

# THEORETICAL AND EXPERIMENTAL INVESTIGATION OF CONTROLLING REGIMES IN CATALYTIC MONOLITHS

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## Summary

It is well known that the performance of a catalytic monolith is bounded by two limits: the kinetic regime at low temperatures (or before ignition) and the external mass transfer controlled regime at high temperatures (or after ignition). We present explicit criteria for determining the operating regimes in terms of various reactor and operating parameters. The criteria are used to evaluate the controlling regimes during the oxidations of hydrogen and propylene on a Pt/Al<sub>2</sub>O<sub>3</sub> washcoated monolith. The analysis reveals that hydrogen oxidation is kinetically limited over a wide range of temperatures whereas the propylene oxidation has a more classical transition between a kinetic and external transport limited regime. The theory also reveals that the existence of an internal diffusion limited regime cannot be ignored in many systems. Finally, we present new experimental data that confirms the theory and a new method for accurate experimental estimation of various controlling regimes in a catalytic monolith.

## Keywords

Micro-reactors, Multiphase reactors, Environmental Reaction Engineering.

## Introduction

It is now well established that the performance of a catalytic monolith is bounded by two limits: the kinetic regime at low temperatures (or before ignition for the case of exothermic reactions) and the external mass transfer controlled regime at sufficiently high temperatures (or after ignition). The washcoat diffusional resistance can also be significant over an intermediate range of temperatures. The transition temperatures at which the controlling regime changes from kinetic to washcoat diffusion to external mass transfer depend on the various geometric properties of the monolith, flow properties, the catalyst loading and washcoat properties. The existing literature criteria on estimation of various regimes and overall mass transfer coefficients in catalytic monoliths have some major limitations. First, they can not be directly extended for arbitrary channel-washcoat shapes and non-linear kinetics. Second, there is a wide range of variation in the experimentally observed Sherwood number in a catalytic monolith ( $Sh_{\text{expt}} \sim 0.05$  to 4) and there is no universal correlation for estimation of  $Sh_{\text{expt}}$ .

In this work, we present accurate description of various regimes in a catalytic monolith based on the recently developed low-dimensional model and the concepts of internal and external mass transfer coefficients

(Joshi et al.<sup>1,2</sup>). We present new experimental data and corroborating theory on the oxidations hydrogen and propylene on a Pt/Al<sub>2</sub>O<sub>3</sub> washcoated monolith. We show that hydrogen oxidation is kinetically limited over a wide range of temperatures whereas the propylene oxidation has a more classical transition between a kinetic and external transport limited regime.

## Mathematical Model

A large number of correlations exist in the literature for estimation of external mass transfer coefficient in catalytic monoliths. A common method to measure the external mass transfer coefficient in a catalytic monolith is to carry out a catalytic reaction at high temperature. Under these conditions, it is often assumed that the reaction is infinitely fast and the reactant concentration at the wall is zero. In such a case, the monolith operates in purely mass transfer controlled regime and the governing equation at the steady state can be written as

$$u \frac{dC_{fm}}{dx} = -\frac{k_{mo}}{R_{\Omega 1}} C_{fm} \quad \dots(1)$$

Thus, measuring the exit concentration enables one to estimate the overall mass transfer coefficient ( $k_{mo}$ ). This experimental method to estimate the external mass transfer

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coefficient under reacting conditions has some limitations, however. When the concentration at the wall is not zero, the mass transfer coefficient calculated will be less than the theoretical upper bound.

In this work, we utilize the recently developed simplified model (Joshi et al.<sup>1</sup>) that is useful for analyzing catalytic reactions in washcoated monoliths of arbitrary shape. Here, we present only model equations and refer the reader to the cited article for further details. The low-dimensional model for a gas-solid system with reaction in the washcoat is described by

$$-u \frac{dC_{fm}}{dx} = -\frac{k_{me}(x)}{R_{\Omega_1}} (C_{fm} - C_s) \quad \dots (2)$$

$$k_{mi} (C_s - \langle C_{wc} \rangle) = R_{\Omega_2} R(\langle C_{wc} \rangle) \quad \dots (3)$$

$$k_{me} (C_{fm} - C_s) = k_{mi} (C_s - \langle C_{wc} \rangle) \quad \dots (4)$$

$$C_{fm} = C_{in} @ x = 0 \quad \dots (5)$$

For first order kinetics, it can be easily shown that

$$\frac{1}{k_{mo}} = \frac{1}{k_{me}} + \frac{1}{k_{mi}} + \frac{1}{kR_{\Omega_2}} \quad \dots (6)$$

$\underbrace{\quad}_{\text{Overall Resistance (} R_t)}$ 
 $\underbrace{\quad}_{\text{External Resistance (} R_e)}$ 
 $\underbrace{\quad}_{\text{Internal Resistance (} R_i)}$ 
 $\underbrace{\quad}_{\text{Reaction Resistance (} R_r)}$

The above model contains three averaged concentrations.  $C_{fm}$  is cup-mixing concentration, which is the transverse-averaged concentration, weighted with respect to the longitudinal velocity,  $C_s$  is the circumferentially averaged concentration at the fluid-washcoat interface and  $\langle C_{wc} \rangle$  is the volume averaged concentration in washcoat.  $R_{\Omega_1}$  is the characteristic length scale for the fluid phase, defined as the ratio of the flow area to the fluid-washcoat interfacial perimeter.  $R_{\Omega_2}$  is the ratio of washcoat cross-sectional area to the interfacial perimeter.  $k_{me}$  and  $k_{mi}$  are position dependent external (gas phase) and internal (washcoat) mass transfer coefficients respectively given by,  $k_{me}(x) = \frac{Sh_e(x)D_f}{4R_{\Omega_1}}$ ,  $k_{mi} = \frac{Sh_i D_e}{R_{\Omega_2}}$ .  $k_{mo}$  can be considered as overall mass transfer coefficient, reciprocal of which is sum of the three resistances of mass transfer.

## Results

We study hydrogen and propylene oxidation in a catalytic monolith with Pt/Al<sub>2</sub>O<sub>3</sub> catalyst deposited in the form of a washcoat. For the hydrogen oxidation experiments shown here, low hydrogen feed concentrations (<200 ppm) were used so that the monolith can be treated as isothermal. Excess oxygen (1%) was used and the reaction was found to be first order in hydrogen. The activation energy of the reaction was found to be 26 kJ/mol. Exit conversion was measured as a function of the monolith temperature as shown in Fig. 1. As temperature increases, the rate of reaction increases and conversion increases. At high temperature, the conversion approaches its maximum value. There is a good agreement between modeling and experimental results. The small discrepancy at high temperature is due to the axial dispersion effects that are neglected in solving the model equations. The overall mass transfer coefficient ( $k_{mo}$ ) or total resistance for mass transfer ( $R_t$ ) can be calculated from the exit

conversion using eq. (1). The overall process of mass transfer comprises of three resistances in series: fluid phase film resistance ( $R_e$ ), internal diffusional resistance ( $R_i$ ) and reaction resistance ( $R_r$ ) as shown by eq. (6). We plot the individual and overall resistances as a function of temperature in Fig. 2. We note that each resistance is a monotonic decreasing function of temperature, though the external and internal mass transfer resistances are nearly independent of temperature. At low temperatures (<80 °C) the reaction resistance is the largest resistance. It can also be observed that the external mass transfer never becomes controlling even at high temperatures. Thus, the process of overall mass transfer is dominated by the reaction resistance over the entire temperature range. In the full article, we will present an additional example of propylene oxidation (higher activation energy) carried out in a catalytic monolith. For this case, it will be shown that purely external mass transfer controlled regime can be attained at high temperatures.

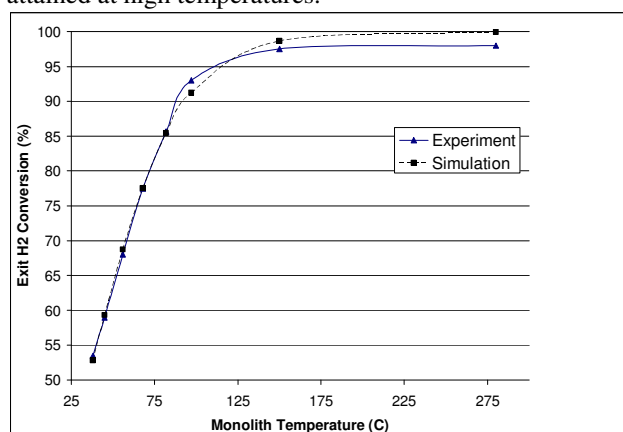


Fig.1 Exit H<sub>2</sub> conversion vs monolith temperature

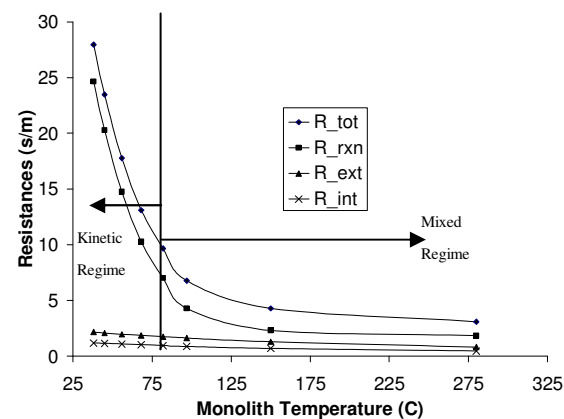


Fig. 2 Various resistances for the process of mass transfer with chemical reaction

## References

- (1) Joshi, S.Y.; Harold, M.P.; Balakotaiah, V. Low-dimensional models for real time simulations of catalytic monoliths. *AIChE J.* **2009**, *55*, 1771.
- (2) Joshi, S.Y.; Harold, M.P.; Balakotaiah, V. On the use of internal mass transfer coefficients in modeling of diffusion and reaction in catalytic monoliths. *Chem. Eng. Sci.* **2009**, *64*, 4976.