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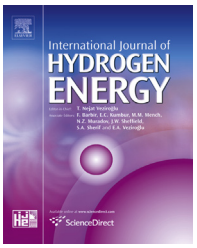

Numerical analysis on steam methane reforming in a plate microchannel reactor: Effect of washcoat properties

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ABSTRACT

The effect of washcoat properties is theoretically investigated for steam methane reforming (SMR) in a plate microchannel reactor. Transport phenomena and reaction within the catalytic washcoat and in the bulk gas phase are modeled using a two-dimensional, comprehensive CFD model with fully resolved catalytic washcoat, coupled with detailed chemistry for SMR over Ni catalyst. Simulation results show that the process is governed by internal mass transfer and reaction, therefore the reactor performance depends markedly on the washcoat structure and dimension. Increasing pore size of the washcoat leads to improved heat coupling, which lowers the hotspot temperature and reduces axial temperature gradients. In the meantime, the role of porosity remains trivial. Further, using a thicker washcoat carrying a greater loading of catalyst can considerably increase the reactor throughput within washcoat thickness of 75 μm, at the expense of certain loss of the catalyst productivity. Optimized washcoat properties would rely on the catalyst activity, price and specific process demands.

Introduction

Steam methane reforming (SMR) remains the world's largest source of industrial hydrogen up to now since its first commercialization over 80 years ago. In centralized plants, this highly endothermic reaction is carried out catalytically in tubular fixed-bed reactors that are placed in gas-fueled furnaces, under high pressure (>20 atm) and temperature (800–900 °C), but with a comparatively slow rate (the residence time is a few seconds) [1]. Despite the fact that industrial technology for SMR is well-established, several downsides are unavoidable; these involve poor heat-transfer from the furnace to the catalyst inside the tube, intraparticle heat and mass transfer limitations [2], and catalyst deactivation [3,4]. The unfavorable energy and matter utilization and the reactor-furnace configuration result in a rather bulky process and a large plant size.

Down-scaling of SMR has been a pressing demand over the last two decades in view of the world's ever growing need for cleaner, safer and more economical hydrogen production processes. Microchannel reactors naturally fit these needs owing to process intensification via miniaturization, which tremendously increases transport rates [5], allowing for processes running at almost the intrinsic rate of chemical kinetics. Regarding SMR, another attraction offered by microchannel reactor is catalytic combustion assisted reforming, in which the proximity of the heat source and heat

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sink benefits a highly integrated and efficient reformer system. Such compact systems find emerging applications in distributed and localized hydrogen/syngas production, including portable fuel cell systems [6], hydrogen fueling stations [7], small-scale GTL process [8] and so on. The overwhelming prospects and feasibility of SMR based on microchannel reactor has been well demonstrated by the leading work of Velocys® Inc. and PNNL [9–11].

Yet process intensification achieved by microchannel reactor is challenging in the context of precisely matching the design to specific process conditions. For instance, SMR can happen over different catalyst systems. Ni, the industrial catalyst, is robust and inexpensive, but relatively easy to deactivate due to carbon deposition and sulfur poisoning [12]. Thus, it dictated prior sulfur removal and high steam to carbon (S/C) ratios on stream, which decrease both the system's energy efficiency and compactness. Rh and other noble metals (Ru, Pd) are orders of magnitude more active for SMR, less prone to coking, and possess high sulfur tolerance, but their expensiveness requires careful usage in a small amount. The point is that process and catalyst intensification must be symbiotic for a downscaled reformer [13]. For washcoated catalyst in microchannel reactor, this intensification implies optimizing both the catalyst's active phase and the porous washcoat (support). For partial oxidation on Rh in monolithic reactors, Stutz and Poulikakos [14] have demonstrated marked effect of washcoat properties and the existence of an optimum washcoat thickness. Similarly, washcoat effect proved to be significant for CO preferential oxidation on Pt in foam-based or honeycomb reactors [15]. Although Stefanidis and Vlachos [16] suggested that Rh-based SMR in microchannel reactor is reaction-controlled, their modeling approach has lumped internal mass transfer and catalytic reaction. Given that partial oxidation is a combination of combustion and SMR [17], it is very likely that effect of washcoat properties is also crucial for SMR in microchannel reactor. That is, despite the fact that the washcoat dimension is considerably small (typically 10–100 μm), intra washcoat mass transfer resistance is significant and not negligible for fast reactions as SMR.

Quantifying the mass transfer resistance for washcoated catalyst in microscale devices is difficult by experimental approach, with which only the overall conversion/yield can be easily measured – which is insufficient for verifying the effect of washcoat properties. Also required are efforts to precisely control and tune the washcoat properties (such as thickness, pore size, etc.) as needed in experiments. These difficulties can be readily overcome, however, by numerical simulation. So far, various modeling schemes have been available for modeling SMR at microscale, ranging from the simplest one-dimensional, plug flow models to three-dimensional, full CFD models [18–24]. To couple gas-phase chemistry and surface catalytic reaction, the instantaneous diffusion approach is the most efficient strategy, which does not necessitate resolving the washcoat geometry; the most sophisticated approach is to solve full reaction-diffusion equations for the catalyst domain. A comprehensive review regarding these approaches can be found in Ref. [25]. Although Irani et al. [26] argued whether the surface-based (instantaneous diffusion approach) or volume-based (solving reaction-diffusion equation) models are preferred for SMR on Ni in a monolithic reactor, Mladenov et al. has shown that for catalytic converters, the latter approach best agrees with the experimental data, and allows discrimination between intrinsic kinetics and mass transfer effects [27]. Anyhow, simulation aiming at optimization of washcoat properties should be washcoat-resolved, if not necessarily. To our best knowledge, most modeling work on SMR in microchannel reactor is limited to the instantaneous diffusion approach. Although some simulations resolved the washcoat geometry [22,28–31], they scarcely discussed the effect of washcoat properties. Another major limitation of the current modeling work is that, with rare exceptions [23,32,33], they used global kinetic models such as that of Xu and Froment [34]. Global kinetics accounts for overall reaction and is deduced with *a priori* assumptions (e.g., the rate-determining step and the most abundant reactive intermediates), which may be invalid under various real reaction conditions. Microkinetics, on the other hand, is developed bottom-up without using condition-dependent assumptions. It can capture behaviors of the reacting system over a wide range of operating conditions. Such reliable detailed chemistry models have been successfully applied in our previous work [35–37].

The objective of this work is to explore the effect of washcoat properties on the performance of a plate microchannel reactor for SMR theoretically. Unlike the aforementioned simulation work, a detailed, washcoat-resolved approach is adopted for momentum, heat and mass transfer within the catalytic washcoat, while catalytic reactions are described by a reliable microkinetics model. We study the basics of reaction and mass transfer within the washcoat, and perform a parametric study with respect to washcoat properties, such as thickness, pore size and porosity. Guidelines for optimization of washcoat are sketched in the context of the reactor's thermal behavior, the catalyst productivity and the reactor throughput.

Mathematical model

An integrated plate microchannel reactor for SMR was modeled with a two-dimensional comprehensive CFD model in which the washcoat was resolved with finite thickness. Catalytic reforming was modeled with microkinetics. Computational domains were specified for a structural unit model and a reduced, single-channel model. Appropriate governing equations, boundary conditions and chemical kinetics were applied for the gas phase, the solid wall and the porous washcoat. This modeling scheme made use of no lumped, correlated transport coefficients. All model parameters were set *a priori* instead of by fitting experimental data. An effective solution method was proposed which iteratively solve the set of differential-algebraic equations forming the mathematical model, ensuring good convergence. All these aspects with regards to establishing the mathematical model are detailed in the following sections.

Model geometries and computational domains

The microchannel reactor is composed of alternate, parallel reforming and heating channels with metal walls in between.

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