



## Multi-scale modelling and measurements of diffusion through porous catalytic coatings: An application to exhaust gas oxidation

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### ABSTRACT

Novel experimental and computational methods to investigate diffusion in catalytic coatings are presented and demonstrated with Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> oxidation catalyst. The catalytic layer with defined particle and pore size distributions is coated on metal plates and subsequently overlaid by an inert layer acting as an additional diffusion resistance. The samples are tested in a lab reactor for CO oxidation and diffusion-limited regime is reached above the light-off temperature. Comparisons of the results obtained with the samples coated by active layer only and the samples additionally coated by an inert layer reveal the extent of diffusion limitations.

The computational part is based on digital reconstruction of the porous layer as a 3D matrix; this is achieved using macroporosity obtained from SEM cross-section images, and measured particle size distributions. Reaction and diffusion are then simulated within a small layer section and the spatially averaged results are employed in the full-scale model of the entire reactor. The simulated light-off curves are in good agreement with the experimental data. Depending on the actual  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> particle size distribution, the predicted effective diffusivities of CO at 298 K are  $2.6 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$  and  $4.2 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$  (for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> particles  $d_{90} = 7 \text{ }\mu\text{m}$  and  $d_{90} = 22 \text{ }\mu\text{m}$ , respectively), whereas the classical random pore model predicts approximately 25–45% lower diffusivities.

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### 1. Introduction

Transport limitations inside the catalytic layer may influence reactor light-off and overall conversions even in the case of relatively thin layers used on monoliths for conversion of automotive exhaust gas. With the gradual development of detailed models, the importance of computer-aided catalyst design and optimization of porous structures increases. It is desirable to first test the influence of the catalyst structure on its end-use performance using mathematical models, and consequently suggest design criteria for the preparation of optimal catalyst structures for a given purpose.

The structure of a  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> porous support is controlled on two levels: (i) the level of mesoporous structure, which can be determined by the use of specific synthesis, e.g., sol-gel method [1,2] or pore-templating method [3] and (ii) the level of macroporous structure, which is influenced by the particle size distribution of

mesoporous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in a slurry that has undergone a specific thermal treatment. The porous support structure is then impregnated by active metal(s) in the form of crystallites whose size and space distribution depends on the preparation conditions [4,5], in turn the reaction rate is often determined by the size of the active crystallites [6].

Development of electron microscopy (SEM, TEM) and other high-resolution imaging techniques in recent years has enabled researchers to focus on the detailed modelling of porous catalyst structures and its influence on the reactor performance [7,8]. One particular class of detailed models is based on digital, computer-aided reconstruction of porous media that can provide a realistic description of catalyst morphology [9,10]. Such a model can subsequently be used to simulate reaction and transport processes inside the reconstructed system [11]. Specific applications of this approach include, for example, simulation of diffusion [12], permeation, heat conduction [13], adsorption [14,15], combined reaction and transport processes in both heterogeneous [16,17] and multi-phase [18,19] systems.

This paper presents a novel approach to experimental and computational evaluation of diffusion effects in porous catalytic

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**Nomenclature**

$A$	area ( $\text{m}^2$ )
$a$	geometric surface area density (in reactor) ( $\text{m}^2 \text{m}^{-3}$ )
$c$	gas concentration ( $\text{mol m}^{-3}$ )
$c_p$	heat capacity ( $\text{J kg}^{-1} \text{K}^{-1}$ )
$C_{\text{Pt}}$	concentration of active catalytic sites (Pt) ( $\text{mol m}^{-3}$ )
$d$	diameter (m)
$D$	diffusion coefficient ( $\text{m}^2 \text{s}^{-1}$ )
$E_a$	activation energy of reaction step ( $\text{J mol}^{-1} \text{K}^{-1}$ )
$E_{\text{inh}}$	inhibition exponential factor (K)
$k$	kinetic constant of reaction step ( $\text{K s}^{-1}$ )
$k_0$	pre-exponential factor of kinetic constant ( $\text{K s}^{-1}$ )
$k_c$	mass transfer coefficient ( $\text{m s}^{-1}$ )
$k_h$	heat transfer coefficient ( $\text{J m}^{-2} \text{K}^{-1} \text{s}^{-1}$ )
$K_{\text{inh}}$	kinetic constant of inhibition (1)
$K_{\text{inh}0}$	pre-exponential factor of inhibition (1)
$L$	length (m)
$M$	molar weight ( $\text{kg mol}^{-1}$ )
$p$	pressure (Pa)
$r$	transverse coordinate in the coated layer (m)
$R$	reaction rate ( $\text{mol m}^{-3} \text{s}^{-1}$ )
$R^g$	universal gas constant, $8.314 \text{ J mol}^{-1} \text{K}^{-1}$
$t$	time (s)
$T$	temperature (K)
$V$	volume ( $\text{m}^3$ )
$x$	spatial coordinate (m)
$y$	spatial coordinate (m)
$Y$	component mole fraction (1)
$z$	spatial coordinate (longitudinal in case of monolith) (m)

**Greek letters**

$\gamma$	tortuosity (1)
$\varepsilon$	porosity (1)
$\eta$	effectiveness factor (1)
$\delta$	layer thickness (m)
$\Delta H_r$	reaction enthalpy ( $\text{J mol}^{-1}$ )
$\varphi$	volumetric fraction (1)
$\varphi^w$	vol. fraction of coating in entire solid phase (incl. wall) (1)
$\lambda$	heat conductivity ( $\text{J m}^{-1} \text{s}^{-1} \text{K}^{-1}$ )
$\nu$	stoichiometric coefficient (1)
$\rho$	density ( $\text{kg m}^{-3}$ )
$\sigma$	diffusion volume ( $\text{m}^3 \text{mol}^{-1}$ )

**Subscripts and superscripts**

bnd	boundary
eff	effective
g	bulk gas in monolith channel
$i$	index of gas component
$j$	index of reaction
m	monolith
M	macropores
$\mu$	mesopores
Pt	platinum particles
s	solid phase (wall + coating)
t	total
w	coated porous layer, washcoat

coatings. Catalytic layers were coated on metal plates and subsequently overlaid by an inert layer acting as an additional transport barrier. The samples were then tested in a lab reactor and CO oxidation light-off curves were measured. A diffusion-limited regime was reached above the light-off temperature. Comparisons of the results obtained with the samples coated by active layer only and the samples additionally coated by an inert layer revealed the extent of diffusion effects in dependence on porous structure and thickness of the layer.

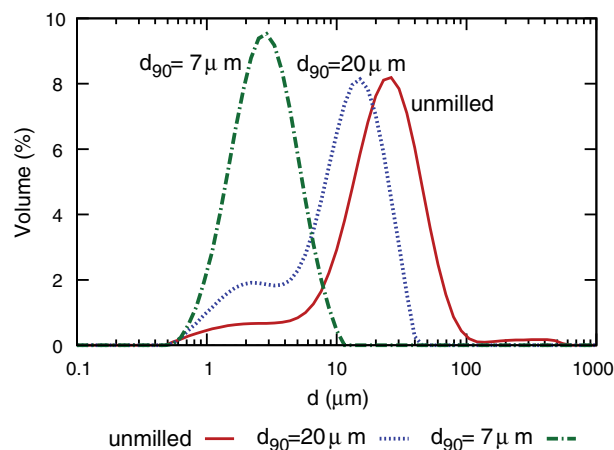
The computational part focuses on prediction of effective diffusivity using a detailed pore-scale model of the coating. The porous layers are digitally reconstructed as 3D matrices using the information from cross-section SEM and particle size analyser. Reaction and diffusion are then simulated within a small section of the porous layer and the spatially averaged results are employed in the full-scale model that can predict the behaviour of entire reactor.

**2. Experimental**

The Pt/ $\gamma$ - $\text{Al}_2\text{O}_3$  catalysts coated on metal plates have been investigated using CO oxidation as a probe reaction to study transport limitations in the porous layer. First, the active base Pt/ $\gamma$ - $\text{Al}_2\text{O}_3$  layer was coated, using a pre-defined alumina particle size distribution and a chosen amount of Pt. This active layer was then overlaid with an additional inert layer of  $\gamma$ - $\text{Al}_2\text{O}_3$  (that did not contain Pt). Two different  $\gamma$ - $\text{Al}_2\text{O}_3$  particle size distributions were used to observe their impact on the layer porosity and effective diffusivity. The thickness of the layers was also varied in a controlled way.

**2.1. Washcoat preparation and characterization**

Commercially sourced  $\gamma$ - $\text{Al}_2\text{O}_3$  micro-particles of the type SCFa140 (Sasol) have been used as a raw material for the porous support. The size of the internal mesopores was evaluated by nitrogen adsorption (Autosorb-1, Quantachrome Instruments), showing the mean mesopore diameter  $d_\mu$  to be 13 nm with very narrow distribution and mesoporosity  $\varepsilon_\mu = 43\%$ . This alumina was impregnated with Pt(IV) nitrate (Johnson Matthey) and the final quantity of platinum was 2% by weight. After calcination at temperature of  $500^\circ\text{C}$  for 2 h, the catalytic material was divided into two parts. Each part was milled in the form of a water suspension in mini motor-mill with 1 mm YTZ beads (Eiger Torrance) for a different period so that two different particle size distributions were obtained:  $d_{p,90} = 7 \mu\text{m}$  and  $d_{p,90} = 22 \mu\text{m}$  (particle sizes were analysed with MasterSizer 2000, Malvern Instruments), cf. Fig. 1.



**Fig. 1.** Particle size distributions of the unmilled (original) and two differently milled alumina dispersions.

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