

Multistructural aspects of catalytic soot oxidation

Souzana Lorentzou^{1,2}, Margaritis Kostoglou^{1,3}, Athanasios G. Konstandopoulos^{1,2}

¹Aerosol and Particle Technology Laboratory (APTL), Center for Research and Technology Hellas, Chemical Process Engineering Research Institute (CERTH/CPERI), 6th km Charilaou-Thermi rd. 57001, Thessaloniki, Greece

²Department of Chemical Engineering, Aristotle University, P.O. Box 1517, Thessaloniki 540 06, Greece

³Department of Chemistry, Aristotle University, P.O. Box 116, Thessaloniki 541 24, Greece

Introduction

In the history of Diesel Emission Control several routes have been developed in order to achieve reduction of particulate emissions. The Diesel Particulate Filter (DPF), and more specifically the wall-flow configuration, is considered to be the most effective means of preventing the emission of engine soot nanoparticles to the atmosphere. However, DPFs have a limit in their operation since soot accumulation inside the pores and on the filter wall leads to the increase of the backpressure in the engine. It is, therefore, essential to “regenerate” (clean) the filter from the accumulated soot. Many pathways are being investigated for the efficient regeneration of the DPFs that involve engine measures, generations of reactive gas species that can oxidize soot, as well as catalytic reactions between soot and catalytic particles.

In the present work soot-catalyst interaction is investigated on the particle-scale considering specific microstructural descriptions of the interaction of soot particles with catalysts. This entails both interaction of soot primary particles with fuel borne-catalytic nanoparticles (occluded in their bulk and/or deposited on their surface), as well as the population dynamics of soot-catalyst contacts on the walls of catalyst coated filters. Conversion dependent soot oxidation phenomena are further described by employing the so-called Two-layer Model [1], extended for the description of multiple contact states between soot and the catalyst on the porous wall.

Fuel-borne catalyst assisted soot oxidation

In the case of fuel-borne catalyst assisted soot oxidation, the major issue is the geometry of the soot-catalyst aggregates. This geometry is dominated by the in-cylinder soot generation and soot-catalyst coagulation process. In general, if the amount of catalyst is small (relative to soot amount), the catalytic particles are expected to be dispersed on the surface of the primary soot particles. If it is larger, the catalyst nanoparticles can be found on the soot primary particle surface in the form of aggregates. For even larger amounts of catalyst, catalyst nanoparticles are also occluded in the bulk of the soot primary particle. A mechanistic model for the oxidation of the soot primary particles under fuel-borne catalyst assisted oxidation, is presented accounting for the evolution of the volume of the soot particle during oxidation taking into account both surface recession by the oxidation reaction as well as density changes due to mobility of catalyst nanoparticles from the surface into the bulk. As the model includes mechanisms of surface and volume reactions it can recover both limiting cases of oxidation models, ie the shriking core and shriking density configurations, depending on values of the governing parameters. The model can describe the patterns of conversion dependent soot oxidation rates seen in experiments [2].

Soot oxidation on catalyst coated filters

Based on microscopic observations it can be assumed that there are multiple contact states among soot particles and the catalyst sites, and the evolutionary dynamics of these contacts determines the overall soot oxidation rate. The population dynamics of soot-catalyst contacts (the “making and breaking” of contacts) is modeled with two mechanisms. The first mechanism is a transition mechanism responsible for the replacement of oxidized soot particles in a higher contact state by

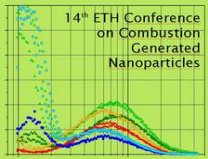
particles in a lower contact state. The second mechanism is oxidative fragmentation. This may cause transfer of soot from lower to higher contact states. The transition and the fragmentation mechanism depend on the structure of the catalyst coating. The model can describe the patterns of conversion dependent soot oxidation rates seen in experiments [2].

Conclusions

The Two-layer model [1], a relatively simple and flexible mathematical model, has been successfully extended further to describe the complex conversion dependent phenomena that appear during fuel-borne catalyst soot oxidation as well as on the surface of catalyst coated filters, by explicitly incorporating mechanistic and microstructural interactions between soot and catalyst particles.

References

1. Konstandopoulos A.G., Kostoglou M., "A mathematical model of soot oxidation on catalytically coated ceramic filters" *Advances in Vehicle Control and Safety*, Amiens, France, 137-143, 1998.
2. Konstandopoulos A.G., Kostoglou M., Lorentzou S., Pagkoura C., Papaioannou E., Ohno K., Ogyu K., Oya T., "Soot Oxidation Kinetics in Diesel Particulate Filters", in *SAE Tech. Paper*, No. 2007-01-1129, SAE SP, 2140 Diesel Exhaust Emission Control Modeling. Also in *SAE Trans.* 116 (J. Fuels & Lubricants), pp. 173-181.



14th Conference on Combustion Generated
Nanoparticles
1-4th August 2010, Zürich

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Outline

- Motivation
- The Two-layer model
- Description of Experiments with the Two-Layer model
 - on catalyst coated filters
 - on fuel-borne catalysts
- Conclusions

Trends in OEM Diesel Particulate Filter Technology

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 to NO₂ conversion and NO₂-assisted oxidation of soot (*indirect action of catalyst*).

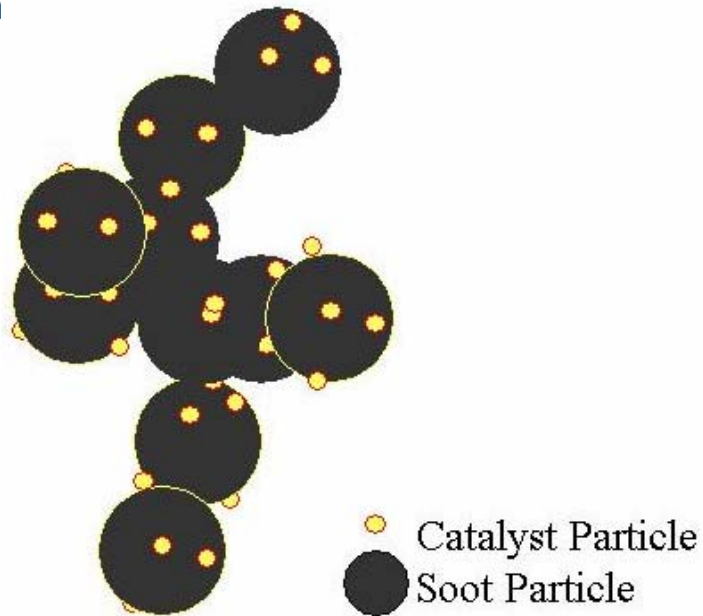
2010... Targeting of *direct soot oxidation* by oxygen transfer from base metal oxide catalysts. **Reduction/elimination of PGM**.

Higher porosity substrates to accommodate larger (multi-functional) catalyst loads and provide better soot-

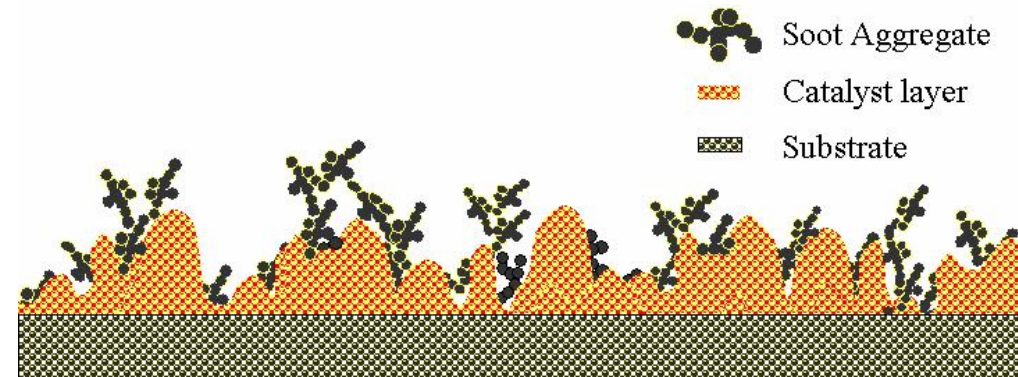
Direct Catalytic Soot Oxidation Kinetics

Soot-Catalyst contact is recognized as a major factor since 1981

Fuel Borne Catalyst (FBC)



Catalyst Coated Filter



The Two-Layer Model of Soot Oxidation in a Catalytic Coating

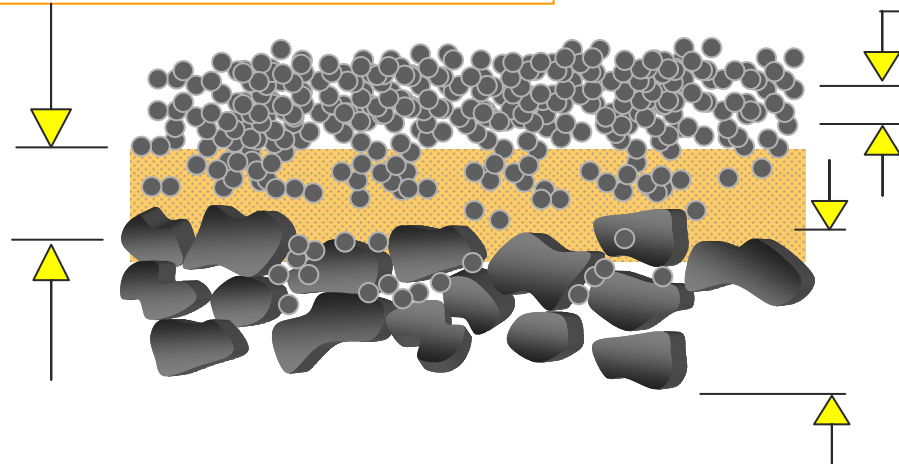
Layer I: Catalyst affected “layer”

Catalyst coating can interpenetrate/overlap partially with top part of the wall. Hence better to describe it in terms of a spatial “field of catalyst activity”.

Particles oxidize when found within the “field of activity” are considered *in contact* with the catalyst. Fraction $\beta \in [0-1]$ of the soot surface in contact with the catalyst depending on coating structure.

Layer II: Soot “layer”

Soot particles form a “queue” on top of the filled-up catalyst layer. They can enter into catalyst affected layer depending on an interaction parameter $\xi \in [0-1]$.



Filter wall

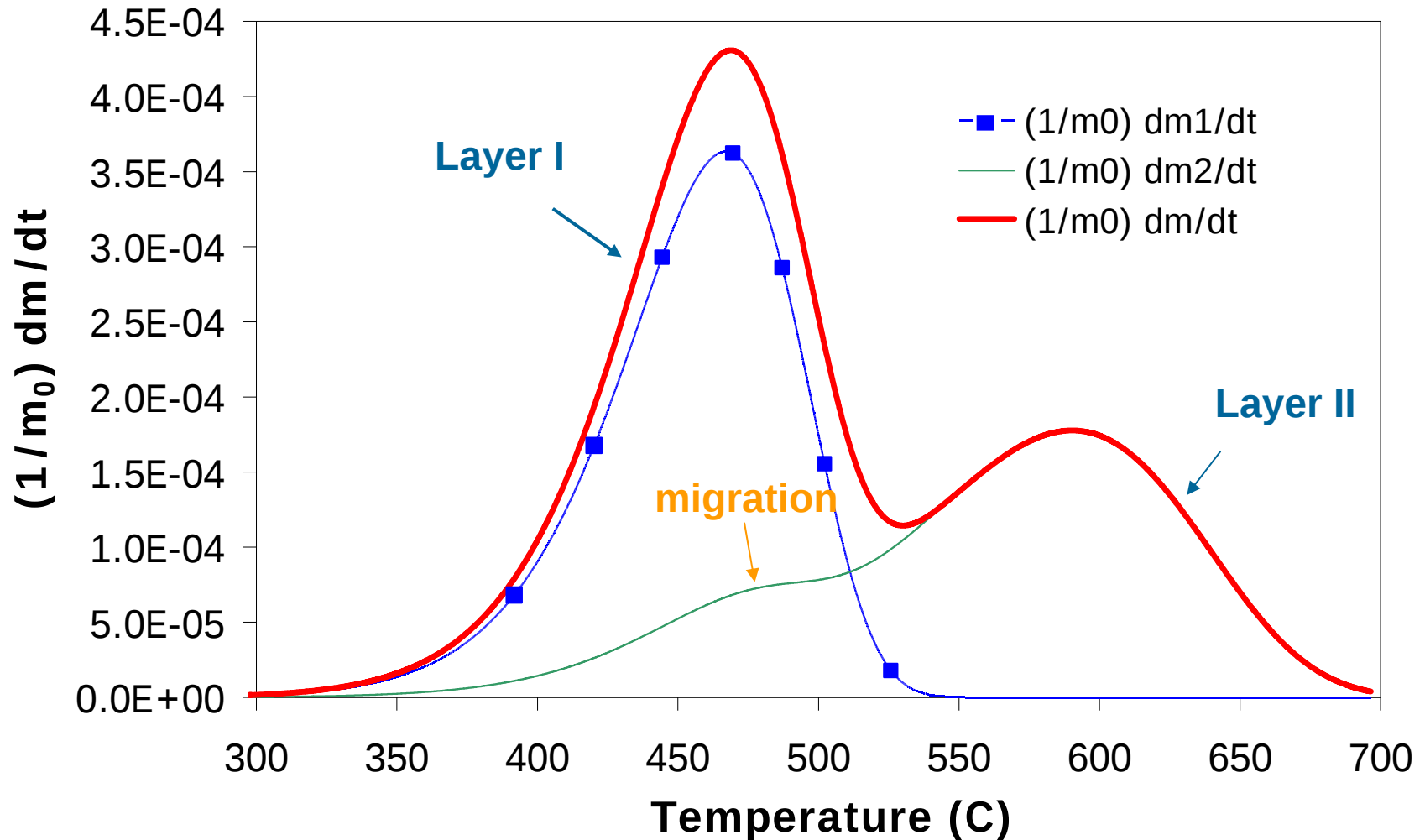
Very small amount of particles stay in the wall of catalyzed DPFs. Exponentially distributed across the wall thickness.

$$\frac{dm_1}{dt} = (-k_{cat}\beta m_1 - k_{th}(1-\beta)m_1)(1-\xi)$$

$$\frac{dm_2}{dt} = -(k_{th}m_2 + \xi(\beta k_{cat}m_1 + (1-\beta)k_{th}m_1))$$

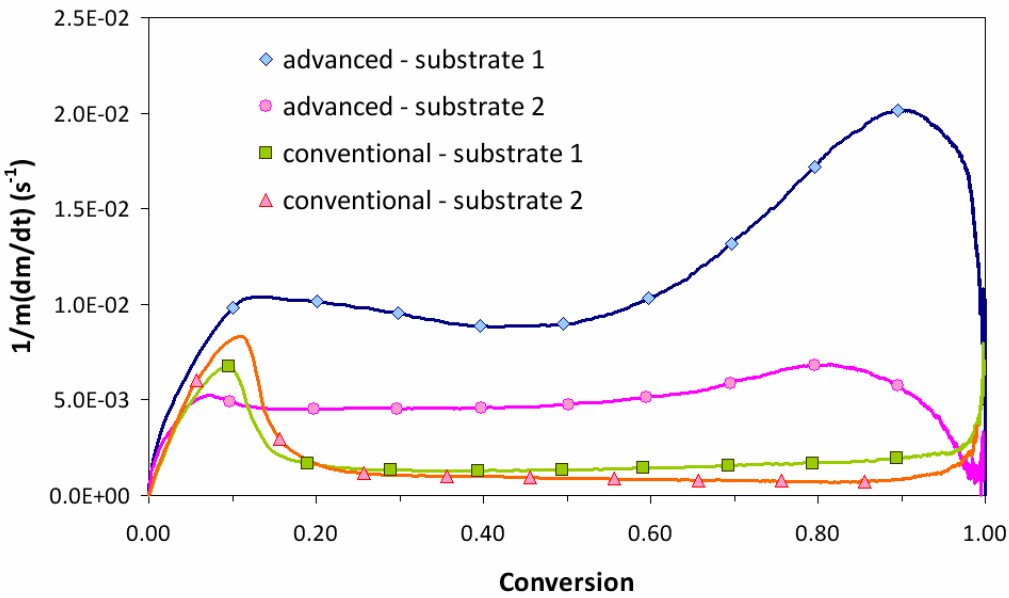
For FBC only
Layer I is applied

Soot oxidation rate based on Two-Layer Model

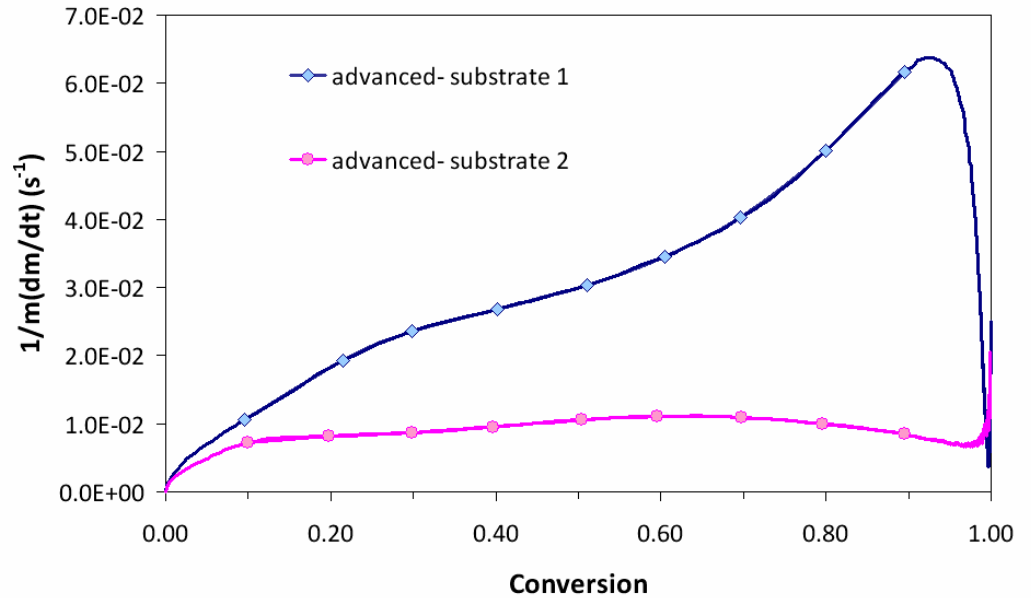


Conversion Dependent Soot Oxidation on Catalyzed DPF

T = 620C



T = 650C



Two-Layer Model: Population Dynamics of Multiple Contact States

Soot oxidation rate $\left(\frac{dm_i}{dt}\right)_{\text{ox}} = -k_i m_i = -\beta_i k m_i$ for $i=1$ to n , $k_i > k_{i+1}$

Mobility
mechanisms

Transition $\left(\frac{dm_{i+1}}{dt}\right)_{\text{trans}} = \xi_i \left(\frac{dm_i}{dt}\right)_{\text{ox}}$

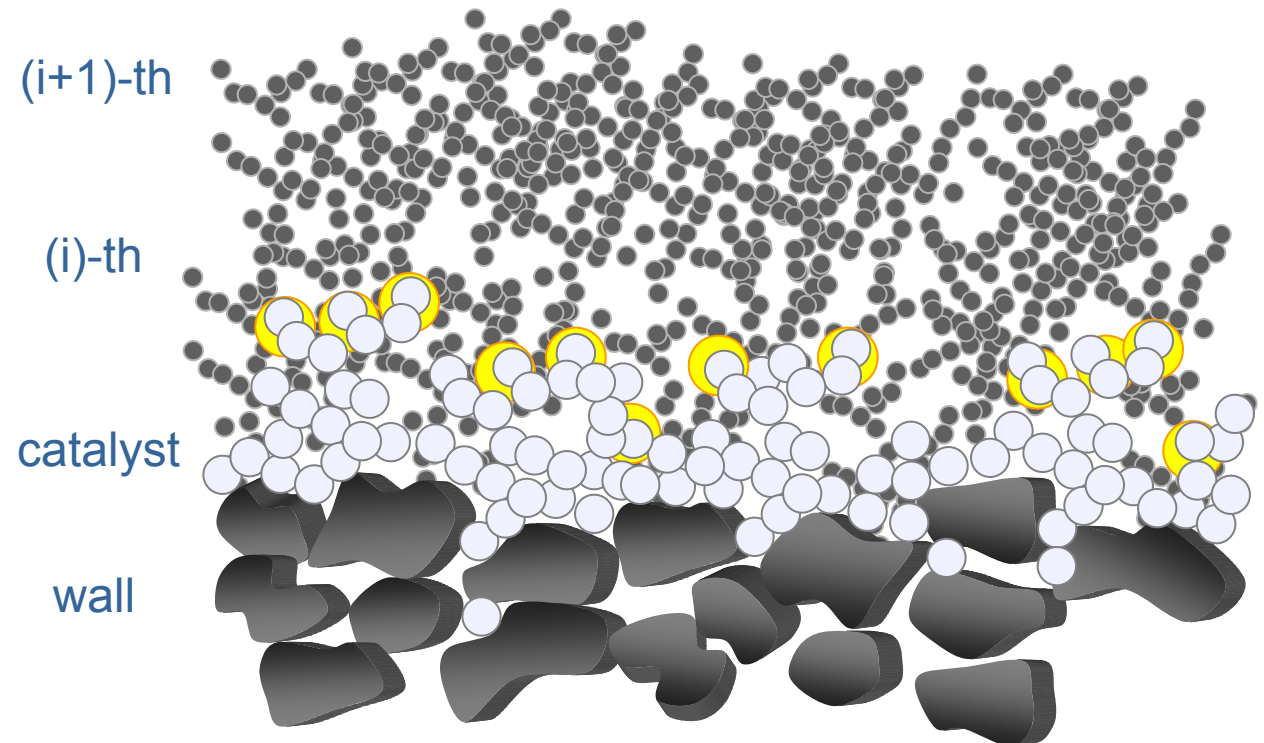
Fragmentation $\left(\frac{dm_i}{dt}\right)_{\text{frag}} = -f_i m_i^c$

Two-Layer Model: Population Dynamics of Multiple Contact States

Transition

$$\left(\frac{dm_{i+1}}{dt} \right)_{\text{trans}} = \xi_i \left(\frac{dm_i}{dt} \right)_{\text{ox}}$$

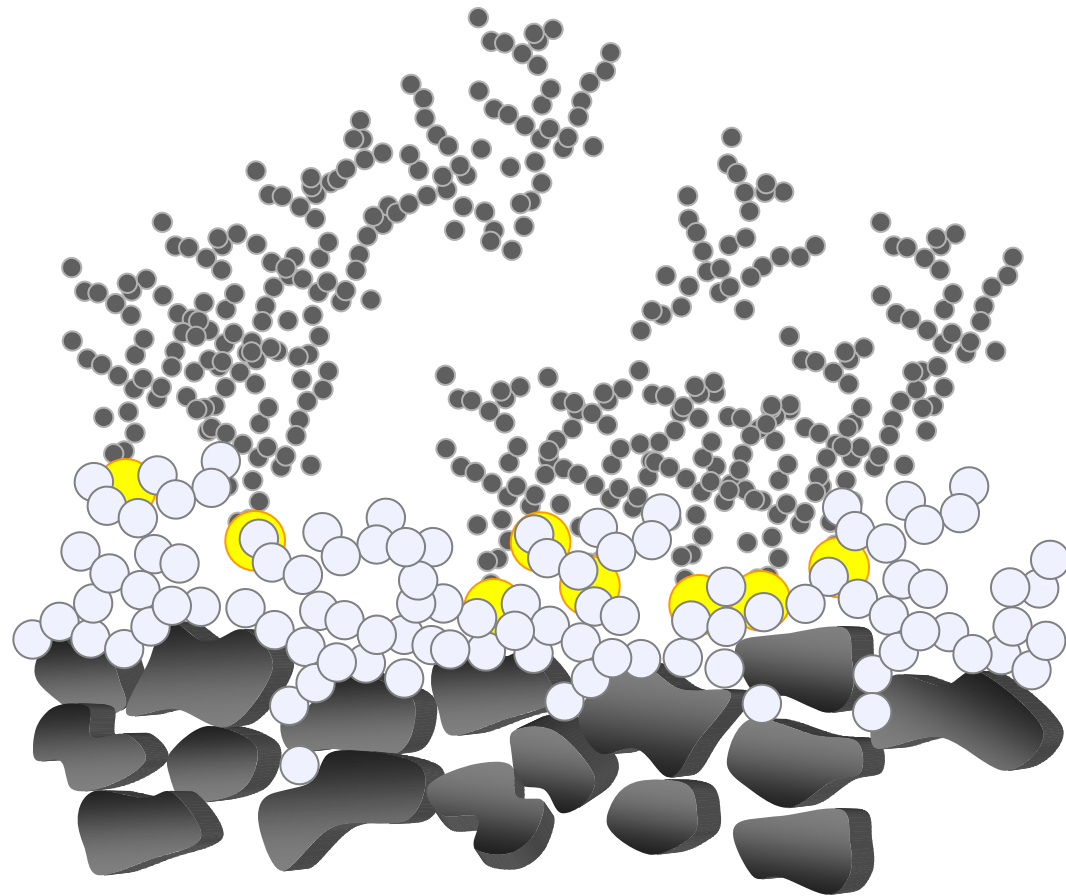
partial replacement of the oxidized soot in the i -th state by soot from the $(i+1)$ -th state – Transition mechanism (as before) see also videos by Hanamura et al (2008).



Two-Layer Model: Population Dynamics of Multiple Contact States

Fragmentation

$$\left(\frac{dm_i}{dt} \right)_{\text{frag}} = -f_i m_i^c$$



(percolative fragmentation, Konstandopoulos and Kostoglou, 2003)

Two-Layer Model: Population Dynamics of Multiple Contact States

Soot oxidation rate $\left(\frac{dm_i}{dt}\right)_{\text{ox}} = -k_i m_i = -\beta_i k m_i \quad \text{for } i=1 \text{ to } n, k_i > k_{i+1}$

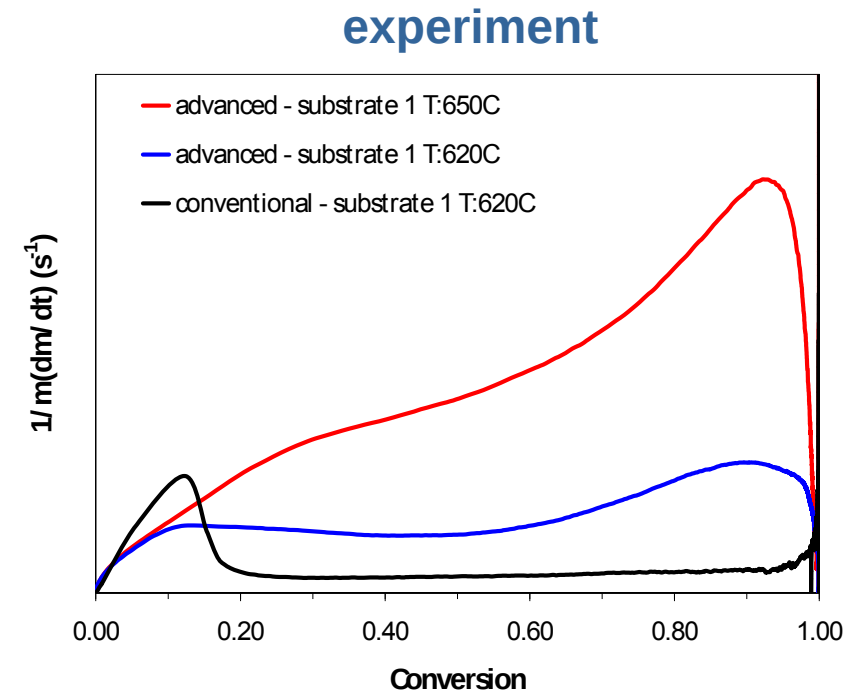
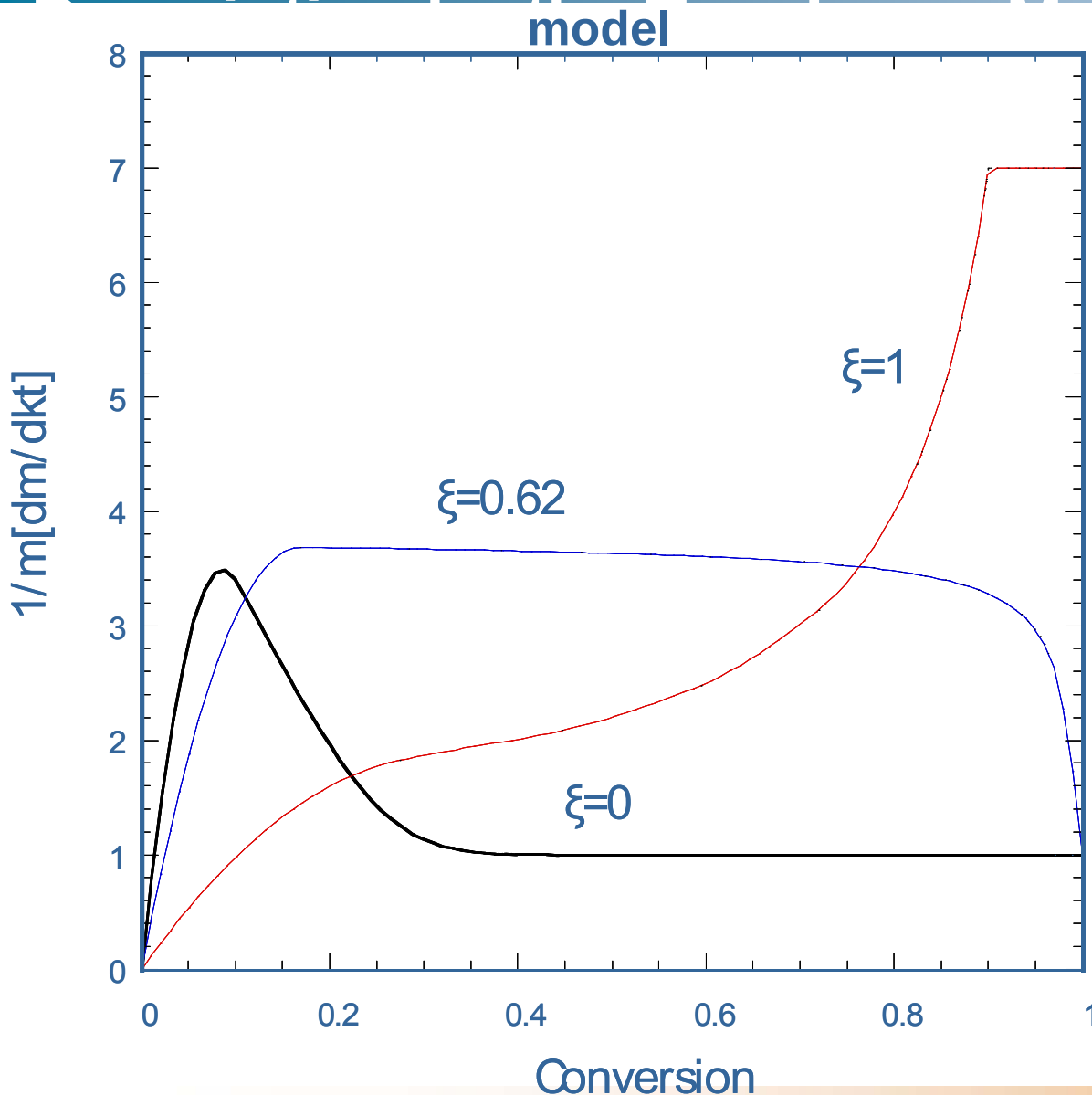
Mobility mechanisms

$$\left\{ \begin{array}{l} \text{Transition} \quad \left(\frac{dm_{i+1}}{dt}\right)_{\text{trans}} = \xi_i \left(\frac{dm_i}{dt}\right)_{\text{ox}} \\ \text{Fragmentation} \quad \left(\frac{dm_i}{dt}\right)_{\text{frag}} = -f_i m_i^c \end{array} \right.$$

Sum up all rates

$$\left\{ \begin{array}{l} \frac{dm_1}{dt} = -(1 - \xi_1) k_1 m_1 + \sum_{j=2}^n p_{1,j} f_j m_j^c \\ \frac{dm_i}{dt} = -(1 - \xi_i) k_i m_i - \xi_{i-1} k_{i-1} m_{i-1} - f_i m_i^c + \sum_{j=i+1}^n p_{i,j} f_j m_j^c \\ \frac{dm_n}{dt} = -k_n m_n - \xi_{n-1} k_{n-1} m_{n-1} - f_n m_n^c \end{array} \right.$$

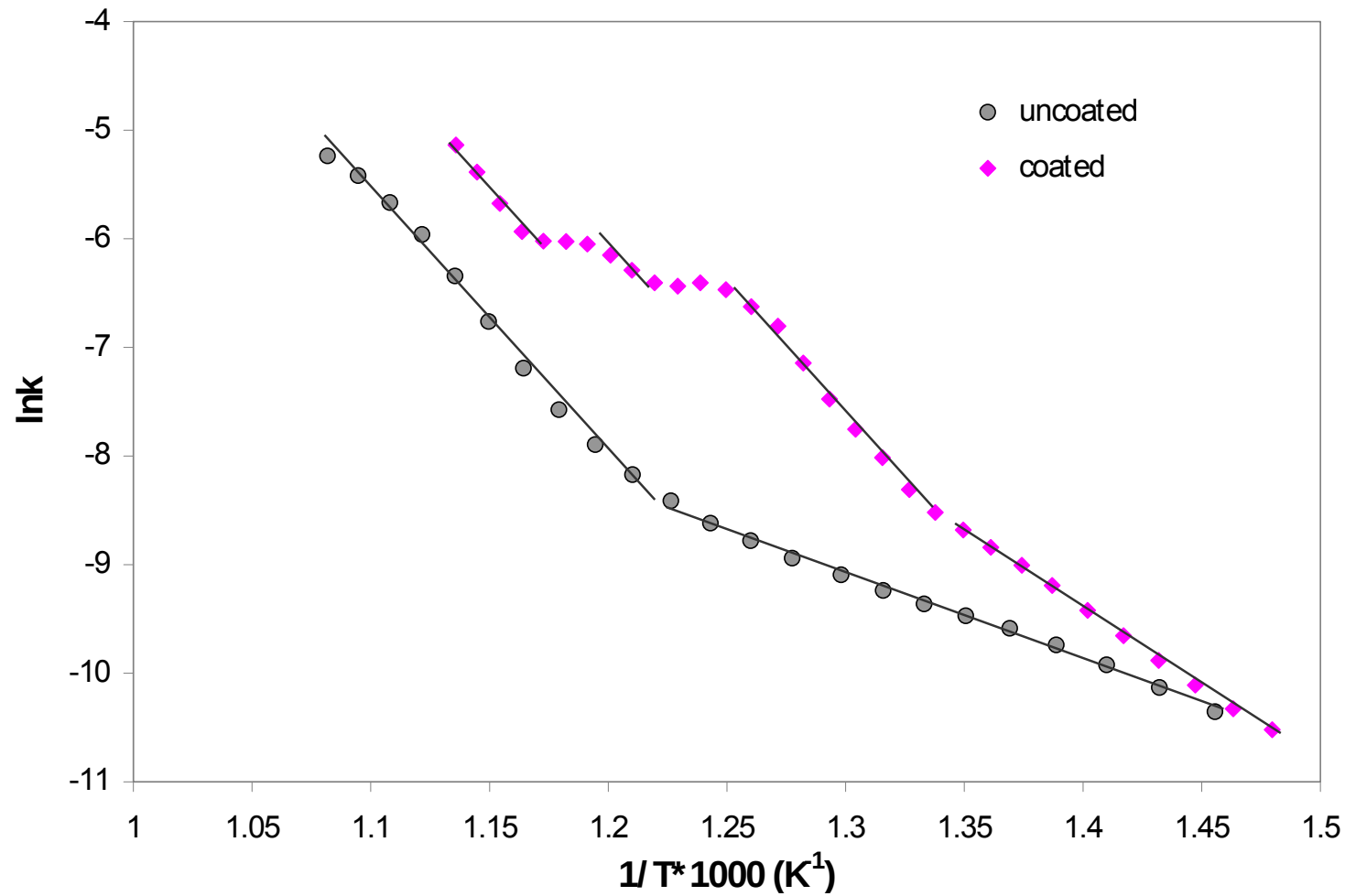
Conversion Dependent Soot Oxidation on Catalyzed DPF



Prediction of the basic patterns that appear in the experimental results. ξ increases with the increase of temperature and it is higher for the advanced than the conventional coating.

Direct Soot Oxidation on Catalytic DPF

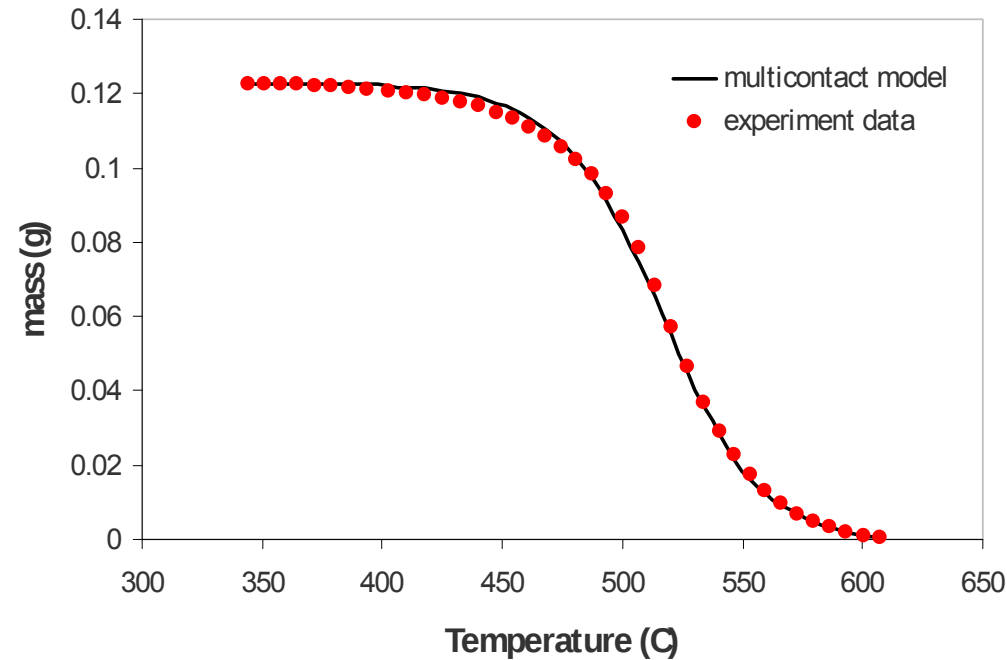
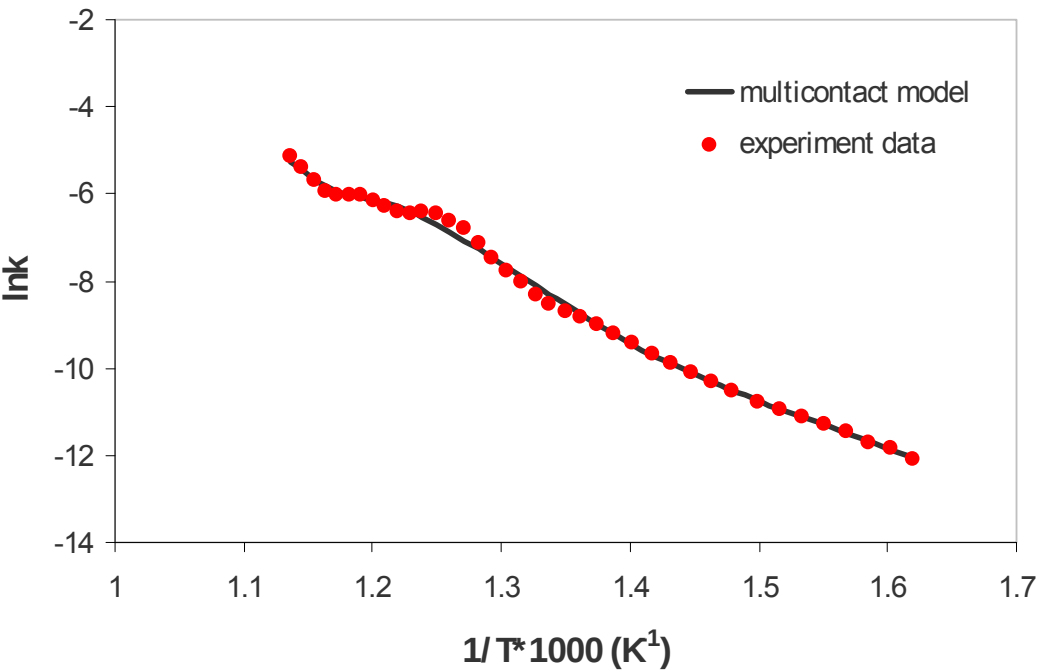
Temperature programmed experiments



Presence of multiple states

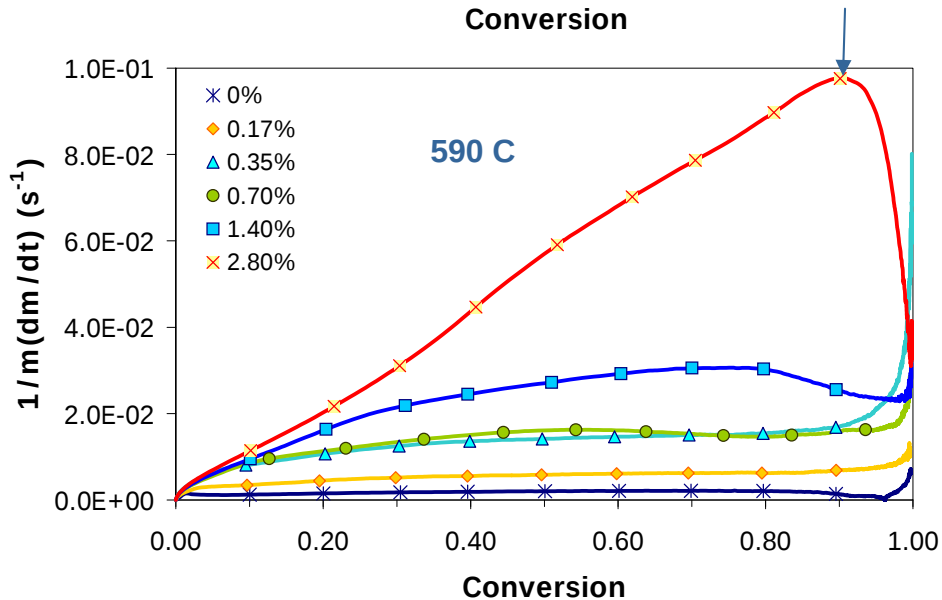
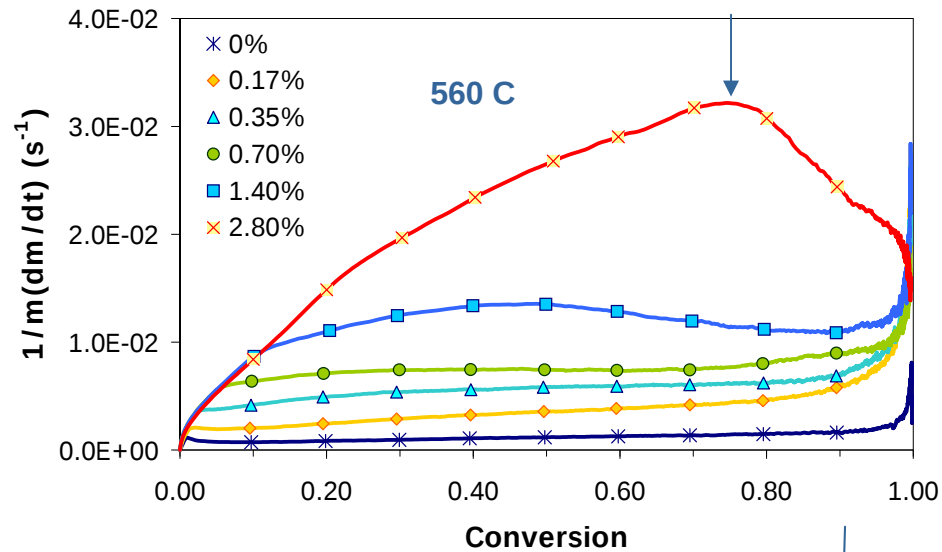
Application on Catalytic DPF

3 population model



Good agreement of the experimental data with the theoretical fit.

Soot Oxidation by FBC – Isothermal experiments



SAE 2004-01-0071, Rhodia

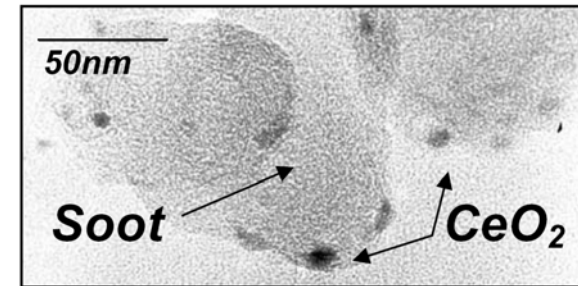


Fig. 3: Ceria distribution in the soot

Song et al. (2006) Comb. Flame

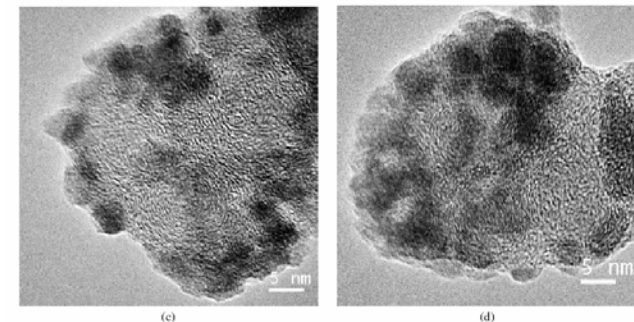


Fig. 4. High-resolution TEM images for the interfacial structure of two catalyzed soots: (a, b) FBC-doped soot at 75% load; (c, d) FBC-doped soot at 25% load.

Occluded/Deposited Nanoparticle Catalyst Model

Extension of: “Size distribution dynamics of fuel-borne catalytic ceria nanoparticles” Kostoglou, Konstandopoulos and Bartscher (2007)

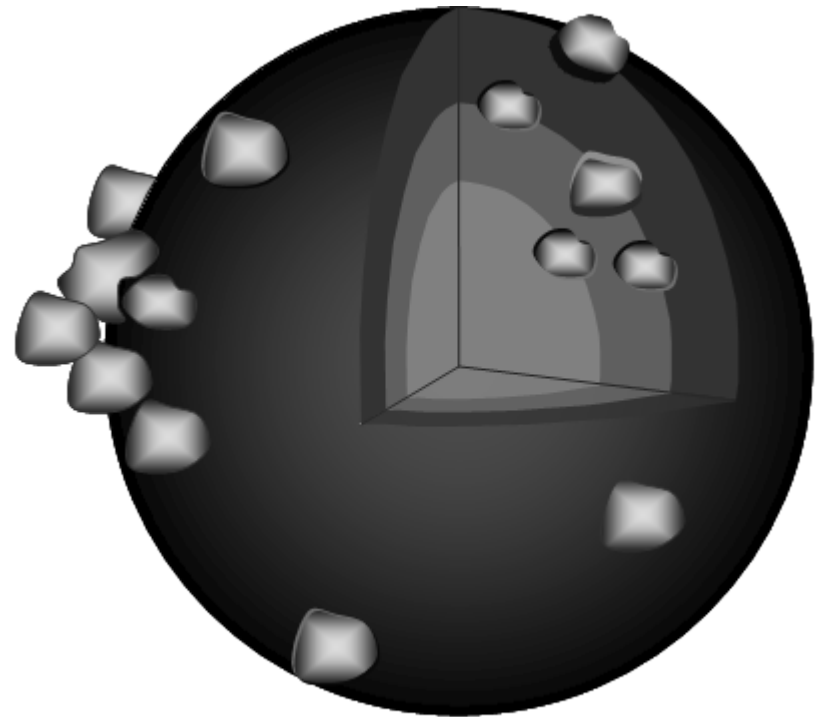
- FBC nanoparticles exist on the surface and in the bulk of soot primary particles depending on the FBC concentration
- Both volume and density of soot primary particle can vary

Volume evolution equation

$$\frac{dV}{dt} = -k_s A c_s (1 - e^{-(c_{crit} / c_s)^n})$$

Density evolution equation

$$\frac{d\rho}{dt} = -k_v c_{in} \rho e^{-\alpha(c_{in} / \rho)}$$



Occluded/Deposited Nanoparticle Catalyst Model

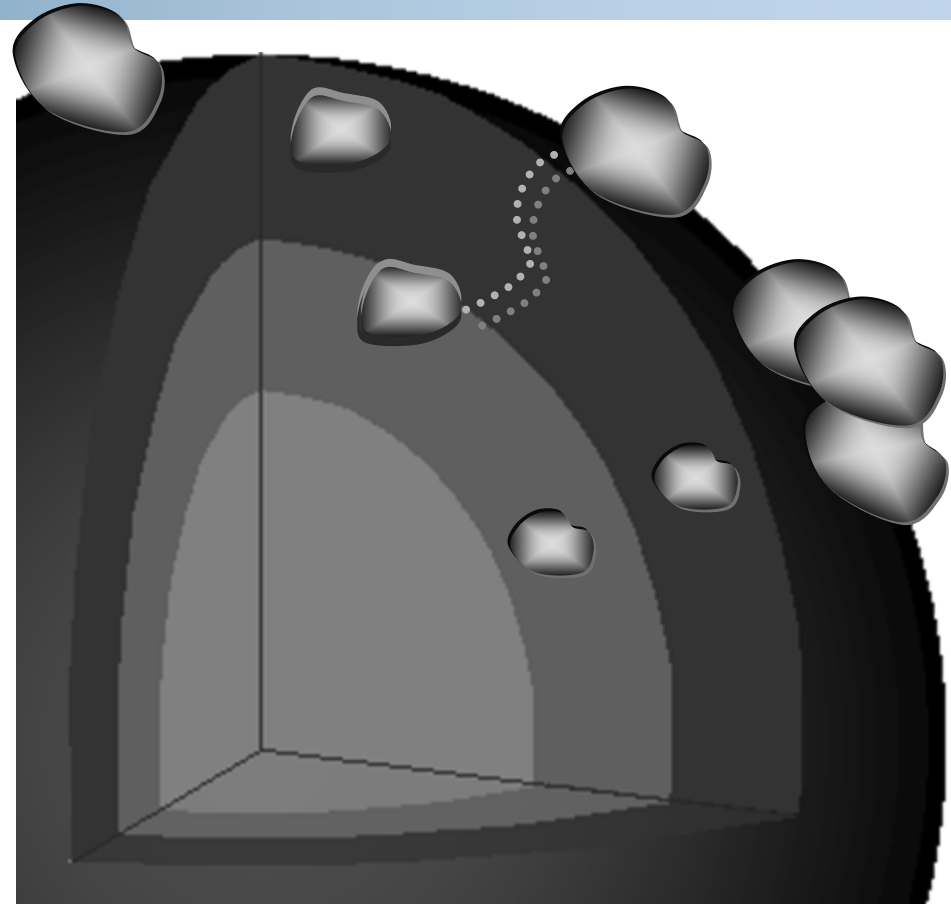
- Surface nanoparticles enter the bulk as the volume is oxidized (“worm in an apple”)
Surface FBC nanoparticle concentration

$$c_s = \frac{A_o c_{so}}{A} F_1(V/V_o)$$

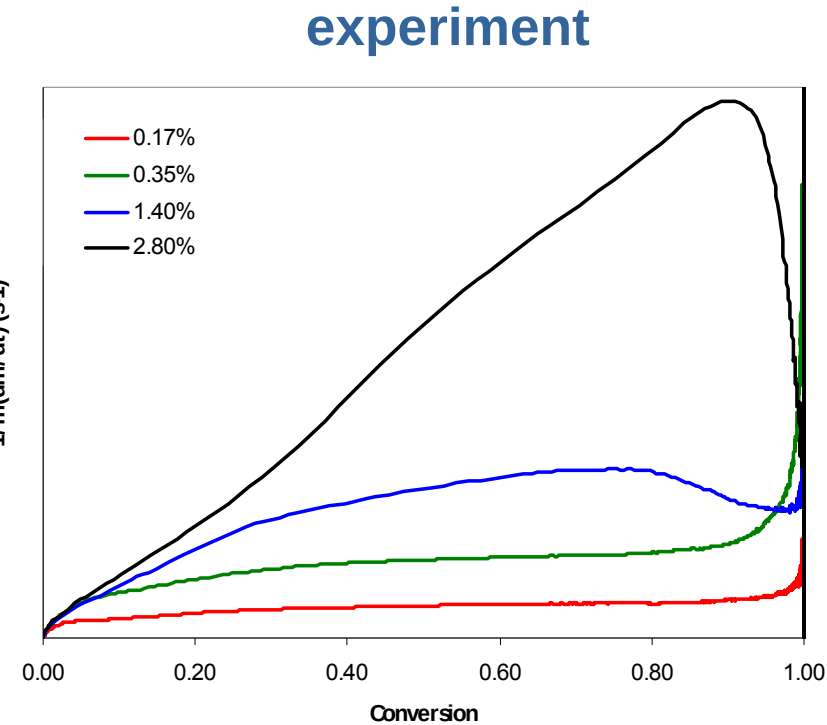
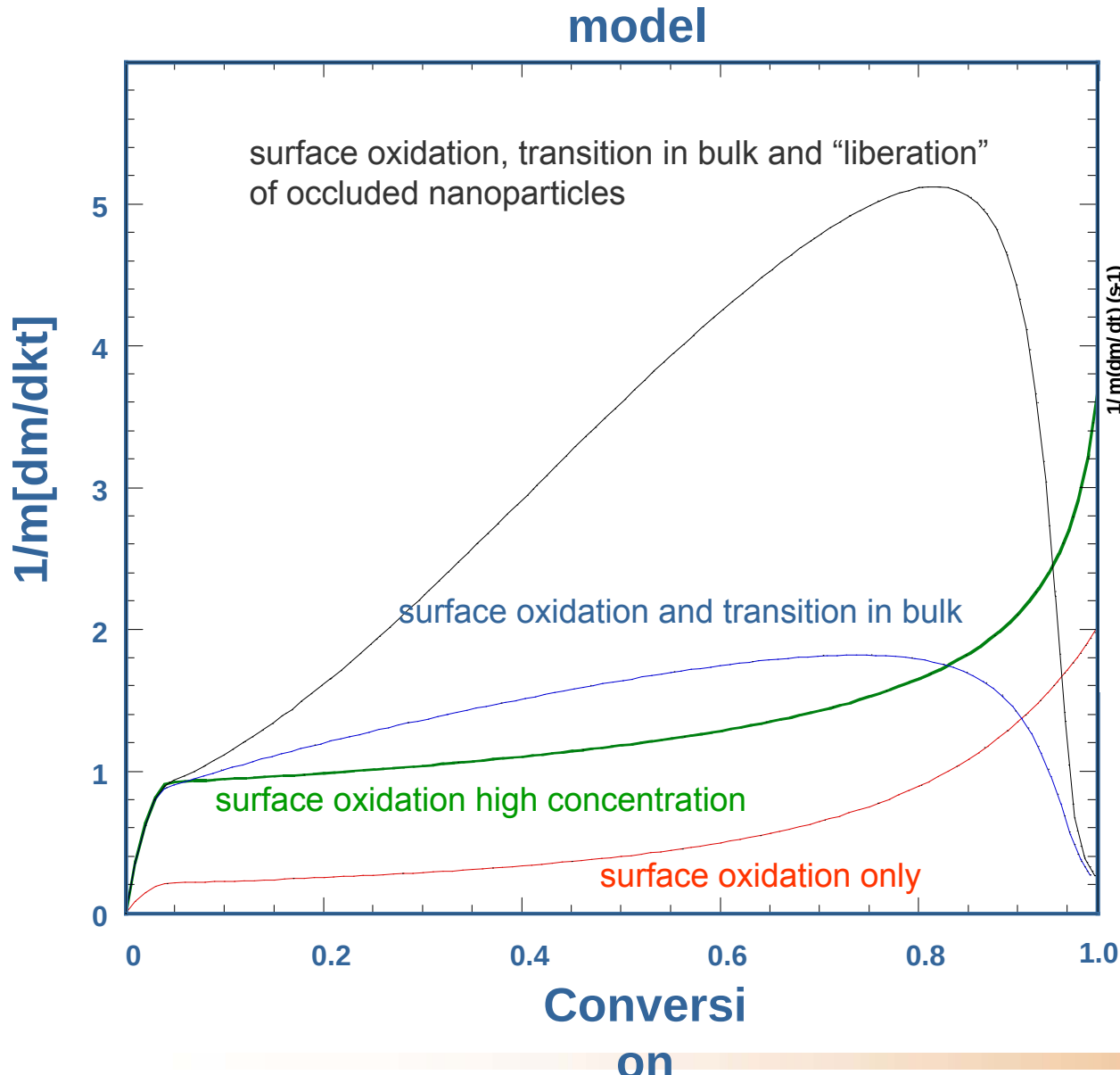
- Bulk nanoparticles become liberated as volume is reduced (acceleration of rate)

Bulk FBC nanoparticle concentration

$$c_{in} = (1 - F_1(V/V_o)) \frac{m_s}{V} + (1 - F_2(\frac{\rho}{\rho_o})) \frac{m_o}{V}$$



Classes of Behaviors Obtained



Prediction of the basic patterns that appear in the experimental results.

Conclusions

- The different behaviors of the catalytic oxidation of soot can be interpreted by the microstructural changes in the spatial interaction of soot and the catalyst particles.
- The Two layer model is extended further to describe the complex phenomena that appear during regeneration of catalyst coated filters as well as during fuel-additive assisted soot oxidation.
- It represents a tool for an intelligent design of catalytic layers on DPFs and the optimization of fuel-additive soot control strategies.

Thank you for your attention!

