Multiscale methodology for evaluation of effective diffusivity in porous catalytic coatings

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Introduction

The microstructure of the support determines a key property of porous catalysts - effective diffusivity. Typically, supporting materials with bimodal pore size distribution are used that involve both meso- and macro-pores. Spatial distribution of active metal crystallites within the porous support then influences reaction rates and conversions. In order to optimize the catalyst support microstructure and ultimately the whole catalyst, it is necessary to relate quantitatively the morphological features of the porous structure both to its preparation conditions and to the final transport properties and catalyst performance.

Experiments

The Pt/γ-Al₂O₃ catalyst coated on metal plates and CO oxidation reaction have been chosen to study transport limitations in the porous catalyst layer. The proposed approach is generally applicable to other porous supported catalysts and different reactions. First, the basic Pt/γ-Al₂O₃ layer was coated, using defined alumina particle size distribution and chosen amount of Pt (2% w.). This active layer was then overlaid with inert layer of γ-Al₂O₃, acting as an additional diffusion barrier. Two different γ-Al₂O₃ particle size distributions were used to investigate their impact on the layer porosity and effective diffusivity, cf. Fig. 2. The thickness of the layers was also varied in a controlled way.
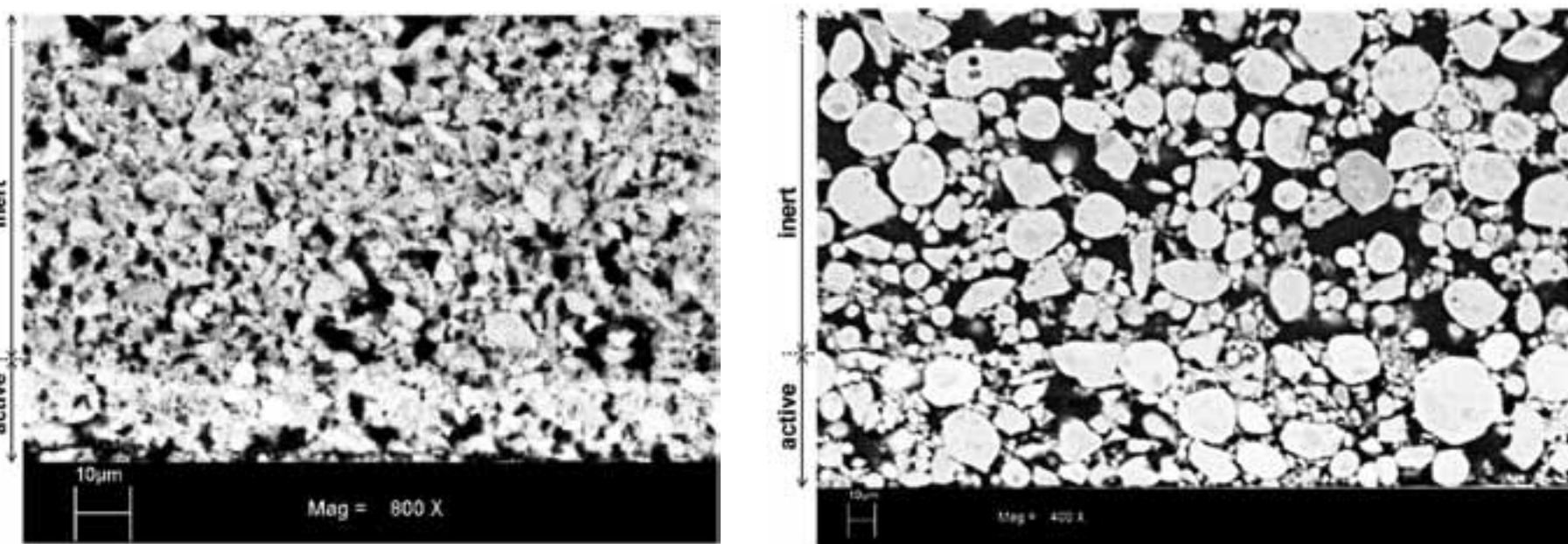

Fig. 1. SEM images of the porous catalyst layers A15+I50 (alumina particles $d_{p,90}$=7 μm) on the left, and A40+I240 (alumina particles $d_{p,90}$=22 μm) on the right. In each image, the active layer is on the bottom side and the overlaid inert layer is on the top side.
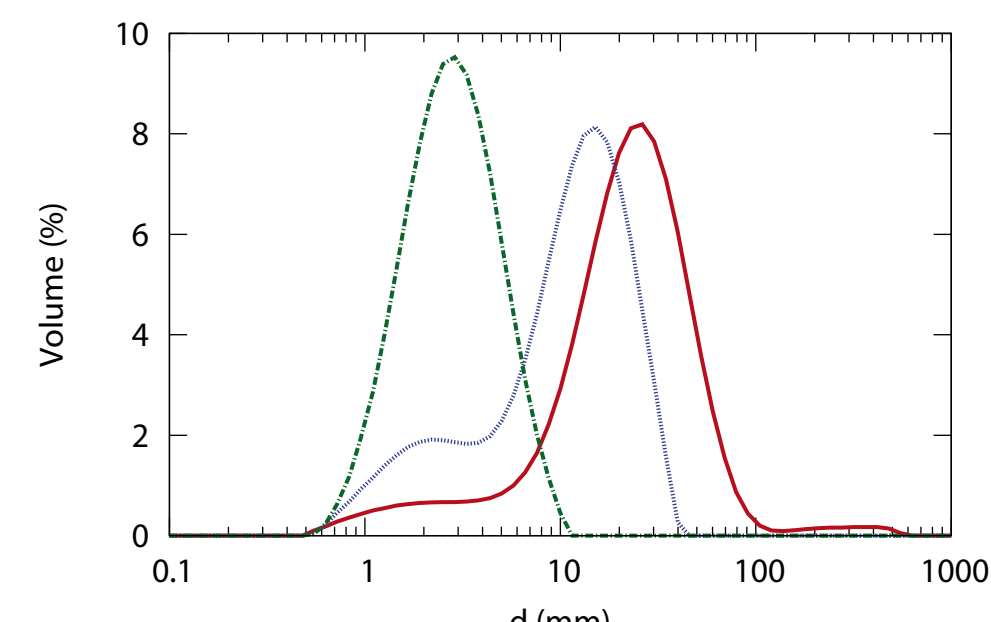
Fig. 2. Particle size distributions of the unmilled (original) and two differently milled alumina powders

Thickness and macro-porosity of the prepared samples was evaluated from cross-section SEM images (cf. Fig. 1).

CO oxidation experiment was performed in a nearly isothermal mini-reactor, Fig. 3. Four coated plates of the same kind were separated with cca 1 mm high metal pads. Slow temperature ramps (3 K/min) were performed in the range 100–350°C to obtain a complete CO light-off curve.

Tab. 1. Coated layers configuration of the tested samples:
A=active layer Pt/γ-Al₂O₃, I=inert γ-Al₂O₃ layer coated on top of the active layer.

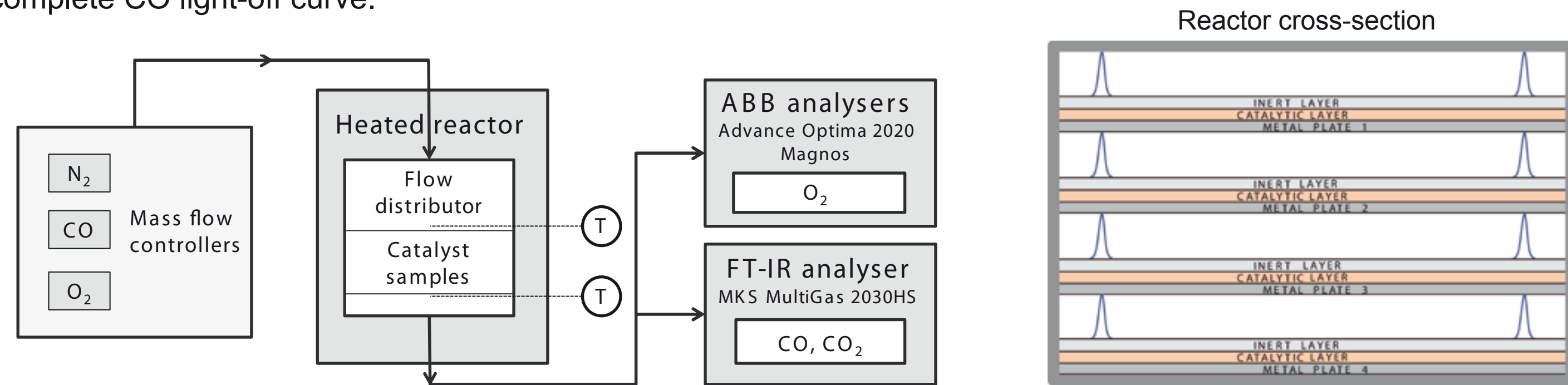| Sample type	A layer thickness	I layer thickness	macroporosity ε^M
A15 ($d_{p,90}$ = 7 μm)	15 μm	—	26 %
A15+I50 ($d_{p,90}$ = 7 μm)	15 μm	50 μm	26 %
A40 ($d_{p,90}$ = 22 μm)	40 μm	—	36 %
A40+I240 ($d_{p,90}$ = 22 μm)	40 μm	240 μm	36 %

Fig. 3. Scheme of lab reactor used for the measurements of catalytic CO oxidation and diffusion in coated layers.

Multi-scale mathematical modeling

Two approaches to mathematical modeling of reaction and transport in catalyst layer are used here. The **detailed model** is based on 3D digital reconstruction of porous catalyst structure and simulations in pore-scale, while the classical approach (**standard model**) treats the catalyst layer as a pseudo-homogeneous slab with effective diffusion coefficient estimated from a suitable correlation (e.g., the random pore model). Both catalyst layer models are then combined with a commonly used 1D heterogeneous model of plug-flow reactor. The proposed methodology links together several models at three different length-scales: nanometers, micrometers, and macroscopic scale.
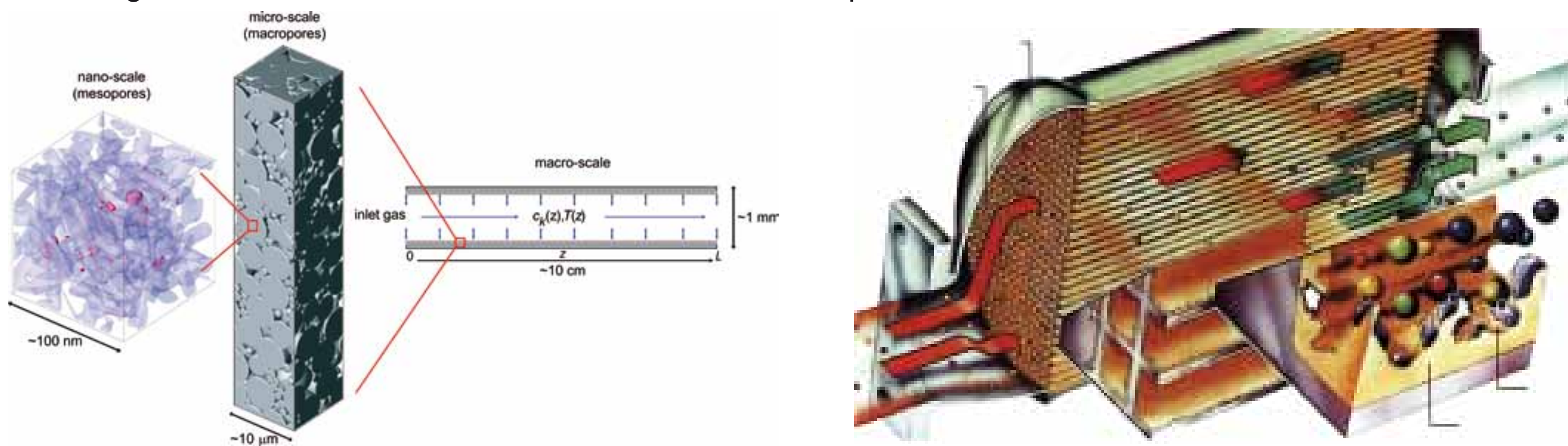

a) Standard 1D+1D model of the coated layer

In this model, the porous layer is treated as pseudo-homogeneous, described by its thickness and effective diffusivity. Transverse spatial coordinate r is distinguished in the porous layer, the reaction kinetics is used directly according to standard rate laws and solved together with simplified diffusion model. The balance of the gas in the washcoat is then replaced by the following equation together with the correlation for the overall effective diffusivity (random pore model):

$$\frac{\partial c_k^s(z,r,t)}{\partial t} = \frac{D_k^{\mathrm{eff}}}{\varepsilon^s}\frac{\partial^2 c_k^s}{\partial r^2} + \frac{1}{\varepsilon^s}\sum_{j=1}^J \nu_{k,j} R_j, \quad k = 1...K \qquad D_k^{\mathrm{eff}} = \varepsilon_M^2 D_{k,M} + \varepsilon_\mu^2 D_{k,\mu} + 4(\varepsilon_M - \varepsilon_M^2)\left/\left(\frac{1}{D_{k,M}} + \frac{(1-\varepsilon_M)^2}{\varepsilon_\mu^2 D_{k,\mu}}\right)\right.$$

M = macropores; μ = mesopores

b) Detailed 3D model of the coated layer

3D digital reconstruction of porous catalyst is based on simplified simulation of the processes occurring during real catalyst preparation. Here we utilize random packing of spherical γ-Al₂O₃ particles with defined particle size distribution. Final reconstructed porous medium is represented by a discrete phase function in the form of 3D matrix containing the information about the phase in each volume discretization element – voxel.
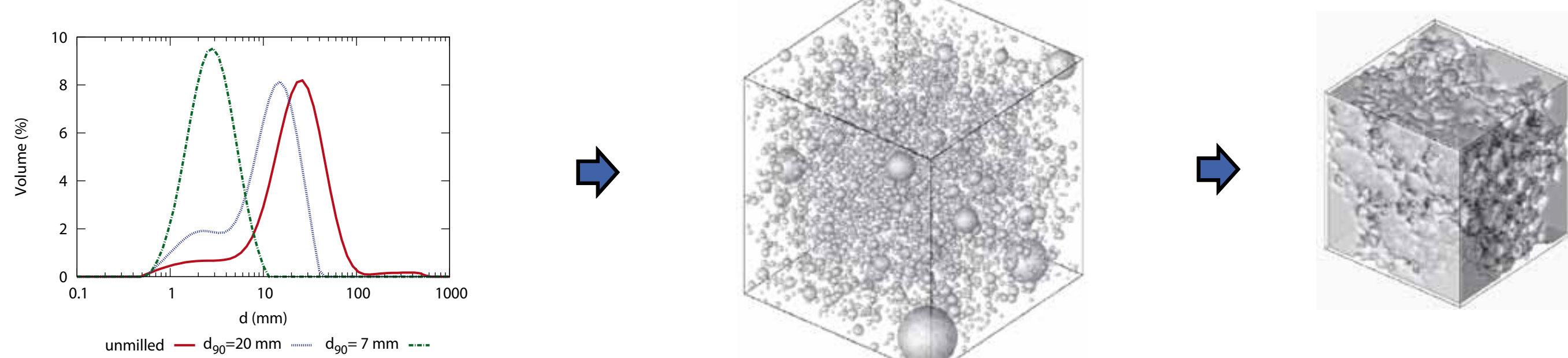
Reaction-transport processes are then simulated in the reconstructed system. The "solid phase" includes implicitly internal mesopores so that the balances for the gas components considered there. The evaluated size of meso-pores, active metal sites concentration are used. The spatially 3D reaction-diffusion model is described by the following mass balances:

$$\nabla \cdot (D_k c \nabla Y_k) + \sum_{j=1}^J \nu_{k,j} R_j = 0$$

In the macro-pores, volume diffusivity in the reference gas used:

$$D_k^M = \frac{144.9 T^{1.75}/p}{\sqrt{2/(10^{-3}/W_k + 10^{-3}/W_{ref})}\left(\omega_k^{1/3} + \omega_{ref}^{1/3}\right)^2}$$

In the mesopores, Knudsen diffusion is considered:

$$D_k^\mu = \frac{\varepsilon^\mu}{\gamma^\mu}\frac{d^\mu}{3}\sqrt{\frac{8R^g T}{10^3 W_k \pi}}$$

Simulation results of the detailed model

Examples of reaction rate profiles are shown in Fig. 5. Typical calculated dependences of effectiveness factor and average reaction rate on the temperature and boundary CO concentration are depicted in Fig. 6.
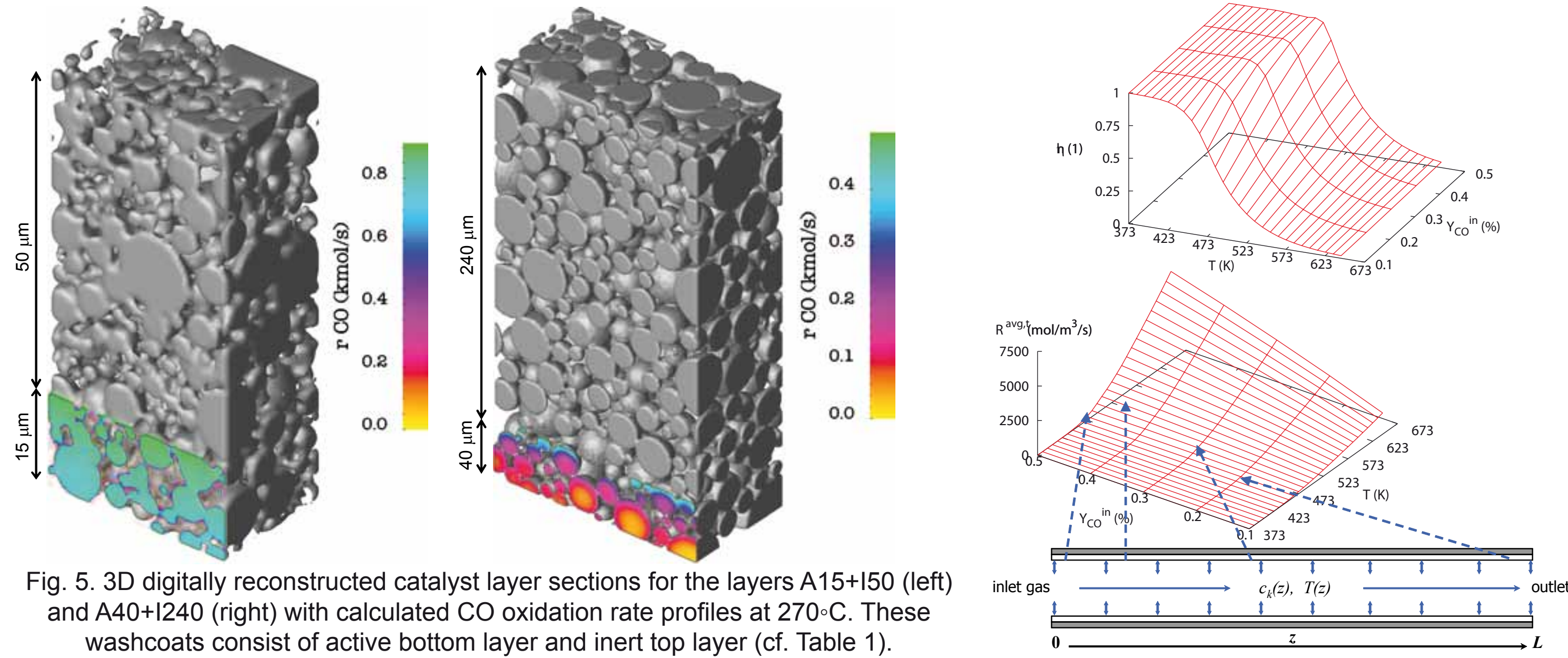

Fig. 5. 3D digitally reconstructed catalyst layer sections for the layers A15+I50 (left) and A40+I240 (right) with calculated CO oxidation rate profiles at 270°C. These washcoats consist of active bottom layer and inert top layer (cf. Table 1).

The precalculated average reaction rates from the microscale simulations (that already include internal diffusion effects for the given porous structure) are provided in the form of a table. The actual local reaction rates in the 1D model of the reactor are evaluated by interpolation in dependence on the local temperature and concentration of key reactants.

Results of experiments, comparison with simulations

The single active layer made from alumina particles with $d_{p,90}$=7 μm (A15) is only 15 μm thick(cf. Table 1). Therefore, the coating diffusion limitations do not affect the CO oxidation light-off on the A15 sample (Fig. 7) and the measured data can be used for adjustment of the actual CO oxidation kinetic parameters. The assumption of negligible transport limitation for the thin active layer was validated by the spatially 3D reaction-diffusion model of the digitally reconstructed catalyst layer— both detailed and standard models give identical results (cf. Fig. 8).

The experiments and simulations for the two samples with overlaid inert layer (A15+I50 and A40+I240) are shown in Fig. 9, respectively. The inert layer makes an additional barrier for the transport of reactants to the active catalytic sites, see Fig. 5. The first onset of the reaction is very similar as for the single active layer only. However, after the light-off temperature is reached, the operation becomes diffusion-limited. This results in a long "tail" of outlet CO concentration that decreases only slowly with the increasing temperature. The detailed model is in a good agreement with experiments, while the classical random pore model predicts too high diffusion limitations (i.e., lower effective diffusivity).
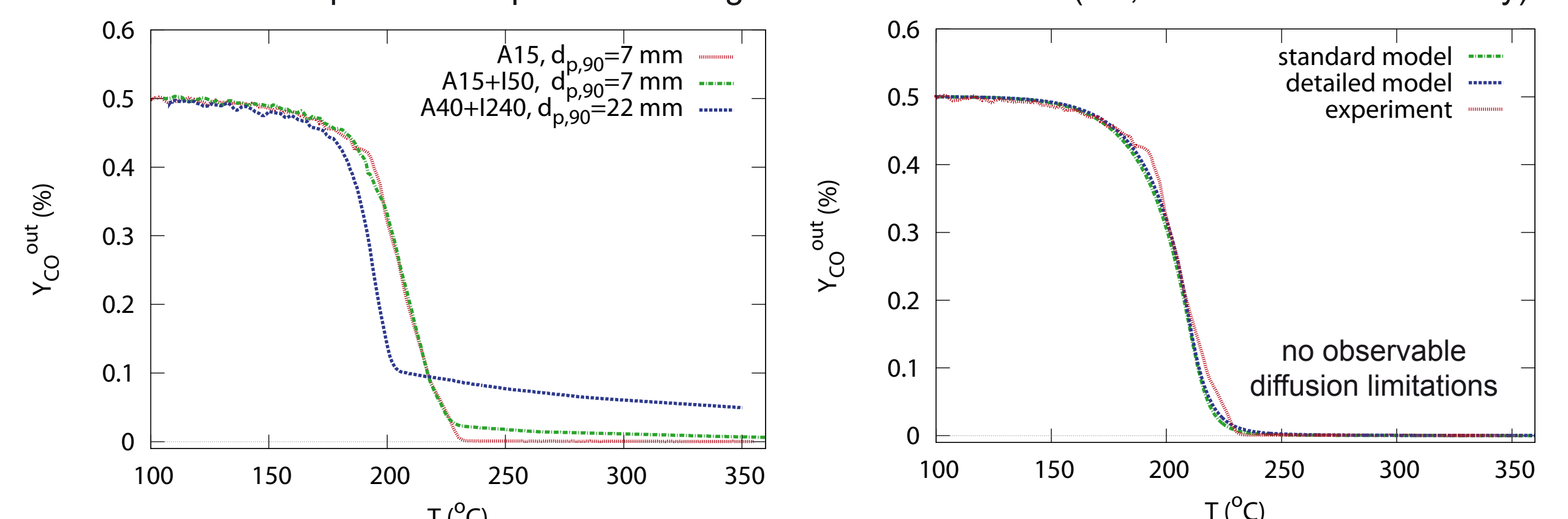

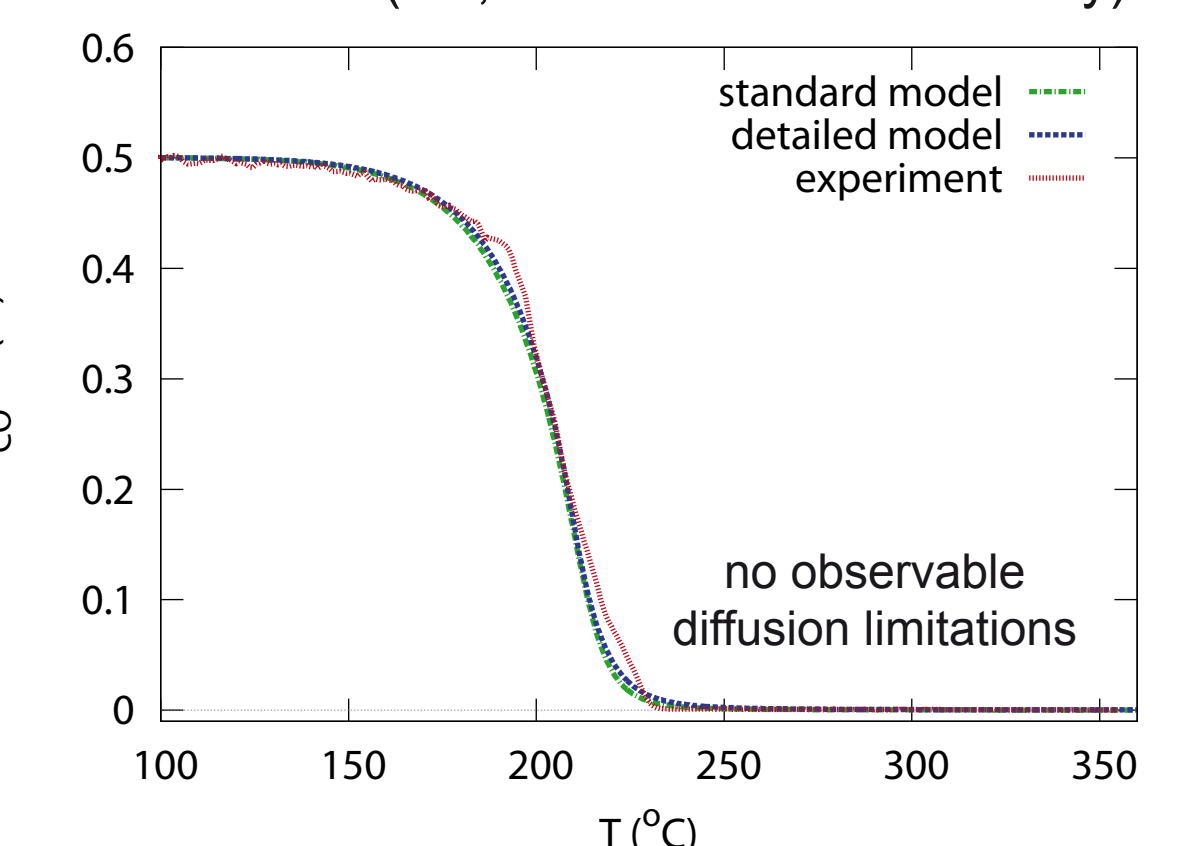Fig. 7. Measured light-off curves for the catalysts described in Tab. 1.

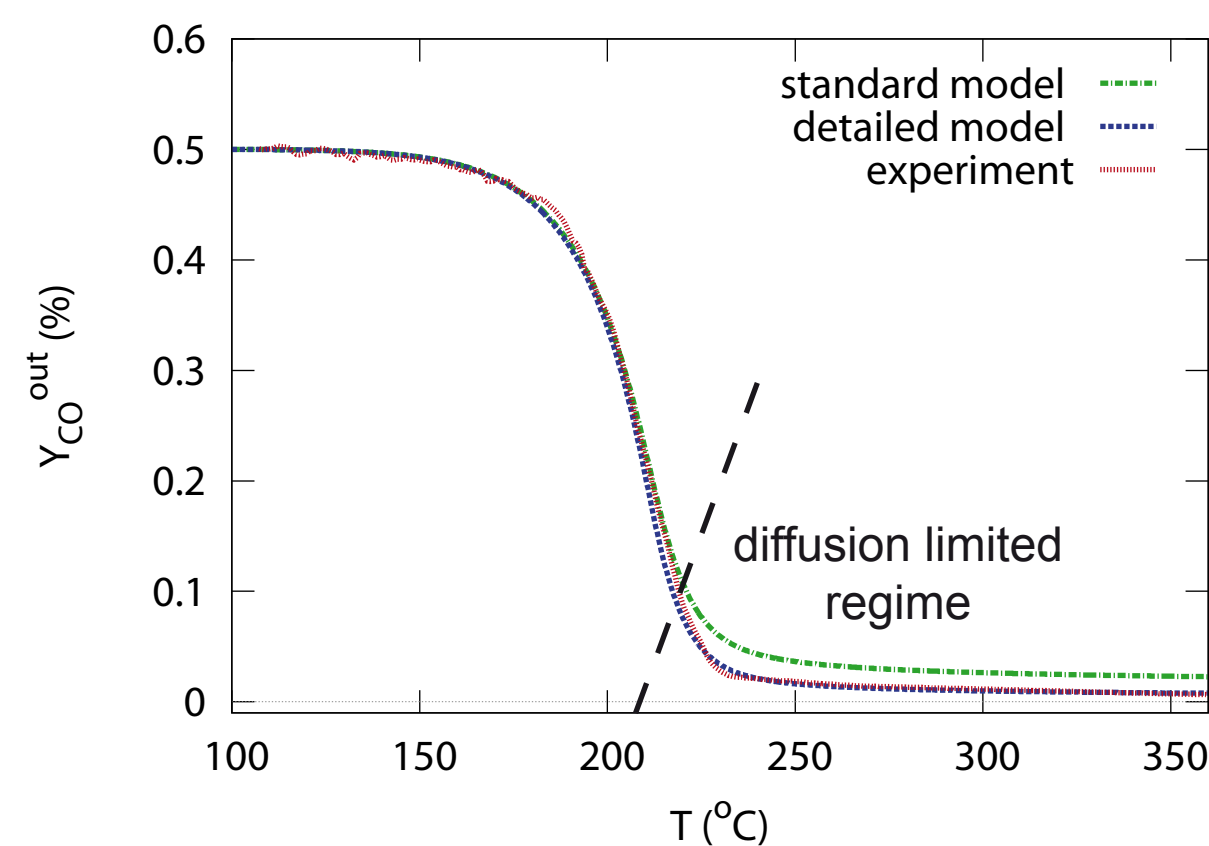Fig. 8. Simulated and measured light-off curves for catalyst layer A15 ($d_{p,90}$=7 μm)

Fig. 9. Simulated and measured light-off curves for the catalyst layers A15+I50 ($d_{p,90}$=7 μm)
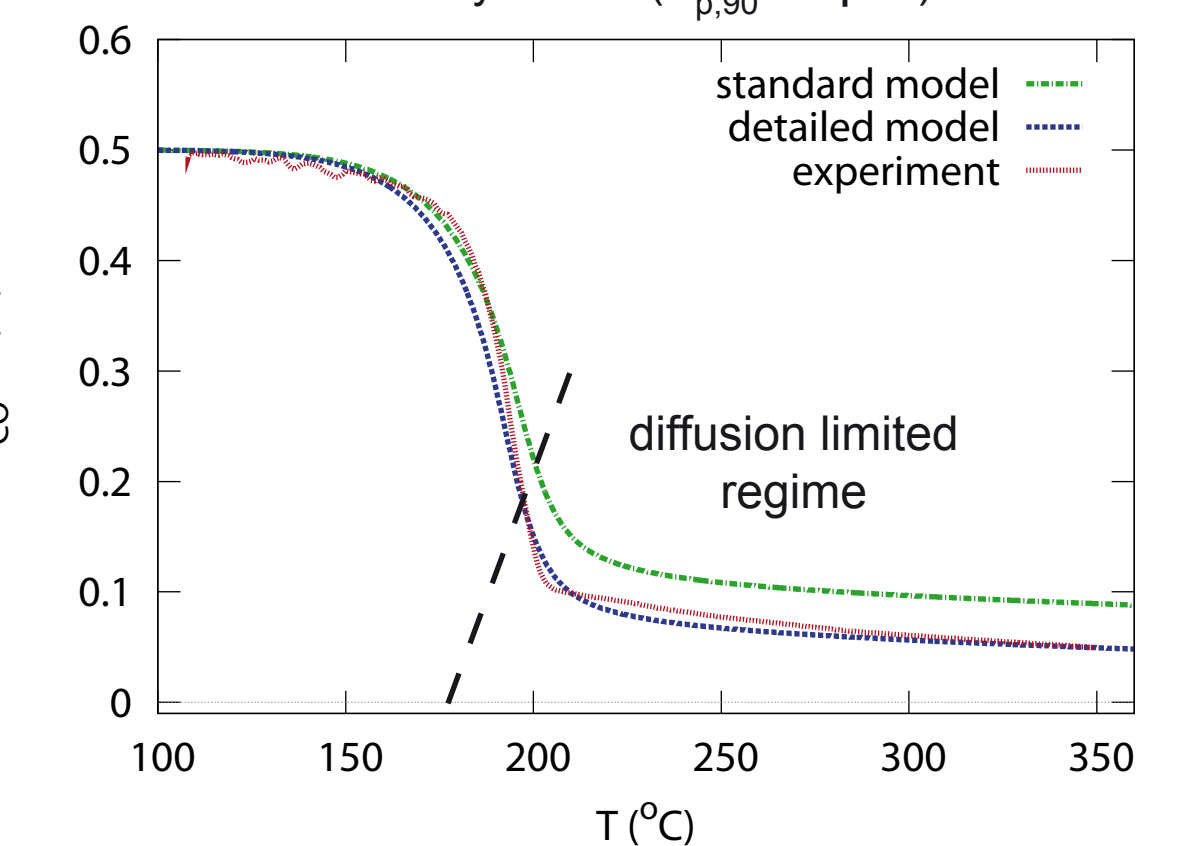
Fig. 10. Simulated and measured light-off curves for the catalyst layers A40+I240 ($d_{p,90}$=22 μm)

Evaluated effective diffusivities

The evaluated effective diffusivities at room temperature are summarized in Tab. 2. Overall effective diffusivity through the catalyst layer formed by large γ-Al₂O₃ particles ($d_{p,90}$=22 μm) is higher than that of the layer formed by smaller particles ($d_{p,90}$=7 μm). This is in line with the higher macro-porosity of the layer consisting of the big particles (36 % vs. 26 %, respectively). However, too big γ-Al₂O₃ particles may exhibit a larger local diffusion limitations for reactants diffusing into their center through meso-pores.

Tab. 2. Evaluated overall effective diffusivity D^{eff} of CO at 298 K through the coated alumina layer

Alumina type	Random pore model	3D digital reconstruction
$d_{p,90}$ = 7 μm	1.5×10^{-6} m².s⁻¹	2.6×10^{-6} m².s⁻¹
$d_{p,90}$ = 22 μm	3.1×10^{-6} m².s⁻¹	4.2×10^{-6} m².s⁻¹

Summary and conclusions

A novel methodology for the study of diffusion in coated porous layers has been proposed. Catalytic layer is coated on metal plates and subsequently overlaid by an inert layer. The samples are then tested in a lab reactor and light-off curves are measured. Effective diffusivity through the catalyst layer can be then evaluated from the conversions measured in diffusion-limited regime.

The detailed 3D model of porous layer gives more accurate predictions of effective diffusivity than the standard random-pore correlation that tends to overestimate diffusion limitations. The used multi-scale methodology enabled to predict the influence of microscopic properties of the catlytic coating on the overall reactor performance.

Acknowledgements

Reference for citation of the presented results

Novák V., Kočí P., Marek M., Štěpánek F., Blanco-García P., Jones G. Multi-scale modelling and measurements of diffusion through porous catalytic coatings: An application to exhaust gas oxidation. *Catalysis Today* (2012), in press, http://dx.doi.org/10.1016/j.cattod.2012.03.049