Assessing Intrusion by the Capillary During Spatially Resolved Mass Spectrometry Measurement

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Abstract

The impact of the capillary probe of a spatially-resolved mass spectrometer system (SpaciMS) on the measured reactant conversion is reported using propylene oxidation over Pt/Al₂O₃ washcoated monoliths. The findings suggest that the invasive nature of SpaciMS depends on its configuration and application. Using monoliths with a range of cell densities (100 to 600 cells per square inch, CPSI), the concentration profiles of propylene sampled with probes of two different outer diameters (170 and 363 μm) are compared with the temperature measured using coherent optical frequency domain reflectometry (c-OFDR). The comparison indicates that flow blockage has a negligible effect if the limiting propylene is depleted in the downstream reactor section. Suction by the probe compensates for the blockage for certain combinations of the channel diameter and probe size. In such cases the profile measured by a probe with the larger outer diameter (363 μm) is similar to that measured by a smaller capillary (170 μm). The experiments reveal that the axial position of the probe does not influence the flow profile in a 100 CPSI monolith channel, nor does it affect the amount of flow deflected to surrounding channels for a 600 CPSI monolith. Under some conditions the results are impacted by transverse concentration gradients. Their existence complicates the interpretation of the SpaciMS data. The difference between the location of propylene depletion and temperature maximum provides a useful metric for capturing the collective impacts of flow deflection and transverse gradients. The complexity of the flow, transport and reaction suggests that at least three dimensionless groups are needed to bound the operating regions in which the presence of the probe has minimal impact on the measured concentration.

Keywords: propylene; oxidation; monolith; mass spectrometry; SpaciMS, c-OFDR

Introduction

Experiments resolving in-situ spatial distributions of concentration and temperature provide a deeper understanding of complex catalytic reaction systems [1]. The spatially-resolved capillary inlet mass spectrometry, commonly referred to as SpaciMS, developed by Partridge and coworkers at Oak Ridge National Laboratory (ORNL) [2], enables in situ measurement of reacting species concentration inside catalytic reactors. This method involves the insertion of a fused-silica capillary tube into a continuous void in the reactor, such as a drilled hole in ceramic foam or the channel of a monolith. The local reactive gas is sucked by the capillary toward a mass spectrometer for sampling. This technique has been instrumental in clarifying certain mechanistic features in various reactor systems: e.g., Partridge's group studied the effect of sulfur on a NO_x reduction catalyst and found that the sulfation increased the ammonia production rate due to the shrinkage of the downstream oxygen storage zone [3]. Soran et al. used a SpaciMS to validate the global kinetic model that predicts the formation and utilization of ammonia in the NO_x storage and reduction catalyst [4]. Li et al. [5] used SpaciMS to resolve species concentrations in a sequential Lean NO_x Trap and Selective Catalytic Reduction (LNT + SCR) reactor system, while Bugosh et al. [6] the same technique to study the anomalous steady state for methane oxidation on Pt/Pd/Al₂O₃ monolith reactor. These and other insightful studies demonstrated the usefulness of the SpaciMS technique.

The SpaciMS probe may affect the flow in a monolith channel, the void of a foam, etc. and therefore alter the axial concentration profile. This potential intrusion has led to an ongoing debate on the accuracy of the method. Resolution of the debate is exacerbated by differences in SpaciMS configurations and implementations as well as experimental methods. Complicating factors include the extent of flow blockage and variations in the suction rate by capillary probe,

boundary layer transport limitations, among other factors. Sa et al [7] used computational fluid dynamics (CFD) to simulate the influence of the probe during CO oxidation. Assuming that the inlet velocity is the same for all monolith channels, they concluded that the probe's influence was negligible. On the other hand, Hettel et al. [8] argued that the assumption of equal flow distribution in all the monolith channels may not be valid. Using CFD simulations of the catalytic partial oxidation of methane, they showed that the blockage caused the conversion in a channel containing the probe to exceed that in a channel without a probe. The simulations reveal that the blockage impact is significant even when the probe occupied only 3.5% the channel area. Goguet and Partridge et al. [9] argued that the SpaciMS method provides an accurate measurement of the concentration with negligible intrusion. Morgan et al. also conducted several experiments to check the invasiveness nature of the capillary probe [1]. The extent of blockage depends on the position of the probe within the channel cross-section, with the largest impact when the probe is at the channel center [8]. For reactors that are positioned horizontally the probe tends to lie on the bottom wall of the channel due to gravity while for vertical reactors the flexible nature of the probe casts doubt on its location. Thus flow blockage by the probe is difficult to predict without knowing its position.

In the current study, to gain a deeper understanding with the goal of providing some guidance, we conducted experiments using SpaciMS comprising two different capillary probe sizes to measure the intra-channel concentration profile during the complete oxidation of propylene on Pt/Al₂O₃ washcoated monoliths of several different CPSIs. The experiments were targeted to assess the impact of the capillary probe in different combinations of monolith cross-section sizes and capillary diameters. Spatial intra-channel fluid temperature profiles were measured using the coherent Optical Domain Reflectometry (c-OFDR), a technique described

elsewhere [10]. In the absence of a probe, a linear relation exists between the limiting reactant conversion in one channel and the temperature in the adjacent channel. A position difference between the propylene depletion point and the local temperature maximum would suggest that the concentration measurement is affected by the probe. Additional experiments are conducted to assess the impact of transverse concentration gradients. To this end, the findings of this study provide useful guidance on the veracity of SpaciMS as an *in situ* reactor diagnostic tool for various configurations and applications. The invasiveness extent may be assessed to determine the costs and benefits of a particular design change. For example, an increase in the capillary size and sampling rate may benefit the temporal resolution at the expense of flow blockage. This can guide experimentalists to make the best design decisions for a particular application.

Experimental Setup and Procedure

The complete oxidation of 0.17 vol. % propylene and 10 vol. % O₂ was conducted in a 7.5 cm long, 2.54 cm diameter catalytic cordierite monolith catalyst with channel densities of 100, 200, 400 and 600. Blank monoliths (100, 200, and 600 CPSIs) were provided by Corning Inc. (Corning, NY). A Pt/Al₂O₃ catalytic washcoat was deposited on these monoliths via a dip coating method described in [11] to achieve a washcoat loading of 2.3 g/in³ and a Pt loading of 23.8 g/ft³. A commercial 400 CPSI monolith was provided by BASF (Iselin, NJ). This monolith has 2.3 g/in³ washcoat loading and 96 g/ft³ Pt loading. Table 1 summarizes the structural characteristics of the different CPSI monolith reactors.

Table 1.

The experimental setup using both a SpaciMS and c-OFDR is described elsewhere [12]. Figure 1 shows a schematic and a picture of the sampling system in the vicinity of the upstream of the monolith. The temperature profile was measured by a stationary 125 μm outer diameter

optical fiber placed in the center channel of the monolith. Temperature measurement by the c-OFDR has several advantages compared to that by thermocouples; i.e., it is not subject to heat conduction along the fiber's body. The small fiber size, fast sampling rate, and distributed temperature measurement capability enables its use in both transient and steady state studies. The fiber provides a continuous spatial temperature profile with $\pm 1^\circ\text{C}$ accuracy. It is essential to accurately identify the entrance location of the monolith to enable accurate comparison of the spatial temperature and concentration profiles. Thus, a portion of the fiber near the entrance was coated with AquadagTM that increases its laser absorbance. A 200 mW GX3 green laser pointer (beam diameter ~ 2 mm) directed to this position created a local hotspot, which was detected on the measured temperature profile. Using this technique, the axial position of the measured temperature profile is off by at most ± 2 mm. The feed entrance temperature was also monitored by a K-type Omega stainless steel sheathed thermocouple (OD = 0.5 mm), positioned 0.5 cm upstream of the monolith front face. That signal was used to monitor the feed temperature and calibrate the optical fiber before the start of each experiment.

Figure 1.

Two fused silica SGE capillary tubes (OD = 363 μm , ID = 150 μm & OD = 170 μm and ID = 110 μm) were used to measure the concentrations. The suction rates of the capillary tubes depend on the capillary internal diameter and other factors. These are estimated and provided later in the paper. The capillary was inserted into a septum in the downstream section of the reactor channel. The other end was mounted on a linear translation stage and connected to the mass spectrometer through a micro Valco[®] fitting. The gas flowed under suction into the probe and through the fiber to a quadrupole mass spectrometer (QMS-Omnistar GSD 300). The position error associated with the spatial concentration profile was about ± 2 mm.

The reactor reached a steady state profile after two hours. A typical concentration profile was established as follows. The capillary probe was moved from the upstream to the downstream end to construct a complete concentration profile. At each axial sampling point, the propylene concentration was measured for ~10 minutes, allowing the value to reach a time-invariant level. The spatial concentration was reported by averaging the values over a period of at most two minutes. The reported dimensionless concentration is the ratio between the measured to inlet concentration. The use of dimensionless concentration improved the accuracy of identifying the depletion location of propylene gas. To ensure that channel concentration profiles were representative of the overall monolith, the experiment was conducted in different channels, which were randomly chosen among eight channels surrounding the reference channel, to confirm an observed trend. This minimized the likelihood of atypical data due to non-uniformity in washcoat thickness between the channels that can produce regions of different catalytic activity.

Unless otherwise stated, the propylene oxidation was conducted under steady state conditions with a feed comprising 0.17 vol. % C_3H_6 , 10 vol. % O_2 and the balance Argon. Both the total flow rate and feed temperature were between 8000 to 11000 sccm and 50 to 250 °C, respectively. The adiabatic temperature rise for this feed composition is estimated to be 158 °C. The gas hourly space velocity (GHSV) range corresponding to this range of flow rates is 12640 to 17380 h^{-1} (standard conditions). The feed temperature was varied by adjustment of the furnace temperature.

Experimental Results and Discussion

Impact of the probe axial position

A set of experiments examined the impact of the axial position of the capillary probe by measuring the temperature profile using the c-OFDR at a given position of the probe. For a 100 CPSI monolith, the measurements were accomplished with the 125 μm c-OFDR fiber and 363 μm SpaciMS probe in the same channel. (Below we discuss the 600 CPSI results shown in Fig. 2.b.) The fiber and probe occupy 0.2% and 1.6% of the channel cross sectional area, respectively. The feed flow rate and temperature in this experiment were 8000 sccm and 200°C, respectively. While the fiber was stationary, the probe was moved along the channel and sampled at about 20 distinct points. The temperature profile was measured while the probe was at either one of these positions indicated in Fig. 2a as upstream (position A), midstream (position B), and downstream (position C). Obviously, the probe occupied a different length or volume fraction of the channel at each axial position. The experiment was conducted to check if the flow rate into the channel and blockage varies with the probe position. In turn, this could affect the gas residence time or alter the measured concentration profile. Specifically, the blockage is expected to be more significant with the probe in position A than that in position C, resulting in a lower flow rate for A than C. This change could be detected by the measured temperature profile. Given the finite thermal conductivity of the fused silica capillary of 1.38 W/(m K) a question raised earlier by Horn et al. [13] is whether heat conduction along the probe may further impact the results. We detected no change in the temperature profile in these steady state experiments. Similar findings were obtained at a higher flow rate of 11000 sccm (not shown here).

It is noted that the measured temperature rise ($\sim 100^\circ\text{C}$) is lower than the calculated value ($\sim 158^\circ\text{C}$) for the given feed concentration of propylene. This is attributed to a couple of factors. First, we cannot rule out heat losses which would suppress the asymptotic value of the

temperature. Second, as we elaborate below, the c-OFDR fiber measures the fluid temperature which is necessarily different (lower) than the solid temperature. The latter would be anticipated to approach the expected value of the temperature rise in the absence of heat losses.

Figure 2.

A similar set of experiments were conducted to check if the probe position affected transient measurements. Fig. 3 shows the evolving temperature profiles when the feed propylene concentration was increased from 0 to 0.17% at $t = 0$ s for a feed temperature of 81°C (Fig. 3A) or at 101°C (Fig. 3B), respectively, with 363 μm OD capillary tube in the commercial 400 CPSI monolith catalyst. Two sets of experiments were conducted: one with the capillary probe fully occupied the channel and the other with the probe removed entirely from the monolith. As in the results in Fig. 2.a, the optical fiber and the capillary tube were contained in the same channel. Reasonably close agreement was obtained between the two temperature profiles when the reaction ignited and the thermal wave propagated upstream. These results indicated the capillary probe position has negligible impact even under transient experiments.

Figure 3.

The steady-state and transient results suggest that the probe axial position for this particular combination of monolith and probe is negligible as the measured temperature profiles were essentially identical when the probe was in different positions. The invariance of the measured temperature profile suggests that the axial position of the probe has a minimal impact on the extent of reaction for low density 100 CPSI monolith.

To examine the generality of these transient results, the same experiment was conducted in a monolith with the highest cell density (600 CPSI). Due to the much narrower channel size, it was not possible to insert both probes into the same channel without influencing the temperature

reading. Hence, the optical fiber was inserted in the channel adjacent to the one housing the capillary probe. Fig. 2b shows that, just as for the 100 CPSI monolith results, the temperature profile in the adjacent channel is not influenced by the position of the capillary tube in channel. This indicates that the axial position of the probe position has a negligible influence over the flow in adjacent channels. These results are consistent with the simulation findings of Hettel et al. [8] and Sa et al. [7] who showed the probe position has only a minor impact on the flow to neighboring channels without a probe. Our findings further suggest that the small amount of gas blocked by the probe is distributed among several adjacent empty channels. The net effect is that the probe position does not cause a significant shift in the flow to the adjacent channels. Finally, it is noted that these experiments do not rule out an impact of the probe position on the measured concentration profile by the probe. This is examined in the next section.

Impact of suction by capillary probe

The gas suction by the capillary is typically a small fraction of the feed to the channel and is therefore ignored. As the suction may counteract the flow blockage by the probe, it is important to estimate and compare the magnitudes of these two effects. The flow by suction can be measured by several methods involving flow meter and transient residence time analysis, such as connecting a manometer to a SpaciMS capillary [13] or by estimating its magnitude with a model. Here we follow the latter approach.

Connecting a capillary probe to the SpaciMS generates a large pressure drop: the sampling point (capillary mouth) is exposed to atmospheric pressure ($\approx 10^5$ Pa), while the outlet is under high vacuum ($\approx 4 \cdot 10^{-6}$ Pa). At very low pressure, the mean free path of a gas molecule is comparable to the probe diameter and significant interaction occurs between individual gas molecules and the tube wall. Due to the violation of the no-slip boundary condition, the flow in

the capillary may significantly deviate from the prediction by the classical Navier-Stokes equations. Several investigators attempted to account for the wall effect using the Maxwell slip velocities, but these approaches are often too complicated for the current application [14].

Dongari et.al [15] developed a simple prediction based on the classical Hagen-Poiseuille model of an incompressible laminar Newtonian fluid in a tube. They argued that under isothermal conditions the nonzero fluid velocity at the wall is determined by the boundary condition:

$$\rho U = -\frac{\mu}{P} \left(\frac{dP}{dz} \right) \quad \text{at } r = r_i \quad (1)$$

where U is the fluid velocity at the capillary tube wall (m/s), r_i the inner radius of the capillary (m), and μ (Pa s) and ρ (kg/m³) are the fluid viscosity and density, respectively. Solving the Navier-Stoke equation with this boundary condition and applying the Bernoulli equation predicts the following suction mass flow rate:

$$M_s = \frac{\pi \times r_i^4}{16\mu L_{cap} R_m T_{cap}} \times \left[\frac{P_{atm}}{1 + \frac{F_T^2}{2R_m \times T \times N^2 \times S^4}} \right]^2 \quad (2)$$

where M_s is a mass suction flow rate (kg/s), L_{cap} the length of the capillary tube (m), T_{cap} the isothermal temperature of the capillary tube, R_m the mass-based gas constant (J/(kg K)), F_T the total volumetric flow rate, T the temperature at the tip of the capillary tube, N the number of channels for the monolith reactor, S the side length of a channel, and P_{in} (P_{out}) the inlet (outlet) pressure of the capillary (Pa). A detailed derivation is presented in Appendix B.

The blockage effect caused by geometrical impact of the capillary tube can be compensated for by the suction rate. The extent of that compensation depends on several factors,

the important ones of which are contained in the modified Dongari formula, Eq. (2). The formula implies that an increasing internal capillary tube diameter increases the suction rate, but increasing the total flow rate decreases the suction, causing the blockage to be more significant. This prediction agrees with the Hettel et al. claim that the blockage impact increases at high space velocity [8].

We utilized Eq. (2) to estimate the ratio of the flow rate caused by suction into the probe and that blocked by the probe. This estimate helps interpret data shown below. The values of various model parameters are provided in Table 2.

Table 3 reports the estimates of the ratio between the flow rates caused by suction (using Eq. 2) and blocked by the probe. These were obtained for several different combinations of channel size (CPSI), probe size (d_o , d_i), and a total feed rate of 8000 sccm. The predictions describe the impact of:

- Channel flow rate without a probe (Q_{ref}),

$$Q_{ref} = \frac{F_T}{N} \quad (3)$$

where N is the number of channels.

- The percentage of the channel cross section area occupied by the capillary probe

$$\% \text{ Occupied} = \frac{\pi d_o^2}{4 \times S^2} \times 100\% \quad (4)$$

This expression assumes the blockage is caused only by the cross-sectional area (S^2) occupied by the probe.

- The blocked flow rate (Q_b) is

$$Q_b = Q_{ref} \times (\% \text{ Occupied})/100 \quad (5)$$

The amount of fluid being deflected by the capillary probe is due to the reduction of cross-sectional area in a monolith channel, a boundary layer is formed at the probe's surface, among other factors. A numerical (CFD) analysis of the boundary effect caused by the probe is required as described by Hettel et al. [8] and Gossler et al. [16]. We assume the conservative estimate given by the cross-sectional area reduction caused by insertion of the probe. Thus ratio of the blockage to suction flow rates (Q_b / Q_s) where $Q_s = \rho_s M_s$ with M_s given by Eqn. (2), likely is an underestimate. A ratio of order unity indicates that the suction compensates for the blocked flow; a ratio much smaller than unity indicates that suction over-compensates for the blocked flow; a ratio greatly exceeding unity indicates that the blocked flow is not influenced by suction.

Table 2.

Table 3.

With this in mind, we investigated the competing effects of blockage and suction during propylene oxidation in the 400 CPSI monolith reactor. The gas was sampled using two different probes ($d_o = 170$ and $363 \mu\text{m}$) to assess the competition. The feed flow rate was 8000 sccm and contained 0.17 vol. % C_3H_6 , 10 vol. % O_2 , and balance Ar. The feed temperature was 180°C . Fig. 4a shows the surprising result that the concentration profiles measured by the two probes are essentially the same, i.e., the probe size did not affect the propylene conversion. A larger probe is expected to increase the blockage and hence alter the residence time in the channel, and consequently shifts the concentration profile upstream. That this did not occur suggests that the increased blockage was compensated by the suction. The suction flow rate prediction (Eqn. (2)) predicts that $M_s \propto r_i^4$ when the non-unity term in the denominator is negligible. For these

conditions a larger internal diameter of the capillary probe increases the suction rate by a factor of 3.5 ($= 150/110$)⁴. The estimated ratio of the deflected and suction flow rates is of order unity (1.04 for the 170 μm OD probe). Thus, any blocked flow is compensated for by the suction. This likely explains why the change in the probe size minimally affected the residence time and conversion in the channel. The results underscore the need to account for suction when assessing the net invasiveness extent.

Fig. 4b shows that when the experiment was repeated at a higher flow rate ($F_T = 11000$ sccm) the concentration profile corresponding to the larger outer diameter probe ($d_o = 363$ μm) was shifted by 1 cm upstream from the profile obtained with the smaller probe ($d_o = 170$ μm). An increase in the total flow rate to the channel increases the magnitude of the Q_b/Q_s ratio. At the higher flow rate the suction flow rate decreases (Eq. (2)). In turn the larger diameter probe increases Q_b . Thus blockage is not compensated by suction to the same degree as at 8000 sccm. The shift in the propylene concentration upstream reflects an increased conversion as a result of the increased residence time. This result is expected when suction is not important.

Figure 4.

We repeated the experiments reported in Fig. 4a in a 600 CPSI monolith with a feed temperature of 240°C. Fig. 4c shows that the propylene concentration measured by the smaller outer diameter probe (170 μm) is upstream of that using the larger probe (363 μm). The large probe occupies about 6% (10%) of the channel cross section in the 400 (600) CPSI monolith (Table 1). It is surprising that the conversion is lower for the larger probe, which has a longer residence time. We attribute this non-intuitive result to an external mass transfer limitation that generates a transverse concentration gradient within the channel at this higher feed temperature.

That is, the smaller capillary probe samples gas that is closer to the surface than that by the larger probe. Hence, for the same center channel reactant concentration the smaller probe measures a lower concentration than the larger probe. It is noted that the results obtained for the 400 CPSI monolith (Figs. 4A, 4B) are also impacted by transverse concentration gradients but perhaps not to the same degree at the lower temperature. There are competing effects. The flow blockage reduces the flow rate, leading to a larger residence time and conversion. On the other hand, the suction by the probe and the above-mentioned sampling effect in the presence of a transverse gradient effect tend to shift the concentration profile downstream; i.e. conversion decrease. Thus, any comparison of two different probe sizes requires consideration of these interacting effects. For the more porous monolith (400 CPSI) these interacting factors result in similar concentration profiles at the lower flowrate (Fig. 4A) while the blockage effect is more prominent at the higher flowrate (Fig. 4B). Finally, at higher temperature with the high density monolith (600 CPSI) the transverse gradient effect causes a qualitative shift in the impact of the probe size (Fig. 4C).

Transverse concentration gradients

An intra-channel concentration gradient transverse to flow can be detected as follows. We measured using the smaller probe the concentration at the end of the channel and about 3 mm from the channel outlet. This concentration is referred to as the cup mixing concentration, a term used to describe the concentration that results if the entire stream is collected in a cup, mixed, and the concentration measured. The concentration difference between the two points provides an estimate of the extent of transverse gradients. Our interpretation of these data assumes that the sampling concentration 3 mm beyond the channel exit enables sufficient mixing to distinguish the composition near the channel wall from that of

the mixed effluent stream. Figs. 5a and 5b report the results for the 100 and 200 CPSI monoliths, respectively. Fig. 5a shows a significant difference in the propylene conversion at the end of the monolith (93%) and the cup mixing value (54%). The rather large conversion gap for the 100 CPSI monolith is attributed to an external mass transport resistance transverse to the axial flow in the 100 CPSI monolith, which has a wide channel and hence a longer diffusion distance. Fig. 5b shows that the conversion gap decreased when the same propylene mixture was fed to the 200 CPSI monolith reactor at the same flow rate and at the lower feed temperature of 131°C. In this case, the outlet conversion was about 95%, while the cup mixing conversion was 80%. Thus, the SpaciMS measurement enables an estimate of the transverse concentration gradient. This information is useful for data interpretation. It is noted that we measured (results not shown here) no concentration (conversion) difference between the end of channel and the effluent when the experiment was conducted at the much lower temperature the $T_f = 65\text{ }^{\circ}\text{C}$ for the 400 CPSI monolith, and $T_f = 150\text{ }^{\circ}\text{C}$ for 600 CPSI monolith. We attribute the higher transverse mass transfer rate in monoliths with a higher cell density to a decrease in the hydraulic diameter, and increase in the specific surface area of the substrate channels.

Figure 5.

A similar experimental approach was proposed by Morgan et. al. [1]. However, in that study the concentration difference was attributed the decreasing conversion beyond the exit point to invasiveness of the probe. In the current study, we attribute the trend to the difference between the cup mixing effluent concentration and the intra-channel concentration. That difference increases with an increase in the channel size of the monolith (CPSI increase).

We now revisit an earlier result in Fig. 4c which was attributed to a transverse concentration gradient. The relative size of the probe and the channel width (hydraulic radius)

may impact the measured concentration: the probe samples a local concentration that is determined in part by its size relative to that of the channel and, as a result, may lead to misleading results under a steep concentration gradient. In contrast, if the probe is positioned in the center of channel, it is more likely to measure a higher reactant concentration than if located near the wall. A peripherally-nonuniform washcoat thickness may also cause differences between the gas sampled near the channel corner and at the midpoint along the wall. That said, peripheral variations are not likely to occur under strong external transport control since the surface concentration would be low around the channel periphery.

The extent and impact of the transverse transport in the capillary probe can be estimated by ϕ , defined as the ratio between the transverse diffusion time (τ_d) and the reaction time (τ_r):

$$\phi = \frac{\tau_d}{\tau_r} \quad (6)$$

ϕ is a product of the transverse Peclet number (Pe_t) and the Damkohler number (Da):

$$\phi = \frac{\tau_d}{\tau_c} \times \frac{\tau_c}{\tau_r} = Pe_t \times Da \quad (7)$$

where τ_c is the characteristic axial convection time. A small ϕ corresponds to kinetic control and a negligible concentration gradient, while a large ϕ corresponds to transverse diffusion control and a steep concentration gradient.

The characteristic transverse transport time (τ_d) is an estimate of the diffusion time of the reactant propylene from the channel center to the wall. In the absence of a probe, τ_d is the ratio of the square of the diffusion distance and the reactant gas phase bulk diffusivity (D_f):

$$\tau_d = \frac{R_{\Omega_1}^2}{D_f}, \quad (8)$$

where the effective transverse length R_{Ω_1} is $\frac{A_{\Omega}}{P_{\Omega}}$, where A_{Ω} is the cross sectional channel area

open to flow and P_{Ω} is the wetted perimeter. For a square channel $A_{\Omega} = S^2$ and $P_{\Omega} = 4S$ where S is the effective length of a square channel, assuming a uniform washcoat thickness. In the

presence of a probe, $R_{\Omega_1} = \frac{S^2 - \frac{\pi d_o^2}{4}}{4S + \pi d_o}$, where d_o is the outer diameter of the capillary probe. Thus,

the effective diffusion length and the diffusion time are shorter in the presence of the probe.

The reaction time (τ_r) of propylene oxidation requires knowledge of the reaction kinetics. In excess oxygen, Pt-catalyzed propylene oxidation rate, R_P , is described by the Langmuir-Hinshelwood rate law

$$r_P = \frac{k_1 Y_s}{(1 + k_2 Y_s)^2} \text{ (mol/m}^3 \text{ washcoat/ s)} \quad (9)$$

where Y_s is a circumferentially averaged mole fraction at the fluid-washcoat interface, and k_1 and k_2 are temperature-dependent kinetic parameters that satisfy the Arrhenius temperature dependence:

$$k_1 = b_1 \times \exp\left(-\frac{b_2}{T_s}\right) \quad k_2 = b_3 \times \exp\left(-\frac{b_4}{T_s}\right) \quad (10)$$

The rate predicts a maximum at an intermediate value of Y_s , consistent with previous experiments [17]. The limiting apparent propylene reaction order is unity for $k_2 Y_s \rightarrow 0$ and -1 for $k_2 Y_s \gg 1$. For example, under strong transverse diffusion limitations, Y_s approaches 0 and the reaction order is unity. In general, τ_r depends on the propylene concentration and therefore on the axial position. The characteristic reaction time is given by

$$\tau_r = \left(\frac{r_{p,s}}{C_T \times Y_f} \right)^{-1} = \left[\frac{\left(\frac{k_1 Y_s}{(1 + k_2 Y_s)^2} \right)}{C_T \times Y_s} \right]^{-1} \quad (11)$$

Where C_T is the total molar concentration. One may estimate τ_r at the point of depletion of propylene ($Y_s \rightarrow 0$). Under these conditions the kinetics are linear and τ_r simplifies to:

$$\tau_r = \lim_{Y_s \rightarrow 0} \left(\frac{r_{Pr}}{C_T \times Y_s} \right)^{-1} = \frac{C_T}{k_1} \quad (12)$$

Substitution of Eqns. (8) and (12) into Eqn. (6), gives

$$\phi(Y_s \rightarrow 0) = \frac{R_{\Omega_1}^2 \times k_1}{D_f \times C_T} \quad (13)$$

Estimation of k_1 (b_1 , b_2 in eqn. (10)) requires a fit of monolith reactor data under differential conditions. We describe the monolith model used for this estimation in Appendix A. The reactor model used is a 1-D low dimensional model following Joshi et al. [17], which has been successful in predicting a variety of different catalytic reaction systems, including NO_x reduction by LNT catalysts [18], dynamic hysteresis of co-oxidation of CO and C_3H_6 [19], among others [20]. Diffusion and reaction in the washcoat is approximated by an internal mass transfer coefficient derived by averaging the washcoat differential mole balance [21]. The model is based on the following assumptions: (i) the cross section of the channel and the washcoat thickness remain constant, (ii) ignores axial diffusion and conduction in the fluid phase, (iii) laminar flow in the channel, (iv) constant physical properties of the gas and solid phases, and (v) ignores heat conduction in the solid phase.

The experiments to extract the kinetic parameters were conducted at sufficiently low feed temperatures to minimize mass transfer intrusion, and the propylene conversion was kept below 15%. The experiments were conducted in the 200 CPSI monolith with a feed of $C_3H_6 = 0.3$ vol. %, $O_2 = 10$ vol. %, $T_f = 152$ °C, and $F_T = 11,600$ sccm. The invasiveness of the probe in this case is mainly a result of its sampling position near the wall. fluid temperatures. Here the probe's invasiveness is mainly a result of its sampling position along the wall of the channel. Fig. 6a and 6b report the SpaciMS (170 μ m) and c-OFDR measured propylene concentration and intra-channel temperature, respectively. The experimental conversion was 13%, while the temperature rise was 30 °C.

The corresponding monolith model predictions are also shown in Fig. 6 in terms of fluid and surface propylene concentrations (C_s , C_f ; Fig. 6A) and temperatures (T_s , T_f ; Fig. 6B). A reasonably good fit of the data is evident. The experiments indicate that the concentration is essentially bounded between the average bulk and surface concentrations. Here the probe's invasiveness is mainly a result of its sampling position along the channel wall. Fig. 6B shows that the experimental temperature was within 6°C of the predicted fluid and surface temperatures, indicating that the model described reasonably well the non-isothermal behavior. The kinetic parameters obtained for the 200 CPSI were used to predict the fluid and surface temperatures.

Figure 6.

Following this scheme, we estimated the kinetic parameter constants for the 100, 400 and 600 CPSI monolith reactors at low conversion (conversion < 15%), and low temperature rise ($\Delta T < 40$ °C). For each monolith a set of experiments was conducted and the parameters estimated. Table 4 reports the estimated kinetic parameters for each monolith while the Supplementary Material provides the plots for the three other monoliths. The estimated value of the pre-

exponential constant b_1 for the 400 CPSI monolith are of the order of 10^{17} (mol/m³ s), which is ~100 times larger than of the other monoliths. This difference is attributed to the three-fold higher loading of Pt in the commercial 400 CPSI. The average estimated value of the parameters b_2 and b_4 for the C₃H₆ oxidation were about ~12,000 K and ~ -100 K, respectively. For comparison, Voltz et al. [22] reported these values as 11,427K and -361 K based on experiments in a fixed bed integral reactor containing Pt/Al₂O₃ catalyst. It is noted that the confidence limits for some of the parameters are rather large. This reflects the limited number of points used to estimate the parameters. Obviously, the large confidence limits would preclude their use to use them to simulate the reactor. However, our intent is simply to estimate the reaction time constant (eqn. (12)) in the creation of the ΔZ map described next.

Table 4.

Assessing impact of the probe: ΔZ map

The spatial profiles of propylene concentration and temperature were measured for different feed conditions distributed among these four monoliths and two capillary probes. The objective was to identify and relate trends in the spatially-resolved data to an impact of the capillary probe. We describe below how to assess the probe impact from the relationship between the concentration and temperature profiles.

When a single irreversible reaction occurs in an adiabatic reactor, a linear relationship exists between the fluid temperature rise and the limiting reactant conversion

$$\Delta T = \frac{(-\Delta H)X C_f}{\rho C_{pf}} \quad (14)$$

Under adiabatic conditions the temperature rise ΔT approaches the adiabatic temperature rise at complete conversion of the limiting reactant; i.e., $\Delta T (X \rightarrow 1) = \Delta T_{\text{ad}}$. [Note: If any heat losses occur then Eqn. (14) is no longer valid and the temperature profile may achieve a maximum along the length of the monolith channel.] Under this linear dependence between ΔT and X inferred by Eqn. (14), the reactant concentration profile is essentially a mirror image of the temperature profile. We contend that the SpaciMS capillary probe is non-invasive if the linear dependence is achieved in an experiment. The rationale is that any blockage by the probe would increase the residence time in the channel. As a result, the temperature profile in a neighboring channel containing the c-OFDR fiber will be shifted downstream from the concentration profile. Any deflected flow would increase the flow rate in neighboring channels, which would further shift the temperature profile downstream. Clearly this methodology relies on all channels having identical dimensions, washcoat loading, and activity. Another assumption is that the optical fiber is sufficiently fine so that it has only a negligible effect on the flow in the channel in which it is contained.

A convenient way of assessing the linearity between the conversion and temperature rise is by the metric ΔZ , defined as the difference between the axial position of the temperature maximum or threshold temperature ($Z_{T_{\text{max}}}$) measured by the c-OFDR optical fiber, and the axial position of the propylene depletion position ($Z_{c=0}$) measured by the SpaciMS probe

$$\Delta Z = Z|_{T_{\text{max}}} - Z|_{c=0} \quad (15)$$

Thus, $\Delta Z \rightarrow 0$ implies that the SpaciMS probe is non-invasive, while $\Delta Z > 0$ is a result of contributions from the probe's invasive nature and radial sampling when a transverse concentration gradient exists. We showed earlier that the capillary probe samples the surface

concentration. This in itself is not problematic, but when combined with the fact that the optical fiber measures more closely the fluid temperature in the center of a channel, leads to a non-zero ΔZ . We illustrate these concepts in more detail below. Finally, it should be mentioned that the error associated with the spatial measurements by the capillary probe and the optical fiber are ± 0.5 mm and ± 2 mm respectively. Thus, the experimental error for ΔZ is ± 2.5 mm.

Fig. 7a shows the results of an experiment in which a feed containing 0.17% propylene and 10% O_2 was fed at 8,000 sccm at a temperature of 200 °C. The lowest cell density (widest channel) monolith (100 CPSI) and larger probe were used (363 μ m o.d.). The data show that the concentration and temperature profiles are essentially mirror images of each other and $\Delta Z \sim 0$. In this experiment, we conclude that the capillary probe is not invasive. Fig. 7b is another example in which a hotter gas ($T_f = 246^\circ$ C) was fed to the 100 CPSI monolith, while employing the smaller capillary probe (170 μ m OD). All other feed conditions were the same as in Fig. 7a. A rather large shift between the two profiles is evident in this experiment, with $\Delta Z \sim 16$ mm. We conclude that the large ΔZ is due to an invasive sampling arrangement, shorter hydraulic diffusion length and steeper radial concentration gradient.

Figure 7.

Table 5 lists 37 distinct experiments in terms of the monolith cell density (CPSI), dimensions of the capillary probe (d_i , d_o ; μ m), feed gas temperature (T_f ; °C) and total volumetric flow rate (F_T ; sccm). Values of $\log(\phi)$, dimensionless propylene depletion point (Z') and the invasiveness metric ΔZ is also provided. Feed composition of experiments denoted without an asterisk (*) is 0.17 vol. % C_3H_6 and 10 vol. % O_2 , while of those denoted with asterisk is 0.3 vol. % C_3H_6 and 10 vol. % O_2 . A plot of ΔZ as a function of a single dimensionless parameter such as

ϕ did not show any obvious trend, such as a monotonic shift from low to high ΔZ values upon increasing ϕ . We tried with limited success to use several other dimensionless groups to identify a coherent correlation of the ΔZ data. This suggests that at least one more parameter is needed to correlate the ΔZ data.

Table 5.

An informative result was achieved with a two-dimensional map of ΔZ in the plane of the Z' and $\log(\phi)$. Z' is defined as the dimensionless position of propylene depletion; i.e.

$$Z' = \frac{Z|_{C=0}}{L} . \quad (16)$$

where L is the length of the monolith, such that $0 \leq Z' \leq 1$. Figure shows the ΔZ map as a function of Z' and $\log(\phi)$. (The map was constructed by Origin 9.0[®] software, using Color Fill Contour Plot feature.) The data points on the ΔZ map correspond to the numbers in Table 5. Thus one can interpret the impact of the various operating parameters by referring to Table 5. The Z' axis is divided into three zones; a *downstream zone* ($Z' > 0.6$), a *midstream zone* ($0.2 < Z' < 0.6$), and *upstream zone* ($Z' < 0.2$). The $\log(\phi)$ axis spans values from 1.9 to ~3.9, or $80 < \phi < 7900$. As defined earlier, ϕ is the ratio of transverse diffusion to reaction time. One reason for the wide range of values is that the measured temperature at the depletion point was used to estimate k_1 . For small values of ϕ (< 1) there are no transverse gradients as the diffusion time is smaller than the convection time; for intermediate values of ϕ ($1 < \phi < 100$) the reaction is moderately transport limited, while for very high values of ϕ (> 100) the reaction is essentially instantaneous and mass transport limited and has the steepest transverse gradient.

Figure 8.

The main ΔZ map features are:

- The smallest values of ΔZ ($0 \leq \Delta Z \leq 4$) occur when propylene is depleted in the downstream zone ($Z' > 0.6$).
- The lone black region occurs for $Z' > \sim 0.7$ and $\log(\phi) > \sim 3$.
- In the midstream zone ($0.2 \leq Z' \leq 0.6$), the ΔZ values are moderate to high (4 to 12 mm). One exception is the small blue region ($\Delta Z \sim 0$ to 4 mm) encountered for lower ϕ values ($\log(\phi) \sim 1.9 - 2.1$).
- For most of the upstream zone ($Z' < 0.2$) moderate to significant ΔZ values are encountered ($\Delta Z \sim 4$ to 20 mm). This trend is similar to the findings of Morgan et al. [1]. They tested five different reactor setups with various degree of probe's blockage and found that the more invasive nature of the probe was encountered for the smaller reactant concentrations measured in the upstream region.

When the propylene is depleted in the downstream zone, fluid and solid temperatures approach each other and the steady state temperature. The optical fiber senses a temperature bounded by these two values. Earlier we established that the smallest capillary probe measures a concentration that is closer to that of the surface than to that of the bulk. In the absence of a transverse temperature gradient and applying Eq. (14), a nonzero ΔZ suggests that the blocking effect is the main cause in this region. Indeed, $\Delta Z \sim 0$ for the group of Experiments 5 – 8, and 16 – 19, all of which involved either the 100 or 200 CPSI monoliths. Their wider channel size was apparently sufficient to prevent any blockage by the capillary. For Experiments 5-8 in the $\Delta Z =$

0 region correspond to mixtures fed to the 100 CPSI monolith (no blockage). On the other hand, upon decreasing ϕ for fixed $Z' \sim 0.9$, nonzero ΔZ values are reported. For example, Experiments 34 and 35 in the blue region were obtained for feed temperatures of 140 -160 °C using the 600 CPSI monolith. Indeed, most of the experiments in this blue region involved the 600 CPSI monolith. The smaller ϕ reflects the lack of transverse concentration gradient. The fact that $\Delta Z > 0$ suggests that flow blockage is the root cause.

The trends observed in the midstream zone are not as discernible and must have higher values of ΔZ . In this region, the temperature gradient between the fluid and the surface at the depletion concentration location is small. A careful inspection of Experiment 36 shows that insertion of the probe caused a small but measureable upstream shift in the concentration profile (see Fig. 9A). We conjecture that this upstream shift is not due to flow blockage by the probe but rather to an increase of the external mass transfer rate due to the shorter hydraulic channel length resulting from the presence of the probe. For $\log(\phi)$ values between 2.2 and 3.8 the ΔZ map does not provide clear insight about the probe impact. In this zone, steep transverse concentration gradients lead to a large discrepancy between the solid and fluid temperatures. Here the probe's invasiveness is mainly a result of its sampling position along the wall of the channel. This claim deserves some elaboration. The data suggest that the c-OFDR temperature measurement is closer to that of the fluid than of the solid. While the optical fiber rests on the wall of the monolith, most of its surface is exposed to the fluid. Thus, for cases in which the fluid temperature is lower than that of the solid the optical probe may sense a temperature closer to that of the fluid temperature. On the other hand, as we showed in the context of Fig. 5 the SpaciMS measures a concentration close to that of the surface. As a result, at the point of measured propylene depletion the local solid temperature should approach the adiabatic

temperature rise. But as the temperature measured by the fiber is of the fluid and not the solid, this results in a mismatch between the maximum solid temperature and measured fluid temperature. Finally, it is worth noting that were the fiber probe to measure the solid temperature, one would expect the temperature profile to be qualitatively different. Instead of increasing with distance down the length of the monolith the solid temperature would be hottest near the entrance and decrease along the monolith, eventually approaching the same level as the increasing fluid temperature.

Following this reasoning, one may conclude that a large value of ϕ for a fixed value of Z' should result in a large ΔZ . However, a comparison between Experiments 20, 21, and 4 shows the opposite trend; i.e., for essentially at the same depletion location ($Z' \sim 0.2-0.3$), the ΔZ value obtained in Experiment 4 (reduced concentration gradient) exceeds that obtained in Experiments 20 and 21 in spite the latter experiments had a steeper concentration gradient than in Experiment 4. This unexpected result suggests that the two parameters (ϕ and Z') are not sufficient to account for all of the ΔZ trends. A potential explanation has to do with the fact that Experiments 20 and 21 were obtained for the commercial catalyst (400 CPSI) for which the Pt loading was about three-fold higher than that of the catalyst used in Experiment 4 (100 CPSI monolith). Thus to obtain the same depletion location, the feed temperature in Experiment 4 was necessarily higher ($T_{4,f} = 224^\circ\text{C}$ vs. $T_{20,f}$ and $T_{21,f} \sim 181^\circ\text{C}$) than that in Experiments 20 and 21 in order to achieve the same activity. However, the higher operating temperature led to a complex heat transfer impact such as potential heat losses to the environment and thermal gradient among monolith channels. These thermal effects may contribute to the larger ΔZ .

In the upstream region ($Z' \sim 0$ to 0.2) ΔZ is typically high (> 12 mm) with the highest values (16 – 20 mm) encountered in a range of $\log(\phi)$ between ~ 2.8 and 3.2 . The data in this

zone push the limits of ΔZ methodology ability to assess the degree of invasiveness. When the limiting reagent is depleted at catalyst front, the solid temperature is likely hotter than the fluid temperature by 10's °C. For example, Dario et al. [28] used a thermocouple to measure the gas temperature and a pyrometer to measure the solid temperature during the catalytic partial oxidation of methane. They observed that when the hot spot occurred at the entrance, the maximum temperature measured by the pyrometer was higher and located a few millimeters upstream of the maximum temperature measured by a sliding thermocouple. The maximum temperature measured by the pyrometer was ~ 920 °C and ~ 800 °C as measured by the thermocouple. The large ΔZ observed in our study is attributed to the above-mentioned heterogeneous effect; i.e. while the optical fiber sensed the fluid temperature the capillary probe measured the surface concentration.

To expand on this point, we inspected Experiment 2 closely (refer to Fig. 9b). In this experiment the most open monolith was used (100 CPSI) together with the smaller of the two probes ($d_o = 170$ μm). At first glance one would think with this probe/monolith combination for which only 2% of the channel area is blocked by the fiber that the invasiveness of the probe should be minimal, at least from the standpoint of flow blockage. Nevertheless, a rather large ΔZ of 17 mm was observed. Obviously, this result is not due to flow blockage. Assuming that some other effect such as nonuniform washcoat deposition is not responsible, the only explanation is the aforementioned heterogeneous effect: the optical fiber sensed the fluid temperature while the capillary probe that measured the surface concentrations.

An additional explanation for large ΔZ in the upstream region is that the probe insertion length increases when the depleted concentration location moved upstream. While this effect has

been discussed in relation to the earlier results obtained for the 100 CPSI monolith (refer to Fig. 2), it may play a role for higher pore density monoliths.

Figure 9.

It is noticed that a small blue region for $Z' < 0.2$ that exists in which ΔZ has a low to moderate value (4-8 mm). Some insight of the origin of this result is provided by a comparison of experiments 12 and 29. Experiment 29 was conducted with the 600 CPSI monolith and large probe (363 μm) at a flow rate of 8000 sccm and feed temperature of 239° C. The only difference with Experiment 12 is the use of the more open 200 CPSI monolith. The larger ΔZ obtained for the 600 CPSI monolith (15 mm) than for the 200 CPSI monolith (7 mm) suggests a more severe impact of the probe blockage effect for the former.

The ΔZ map is a useful for classifying the impact of the SpaciMS capillary probe for a range of operating conditions, monolith structures, operating conditions, and reactor regimes. Depending on the hot zone location inside the reactor, a SpaciMS can be implemented either at the front or the back of the reactor to mitigate the exposure of the tube to high temperature region. Our analysis is limited to conditions leading to complete conversion of the limiting reactant and a back reactor SpaciMS implementation (suction flow is in the same direction as reactive flow). As the c-OFDR measures the fluid rather than solid temperature but the SpaciMS measures the surface rather than the fluid concentration, ΔZ is a useful identification of conditions in interpreting data and modeling.

Finally, additional experiments and simulations are needed to provide more detailed information on the conditions under which the probe SpaciMS probe has a minimal invasive impact.

Conclusions

The objective of this work is to study the impact of the capillary probe on the accuracy of SpaciMS concentration measurements. To this end, we carried out propylene oxidation on Pt/Al₂O₃ washcoated monoliths with a range of channel densities (100, 200, 400, and 600 CPSI), and concentration sampling by probes of two different sizes (170 & 363 μm o.d.). The axial position of the probe did not influence the flow profile in the 100 CPSI monolith channel, nor did it alter the amount of flow shifted to surrounding channels for the 600 CPSI reactors.

We investigated the effect of the probe size on the spatial concentration measurement. The SpaciMS concentration measurement in the conventional 400 CPSI monolith reactor at the relevant space velocity of 12 k h^{-1} with two capillary probe sizes showed similar profiles. An analytical prediction of the compressible flow in a capillary was used to estimate the amount of flow suction by the probe. We found that in some experiments the suction flow rate was about the same as the flow deflected by these capillaries. These experiments implied that for certain operating conditions, the measurement even with a larger capillary probe may still be accurate, due to compensation of the blockage by the suction.

We developed an experimental methodology to assess the uncertainty and to some extent the impact of the capillary probe to the measured conversion. This methodology can be used to interpret the SpaciMS data, as well as provide guidance for designing SpaciMS configuration for a specific application. This method employed the metric ΔZ , defined as the difference between the axial position of the temperature maximum and the axial position of the propylene depletion position. $\Delta Z \rightarrow 0$ implies that the SpaciMS probe is non-invasive, while $\Delta Z > 0$ implies the impact of the probe's invasive nature in combination with sampling when a transverse concentration gradient exists. A systematic experimental study provided the ΔZ information for

the 100, 200, 400, and 600 CPSI catalytic monolith at various conditions. When the limiting reactant was completely consumed at the downstream region of the reactor ($> 60\%$ reactor length), $\Delta Z \rightarrow 0$ and the SpaciMS concentration measurements shows minimal impact. The invasive impact of the probe cannot be asserted when the reactant concentration depletion occurred at these regions due to the limitation of our temperature measurement technique and the complex interplay of heat and mass transfer occurring at the upstream of the reactor. Additional experimental and simulation studies are conducted and will be reported in the future.”

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Nomenclature

$\langle u \rangle$	Average fluid velocity in the fluid phase (m/s)
U_f	Fluid velocity at the capillary tube wall (m/s)
P_{in} (P_{out})	Inlet (outlet) pressure of the capillary tube (Pa)
d_o (d_i)	Outer (inner) diameter of the capillary tube (m)
Y_{fm}	Cup-mixing mole fraction of propylene in fluid phase
F_T	Total gas flow rate (sccm)
A_Ω	Cross sectional channel area open to flow (m ²)
P_Ω	The wetted perimeter (m)
R_{Ω_1} (R_2)	Effective transverse diffusion length for flow (washcoat) (m)
k_{mo}	Overall mass transfer coefficient (m/s)
$\langle Y_{wc} \rangle$	Volume averaged mole fraction of propylene in washcoat
k_{me} (k_{mi})	External (Internal) mass transfer coefficient (m/s)
Y_s	Circumferentially averaged mole fraction at the fluid-washcoat interface
C_T	Total concentration in gas phase (mol.m ⁻³)
r_p	Volumetric reaction rate in the washcoat (mol/m ³ washcoat/s)
Sh_e (Sh_i)	External (Internal) Sherwood number
$Sh_{i\infty}$	Asymptotic internal Sherwood number
N	Number of channels
S	Side length of a channel (m)
T_f (T_s)	Gas phase (solid phase) temperature (K)
R_m	Mass-based gas constant (J/(kg K))
R_g	Molar-based gas constant (J/(mol K))
T_{cap}	Isothermal temperature of the capillary tube (K)
$D_{f,e}$	Diffusivity of species in fluid phase (m ² /s)
D_i^{Knu} ($D_{f,i}$)	Knudsen diffusion (effective diffusion) of gas in washcoat layer (m ² /s)
r_{pore}	Pore radius (m)
M_M	Molecular mass (g mol ⁻¹)

r_i	Inner radius of the capillary tube (m)
M_s	Mass suction flow rate of the capillary tube (kg/s)
h_f	Heat Transfer Coefficient (W/ (m ² .K))
Nu_∞	Asymptotic Nusselt Number
p	Transverse mass Peclet number
Le_f	Lewis number
z^*	Dimensionless length
k_f	Heat conductivity of fluid (W/(m K))
L (L_{cap})	Length of monolith reactor (capillary tube) (m)
C_{uff}	Specific heat capacity (J.kg ⁻¹ .K ⁻¹)
ΔH	Heat of reaction (J/mol)

Greek letters

τ	Tortuosity
ε	Porosity of washcoat
μ_f	Viscosity of fluid (Pa s)
ρ_f	Density of fluid (kg/m ³)
τ_d (τ_r)	Transverse diffusion (reaction) time (s)
ϕ	Ratio between the transverse diffusion time and the reaction time
σ_{AB}	Collision integral
Ω_{AB}	Lennard-Jones potential parameter
ϕ_s	Thiele modulus

Appendix A: 1-D Low-Dimensional Model of Catalytic Monolith Reactor

In this section we describe the reactor model used to simulate the propylene oxidation and with which kinetic parameters are estimated. The values of various model parameters are provided in Table 6. The estimated kinetic parameters in Table 4 and the model predictions in Figure 6 for the 200 CPSI monolith. The corresponding fits for the 100, 400, and 600 CPSI monolith catalysts are provided in Figs. S.1 – S.3 in the Supplementary Material.

Table 6.

The 1-D low dimensional model is adopted from previous work of Joshi et al. [17, 21]. It comprises a set of differential material and energy balances that are solved through numerical integration.

The steady state gas phase material balance is

$$\langle u \rangle \frac{dY_{fm}(z)}{dz} = -\frac{1}{R_{\Omega_1}} k_{mo} (Y_{fm}(z) - \langle Y_{wc} \rangle(z)). \quad (17)$$

The corresponding species balance at the surface and inside the washcoat are

$$k_{me} (Y_{fm}(z) - Y_s(z)) = k_{mi} (Y_s(z) - Y_{wc}(z)) \quad \text{and} \quad (18)$$

$$k_{mo} \times (Y_{fm}(z) - Y_{wc}(z)) + \frac{R_2}{C_{Total}} \times (-r_p) = 0, \quad (19)$$

where $Y_{fm}(z)$, $Y_s(z)$, and $Y_{wc}(z)$ are the cup mixing mole fractions of propylene in the fluid phase, the circumferentially averaged concentration at the fluid-washcoat interface, and the volume averaged mole fractions in the washcoat respectively. R_2 is a washcoat thickness, and $\langle u \rangle$ is the average feed gas velocity per channel. The temperature dependent factor $(T_f(z)/273.15)$ accounts for the gas expansion at various fluid temperatures. The overall mass transfer coefficient is given by

$$\langle u \rangle = \frac{F_T}{N \times S^2} \times \left(\frac{T_f(z)}{273.15} \right). \quad (20)$$

$$\frac{1}{k_{mo}} = \frac{1}{k_{mi}} + \frac{1}{k_{me}}, \quad (21)$$

where k_{me} , k_{mi} , and k_{mo} are the external, internal and overall mass transfer coefficients, respectively. The external and internal mass transfer coefficients are defined as

$$k_{me} = \frac{D_{f,e} \times Sh_e}{4R_{\Omega_1}} \quad \text{and} \quad (22)$$

$$k_{mi} = \frac{D_{f,i} \times Sh_i}{R_{\Omega_2}}, \quad (23)$$

where $D_{f,e}$ and $D_{f,i}$ are the fluid phase diffusivity and the effective washcoat diffusivity of propylene, respectively. We used the Chapman-Enskog's formula [23] to compute the propylene diffusivity in the fluid phase (Argon as a carrier gas), over the temperature range of 300 - 900 K,

$$D_{f,e} = 0.0018583 \frac{\sqrt{T_f^3 \left(\frac{1}{M_A} + \frac{1}{M_B} \right)}}{P \cdot \sigma_{AB}^2 \cdot \Omega_{AB}}. \quad (24)$$

D_f , T_f , M , σ_{AB} and Ω_{AB} in Eq. (24), are the bulk diffusion coefficient, the fluid temperature, molecular weight, collision integral, and Lennard-Jones potential parameters, respectively. The bulk diffusion temperature dependence is $T^{1.5}$. For the sake of simplicity, Eq. (24) is reduced to the more convenient form [19]

$$D_{f,e} = 4.237 \times 10^{-6} \times T_f^{1.7844} \text{ cm}^2 / \text{s}. \quad (25)$$

The value of the external Sherwood number, Sh_e , is reported by Gupta et.al [24]. For a fully developed flow in a rounded square channel and small value of the transverse mass Peclet

number ($P = \frac{\langle u \rangle R_{\Omega_1}^2}{LD_f} \approx 10^{-3} - 10^{-2}$), the constant value of $Sh_e = \frac{48}{11}$ is used.

Two types of diffusion contribute to mass transport in the monolith washcoat: volume (molecular) diffusion, and Knudsen diffusion, predicted by Eq. (26) and Eq. (27) respectively.

$$D_i^n = 0.0018583 \frac{\sqrt{T_s^3 \left(\frac{1}{M_A} + \frac{1}{M_B} \right)}}{P \cdot \sigma_{AB}^2 \cdot \Omega_{AB}} \quad \text{and} \quad (26)$$

$$D_i^K = \frac{2}{3} r \times \sqrt{\frac{8 R_g T_s}{\pi M_M}}. \quad (27)$$

D_i^K is the Knudsen diffusion coefficient, r is pore radius, and R_g is the gas constant. In a porous catalytic washcoat, there are both macropores ($r \approx 100\text{-}500$ nm) between the support material particles (i.e., $\gamma\text{-Al}_2\text{O}_3$, zeolites, ceria...), and small meso or micropores ($r \approx 3\text{-}6$ nm) among the catalytic particles. The two most popular effective diffusion models are the random-pore model [25], and the mean transport-pore model by Froment and Bischoff [26]. The latter uses one characteristic pore size and correction factors such as tortuosity (τ) and porosity (ϵ). The tortuosity accounts for the geometrical deviation between straight cylindrical pores and the actual pore length, while porosity is a fraction of the void volume to the washcoat. We used the mean transport pore approach in our simulations. Using the resistance-in series model (Bosanquet's equation), the effective diffusion coefficient in the washcoat is

$$\frac{1}{D_{f,i}} = \frac{\tau}{\epsilon} \left(\frac{1}{D_i^{vol}} + \frac{1}{D_i^{knu}} \right) \quad (28)$$

The internal Sherwood number is evaluated as a function of the Thiele modulus:

$$Sh_i = Sh_{i\infty} + \frac{\Lambda \phi_s^2}{1 + \Lambda \phi_s} \quad (29)$$

here $Sh_{i\infty}$ is the asymptotic internal Sherwood number, obtained in the limit of slow reaction. The constant Λ depends on washcoat geometry ;for the case of a square channel with a rounded square flow area, $Sh_{i\infty}$ and Λ are 2.65 and 0.58, respectively [21]. The Thiele modulus is defined as

$$\phi_s^2 = \frac{\tau_{d,w}}{\tau_r} = \frac{\frac{R_2^2}{D_{f,i}}}{\left(\frac{r_{C_3H_6}|_{surface}}{Y_s \times C_{Total}} \right)^{-1}}, \quad (30)$$

where R_2 is the washcoat thickness, $D_{f,i}$ is the internal washcoat diffusivity computed by Eq. (25).

The energy balance in the fluid phase is

$$\langle u \rangle \rho_f C_{p_f} \frac{dT_f}{dz} + \frac{h_f(z)}{R_{\Omega_1}} (T_f - T_s) = 0. \quad (31)$$

Here, T_f and T_s are the fluid and solid temperatures, respectively. ρ_f and C_{p_f} are the density and specific heat capacity of the fluid phase. The local heat transfer coefficient, h_f , is calculated using the Nusselt number (Nu) correlation

$$h_f(z) = \frac{Nu(z)k_f}{4R_{\Omega_1}}. \quad (32)$$

The position dependent Nusselt number (Nu) is calculated by [27]

$$Nu = Nu_{\infty} + \frac{0.272 \left(\frac{p}{z^* Le_f} \right)}{1 + 0.083 \left(\frac{p}{z^* Le_f} \right)^{2/3}}, \quad (33)$$

where $z^* = z/L$ is the dimensionless length. For a rounded square channel, $Nu_{\infty} = 3.2 \cdot Le_f$ and p are the Lewis fluid and transverse mass Peclet numbers. These quantities are calculated as

$$Le_f = \frac{k_f}{\rho_f C p_f D_{f,e}} \text{ and} \quad (34)$$

$$p = \frac{R_{\Omega_1}^2 \langle u \rangle}{LD_{f,e}}. \quad (35)$$

The energy balance for the solid phase is

$$h_f (T_f - T_s) + R_2 \times r_p \times (-\Delta H) = 0. \quad (36)$$

The solid and fluid temperatures were measured close at the centerline channel. Thus, the assumption of adiabatic is reasonable. In addition, heat conduction along the capillary tube is negligible for the steady state profile.

The initial conditions are

$$Y_{fm}(z=0) = Y_{fm,0}, T_f(z=0) = T_{f0}, T_s(z=0) = T_{s0} \text{ and} \quad (37)$$

$$\left. \frac{\partial T_s}{\partial x} \right|_{z=0} = 0. \quad (38)$$

The system of equations was solved using the BDF method (Backward differentiation formulae), which is implemented in ode15i subroutine (part of the Matlab[®] ODE suite [28]). The ode15i solver can simultaneously adjust both the order of the BDF, the step-size, and maintain

the local error under control. The solving time is of the order of a second on an i5-4300U processor computer. This is effective for finding the reaction kinetic parameters where several iterations of solving the model are needed for parameter fitting. It is noted that inclusion of a heat conduction term in the enthalpy equation for the solid phase (Eq. 36) results in a second order differential equation, requiring solution of BVP (boundary value problem). In that scenario, the preferred method is to solve the transient model, which is described by an ordinary time dependent differential equation, from the start-up of the experiment until converging to a steady state. The solving methodology used is the method of lines. A drawback of this transient approach is that computing the Thiele modulus (Eq. (30)) required knowledge of the surface concentration. Most published papers used an approximation that the fluid concentration was close to the surface concentration, and compute the Thiele modulus at the fluid concentration [29]. This assumption may be adequate for high density monolith reactors (400 and 600 CPSI), but may not be adequate for the 100 and 200 CPSI monolith as due to the large hydraulic diameter, the fluid (bulk) concentration can differ from the surface concentration.

Appendix B: Estimation of the Suction Flow

The Dongari's prediction of the suction mass flow rate is [15]:

$$M_s = \frac{\pi \times r_i^4 \times P_{out}^2}{16\mu L_{cap} RT_{cap}} \left[\left(\frac{P_{in}}{P_{out}} \right)^2 - 1 \right] + \frac{\mu \pi r_i^2}{L_{cap}} \ln \left(\frac{P_{in}}{P_{out}} \right) \quad (39)$$

where M_s is a mass suction flow rate (kg/s), L_{cap} the length of the capillary tube (m), T_{cap} the isothermal temperature of the capillary tube, R the mass-basis gas constant (J/(kg K)), and P_{in} and P_{out} are the inlet and outlet pressures of the capillary, respectively (Pa). For a small pressure drop, $P_{in} \approx P_{out}$, Eq. (39) reduces to the Hagen-Poiseuille equation for incompressible Newtonian fluid. For a large pressure drop ($P_{in} \gg P_{out}$, $P_{out} \approx 0$), the convective term (first term in Eq. (39)) dominates. In this case, the mass suction flow rate is half of that predicted by the Hagen-Poiseuille's equation.

$$M_s = \frac{\pi \times r_i^4}{16\mu L_{cap} RT_{cap}} [P_{in}^2] \quad (40)$$

Bernoulli's equation is used to estimate inlet pressure of the capillary tube:

$$P_{atm} + \frac{1}{2} \rho v_1^2 = P_{in} + \frac{1}{2} \rho \langle u \rangle^2 \quad (41)$$

where P_{atm} is an atmospheric pressure (Pa), ρ fluid density $\left(= \frac{P_{in}}{R_{ideal} \times T} \right)$, $v_1 \approx 0$ m/s, $\langle u \rangle$ is the

linear velocity in the monolith channel $\left(\langle u \rangle = \frac{F_T}{N \times S^2} \right)$. Inserting these values into Eq. (41)

yields

$$P_{atm} = P_{in} + \frac{1}{2} \left(\frac{P_{in}}{R_{ideal} \times T} \right) \times \left[\frac{F_T}{N \times S^2} \right]^2 \quad (42)$$

Substitution of Eq. (42) into Eq. (40) gives

$$M_s = \frac{\pi \times r_i^4}{16\mu L_{cap} R_{ideal} T_{cap}} \times \left[\frac{P_{atm}}{1 + \frac{F_T^2}{2R_{ideal} \times T \times N^2 \times S^4}} \right]^2 \quad (43)$$

Fig. 1. (A) Schematic of the pair of monolith channels containing the SpaciMS capillary probe and c-OFDR fiber. The species concentration profiles are measured with the SpaciMS. In an adjacent channel the temperature profile is measured with the optical fiber. (B) Photograph of the front face of the monolith showing the capillary probe and optical fiber. (C) Example concentration and temperature profiles for propylene oxidation (0.17 vol.% C_3H_6 , 10% O_2) carried out at a space velocity of 17400 hr^{-1} and feed temperature of 195°C using the probe diameter of $363 \mu\text{m}$ in a 100 CPSI monolith reactor. A linear relation exists between the axial temperature rise (ΔT) and propylene conversion (X) as shown by the inset formula.

Fig. 2. Spatial temperature and concentration profiles of propylene oxidation (0.17 vol. % C_3H_6 , 10 vol. % O_2) at the total flow rate of 8000 sccm are measured with capillary ($d_o = 363 \mu\text{m}$) and optical fiber ($d_f = 125 \mu\text{m}$) on (A) 100 CPSI, and (B) 600 CPSI monolith reactor.

Fig. 3. Transient temperature profiles were reported for the case capillary probe ($d_o = 363 \mu\text{m}$) and 400 CPSI monolith at the inlet (solid line), and case where no probe inside the channel (dash line). The optical fiber and the capillary tube are in the same channel. The gas mixture was 0.17 vol. % C_3H_6 , 10 vol. % O_2 and $F_T = 8000$ sccm at (A) $T_f = 81^{\circ}\text{C}$ and (B) $T_f = 101^{\circ}\text{C}$.

Fig. 4. The propylene concentration profiles were measured by two different probe sizes for a mixture of 0.17 vol. % C_3H_6 and 10 vol. % O_2 at $T_f = 180^\circ C$, and $F_T = 8,000$ sccm in a 400 CPSI monolith reactor.

Fig. 5 The propylene concentration profiles were measured by the 170 μm capillary probe for a mixture of 0.3 vol.% C_3H_6 and 10 vol.% O_2 at $F_T = 12,000$ sccm in (A) 100 CPSI, and (B) 200 CPSI monolith reactor.

Fig. 6. Fitted spatial concentration and temperature profiles during propylene oxidation. The gray (orange) curves are surface and fluid, respectively. The experiment was conducted in the 200 CPSI monolith reactor ($C_3H_6 = 0.3$ vol. %, $O_2 = 10$ vol. %, $T_f = 152$ °C, $F_T = 11,600$ sccm). The intra channel concentration was measured with capillary probe (O.D = 170 μ m). (x) is the experimental data, C_f , C_s , T_s , T_f are computed by the model.

Fig. 7. Measured propylene concentration and temperature profiles for two cases in which a gas containing 0.17 vol. % C_3H_6 and 10 vol. % O_2 is fed at 8,000 sccm to 100 CPSI monolith. Other conditions are: (A) 363 μm O.D. probe, $T_f = 201^\circ\text{C}$, (B) 170 μm O.D. probe, $T_f = 246^\circ\text{C}$.

Fig. 8. ΔZ map in the plane of Z' vs. $\log(\phi)$. The data points in the map correspond to the individual experiments (refer to Table 4 for details).

Fig. 9. Measured propylene concentration and temperature profiles using the 170 μm O.D. probe for gas containing 0.17 vol. % C_3H_6 and 10 vol. % O_2 is fed at 8,000 sccm at (A) 205°C to 600 CPSI, and (B) 231°C to 100 CPSI monolith.

Table 1. The structural characteristics of various CPSI monolith reactors.

CPSI	100	200	400	600
Pt Loading (g/ft ³)	23.8	23.8	96	23.8
Number of Channels (N)	78	157	314	471
Channel size [=] mm	2.54	1.80	1.27	1.04
Washcoat thickness (R ₂) [=] μm	47	35	25	20

Table 2. Parameters used in the Dongari model.

Constant	Values
L_{cap}	1.524 m
μ	2.09×10^{-5} (Pa.s)
R	208 (J/ (kg.K))
P_{in}	1.01×10^5 (Pa)
P_{out}	4.0×10^{-6} (Pa)
T	453.15 K

Table 3. The total flow rate is fixed at 8000 sccm. The volumetric flow rate per channel in the case of no probe presence (Q_{ref}), and with the probe presence (blocked flow, Q_b , and suction flow, Q_s) are tabulated.

	CPSI	OD (μm)	ID (μm)	% Occupied	# Channels	Q_{ref} (sccm)	Q_b (sccm)	Q_s (sccm)	Q_b/Q_s
1	100	170	110	0.35	78	102.6	0.36	0.34	1.05
2	100	363	150	1.6	78	102.6	1.64	1.19	1.38
3	200	170	110	0.7	157	51.0	0.36	0.34	1.04
4	200	363	150	3.21	157	51.0	1.64	1.19	1.38
5	400	363	150	6.42	314	25.5	1.64	1.19	1.38
6	400	170	110	1.41	314	25.5	0.36	0.34	1.04
7	600	170	110	2.11	471	17.0	0.36	0.34	1.04
8	600	363	150	9.62	471	17.0	1.63	1.19	1.38

Table 4. Fitted kinetic parameters in the Langmuir Hinshelwood reaction rate of propylene oxidation reaction for various monolith reactors (100, 200, 400, and 600 cpsi). The 95% confidence limits are also provided.

CPSI	b_1 (moles/m ³ /s)	b_2 (K)	b_3 (moles/m ³ /s)	b_4 (K)
100	$8.01 \times 10^{15} \pm 5.11 \times 10^{17}$	$1.19 \times 10^4 \pm 3.55 \times 10^4$	$1.01 \times 10^3 \pm 3.23 \times 10^4$	$-1.13 \times 10^2 \pm 6.26 \times 10^3$
200	$4.40 \times 10^{15} \pm 2.98 \times 10^{15}$	$1.15 \times 10^4 \pm 1.15 \times 10^4$	$5.29 \times 10^2 \pm 5.29 \times 10^2$	$-4.67 \times 10^2 \pm 2.52 \times 10^2$
400	$8.44 \times 10^{17} \pm 9.32 \times 10^{16}$	$1.21 \times 10^4 \pm 3.43 \times 10^4$	$1.04 \times 10^2 \pm 2.39 \times 10^1$	$-1.01 \times 10^2 \pm 2.31 \times 10^1$
600	$4.94 \times 10^{15} \pm 1.52 \times 10^{16}$	$1.21 \times 10^4 \pm 8.56 \times 10^3$	$1.11 \times 10^3 \pm 3.40 \times 10^3$	$-1.00 \times 10^2 \pm 4.42 \times 10^3$

Table Error! No text of specified style in document.**5.** The entire set of 37 experiments conducted in four monoliths and two capillary probes. The asterisk (*) denotes experiments with 0.3% propylene in the feed; those without had 0.17% propylene in the feed.

No.	F _T (sccm)	CPSI	ID (μm)	OD (μm)	ΔZ (mm)	log(φ)	Z'	T _f (°C)
1	8000	100	110	170	16	3.63	0.13	246
2	8000	100	110	170	17	2.88	0.13	232
3	9000	100	110	170	18	3.05	0.13	231
4	8000	100	110	170	11	3.45	0.33	224
5*	12000	100	110	170	0	3.09	0.96	150
6*	10000	100	110	170	0	3.31	0.93	143
7	11000	100	150	363	0	3.54	0.87	202
8	8000	100	150	363	0	3.50	0.73	196
9	9000	100	150	363	6	3.06	0.53	201
10	8000	200	110	170	8	2.66	0.13	233
11	11000	200	110	170	5	2.68	0.20	210
12	8000	200	150	363	7	2.72	0.13	234
13	11000	200	150	363	5	2.51	0.20	210
14	8000	200	150	363	17	2.95	0.11	248
15	11000	200	150	363	6	2.70	0.16	216
16*	11000	200	110	170	0	3.01	0.68	157
17*	11600	200	110	170	0	3.10	0.88	152
18*	12000	200	110	170	0	3.31	0.96	131
19*	10000	200	110	170	0	3.09	0.92	121
20	11000	400	110	170	7	3.95	0.27	181
21	11000	400	150	363	7	3.83	0.27	182
22	8000	400	150	363	13	3.22	0.11	180
23	8000	400	110	170	13	3.34	0.11	180
24*	10000	400	110	170	0	3.77	0.97	65
25	9000	400	110	170	3	2.84	0.84	82
26	9000	400	110	170	6	2.91	0.56	87
27	8000	400	110	170	4	2.77	0.60	80
28	8000	600	110	170	17	2.56	0.12	238
29	8000	600	150	363	15	2.18	0.13	239
30	11000	600	150	363	4	2.13	0.64	200
31	8000	600	150	363	4	1.98	0.60	204
32*	10000	600	110	170	0	2.75	0.96	159
33*	10000	600	110	170	0	2.57	0.96	154
34*	10600	600	110	170	4	2.28	0.91	157
35*	12000	600	110	170	3	2.63	0.93	170
36	8000	600	110	170	3	1.89	0.20	205
37	8000	600	110	170	0	1.87	0.24	181

Table 6. Numerical constants and parameters used in the simulations.

Constant	Value
ΔH	$-1925.9 \times 10^3 \text{ J/mol}$
L	7.5 cm
Sh_e	4.36
Sh_∞	2.65
Nu_∞	3.2
k_f	0.0343 W/m/K
τ	3
ϵ	0.41
r	$5 \times 10^{-7} \text{ cm}$
Λ	0.58