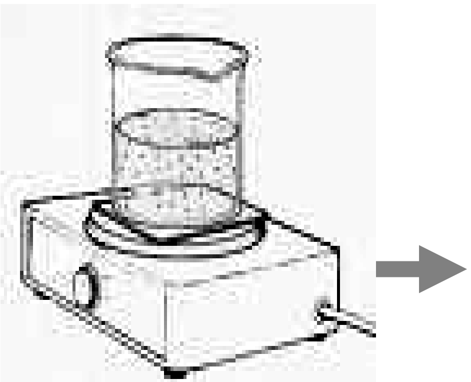
2003 Introduction of **catalyst coated DPF**. PGM-based catalysts aiming at NO/CO/HC oxidation and NO_2- assisted oxidation of soot (***indirect action of catalyst***).

2010 Targeting of ***direct soot oxidation*** by oxygen transfer from base metal oxide catalysts. Reduction/elimination of PGM. Higher porosity substrates to accommodate larger (multi-functional) catalyst loads and provide better soot-catalyst contact.

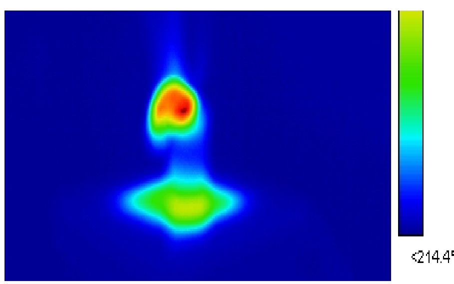
>2010 **Integration** of additional functionalities (NOx treatment, nanoparticle number emissions compliance), reduction of emission control system size and cost.

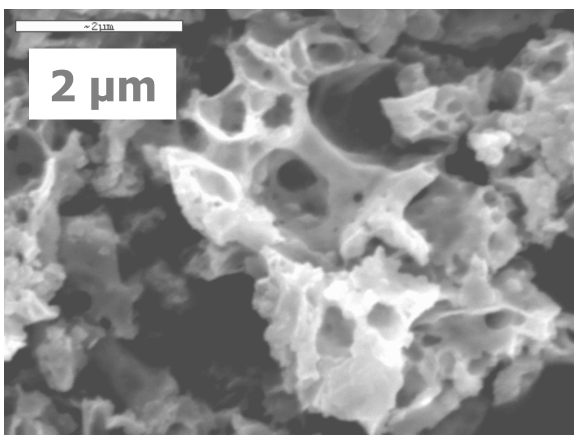
Catalyst Synthesis Techniques Employed

Liquid Phase Self Propagating High- temperature Synthesis **(LPSHS)**

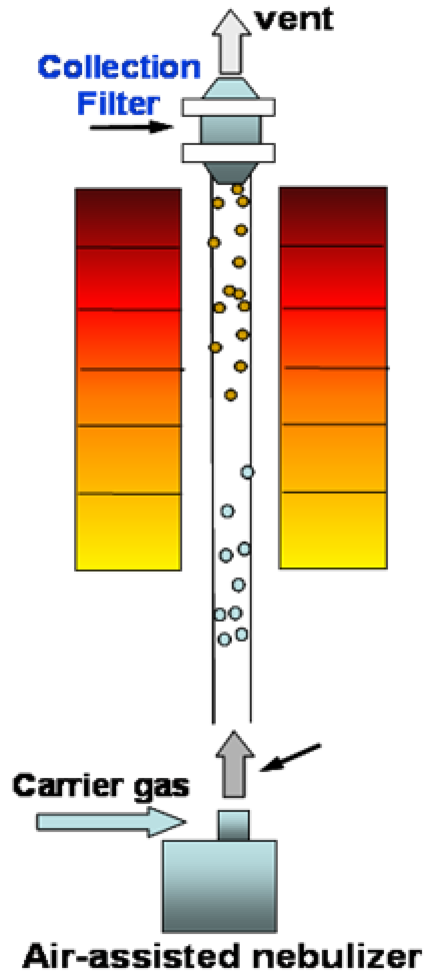


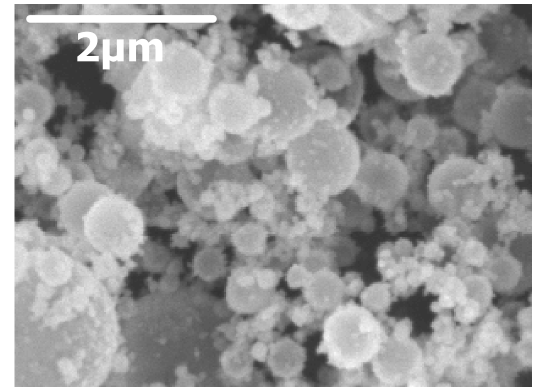
Flame front in the precursor solution

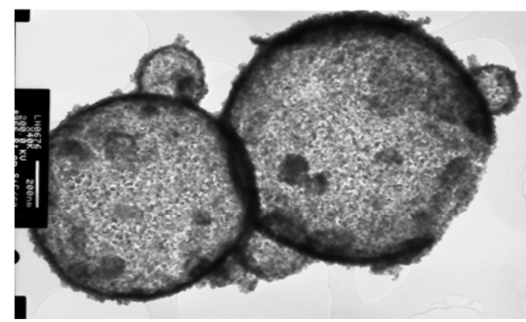




Aerosol Based Synthesis **(ABS)**







Ceria Nanoparticle Coated Filters for Soot Emission Control, PARTEC 2001
K. Karadimitra, G. Macheridou, E. Papaioannou, A. G. Konstandopoulos

Catalyst Evaluation Protocol

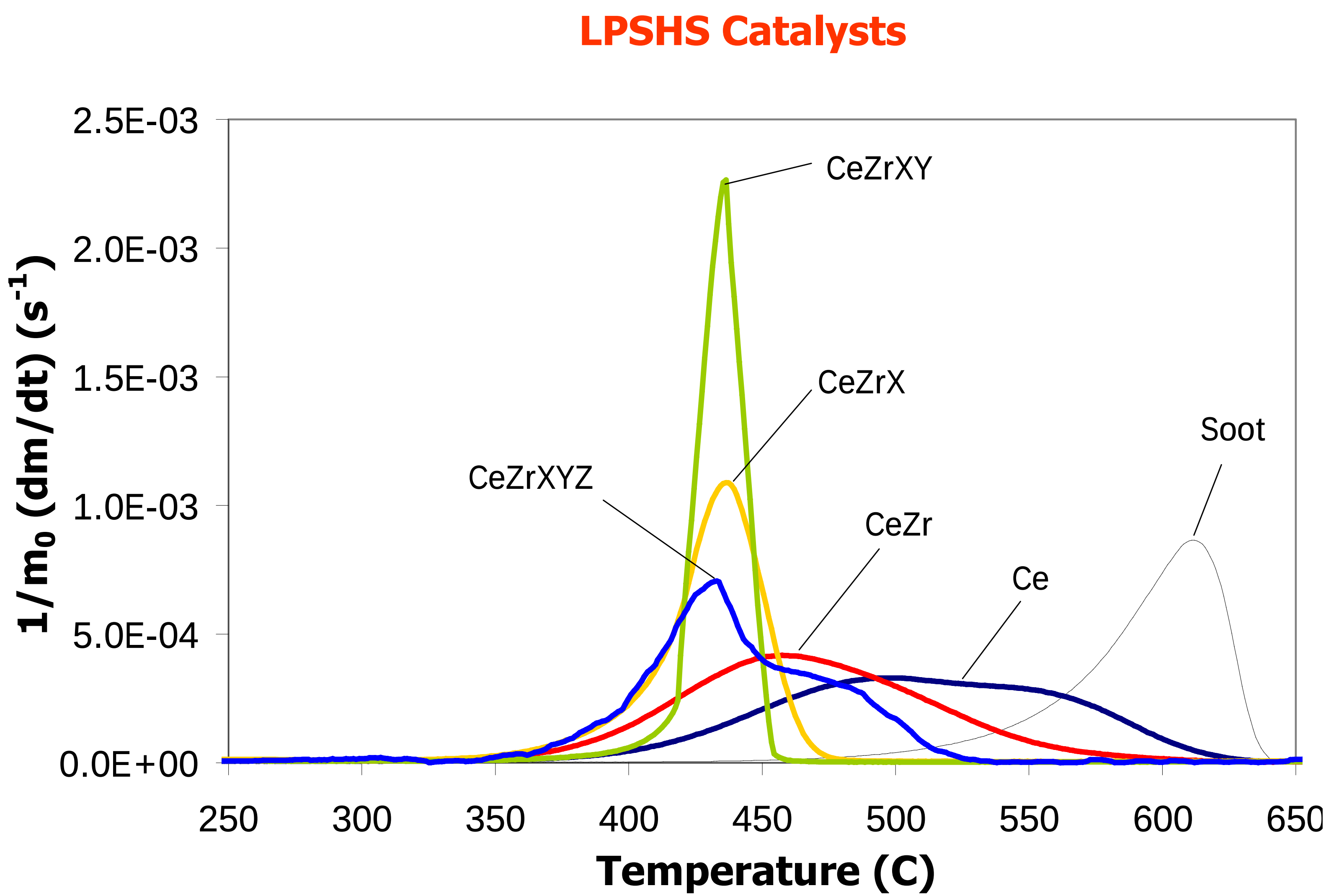
Powder Scale

- Thermogravimetric Analysis (TGA)
  - Soot-catalyst mixtures (1:2 in tight contact)
  - Increase of temperature from 150-700 C with 3 C/min, under 20% O_2 in N_2.

Monolith Scale

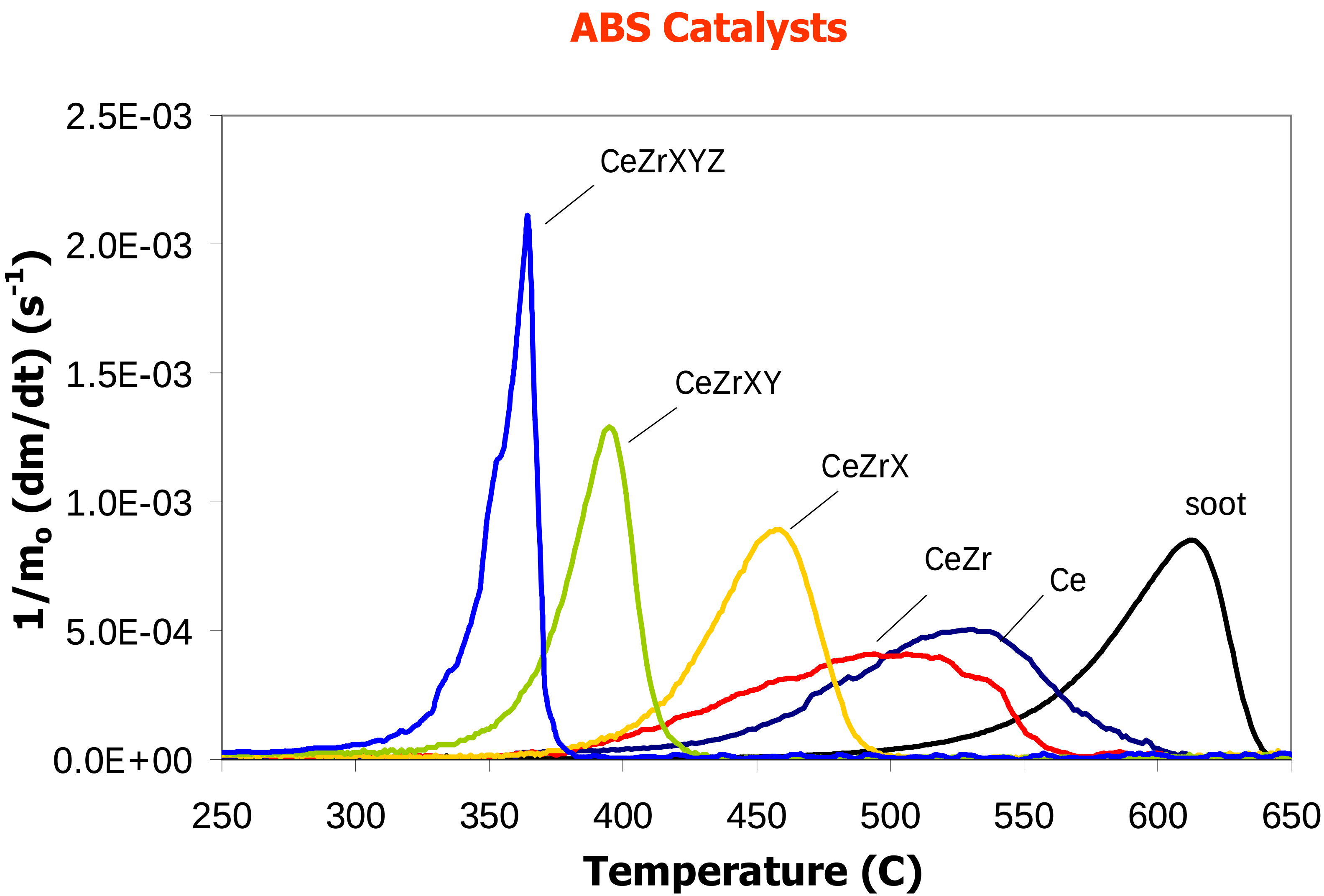
- Diesel Engine Test Cell (1.9L TDI, common rail)
  - Catalyst deposition on wall-flow filter segments
  - Filtration efficiency
  - Soot loading
  - Soot oxidation

Soot oxidation activity – CeO_2 Based Oxides



SAE-2008-01-417

Soot oxidation activity – CeO_2 Based Oxides



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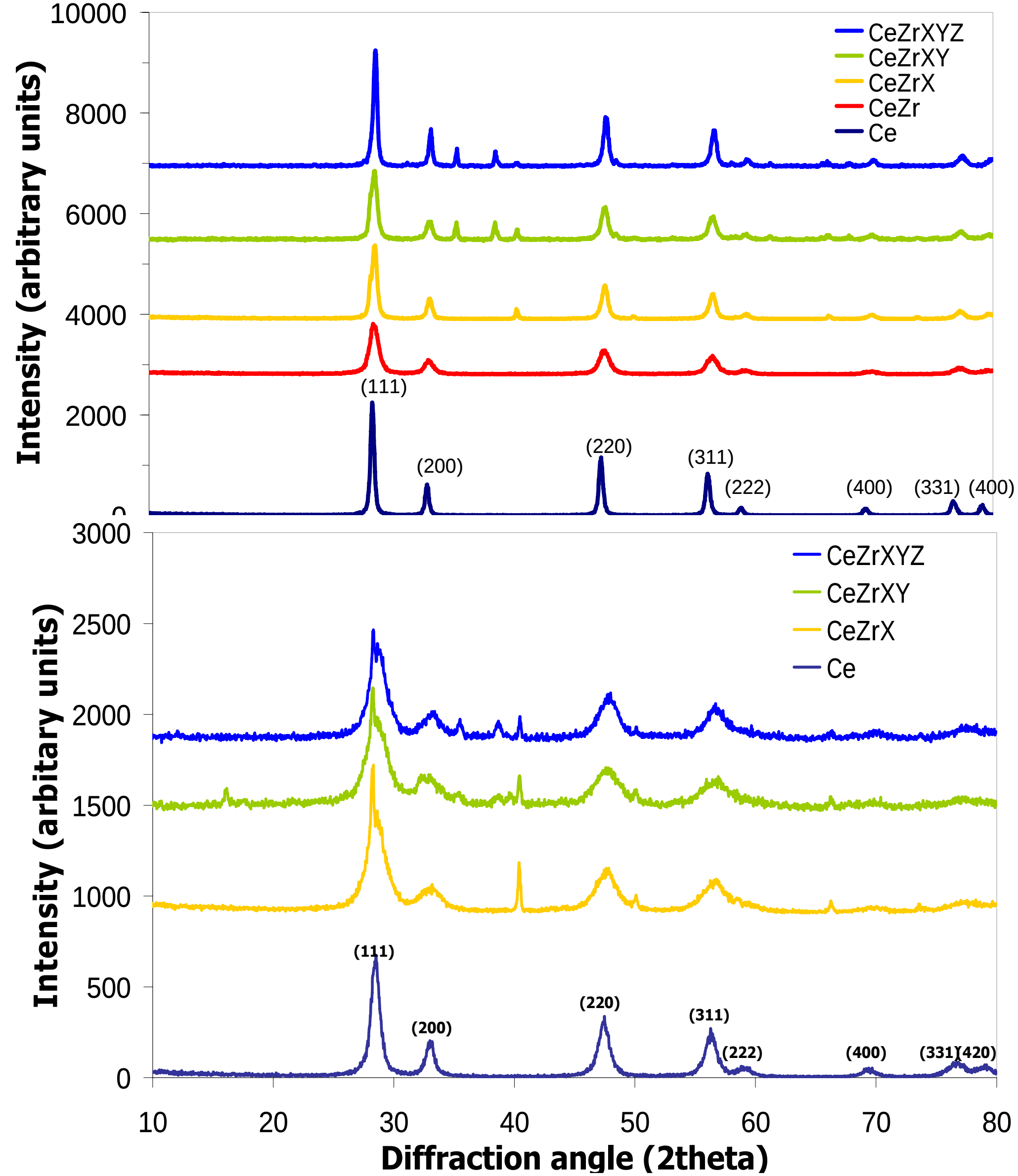
XRD – CeO_2 Based Mixed Oxides

LPSHS :

- well crystallized
- cubic-fluorite cerium oxide,(111) orientation

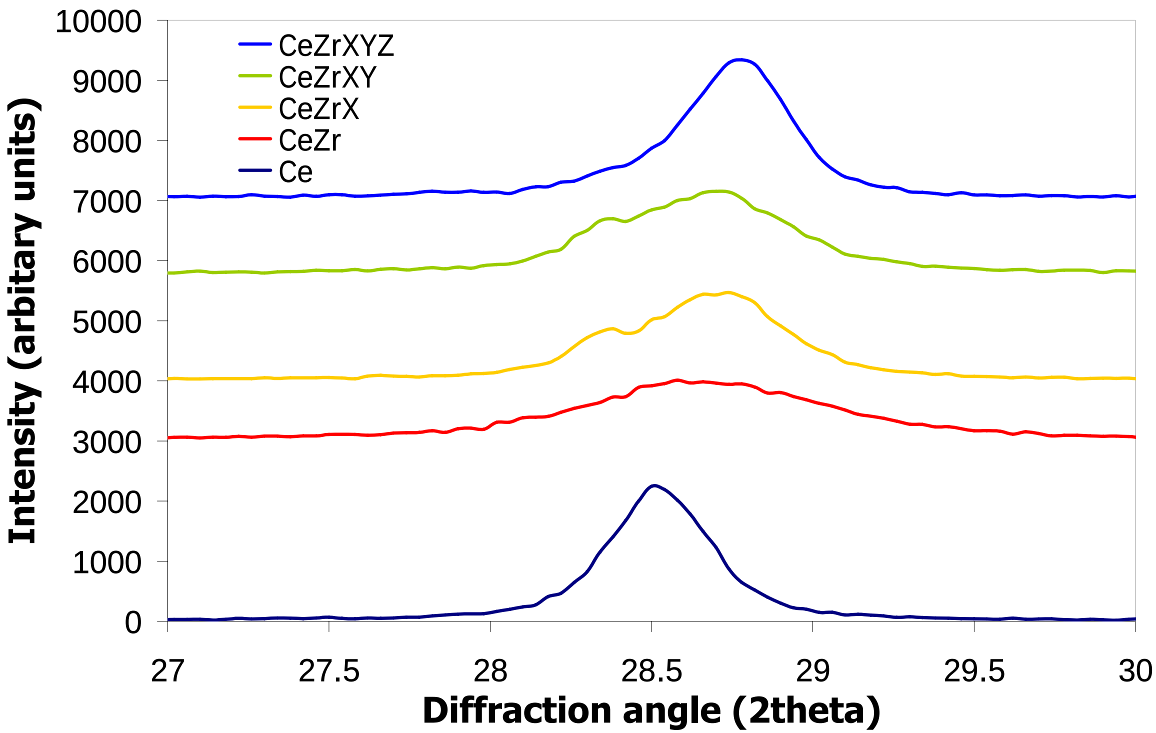
ABS :

- typical low degree of crystallinity
- cubic-fluorite cerium oxide,(111) orientation



XRD – CeO_2 Based Mixed Oxides

Doping of cerium oxide with other metals generally causes a shift of the cerianite (CeO_2) peak to higher diffraction angles.



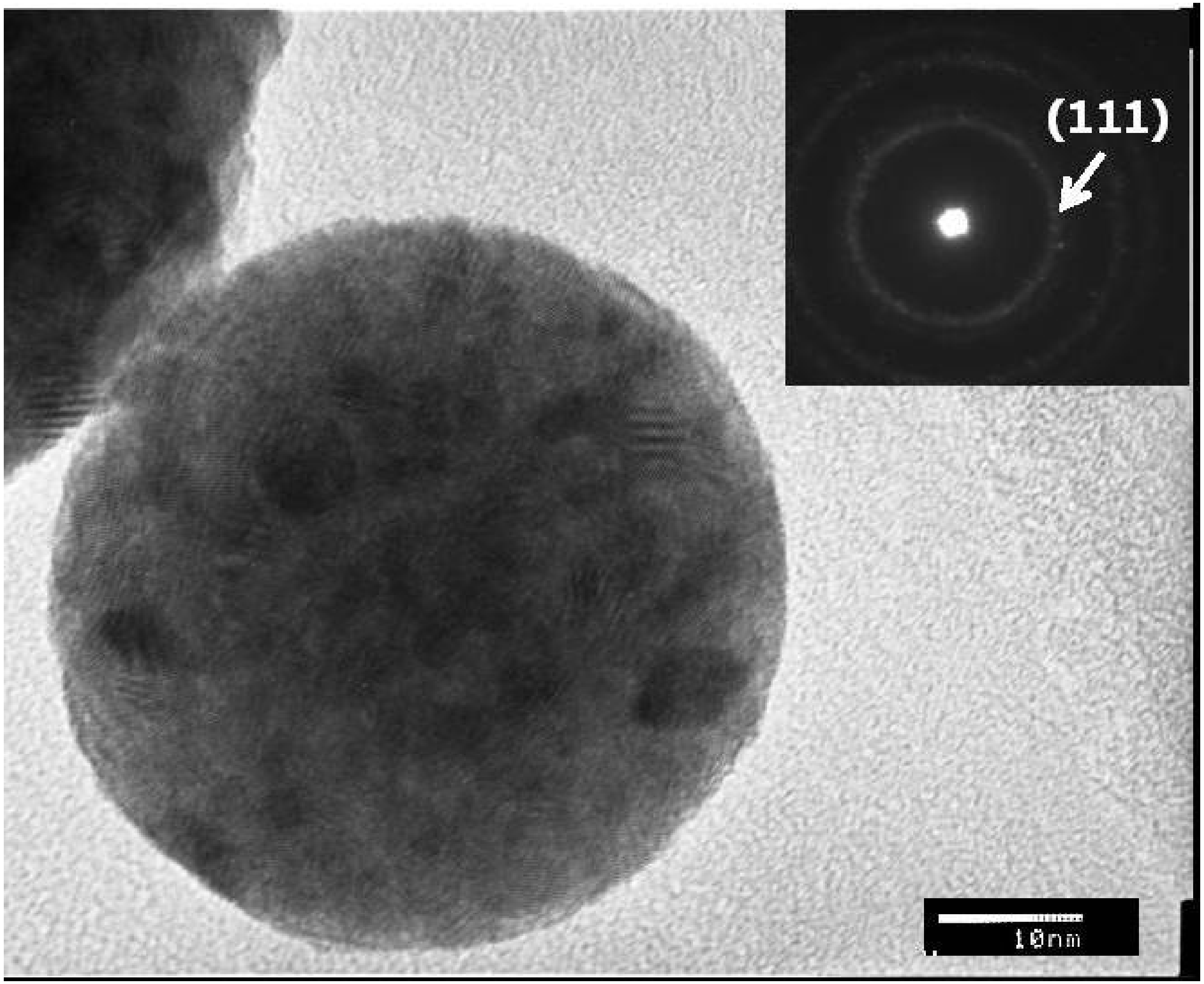
Crystallite Size			
ABS	Ce	9.51	nm
ABS	CeZrX	7.16	nm
ABS	CeZrXY	3.66	nm
ABS	CeZrXYZ	4.77	nm
LPSHS	Ce	21.44	nm
LPSHS	CeZX	12.04	nm
LPSHS	CeZrXY	11.10	nm
LPSHS	CeZrXYZ	20.12	nm

Crystallite size :

- ABS: 4-10 nm with the size decreasing with the increase of the dopants.
- LPSHS: crystallites with larger size 10-20nm.

TEM – CeO_2 Based Mixed Oxides (ABS)

- Nanocrystalline structure detected by TEM and electron diffraction pattern.



Catalyst Functions

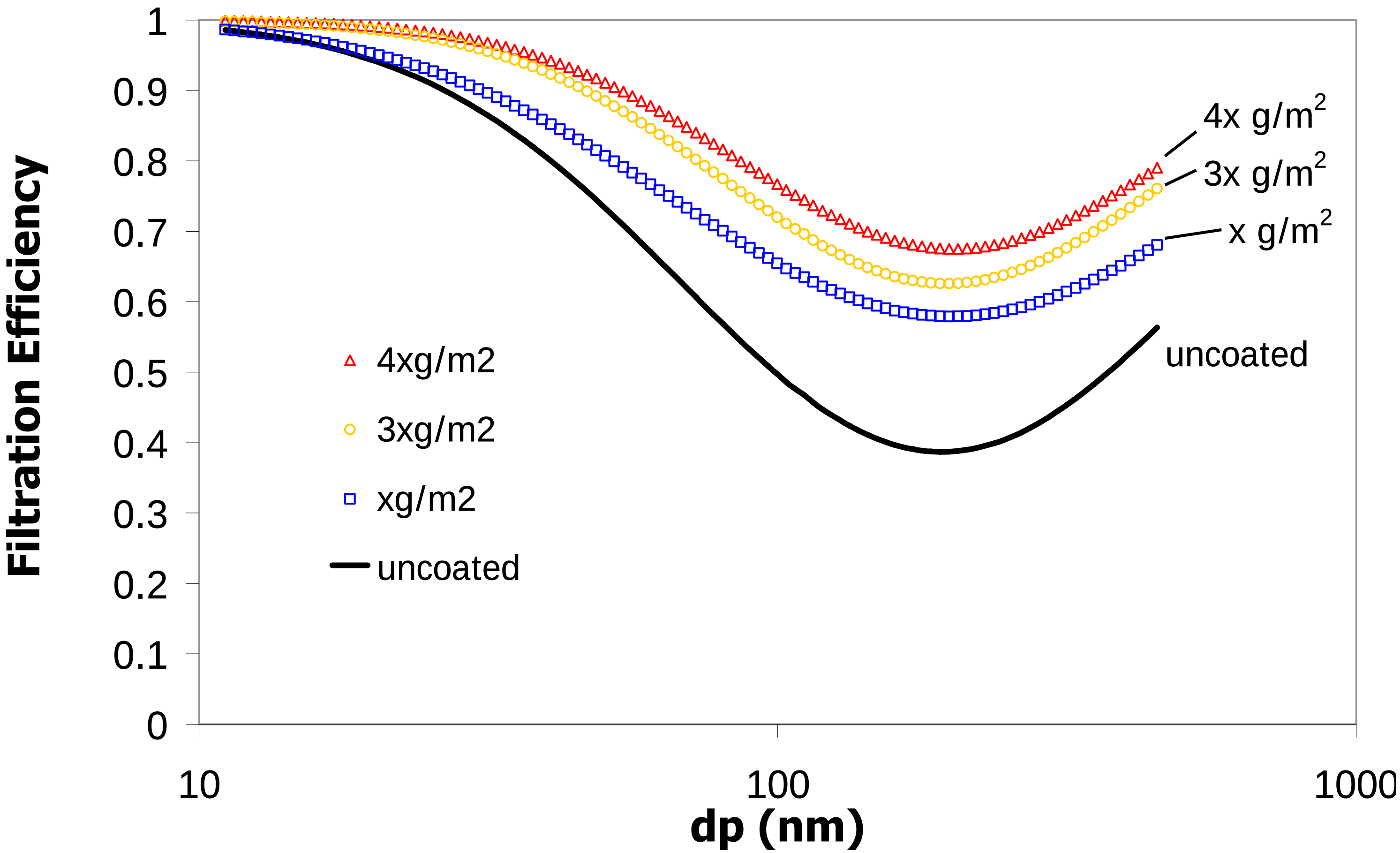
Direct Soot Oxidation Catalyst

Material with redox/oxygen storage ability such as Ce-based metal oxides e.g. Ce/Zr/other metals, referred to as Mixed Oxide Catalysts, MOC.

Indirect Soot Oxidation Catalyst

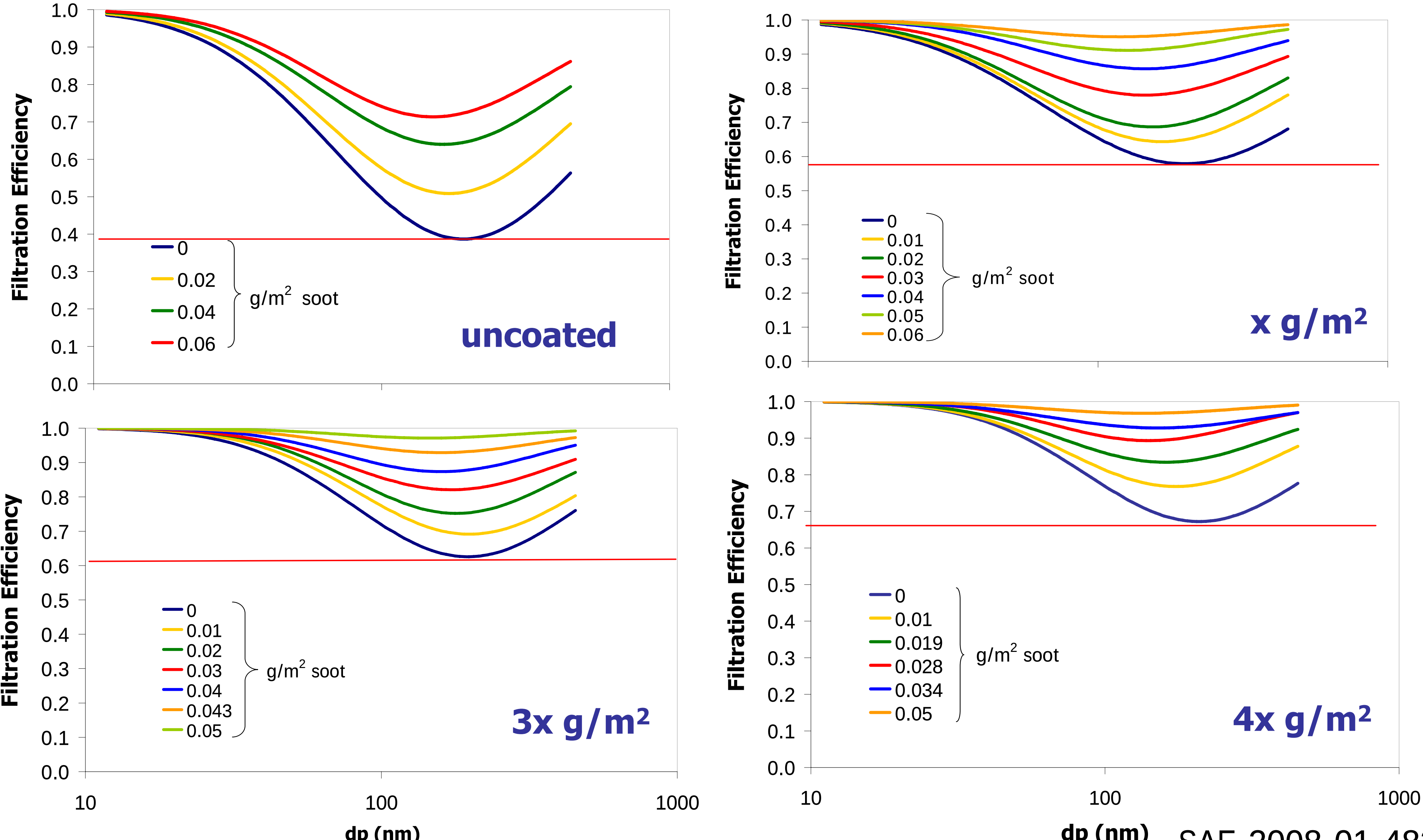
PGM-based material promoting $NO \rightarrow NO_2$ oxidation, CO and HC conversion

Initial Filtration Efficiency vs. Catalyst Amount



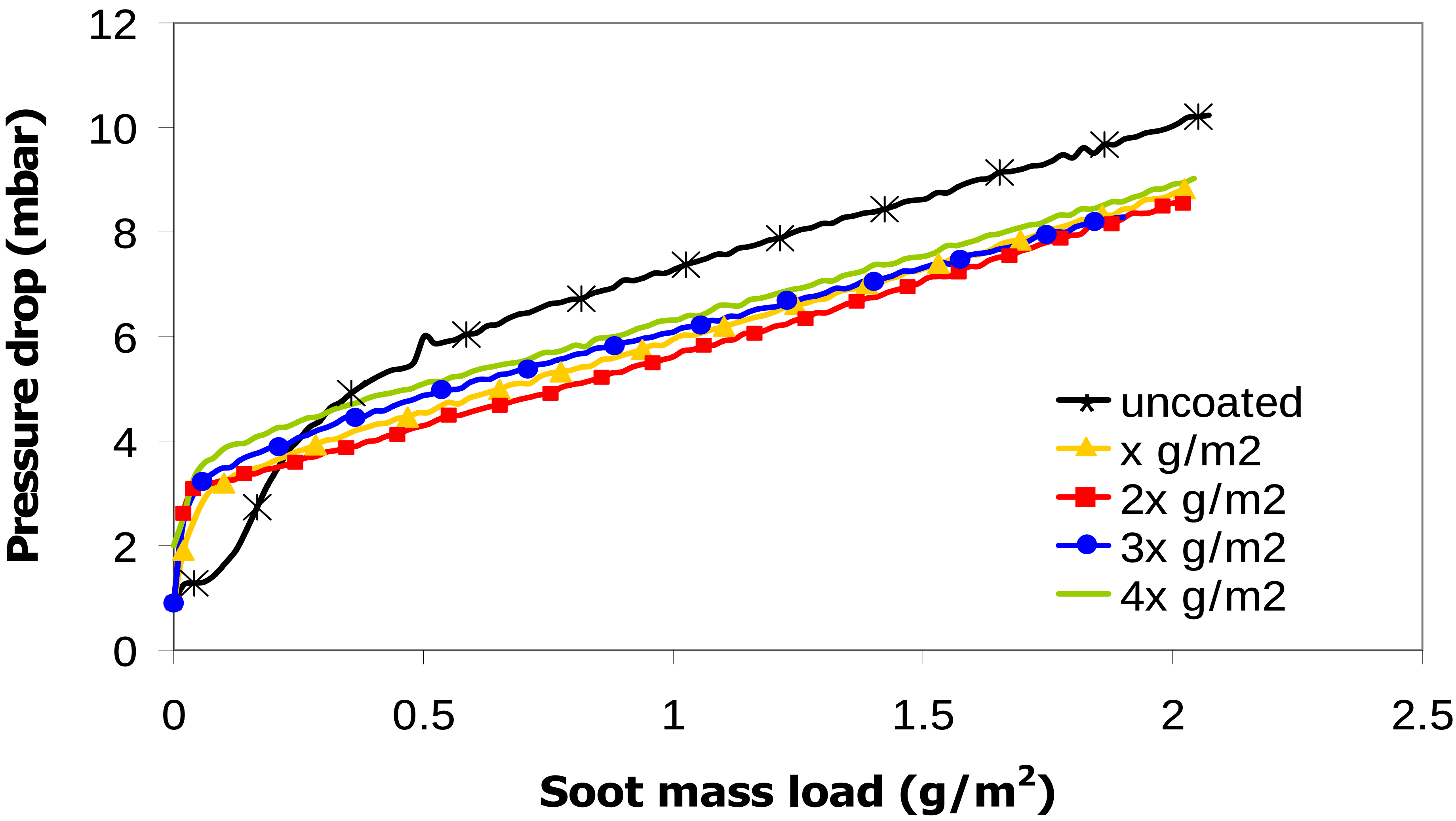
- Increase of the clean filtration efficiency with the increase of the catalyst amount.

Filtration Efficiency of Coated DPF



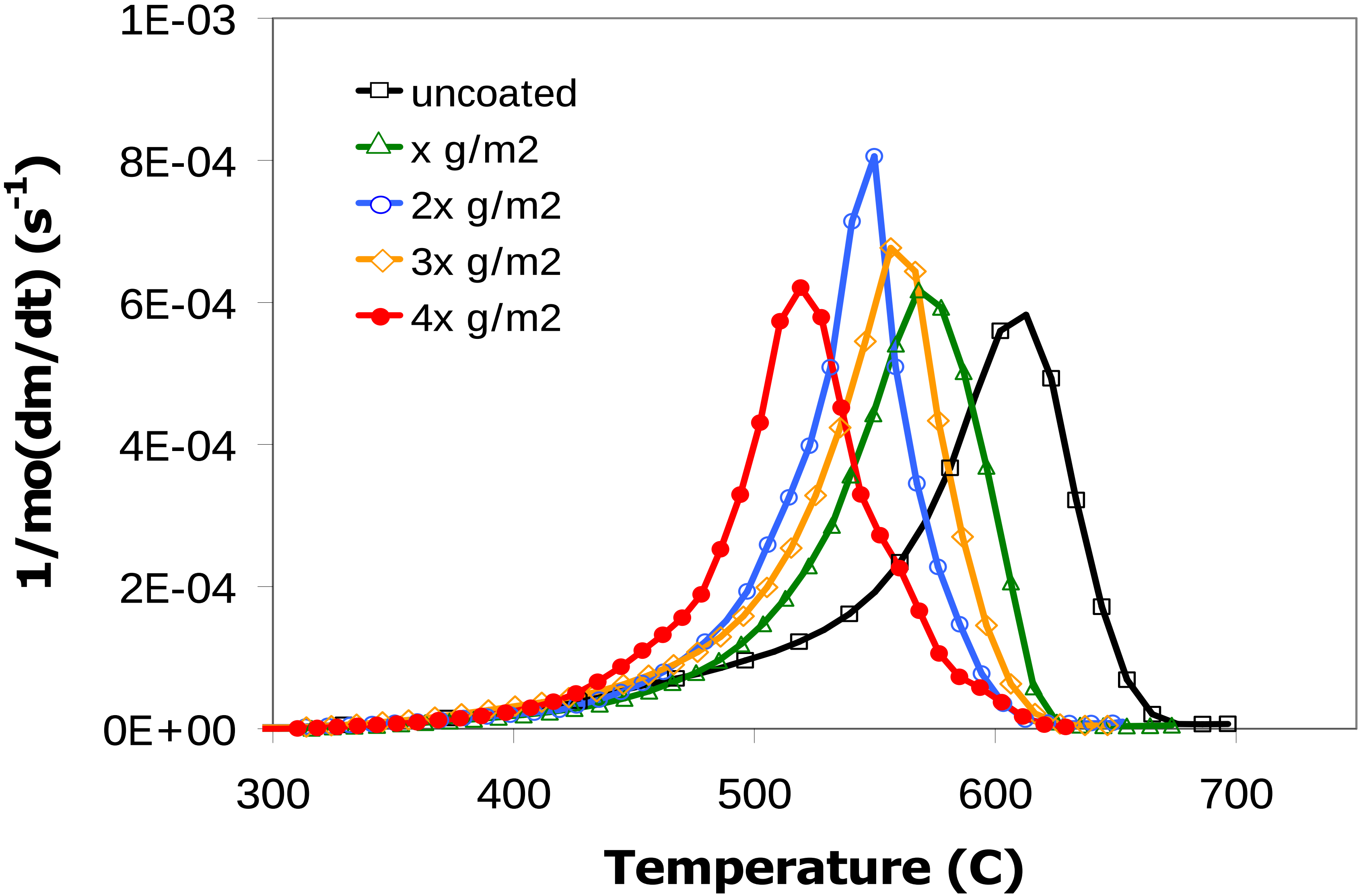
SAE-2008-01-483

Catalyst Amount Effect on Soot Loading



JSAE-2007-01-7334

Catalyst Amount Effect on Direct Soot Oxidation

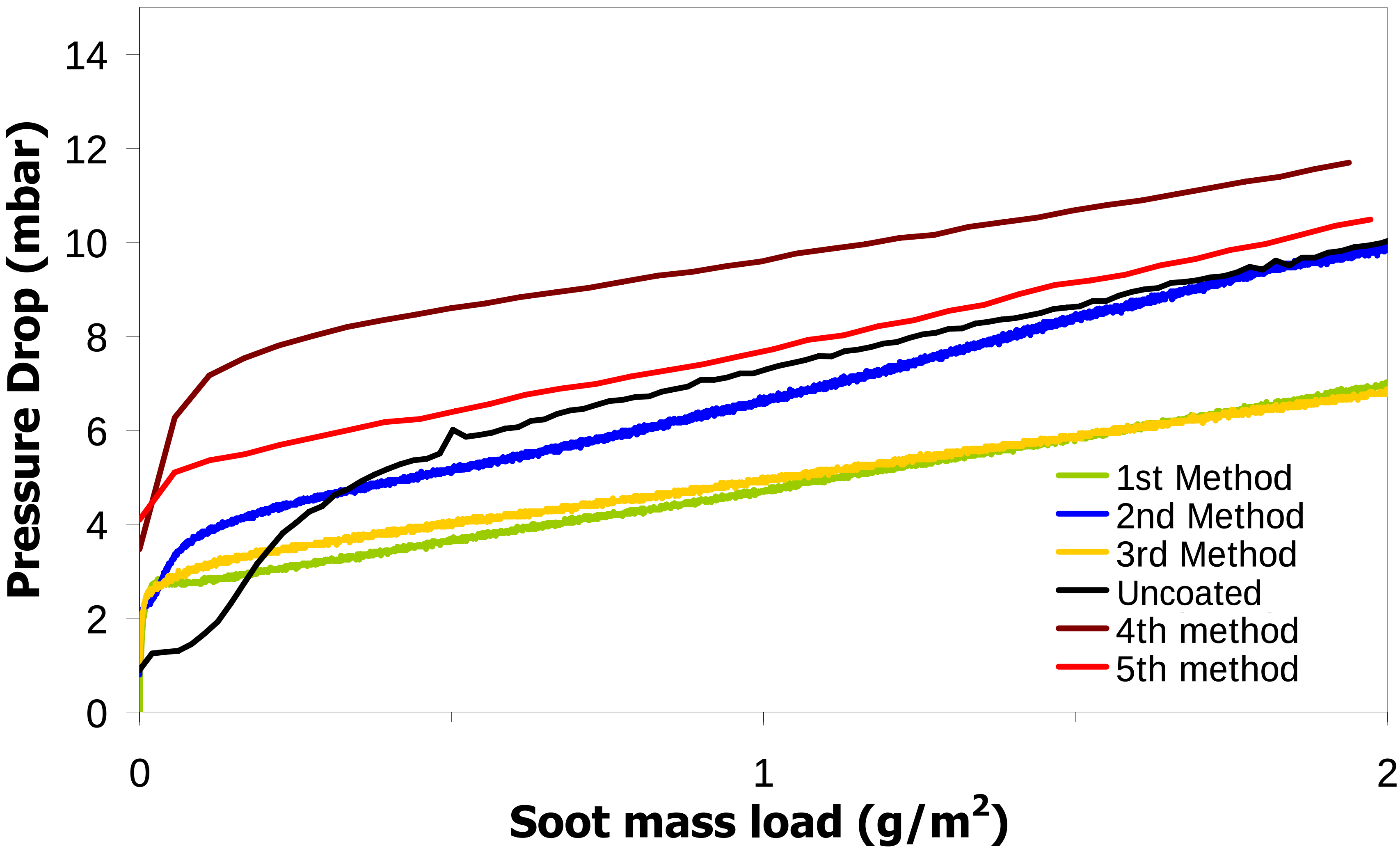


PGM addition methods

1. **Simultaneous deposition** of PGM and MOC
2. **Sequential coating-A:** MOC followed by PGM deposition.
3. **Sequential coating-B:** MOC followed by PGM deposition (lower temperature process)
4. **Sequential coating-C:** MOC followed by PGM deposition (different solution properties)
5. **Optimized coating-D:** Combination based on above knowledge

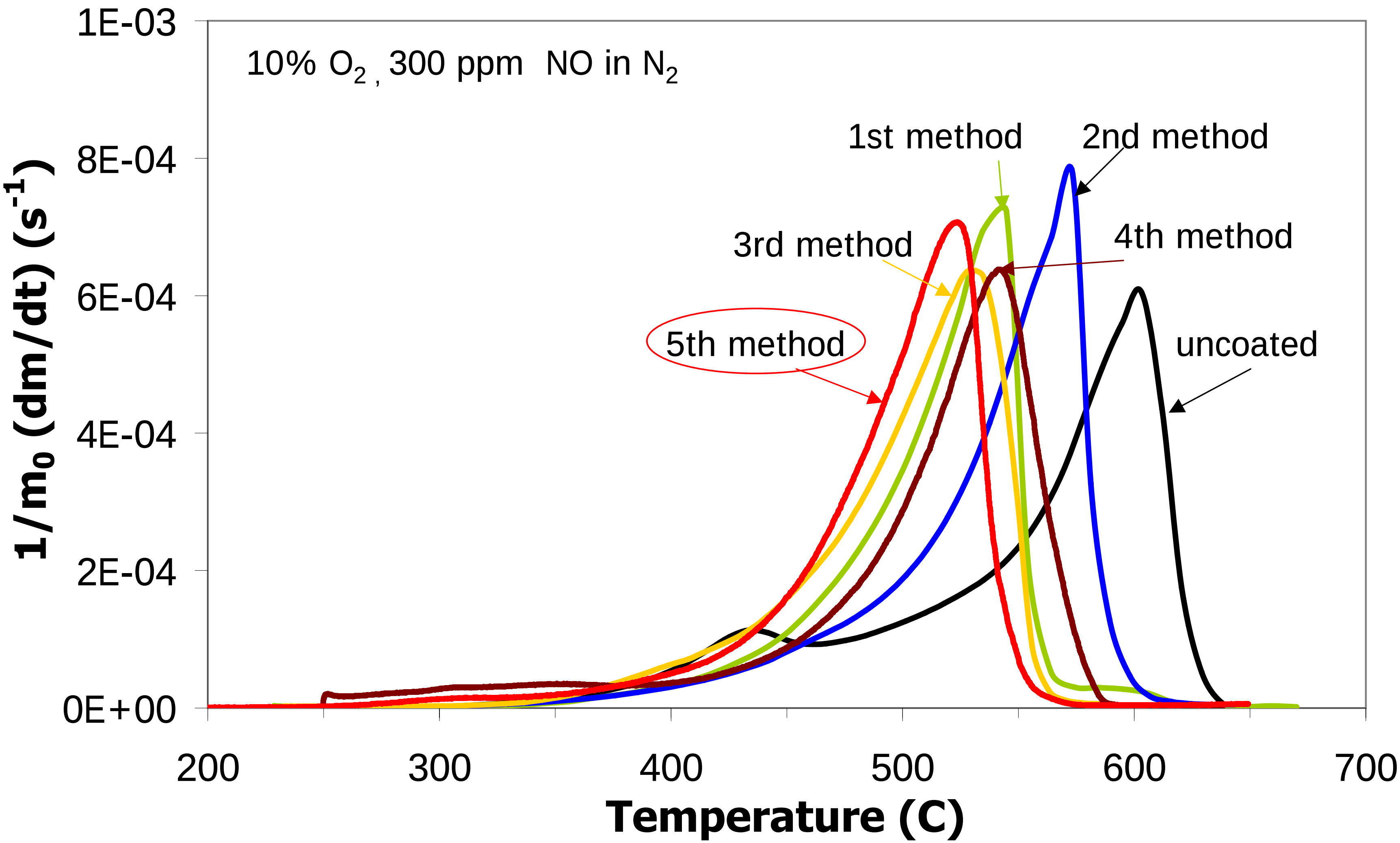
PGM loading is the same in all cases

Effect of PGM addition method on soot loading behavior

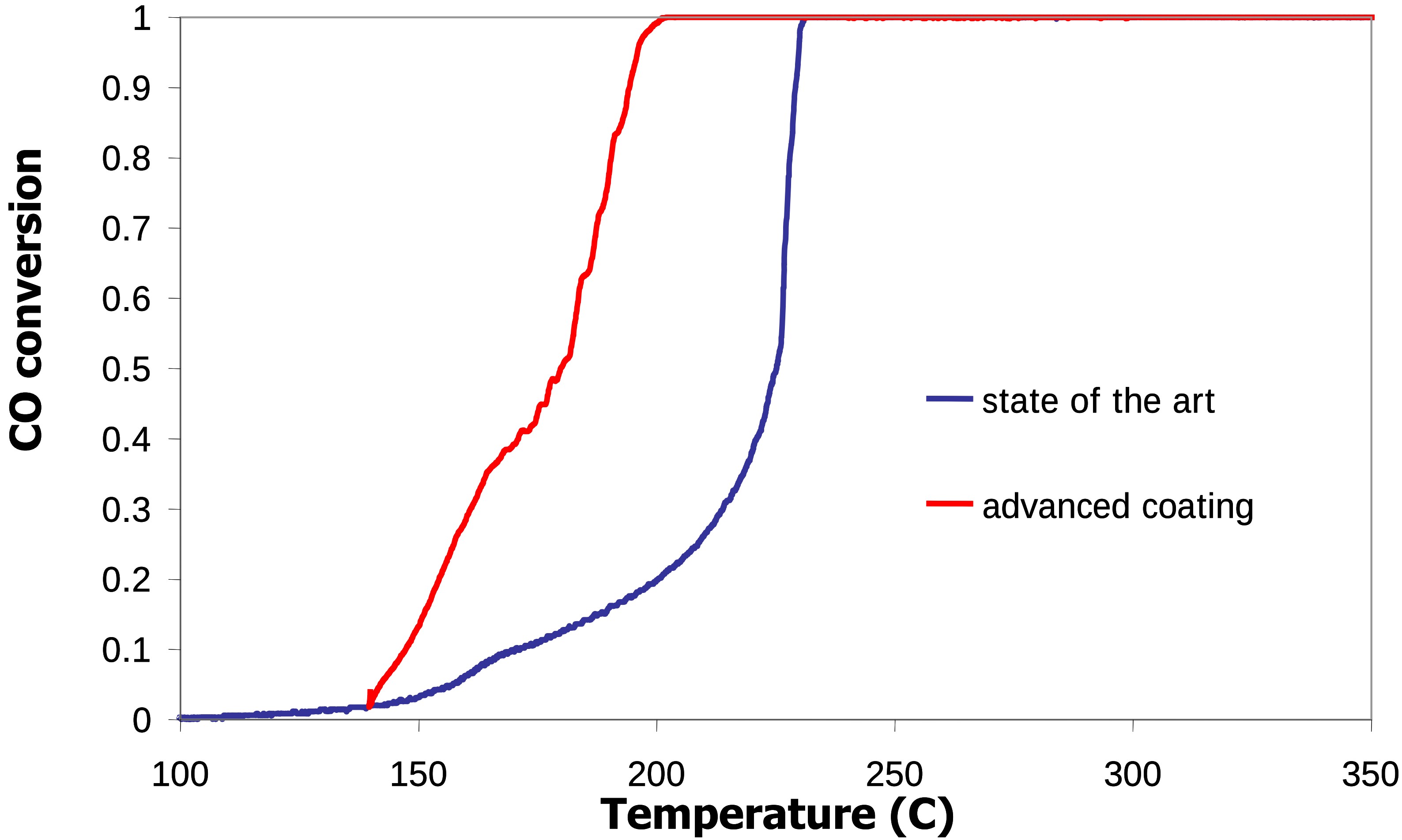


Filtration velocity = 1.36 cm/s
$T_{loading}$ = 250 C

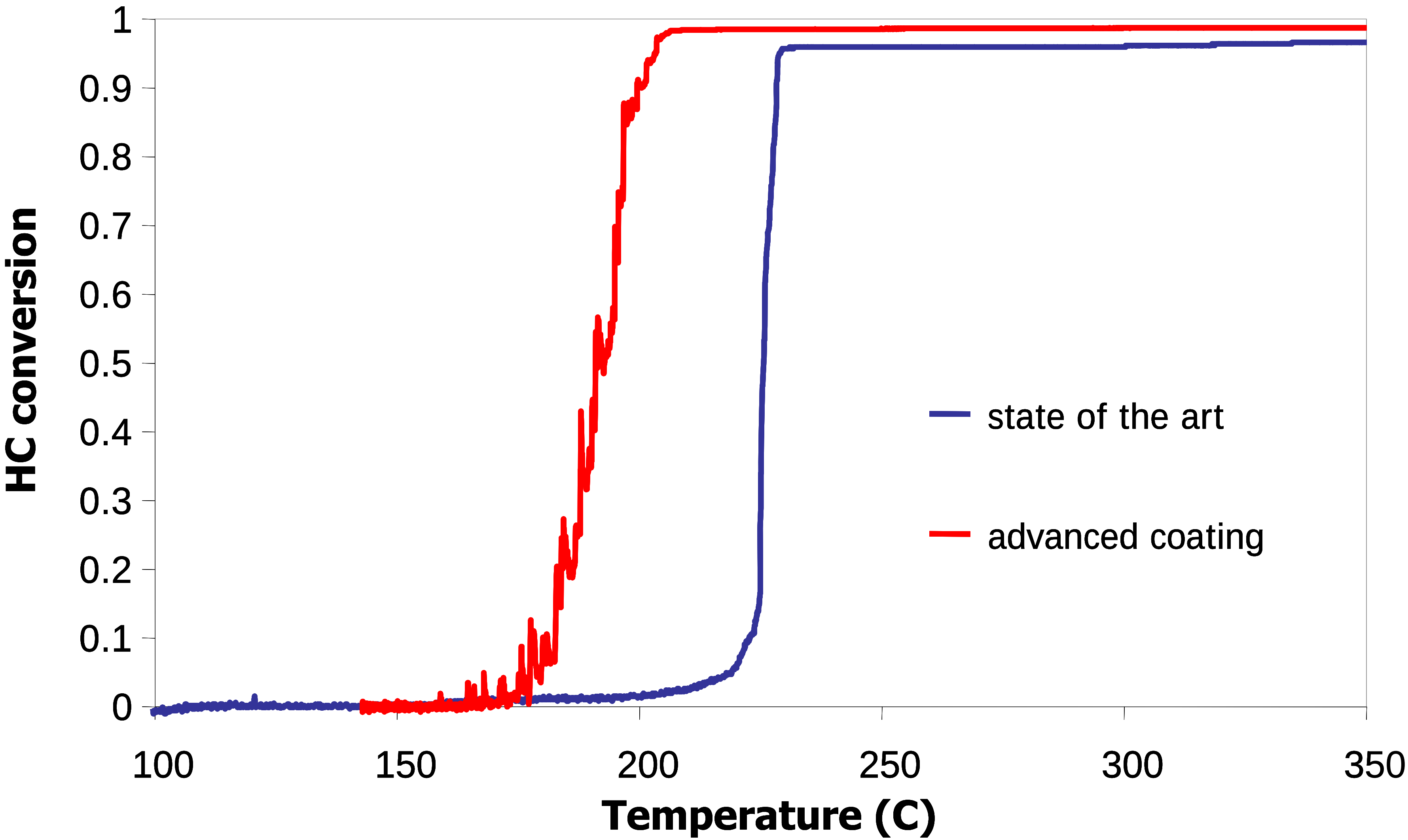
Effect of PGM addition method on soot oxidation



CO conversion

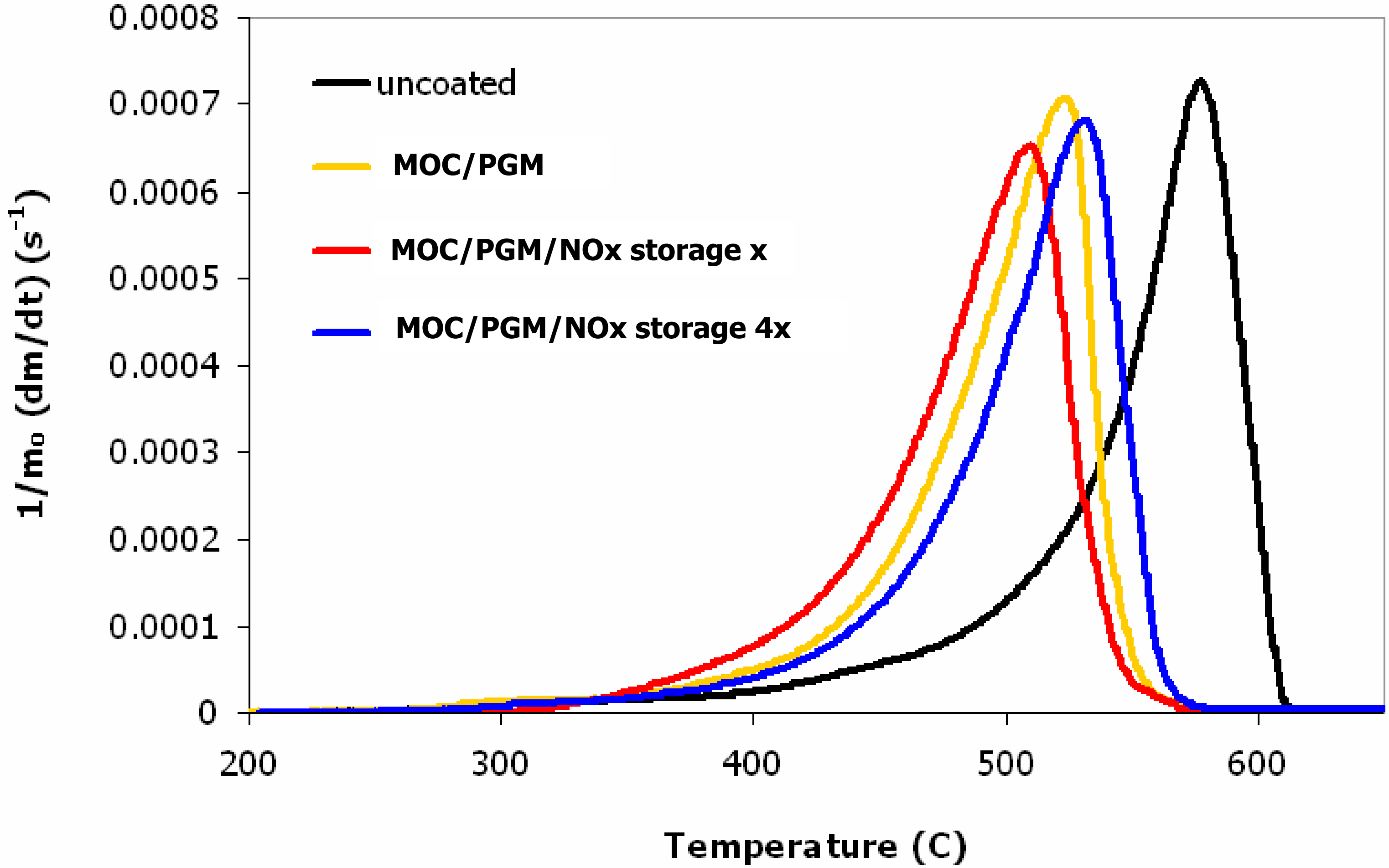


HC conversion

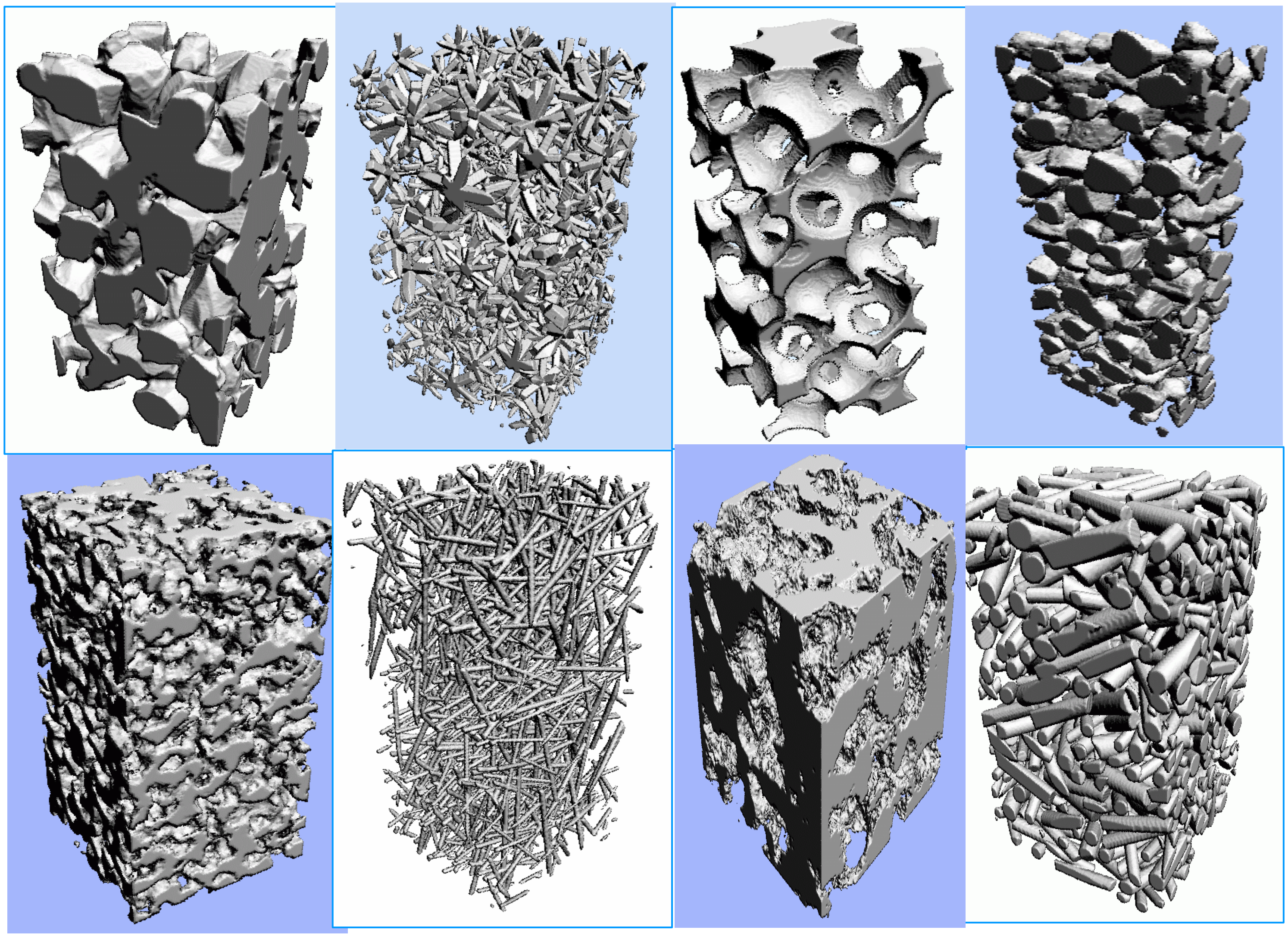


Addition of NOx storage material on soot oxidation

10% O_2 , 300 ppm NO

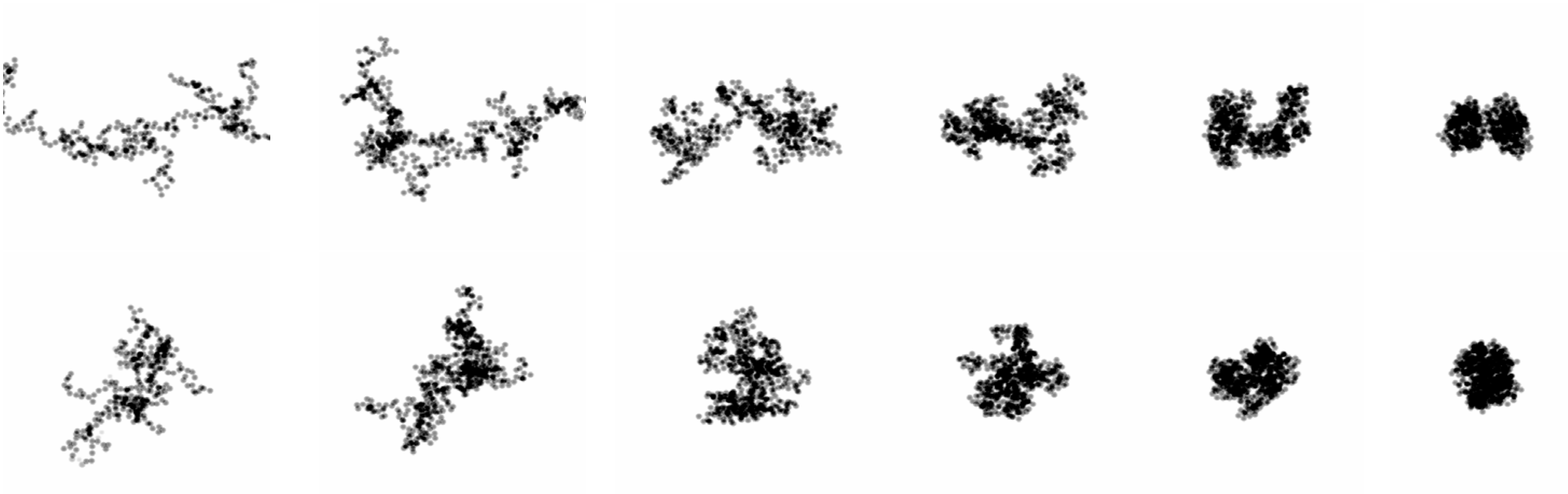


DPF Digital Materials



SAE 2006-01-0260

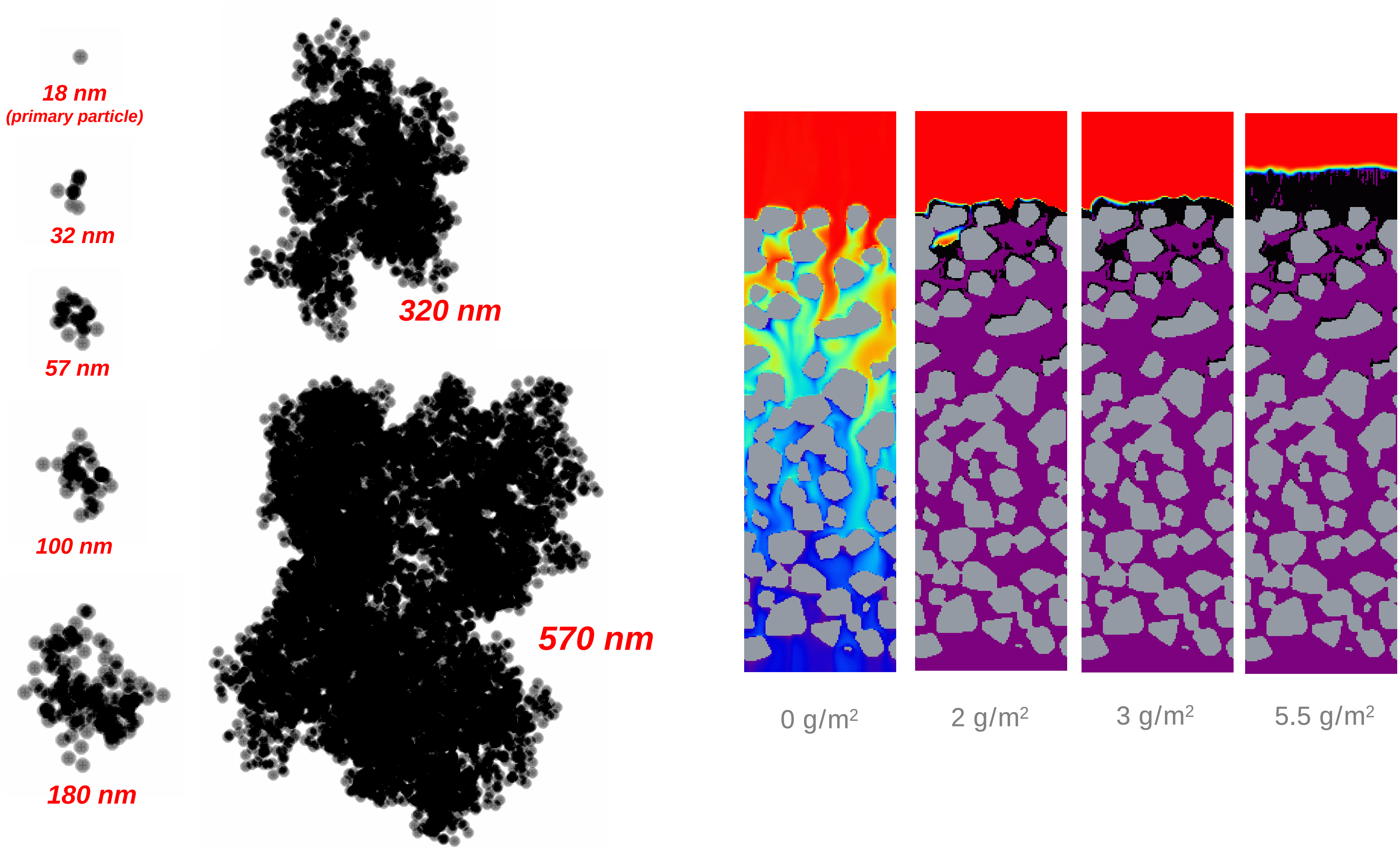
Tailored Aggregate Generator



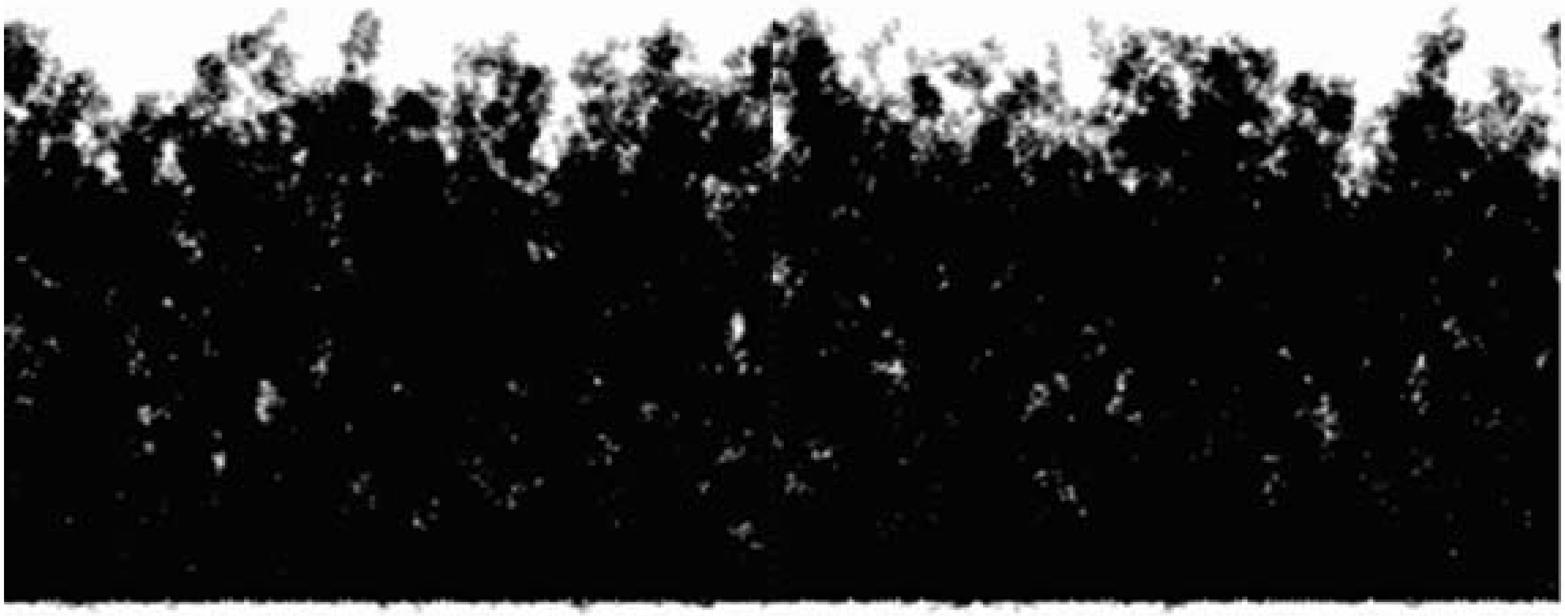
D_f=1.6 D_f=1.8 D_f=2 D_f=2.2 D_f=2.4 D_f=2.6

k_f = 1.5 N_a = 500

Soot loading simulation with actual soot aggregate geometry

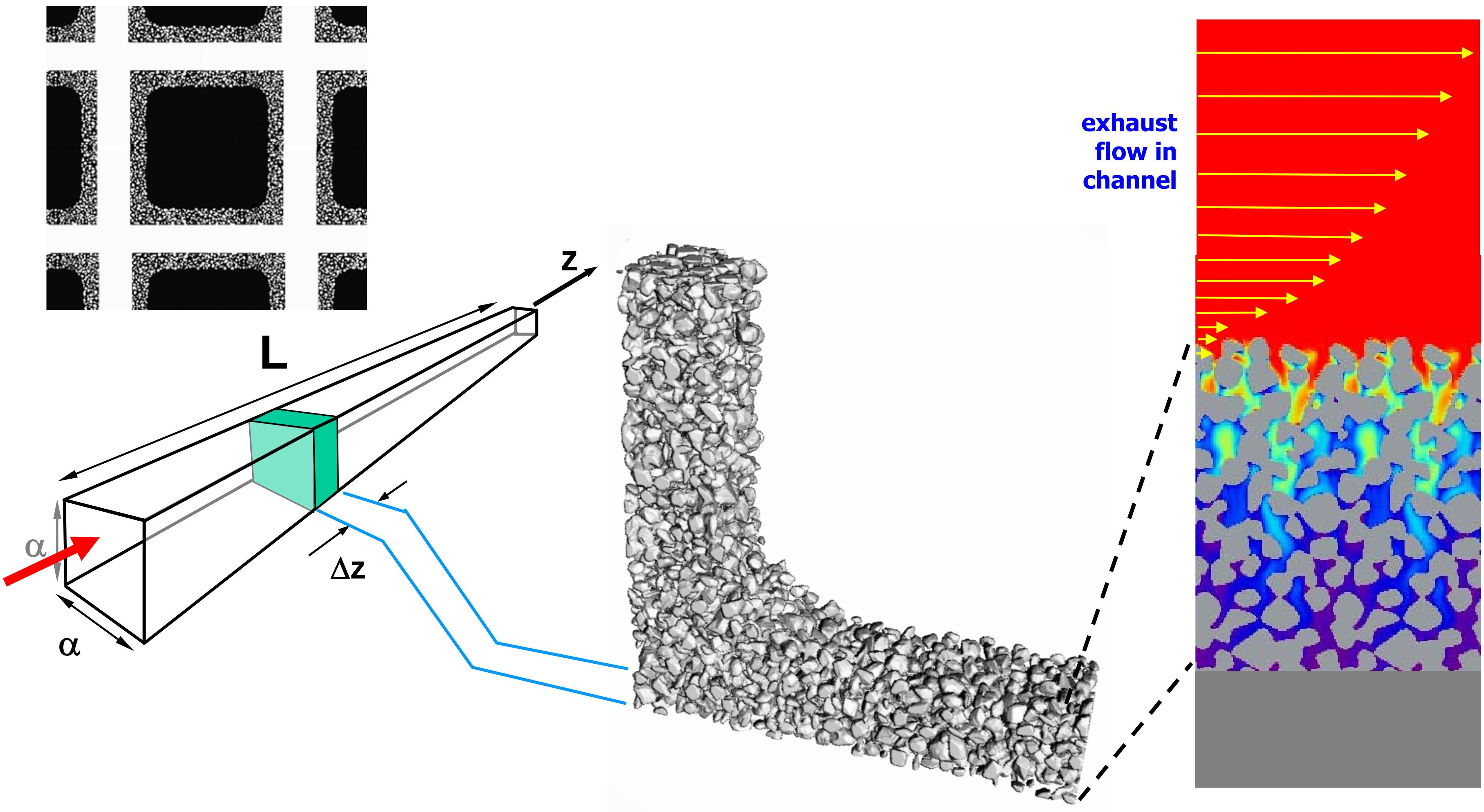


Soot loading simulation with actual soot aggregate geometry

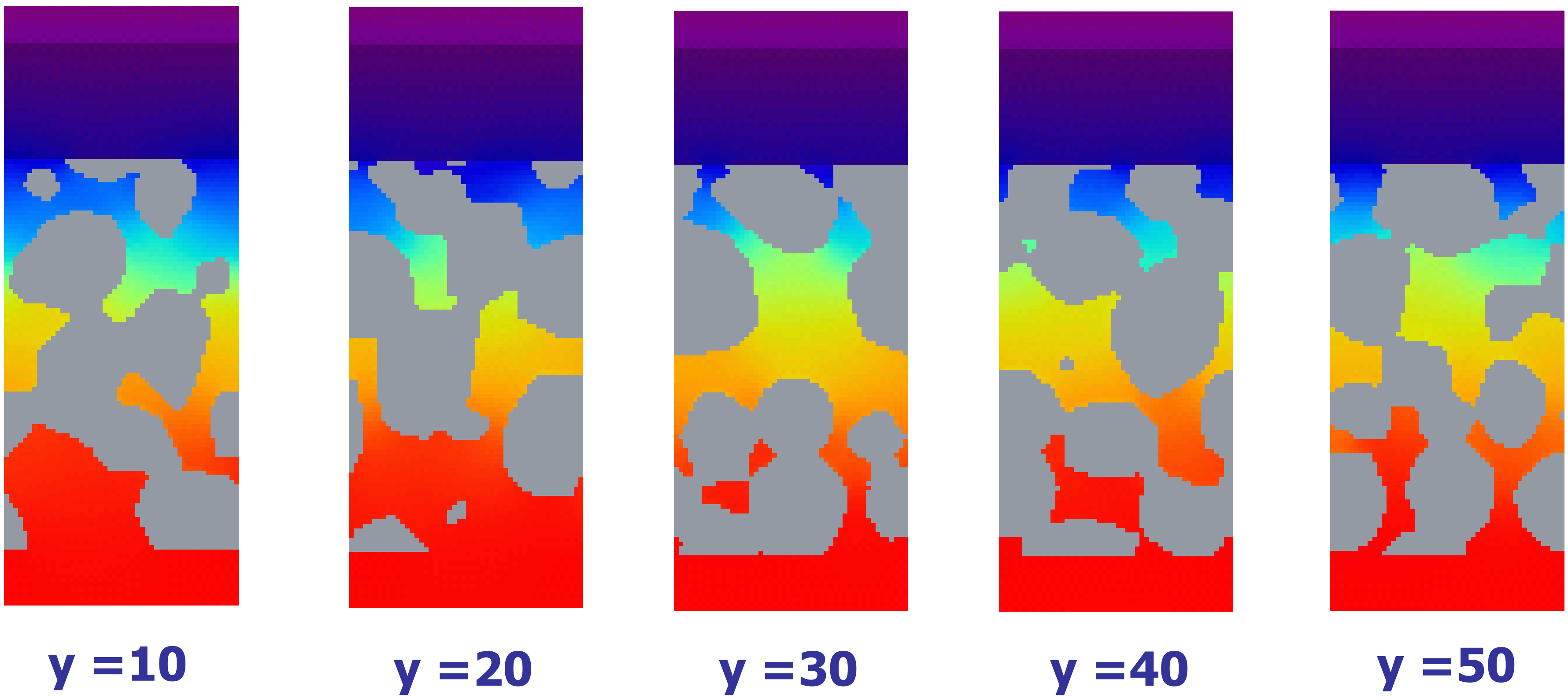


True to geometry studies of coatings

Coupled transport/reaction/separation phenomena



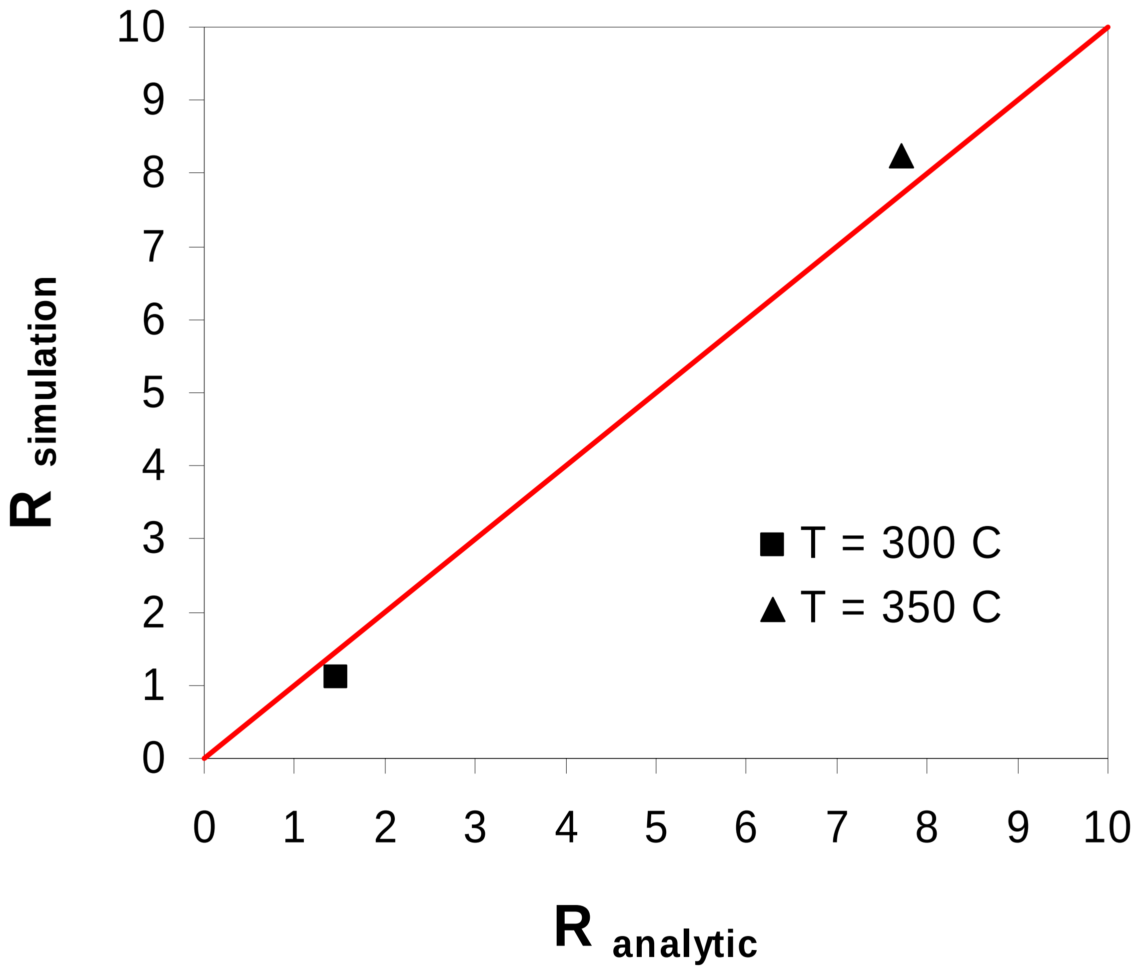
Simulation of 3-D DPF wall



NO_2 concentration through wall with catalyst at 300 C

SAE-2008-01-0442

NO_2 turnover, R: analytical vs. 3-D simulation



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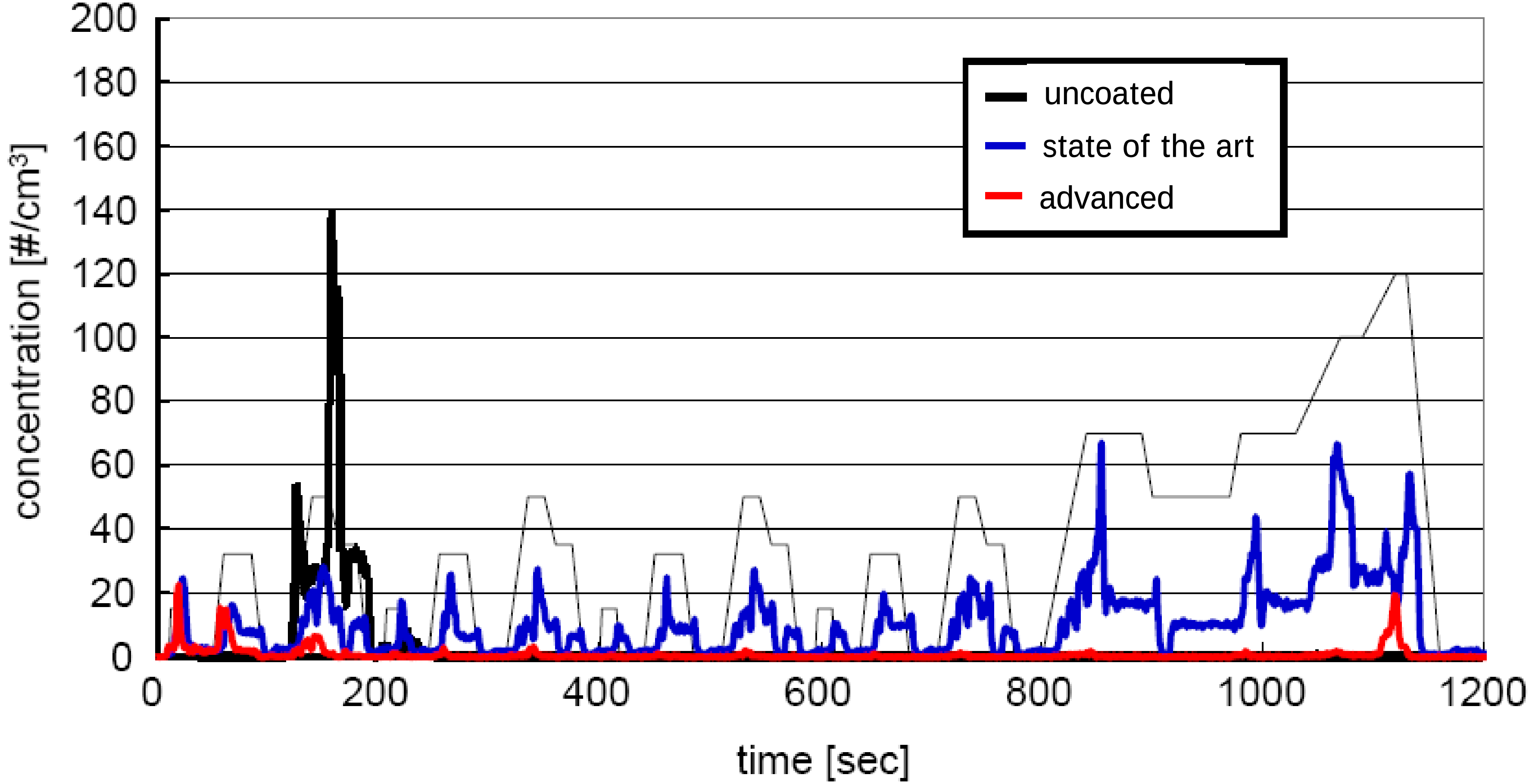
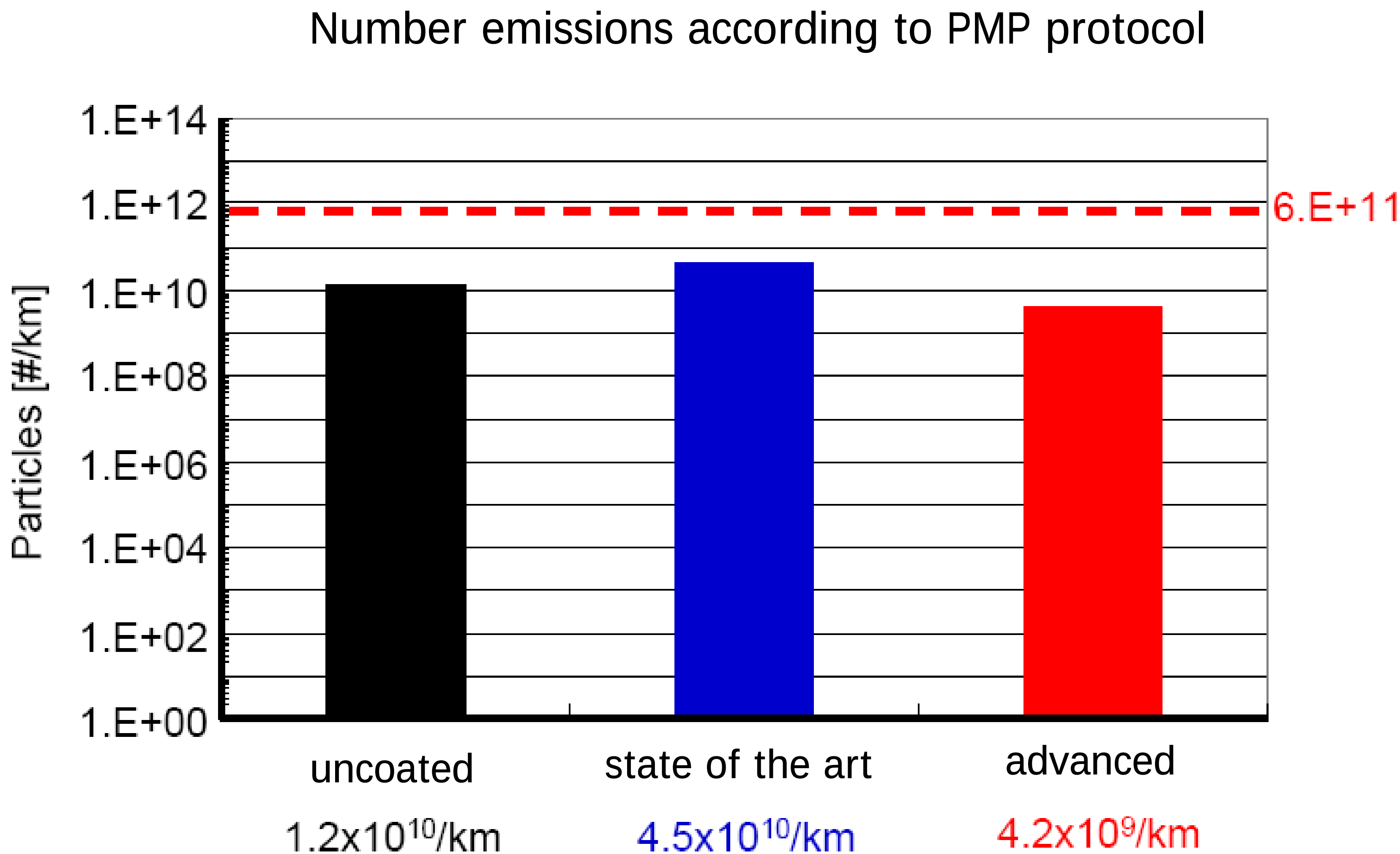
NEDC Testing of C-DPFs

Number emissions according to PMP protocol



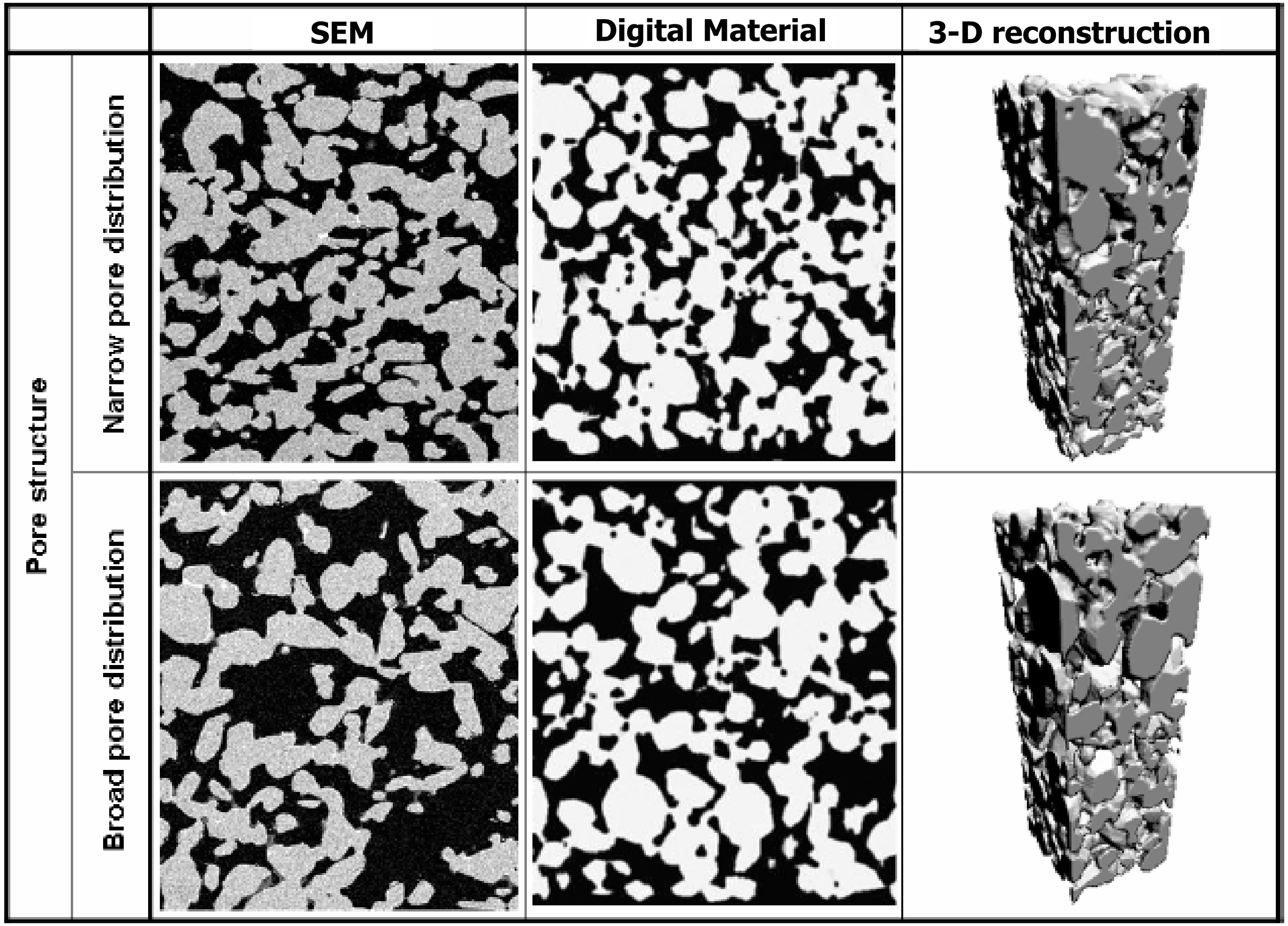
Ogyu et al., GPC 2008

NEDC Testing of C-DPFs



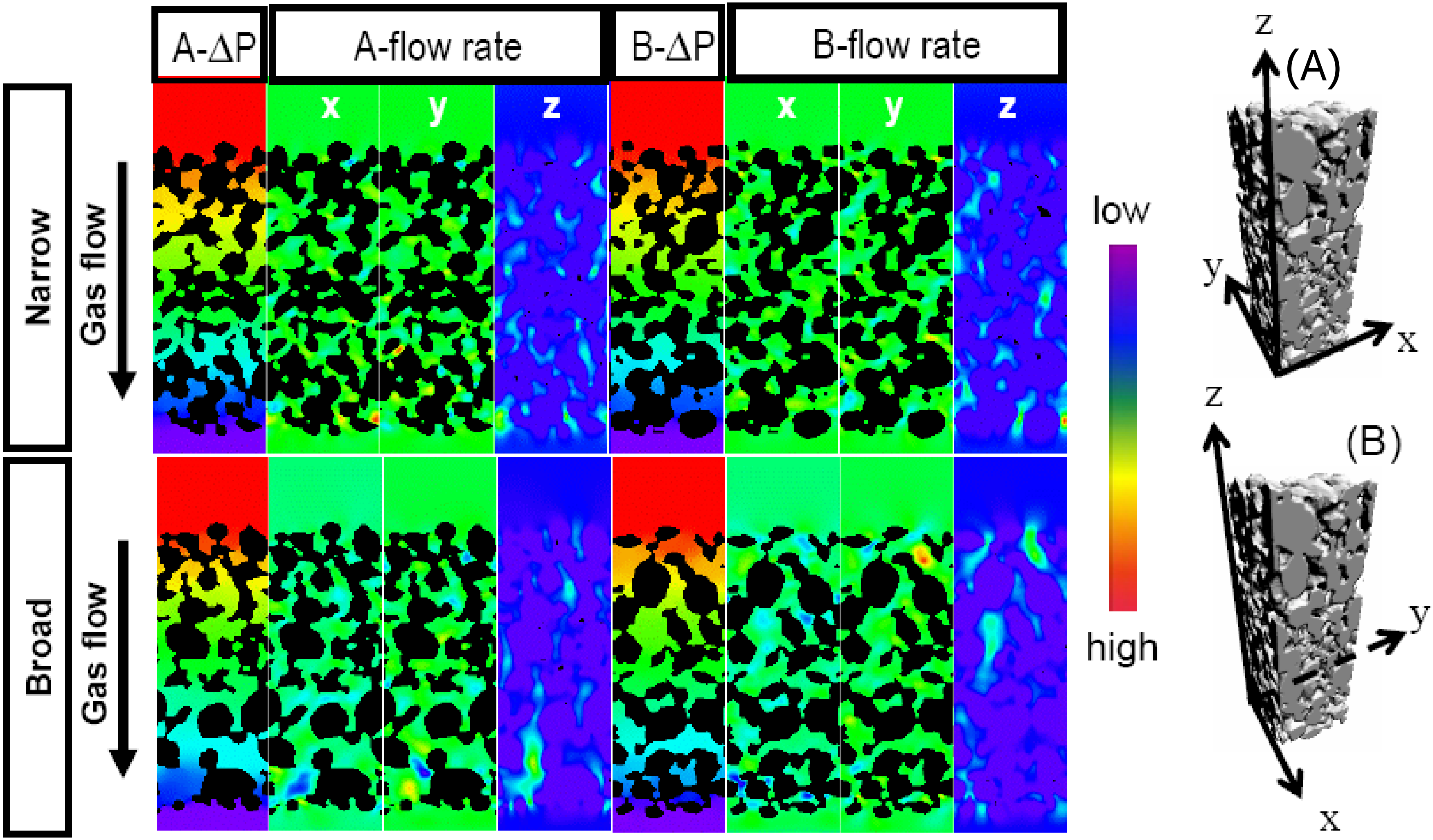
Ogyu et al., GPC 2008

Effect of Structure on Flow Distribution



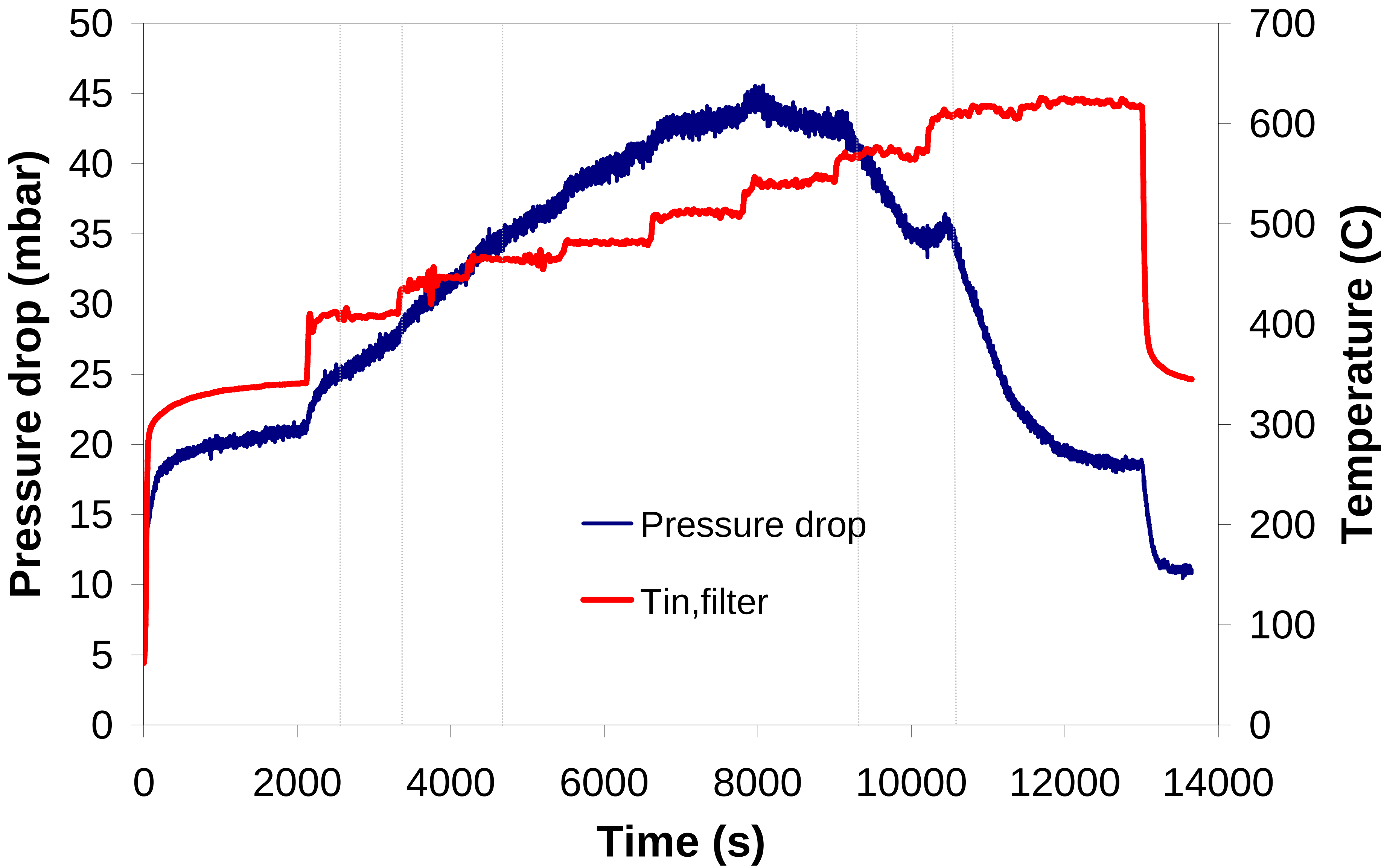
Ogyu et al., GPC 2008

Effect of Structure on Flow Distribution

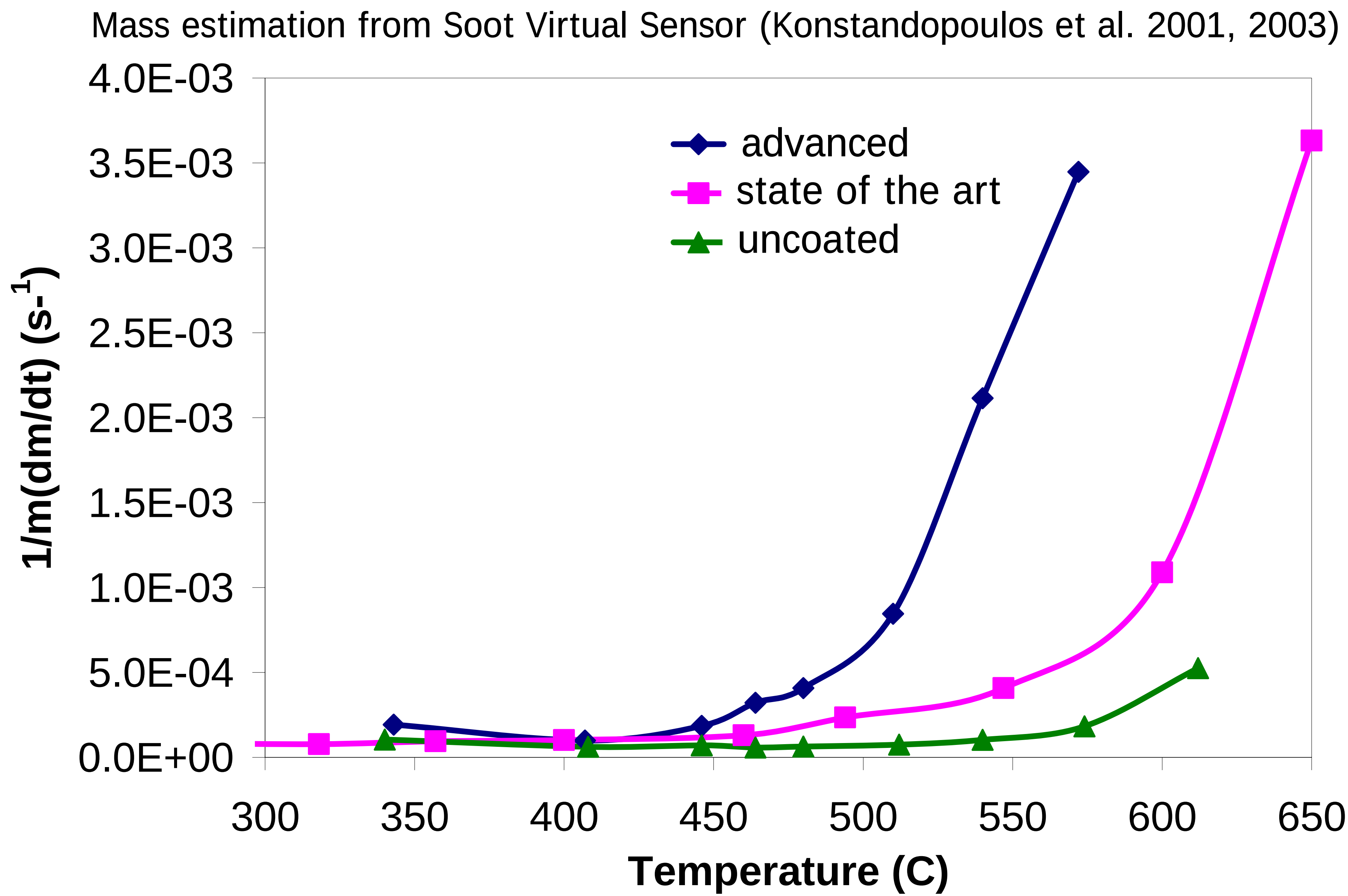


Ogyu et al., GPC 2008

DPF regeneration by HC exhaust port injection



Evolution of the soot oxidation rate with temperature



Conclusions

- A direct soot oxidation catalyst formulation (designated as MOC) was developed and tested at the powder scale and on wall flow monoliths.

- The MOC coated filter exhibited lower pressure drop during soot loading than the uncoated filter. Increase of the catalyst amount increases significantly the filtration efficiency of the filters, while the filtration efficiency attains rapidly a high value with the accumulation of only a small amount of soot on the filter.

- Total soot oxidation consists of the NO_2 oxidized soot plus the direct-catalytically oxidized soot. Optimization of PGM-MOC based multifunctional coatings must take into account the composite effect of the indirect and direct-catalytic soot oxidation. The method of preparing PGM-MOC catalytic coatings and the sequence of the material deposition on the filters plays an important role on the NO to NO_2 conversion.

- In depth understanding of the coupled transport – reaction phenomena occurring inside the microstructure of the coated walls of DPFs is highly aided by employing computational approaches based on realistic representations of all “actors” involved: nano and microstructured porous substrates/filters, catalyst coatings and dispersions and soot nanoparticle aggregates.

Acknowledgements

- European Commission for partial support of our work in emission control through projects: IPSY, ATLANTIS, PAGODE, TOP-EXPERT
- S. Lorentzou and D. Zarvalis (APT Lab)