

Influence of the Washcoat Structure in the Performance of Automotive Three Way Catalysts

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ABSTRACT

Transport limitations inside the porous washcoat layer have an important influence in the light-off and overall conversions even in the case of relatively thin layers used in automotive three way catalysts (TWC). The porous structure of the washcoat layer is controlled at two levels: i) at the level of mesoporous structure, which can be determined by the use of specific synthesis techniques (e.g., sol-gel or pore-templating method), and ii) at the level of macroporous structure, which is influenced by the particle size distribution of mesoporous in a slurry that has undergone a specific thermal treatment. This paper investigates the influence of the washcoat structure in the performance of automotive TWC. Furthermore, the article presents a method that allows to quantify the magnitude of the reaction resistance (chemical kinetics), internal mass transfer resistance (washcoat diffusion), and external mass transfer resistance on the TWC conversions. From experimental data gathered at different operating temperatures (from light-off to 1100 K) and applying the developed methodology for resistances quantification, it was found that the internal mass transfer limitations play a major role in the TWC conversions. The main conclusions from this study are: i) the effective diffusivity strongly depends on the washcoat layer structure, which in turn depends on its preparation process; ii) the resistance quantification analysis reveals that the lower effective diffusivity interval is more adequate for the TWC used in the present investigation, which also indicates that the TWC washcoat has a low percentage of macropores; and iii) to decrease the relevance of the internal mass transfer limitation requires an increase in the effective diffusivity and/or a thinner washcoat layer.

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INTRODUCTION

Monolith supported catalysts are widely used in automotive catalytic converters [1]. Despite ceramic and metallic monoliths having high surface to volume ratios (geometrical surface area - GSA), their specific surface area (m^2/g) (BET - Brunauer, Emmet and Teller) is too low (about $0.3 \text{ m}^2/\text{g}$) to enable the active catalytic metals to be adequately dispersed. To overcome this, a thin layer of a porous material is applied to the channel walls. This layer is referred to as washcoat. Good washcoat materials are characterized by having high BET and thermal stability. The BET of the washcoat materials is typically $100\text{-}200 \text{ m}^2/\text{g}$. Nowadays, the materials used in a TWC washcoat are: i) $\gamma\text{-Al}_2\text{O}_3$, which is employed as a high BET support, that

proved to be the best choice due to its chemical and physical characteristics, widespread availability and relatively low cost; and ii) $\text{CeO}_2\text{-ZrO}_2$ (cerium zirconium mixed oxides) that are often added to the washcoat as oxygen storage promoters and to stabilize the porous structure (thermal stabilizers) - they may also act as active catalytic centers [3].

After adding the washcoat to the substrate, the next requirement is to add controlled amounts of precious metal catalysts (e.g., a platinum group metal - PGM, in the case of the automotive catalysts), which are usually applied in a second step called impregnation. During the impregnation, the washcoated monolith is exposed to a slurry containing catalytic precursors. The washcoat with the catalysts is then dried and calcined to its final form [1]. Depending upon the interaction with the washcoat structure, various techniques

were adopted to introduce accurate quantities of catalysts to the washcoat structure. Meille [2] reviewed the methods to deposit washcoat and catalysts on structured surfaces for monoliths and foams.

Internal mass transfer (intrapphase diffusion) is the transport process whereby reactants/products diffuse into a washcoat layer. Recently, it was demonstrated that this process may have a significant influence on the conversion behavior of the TWC [4,5], and thus the accurate evaluation of the effective diffusion coefficients of the exhaust gases in the washcoat layer is imperative.

The typical γ -Al₂O₃ washcoat layer used in commercial TWC has a bimodal pore size distribution [4,6], with both meso and macropores. The microstructure of the washcoat layer determines the key property of porous structure - the effective diffusivity.

The actual values of the effective diffusivity coefficients (D_{eff}) in the washcoat layer are known only approximately. Experimental results [6, 7, 8, 9], with relatively wide confidential intervals, and different theoretical models applied to bimodal pore size distribution of the washcoat can give large variations in the D_{eff} values.

To optimize the washcoat microstructure and ultimately the whole TWC, it is necessary to relate quantitatively the morphological features of the porous structure (pore diameters, porosity and tortuosity) to the final transport properties (D_{eff}) and catalyst performance under reaction conditions. In this context, this paper investigates the effects of the washcoat structure in the performance of automotive TWC.

WASHCOAT LAYER CHARACTERIZATION

A typical TWC washcoat layer has a thickness of between 15 μ m and 60 μ m. The complex porous structure of real washcoat layers and the differences in the pore size distribution is due to the many factors present in the manufacturing process as well as to the differences in the materials [6, 7, 8, 9]. Recently, a number of studies [6, 7, 8, 9] have used several techniques for obtaining pore transport characteristics in commercial available washcoat layers. Typical sizes of pore diameter in a TWC washcoat range from 6.5 nm to 500 nm [7], so that micropore diffusion may be neglected. Characteristic mesopore diameter of γ -Al₂O₃ particles is commonly accepted to be 10 nm, as confirmed in recent experimental studies [6,8]. On the other hand, the macropores diameters are situated in a wide interval (100-500 nm), which strongly depends on the actual washcoat preparation process [4,6,7].

Effective Diffusivity

Experimental techniques

The key difficulty to undertake effective diffusivity measurements within a monolith washcoat is the complexity

or non-homogeneity of the structure. In addition, the washcoat is a complex porous network consisting of mesopores and macropores.

There are a number of experimental techniques for evaluating the diffusivity of gases in porous materials, which can separate gas diffusivity and catalyst activity. Kolaczkowski [10] provided a review on the techniques that have been used to evaluate the effective diffusivity of gases in washcoat layers, as used in automotive catalytic converters.

The most classical experimental techniques for effective diffusivity measurements are: i) the counter-current diffusion measurement with a Wicke-Kallenbach type cell [6,7]; and ii) the chromatographic method [8]. Since its initial conception, many modifications to the Wicke-Kallenbach type cell have been made, which do allow the direct measurement of monoliths effective diffusivities (e.g., [6,7]).

The major problem with these techniques is that the transport through the washcoat alone is not measured; it is measured together that through both the monolith, e.g., cordierite, and the washcoat. Hence, the effective diffusivity could only be obtained indirectly. By using coated and uncoated monoliths, Zhang et al. [6], Hayes et al. [7] and Starý et al. [8] were able to separate the effective diffusivity of the washcoat layer from that of the monolith wall. The effective diffusivity of the washcoat layer alone was calculated indirectly with the obtained effective diffusivity of the monolith and of the monolith with the washcoat.

Recently, Kato et al. [9] established a technique that allows a direct measurement of the effective diffusivity in the washcoat layer. Because there was no diffusion resistance in a metal support, Kato et al. [9] used a metal mesh instead of cordierite as support.

Effective diffusivity measurements

There are few experimental studies in the literature that have evaluated the effective diffusivity (D_{eff}) of reacting species in the washcoat. Measured values of effective diffusivities in typical γ -Al₂O₃ based washcoat layers used in automotive TWCs vary over a wide range (from 1×10^{-7} to 1×10^{-6} m²/s), depending on the actual washcoat structure [6, 8]. In the washcoat structure, the porosity (ϵ) is the ratio of the void (open) volume to the total volume of the washcoat including the void volume, and the tortuosity factor (τ) describes the deviation of the pore geometry from perfect cylindrical shaped pores, accounting for the tortuous pathways in the structure.

Table 1 shows the proprieties of a γ -Al₂O₃ washcoat structure and the measured effective diffusivity of CO in N₂ at room temperature, $T_{ref} = 290$ K [6, 8]. The table reveals that the mesopores diameter is equal to 10 nm in both studies, but the macropores diameter and porosity is higher in the washcoat characterized by Zhang et al. [6] and the tortuosity is higher in the washcoat characterized by Starý et al. [8]. Table 1 also reveals that the $D_{eff,ref}$ obtained by Starý et al.

[8] is one order of magnitude lower than that obtained by Zhang et al. [6]. This difference is due to the difference in porous structure.

Table 1. Properties of a γ -Al₂O₃ washcoat structure and the measured effective diffusivity of CO in N₂ at room temperature, T_{ref} = 290 K.

Parameter	Zhang et al. [6]	Starý et al. [8]
Washcoat material	γ -Al ₂ O ₃	γ -Al ₂ O ₃
Mesopores, d_μ [nm]	10	10
Macropores, d_M	500	130
Porosity, ϵ [-]	0.41	0.33
Tortuosity, τ [-]	1.2	2.64
$D_{eff,ref}$ [m ² /s]	1.58×10^{-6}	1.13×10^{-7}

Mean transport pore models

In the absence of experimental data for the effective diffusivity, mean transport pore models are frequently used to estimate a value. The principal advantage of using such models is the ability to calculate the effective diffusivity of a gas species in a given temperature range using the washcoat properties, which needs to be measured experimentally. The two most widely applied pore diffusion models for effective diffusivity evaluation are the parallel pore model (PPM) and the random pore model (RPM) [16].

The RPM model assumes a porous material composed of macroscopic particles. The voids between these particles form a system of macropores. The macroparticles themselves are assumed to have a microporous structure. It is further assumed that the macroscopic particles are distributed randomly, and that the diffusion through the porous structure is a combination of diffusion through the open voids and diffusion through the micropores.

The PPM model assumes parallel channels directly connected to the two opposite faces of the material. The PPM model uses the tortuosity (τ), which is an empirical correction factor that allows fitting the PPM model to the experimental data. Furthermore, the tortuosity represents the deviation of the washcoat pores from the ideal cylinder. In a washcoat, it is important to understand that the fluid flow does not follow a straight path. Instead, it twists and turns its way through the pores and this tortuous flow requires modeling. This tortuosity is a methodology of accounting for the additional path length and the resulting increase in the capillary velocity over the interstitial axial velocity.

Many studies [e.g., 7] reported that the RPM model is not appropriated because it overpredicts the effective diffusivity in the washcoat. On the other hand, the PPM model agrees well with the experimental data [6, 8]. Hence, the PPM model is the most adequate for a γ -Al₂O₃ washcoat and was used in the present study.

The temperature dependence of the effective diffusion coefficient differs for volume (gas or bulk) diffusion and

Knudsen diffusion. The transport in the washcoat includes the combination of both types of diffusion.

Bulk diffusion can be calculated as:

$$D_{g,CO} = 9.524 \times 10^{-10} \times T^{1.75} \quad (1)$$

where $D_{g,CO}$ has units of [m²/s].

The Knudsen diffusion can be calculated as:

$$D_K = 48.5 \times d \times \sqrt{\frac{T}{M_{CO}}} \quad (2)$$

where D_K has units of [m²/s], M_i is the molar mass of CO given in [g/mol] and d is the mean pore diameter in [m]. The Knudsen diffusion was calculated either for mesopores ($D_{K,\mu}$) or for macropores ($D_{K,M}$).

In the PPM model, D_i is the diffusion of the gas species used to calculate the effective diffusivity. It takes into account both the Knudsen and bulk diffusion according to:

$$D_i = \frac{V_\mu/V_{Total}}{(1/D_{g,i}) + (1/D_{K,\mu})} + \frac{V_M/V_{Total}}{(1/D_{g,i}) + (1/D_{K,M})} \quad (3)$$

where V_μ/V_{Total} and V_M/V_{Total} are the ratio between the volume of mesopores and total volume and volume of macropores and total volume in the washcoat, respectively.

In the PPM model, the relationship between the diffusion coefficient (D_i) in the pore space and the effective diffusivity based on the total cross sectional area can be calculated as:

$$D_{eff,i} = \frac{\epsilon_p \times D_i}{\tau} \quad (4)$$

where $D_{eff,i}$ is the effective diffusivity in [m²/s], ϵ_p is the overall porosity and τ is the tortuosity.

Effective diffusivity evaluation

As mentioned earlier, experimental values for effective diffusivity for a γ -Al₂O₃ TWC washcoat varies over a wide range (cf. Table 1). The modeling studies also reveal a large variation in the effective diffusivity values considered in the simulations. Here, it was decided to evaluate the effective diffusivity as a function of the temperature using the PPM model for two different washcoat structures that correspond to the lower [8] and upper [6] limits found in the experimental studies available in the literature.

Table 2 presents the proprieties of the two different γ -Al₂O₃ washcoat structures considered and a comparison between the experimental and the PPM model results for the effective diffusivity of CO in N₂ at room temperature, T_{ref} = 290 K.