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Rational modeling of the CPO of methane over platinum gauze Elementary gas-phase and surface mechanisms coupled with flow simulations

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Abstract

The high-temperature catalytic partial oxidation of methane (CPOM) over a platinum gauze reactor was modeled by integrating 3D numerical simulations of the flow field coupled with heat transport as well as detailed micro-kinetic models including gas-phase and surface reaction mechanisms. Model results describe well CPO experiments over Pt-gauzes in the literature. The conversions of CH_4 and O_2 increase with an increased contact time and were constant in the temperature range of 1000–1200 K. The selectivity to CO linearly increases with temperature. H_2 was only observed above 1200 K, below this temperature H_2O was the only hydrogen-containing product. The contribution of heterogeneous steps in the overall process is prominent, but in the later stages of the reactor, gas-phase reactions become important at certain conditions of temperature, pressure and residence time. Simulations predicted significant gas-phase production of ethane and ethylene via methane oxidative coupling upon increasing the total pressure and residence time. Consequently, homogeneous and heterogeneous processes should be simultaneously implemented in order to accomplish a solid reactor modeling.

Keywords: Methane partial oxidation; Pt metal gauze; CFD modeling; Reaction mechanism; Micro-kinetics; Reactor model

1. Introduction

Catalyzed combustion and oxidation processes are characterized by the occurrence of a complex interplay between transport and chemical kinetics [1,2]. Rational modeling of high-temperature hydrocarbon conversions requires a detailed understanding of gas-phase as well as surface mechanisms. These processes are often mass and heat-transfer limited [3] and accordingly integration of physical (transport) and chemical (reaction mechanisms) processes is key in model development so as to accomplish a solid understanding of the overall process.

The high temperature catalytic partial oxidation of methane (CPOM) in short contact time reactors has been intensively investigated because it offers a promising route to convert natural gas into syngas (mixtures of H_2 and CO), which can be subsequently converted to higher alkanes or methanol [4]. Most of these studies including kinetic and reactor modeling have described the process using a global kinetic models or considering a limited number of elementary steps that satisfactorily fit with experimental data. These studies often suffer from two additional constraints: the gas-phase reactions, which are very likely at typical operation temperatures and the effect of the catalyst reactor geometry, are not taken into account.

De Smet and co-workers [5,6] considered some of the geometric effects during the CPOM by performing steady-state tests in a continuous flow-reactor containing single platinum gauze. Although the real three-dimensional geometry of the catalytic gauze was simplified, a detailed surface reaction mechanism purely based on elementary steps was not included and gas-phase chemistry was omitted. Some of us reported CPO modeling inside a single monolith channel coated with

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platinum incorporating both gas-phase and surface mechanisms [7], but this geometry is of considerably lesser complexity as compared to the above-referred gauze.

For the first time, this paper provides a rational approach for modeling the CPO of CH_4 over Pt-gauze reactor. To this end, detailed kinetic schemes for gas-phase and surface chemistries have been developed [8], evaluated and implemented in a three-dimensional gauze reactor model, coupled with the flow field and heat transfer. This model closely describes realistic reactor features. Our results indicate that both homogeneous and heterogeneous processes should be simultaneously implemented in order to accomplish a solid reactor modeling.

2. Reactor modeling

2.1. Gauze reactor and computational domain

The gauze used in our simulations, is schematically shown in Fig. 1. The gauze catalyst consists of two rows of six parallel platinum wires placed on top of each other (Fig. 1(a)). The average distance between the centers of two individual wires (diameter = 0.20 mm) was 8.2×10^{-4} m (Fig. 1(b)). Due to symmetry considerations, only a quarter of a single mesh of the gauze catalyst had been taken into account into the computational grid, including a single contact point between two wires. The domain extends for half of the distance between centers of two individual wires (amount 4.1×10^{-4} m) in the y-direction (Fig. 1(c)). At the reactor inlet, the reactive mixture (volumetric CH_4/O_2 ratio = 2.5 diluted in 80 vol.% He) flows at a uniform inlet velocity of 10 m/s and at 600 K.

2.2. Numerical model

Modeling the gauze reactor involves a numerical solution for the Navier Stokes equations, including the coupling of detailed gas-phase and surface reaction mechanisms by assuming interaction between them via stable and radical species (see Section 3.1) and considering that energy and mass balances should be satisfied at the interface solid–gas. Arrhenius type expressions were adopted to model the reaction rate in the chemical source terms, which were divided into homogeneous (gas-phase) and heterogeneous (surface) reactions. The enthalpy of the species was calculated by integrating the heat capacity at constant pressure (cp) over the working temperature range, the cp values were obtained by a polynomial approach using data from the JANAF thermodynamic database [9]. The flow field was computed using the commercial computational fluid dynamics code FLUENT [10] coupled with external subroutines developed in our group to model gas-phase and surface chemistries. Details on this are extensively described in the DETCHEM manual [11].

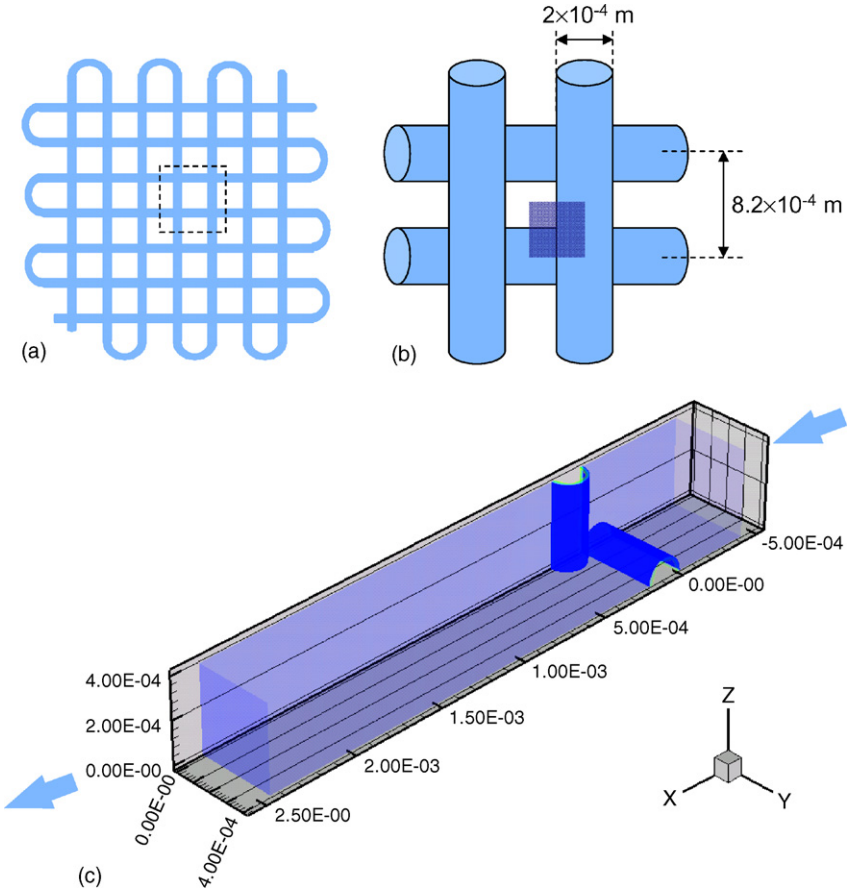

Fig. 1. Platinum gauze modeled in this study: (a) original gauze and (b) detail of wire intersections. Shadow area in (b) corresponds to the selected computational domain presented in (c).