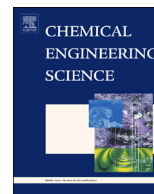




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Enhancing catalyst effectiveness by increasing catalyst film thickness in coated-wall microreactors: Exploiting heat effects in catalytic methane steam micro-reformers



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HIGHLIGHTS

- Investigated impact of increasing catalyst loading in catalytic-wall microreactors.
- New catalyst design rules for catalytic methane steam reforming in microreactors.
- Design rules exploit internal heating of endothermic catalyst washcoatings.
- Theory outlines design space for maximizing both thermal and catalyst efficiency.
- Industrial microreactor simulations confirm benefit of increased catalyst loading.

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ABSTRACT

The potential for increasing endothermic reforming process capacity of a heat-exchanger microreactor without compromising thermal or catalyst efficiency via employing unconventionally-thick catalyst washcoatings is investigated. This is achievable through exploiting the “internal” heating of the catalyst film, i.e. existence of a non-zero heat flux at the wall-catalyst interface at the inner boundary of the film, which is a characteristic of the heat-exchanger microreactor design. Classical one-dimensional analysis of non-isothermal reaction and diffusion in an internally-heated catalyst film identifies minimum values for Prater Temperature and dimensionless activation energy required for internal accumulation of applied heat to be effectively utilized. Under such conditions, analysis confirms the existence of a range of Thiele Moduli, or catalyst film thicknesses, corresponding to complete utilization of internally-supplied heat at catalyst effectiveness greater than unity. Subsequent application of these design rules to a previously validated computational fluid dynamic (CFD) model of an industrial annular micro-channel reformer (AMR) for methane steam reforming confirm that increasing catalyst film thicknesses to values corresponding to Thiele Modulus greater than unity enables intensification of the microreactor performance via increasing reforming capacity while maintaining equivalent thermal efficiency and retaining competitive catalyst effectivenesses.

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1. Introduction

Microchannel reactors pairing methane steam reforming with combustion in a heat-exchanger reactor configuration (Ramaswamy et al., 2006) represent an enabling process intensification technology for natural gas monetization (Economides, 2005; Thackeray, 2002; Holditch, 2003; Khalilpour and Karimi, 2012) and on-board/on-site hydrogen production (Andrews and Shabani, 2012; Balat, 2008; Luk et al., 2012). By reducing the hydraulic diameter

associated with reaction volume, order-of-magnitude improvements in heat and mass transfer rates are achievable, in turn enabling the efficient pairing of endothermic and exothermic reactions within a single, compact unit. This reduced hydraulic diameter (typically ~0.5–5 mm) makes it preferable to use catalyst washcoatings in lieu of a packed bed in order to minimize pressure drop. The dividing wall, which supports the catalytic washcoating, provides the medium for heat transfer between endothermic and exothermic process volumes. The localized addition or removal of heat at the catalyst inner boundary (catalyst-wall interface) may be expected to influence catalyst effectiveness for endothermic processes by providing an additional source of reaction heat to the catalyst film (Honda and Wilhite, 2012).

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Over the past decade, several heat-exchanger microreactor designs have been reported for hydrogen production via methane steam reforming coupled with combustion and/or partial oxidation (Mettler et al., 2010, 2011; Stefanidis and Vlachos, 2009, 2010; Tonkovich et al., 2005; Tonkovich et al., 2007; Tonkovich et al., 2004). To-date, research has aimed at optimizing the methane conversion and hydrogen yield through the variation of design parameters such as temperature, steam to carbon ratio, and residence time (Karakaya et al., 2012; Zhai et al., 2011a) or design parameters such as the thermal conductivity of the supporting wall (Mettler et al., 2010, 2011) or catalyst loading (Zhai et al., 2011a; Zhai et al., 2011b). Additionally, several optimization studies have been conducted in the interest of maximizing methane conversions by investigating the potential of countercurrent flow and the offsetting of reactions zones (Zanfir et al., 2011), the use of stripe combustion catalyst patterning (Jeon et al., 2013), and the use of phase-change media (Pattison and Baldea, 2013, 2015), in order to minimize hotspots. Common to the majority of studies to-date is the assumption of isothermal and/or unity effectiveness catalyst justified by the use of thin catalyst washcoatings. In contrast to this practice, the present study aims to identify new catalyst design rules for maximizing production capacity through exploiting the presence of direct internal heat addition to the catalyst film at the wall-catalyst interface in sufficiently thick washcoatings.

Traditional catalyst design rules are based upon the mathematical treatment of a symmetrical catalyst particle suspended in a fluid supplying both heat and mass to the catalyst, such that heat and mass source conditions (either in form of Dirichlet or Robin-type boundary expressions) are located at the outer boundary of the reaction-transport domain while zero net flux of heat and mass is assumed at an inner boundary corresponding to the center of the symmetry (Aris, 1957a, 1969; Carberry, 1961; Carberry and Kulkarni, 1973; Roberts and Satterfield, 1965; Thiele, 1939). By exploiting shape-, kinetics- and reaction reversibility normalizations (Aris, 1957a, 1969; Carberry, 1962; Carberry and Kulkarni, 1973), a robust rule-of-thumb expression relating expected catalyst effectiveness (η) in terms of the Thiele modulus (ratio of reaction to diffusion rates within the catalyst body) in the absence of external mass or heat transfer resistances is obtained which in turn indicates a maximum value for ϕ of 0.4 to ensure an effectiveness of greater than 95%:

$$\eta_{\text{cat}} = \frac{\tanh(\phi)}{\phi} = 0.95 \rightarrow \phi = 0.4 \quad (1)$$

where ϕ is the normalized Thiele modulus relating catalyst particle size or washcoating thickness to reaction and diffusion rates as follows:

$$\phi^2 = \frac{L^2 r(C_f, T_f)}{C_f D_{\text{eff}}} \quad (2)$$

This results in a sufficiently thin catalyst layer as to prevent significant reduction in internal reaction concentration arising from internal diffusion resistances. However, in the presence of internal heating of the catalyst (such that a finite heat flux condition occurs at the inner boundary), reduction in local reaction rates due to species depletion via diffusional resistances may be countered by local elevation of temperature. In the case of heat-exchanger microreactors, this elevation arises from a combination of heat addition at the inner boundary (catalyst-wall interface) and conductive heat resistances within the catalyst film arising with the use of unconventionally-thick ($\phi > 0.4$) catalyst films. Given that defect-free and smooth catalyst washcoatings of 30–100 μm have been readily achieved in meso-to microscale channels, the use of thicker catalyst coatings is a viable means to exploit heat effects at the catalyst-scale in microreactors (Cybulski and Moulijn, 1994).

This manuscript provides a demonstration of this new design approach as follows. First, a representative non-isothermal one-dimensional reaction-diffusion model with first-order irreversible kinetics is employed to verify the feasibility of enhancing catalyst effectiveness by exploiting internal heat addition and identify parametric design rules. These design rules are validated using a two dimensional computational fluid dynamic (CFD) model, previously described and experimentally validated by the authors (Butcher et al., 2014; Wilhite et al., 2013), of an industrial annular microreactor (AMR). The CFD model is employed to predict local and overall catalyst effectiveness factors alongside overall thermal efficiencies at reformer flow rates corresponding to 95% of equilibrium conversion of methane via MSR over a range of catalyst thicknesses corresponding to $\phi = 0.27$ –2.4 (10–90 μm).

2. Theoretical section

2.1. One dimensional analysis of internally-heated slab catalyst

A one-dimensional reaction-conduction-diffusion model assuming negligible fluid-catalyst transport resistances is employed for parametric analysis of the impact of internal heating of a slab-catalyst upon both local heat utilization and catalyst efficiency for the case of an endothermic unimolecular first-order irreversible reaction. Within the catalyst slab, mass, conduction, and reaction are described by:

$$\frac{d^2 u}{ds^2} = \phi^2 f(u, v) \quad (3)$$

$$\frac{d^2 v}{ds^2} = -\beta \phi^2 f(u, v) \quad (4)$$

with dimensionless boundary conditions

$$\text{at } s = 0 \quad \frac{du}{ds} = 0; \quad \frac{dv}{ds} = \chi \quad (5)$$

$$\text{at } s = 1 \quad u = 1, v = 1 \quad (6)$$

where the Thiele modulus (ϕ), Prater number (β), dimensionless activation energy (γ) and ratio of internal heat addition to conduction (χ) are defined as follows:

$$\phi^2 = \frac{L^2 r(C_f, T_f)}{C_f D_{\text{eff}}}; \quad \beta = \frac{-\Delta H C_f D_{\text{eff}}}{k_{\text{eff}} T_f}; \quad \gamma = \frac{E_A}{R * T_f}; \quad \chi = \frac{q}{T_f} \cdot \frac{L}{k_{\text{eff}}} \quad (7)$$

And the dimensionless rate of reaction is

$$f(u, v) = \frac{k_o \cdot C \cdot \exp\left[\frac{-E_A}{RT}\right]}{k_o \cdot C_f \cdot \exp\left[\frac{-E_A}{RT_f}\right]} = u \cdot \exp\left[\gamma \left(1 - \frac{1}{v}\right)\right] \quad (8)$$

Numerical solution to the above pair of differential equations were obtained using the BVP4C package in the Matlab programming environment and employed to calculate catalyst effectiveness and internal heat utilization. The former, defined as the net volumetric rate of catalytic reaction normalized by the expected rate in the absence of heat and mass transport limitations, may be obtained from derivative analysis of the numerical solution as follows:

$$\eta_{\text{cat}} = \frac{\int_V r(T, C) dv}{r(T_f, C_f) \int_V dv} = \frac{1}{\phi^2} \frac{du}{ds} \Big|_{s=1} \quad (9)$$

The internal heat utilization is defined as the net heat consumption by endothermic reaction within the catalyst slab normalized by the rate of internal heat addition,

$$\eta_{\text{I}} = \frac{\int_0^1 \beta \phi^2 f(u, v) ds}{\frac{dv}{ds} \Big|_{s=0} - \frac{dv}{ds} \Big|_{s=1}} = 1 \quad (10)$$

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