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Characterization of secondary pores in washcoat layers and their effect on effective gas transport properties

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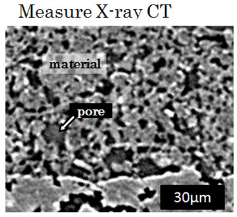
HIGHLIGHTS

- Pore morphology of washcoat layers was analyzed with X-ray computed tomography.
- Effective gas permeability of washcoat layers was measured.
- Effect of pore properties on effective gas permeability was investigated.
- New model for calculating gas permeability of washcoat layers was developed.

GRAPHICAL ABSTRACT

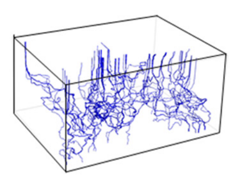
A new model to calculate effective gas permeability of washcoat layer using pore properties obtained from X-ray CT analysis.

Step 1
Measure X-ray CT



Sliced image of washcoat layer

Step 2
Calculate pore connectivity



Visualized percoaltion path

Step 3
Calculate effective permeability with parameters of pore connectivity

Proposed new model

$$K_e = \frac{\varepsilon}{\tau} \frac{\sum_{i=0}^{n} (d_i^2/32)(1 + 8\lambda/d_i)}{n}$$

K_e : effective permeability
ε, n, i, d_i : perameters obtained from X-ray CT
λ : mean free path

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ABSTRACT

It is well known that the performance of monolithic catalysts is limited by gas transport resistance in the washcoat layer. Gases are transported via two types of pores within the washcoat layer: primary pores, which exist inside the particle of catalyst support material (e.g., Al_2O_3), and secondary pores, which are voids among particles of the catalyst support material. Primary pores play an important role in the effectiveness of catalytically active components such as Pt, Rh, and Pd, while secondary pores facilitate gas transport in the washcoat layer. This paper reports the characterization of secondary pores and their effect on gas transport. In order to evaluate the gas transport properties of a washcoat layer, effective gas permeability was measured. Four samples with different pore morphologies were prepared, and their secondary pore properties were characterized with scanning electron microscopy, mercury porosimetry and synchrotron X-ray computed tomography. The obtained pore properties were correlated with the effective gas permeability, and based on the obtained correlation, we formulated a model for the gas permeability of the pores. This new model was compared to the conventional Kozeny-Carman equation.

1. Introduction

Monolithic catalysts are widely employed in the abatement of pollution from moving sources, such as cars, and from stationary sources, such as factories [1]. Other applications of monolithic catalysts include partial oxidation of methane [2], dimethyl ether steam reforming [3], CO-PROX reaction [4] and combustion chambers for gas turbines used in power generation [5].

In many monolithic catalysts, the catalyst layer is applied on the wall of a honeycomb-type substrate. The catalyst layer is thin (10–150 μm), porous, and commonly referred to as the washcoat layer.

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Nomenclature

b	empirical factor that varies in the range 0.6 < b < 2	ΔP	pressure drop (Pa)
d_i	path size of percolation path *i*	U	superficial flow velocity (m s^{-1})
m	empirical cementation that varies in the range 1 < m < 4	V_{total}	volume of domain for calculating percolation path
n	number of percolation paths	Z_{sub}	thickness of substrate (m)
r	pore radius (m)	Z_{wc}	thickness of washcoat layer (m)
$K_{e,a}$	apparent effective permeability (m^2)	D_p	diameter of particles of the porous material (m)
$K_{e,sub}$	effective permeability of the cordierite substrate (m^2)	ε	porosity (–)
$K_{e,wc}$	effective gas permeability of the washcoat layer (m^2)	τ	tortuosity (–)
L	length over which the pressure drop is taking place (m)	μ	viscosity (Pa s)
$L_{path,i}$	length of percolation path *i*	λ	mean free path (m)
$P(r)$	probability density function of pore		

The thinness of the washcoat layer has advantages for reducing gas transport resistance. Nevertheless, it is well known that catalytic performance is limited by gas transport resistance, which takes place within the fluid-washcoat interface (external, interface) and in the washcoat layer (internal, intraface). An internal transport limitation has been reported by many researchers. For example, it was reported that gas transport resistance in the washcoat layer can play an important role in determining the light-off behavior of automotive catalysts [6]. Santos and Costa reported that automotive catalysts operate in a mixed regime, in which both external and internal gas transport resistance play a role, and even at high temperature, the purely external gas transport controlled regime is difficult to obtain [7].

In order to meet emissions regulations, it is necessary to reduce gas transport resistance in the washcoat layer. This needs deep understanding about gas transport phenomena in the washcoat layer. Measurement method of effective gas transport in the washcoat layer is well studied [5,8,9–13]. But the guideline of optimizing the pore properties of the washcoat layer has not been established. This is because the influence of pore properties on the gas transport phenomena, and even the pore properties themselves are not well studied. Since washcoat layers usually consist of porous metal oxide particles (e.g., Al_2O_3, ZrO_2, CeO_2), the pores can be classified into two types according to size: smaller pores, on the order of nm, are voids inside the porous metal oxide particles, and are called primary pores, while larger sub-μm or μm pores are voids among porous metal oxide particles, and are called secondary pores. Primary and secondary pores can be observed as two or three peaks in a pore size distribution graph obtained from mercury porosimetry. For example, Haya et al. reported pore sizes of 5 nm and 250 nm as primary and secondary pores, respectively [5]. We reported two peaks of 5 nm and 200 nm for an experimentally simulated washcoat layer [8]. Stary̌a et al. reported three peaks of 200 nm, 1 μm and 5 μm [9]. Both primary and secondary pores play important roles in catalytic performance. Fig. 1 shows a simple diagram of gas transport in a washcoat layer. The reactants first diffuse through the secondary pores (among secondary particles), and then diffuse through the primary pores (inside a secondary particle), and finally react on active sites (e.g., Pt, Rh, Pd) at the wall of a primary pore. To analyze these gas transport phenomena, conventional mercury porosimetry does not seem to be appropriate. For example, mercury porosimetry has been used to predict effective gas diffusivity with the random pore model (RPM) [14]. Hayes et al. reported that RPM predicts an effective diffusivity of the washcoat layer 8 times higher than the experimentally measured value [5]. The reason for this discrepancy may be due to the fundamental difference between mercury intrusion and gas transport phenomena. The pores of the washcoat layer may be too complicated to analyze with mercury porosimetry. Imaging the 3D structure using a technique such as X-ray CT should therefore give us new perspectives on the pore properties of washcoat layers.

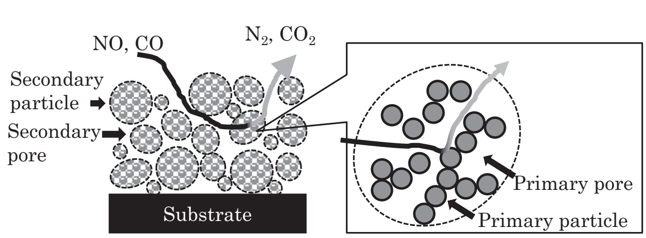

Fig. 1. Diagram of gas transport phenomena in washcoat layer.

Recently, secondary pores of the washcoat layer of a commercial Rh-γAl_2O_3 monolithic catalyst has been studied by Karakaya et al. [15]. They reconstructed the 3D structures from a series of sliced images obtained with focused ion beam – scanning electron microscopy (FIB-SEM). A volume of 26.7 × 13.8 × 37.4 μm^3 was imaged with a spatial resolution of approximately 0.1 μm. From the 3D structure, 3D images of secondary pores are reconstructed. Their morphologies varied significantly, ranging from crevice-like features to tortuous capillary-like features. They developed new model and the model was successfully applied to investigate reaction-diffusion process within the reconstructed 3D secondary pore volume. With this result, Blasi et al. develop macroscale models that can be applied at larger length scale [16]. These studies contributed new quantitative insight about the influence of gas diffusion on the catalytic performance. But the pore properties of primary and secondary pores, and their effect on the gas transport phenomena remains to be researched.

As a first step to reveal all of the pores of washcoat layers and to investigate gas transport phenomena in washcoat layers, in this research, we imaged secondary pores of washcoat layers with synchrotron X-ray CT. The obtained pore properties were compared with those obtained by scanning electron microscopy (SEM) and mercury porosimetry. The gas transport properties were evaluated based on the gas permeability. It is appropriate to investigate the effect of secondary pores only, because primary pores can be neglected in the total permeability, as reported by Salejova et al. [17] The correlation between gas permeability and pore properties was investigated to establish a new model that can link secondary pore properties to gas transport properties.

2. Experimental

2.1. Sample preparation

Four types of monoliths were prepared with washcoating. In the washcoating process, a slurry that included ZrO_2 powder and