



Effective Diffusivity Measurement on a Monolithic Reactor using SPACI-MS Technique



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ABSTRACT

Measuring Effective Diffusivity in the pores of the catalytic washcoat of a monolith reactor is a challenging task. In this work, Spaci-MS technique has been used to measure effective diffusivity in the porous washcoat, and through the porous walls of the cordierite monolith substrate. A mixture of a tracer gas (in this case O₂) was introduced in a center (feed) channel along with a carrier gas, and the axial profile of tracer gas was measured in the neighboring channels. The axial profile of the tracer gas in the neighboring channels depends on the diffusivities in the gas phase, in the washcoat layer and through the substrate wall. A mass balance was made around the 1-adjacent channel to compare the calculated tracer profile with the measured profile, and used to get the value of effective diffusivity. Experiments were done on an uncoated (blank, substrate only) monolith to measure the effective diffusivity in the substrate, and then experiments were repeated for a washcoated monolith to measure the effective diffusivity in the catalytic washcoat layer. The experiments were also repeated at different temperatures to get the temperature dependence of the observed effective diffusivity. The results showed that the monolith substrate was in the bulk diffusion region and the washcoat exhibited Knudsen diffusion. Effective diffusivity of O₂ in substrate was calculated to be $9.28 \times 10^{-6} \text{ m}^2/\text{s}$ and in washcoat to be $2.2 \times 10^{-6} \text{ m}^2/\text{s}$ at 100 °C.

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1. Introduction

The key to understanding transport processes in a porous medium or porous catalyst is the knowledge of effective diffusivity (D_{eff}) of the characteristic molecular species. Diffusional resistance is significant in many gas solid reactions under their operating conditions, such as reactions in zeolites. In automotive applications, the use of zeolites has led to the porous washcoat now generally consisting of macropores, mesopores and micropores, depending on the crystal/particle size in the washcoat. Due to this range of pore sizes, any of Knudsen, bulk or configurational diffusion may be significant. Diffusivity data for various reactant species is required to understand which transport/reaction process limits the extent of the reaction, and to improve reactor performance. Modern reactor design uses an accurate mathematical model of the reactor (with the porous catalyst) which requires an accurate estimate of the diffusivities. Pore size distribution and sizing of the porous catalyst can be optimized so that the diffusional resistances are as small as possible.

There are two kinds of diffusional regimes in pores, the bulk/molecular diffusion and the Knudsen diffusion. Effective diffusivity in a porous catalyst depends on its porosity and tortuosity. While porosity of a medium restricts the cross-sectional area available for transport; tortuosity characterizes the convoluted nature of the porous pathways followed by the diffusing species. Effective diffusivity can be written as

$$D_m = \frac{\varepsilon}{\tau} \times D_o \quad (1)$$

where D_m is the effective diffusivity, D_o is the reference/equivalent diffusivity, ε is the porosity of the material and τ is the tortuosity. In the Knudsen regime, the diffusivity is given by:

$$D_k = \frac{4}{3} K_o \left(\frac{8RT}{\pi M} \right)^{1/2} \quad (2)$$

where D_k is the Knudsen diffusivity, K_o is the Knudsen coefficient, R is the universal gas constant, T is the temperature and M is the Molecular weight of species. The combined reference diffusion coefficient is given by the Bosanquet formula:

$$D_o = \left(\frac{1}{D_b} + \frac{1}{D_k} \right)^{-1} \quad (3)$$

where D_b is the bulk diffusivity.

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Nomenclature

C	Concentration in gas phase (mol/m^3)
D	Diffusivity (m^2/s)
k	Mass transfer coefficient (m/s)
K_0	Knudsen coefficient (m)
M	Molecular weight of gas species
R	The universal gas constant
R_Ω	Hydraulic radius (m)
t	Time (s)
T	Temperature ($^\circ\text{C}$)
u	Linear velocity (m/s)
w	Wall thickness (m)
x	Length (m)
ε	Porosity
τ	Tortuosity
ρ	Density (g/m^3)

There are methods available in the literature to model effective diffusivity in multi-pore size materials [1]. Several methods have also been described to measure the effective diffusivity in the porous catalyst [2–4]. Richardson [2] describes a gas chromatographic method for measuring the effective diffusivity through a porous catalyst bed. A gas sampling valve is used to introduce a pulse of gas at the inlet, and the resulting broadening of the pulse as it passed through the bed was analyzed to get an estimate of effective diffusivity. This method is more useful for a large scale catalyst system. Richardson also found that upon catalyst fouling, the change in tortuosity was only 0.9, whereas the surface area changed by a factor of 5. A Wicke-Kallenbach cell is another frequently used system for a large scale catalyst, where a concentration gradient is applied across a catalyst pellet and effective diffusivity is determined from the concentration profiles (vs. time) on the two sides of the pellet. It offers an easy design and operation, but is not suitable for direct use in measuring effective diffusivities across a monolith wall. Beeckman [3] suggested a method to measure effective diffusivity through the wall of a specially built monolith channel. The diameter of the channel used was 6 mm (much larger than the channel diameter of monoliths used in automotive industry (less than 1 mm)) and was therefore easier to work with for their study. Hayes et al. [4] described how Beeckman's method can be modified to smaller diameter monoliths, but used a special system made of a 7 channel monolith, where the inlet channel was the center channel and the remaining 6 channels (called "out channels") surrounded the inlet channel. It also included a complicated system of adding gases in the inlet and outlet channels through separate connections, and trying to maintain zero pressure drop along the monolith wall. Additionally, it ignored any mass transfer to the outside of the system through the walls of the outer channels. The method described in this work does not need any special monolith. It can be used on any monolith sample available. It uses the SPACI-MS technique [5] to measure the concentrations in the inlet and outlet channels. Further it includes a more complete mass balance on the "adjacent to inlet" channels. The catalyst sample used is also much longer than the shorter (13 mm) sample used in previous studies to allow mass transfer across even a heavily coated monolith wall. The method shown in [6] is more suited to nanopores, and is computationally more intensive. It includes using Confocal Raman Spectroscopy to monitor mass transport and doing a rigorous numerical simulation using the boundary element method.

2. Experimental Methods

One inch (nominal) diameter sample of a cordierite monolith was removed from a full size casting using a diamond hole saw. The cores were typically 0.07 m (or more) in length and typically 0.97 in. in diameter after cutting. The catalyst sample was wrapped with a ceramic cloth to ensure a gas tight fit into a quartz reactor tube of 1 in. (nominal) I.D. The catalyst sample in the reactor tube was then mounted with stainless steel end caps to allow the gastight delivery of gaseous flow through the reactor tube and catalyst sample. Special fittings allow for the introduction of small diameter stainless steel capillary tubing into the reactor volume and to be inserted at various depths within the catalyst channels of the sample. These interface fittings were built from Swagelok™ fittings of various sizes and of configurations to allow the flow of both bulk gas and the movement of the capillary tubing (Fig. 1).

The uppermost capillary interface includes an inlet port for bulk carrier gas (N_2 at 12–15 L/min) and a capillary flow of O_2 at 20 mL/min or less. The upper (single) capillary delivering the O_2 tracer gas was positioned at the inlet of the catalyst sample in a center channel and approx. 0.5 mm into the front edge of the catalyst channel. The flow of tracer gas was controlled by a NIST certified calibrated mass flow controller (MKS) and a three way, fast-acting, micro switching valve. Tracer gas flow is vented to exhaust through the valve until such time as the experiment is started, when a digital signal is used to switch the valve and precisely record the switching event using a digital/analog interface control and Labview software (National Instruments) algorithms.

Three additional capillaries were inserted from the outlet side of the catalyst and reactor tube through an identical custom built interface that also allows the manipulation of these sampling capillaries. The trio of capillaries inserted from the outlet side of the reactor all terminate in a Swagelok assembly that also has sources of nitrogen diluent gas and a sample line connection to a V&F CIMS, a specialty mass spectrometer that uses charge exchange ionization to selectively ionize trace gases in the presence of bulk nitrogen gas [7,8].

The sampling capillary interface tubes were inserted into channels arranged around the center channel receiving the O_2 tracer gas, in three distinct patterns. Pattern 1 (1-Adjacent channels, as shown in Fig. 2) was where the gases were sampled in channels that shared an adjacent channel wall with the center channel receiving the tracer gas. Pattern 2 (Diagonal channels) is where all channels shared a corner with the center channel. Pattern 3 (2-Adjacent channels) is where the sample capillaries are one channel removed from the center channel, with 2 walls between the source channel and the measurement channel.

In a typical experiment the sampling capillaries would be inserted through the catalyst in individual channels, until their tips were observable flush with the front edge of the channels of the catalyst sample. A magnifying lens was used to observe and adjust them precisely to be flush with the leading edge of the catalyst. Once positioned, the gap between two fittings on the outlet capillary interface was measured with a Machinists digital caliper. As the sampling (outlet side) capillaries were repositioned during the measurement of the tracer gas diffusional concentration, the fitting gap was measured to determine the location of the assembly. A graphite Vespel ferrule in a Swagelok tube fitting allowed adjustment of the position of the MS sampling interface and the capillary tube inlet locations could be adjusted incrementally from the front face of the catalyst sample to its rear face with its location known within about 0.05 mm accuracy. The flowrates of the capillaries for both the inlet and the outlet interfaces were determined using a NIST certified bubble flowmeter (STEC) with an accuracy of + or –1% of reading. Gas temperatures were measured and controlled using a 1/32" type K thermocouple inserted into the front face of the

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