

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 CH₄ and O₂ 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. H₂ was only observed above 1200 K, below this temperature H₂O 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.

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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 H₂ 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].

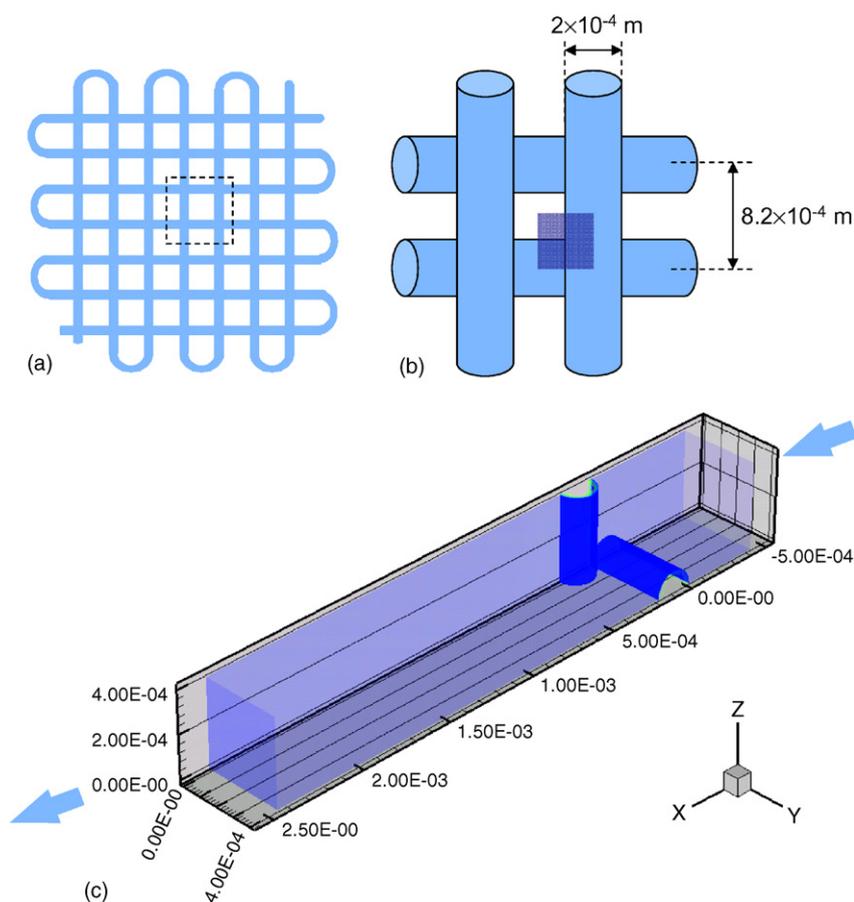


Fig. 1. Platinum gauze modeled in this study: (a) original gauze and (b) detail of wire intersections. Shadow area in (b) corresponds to the selected computational domain presented in (c).

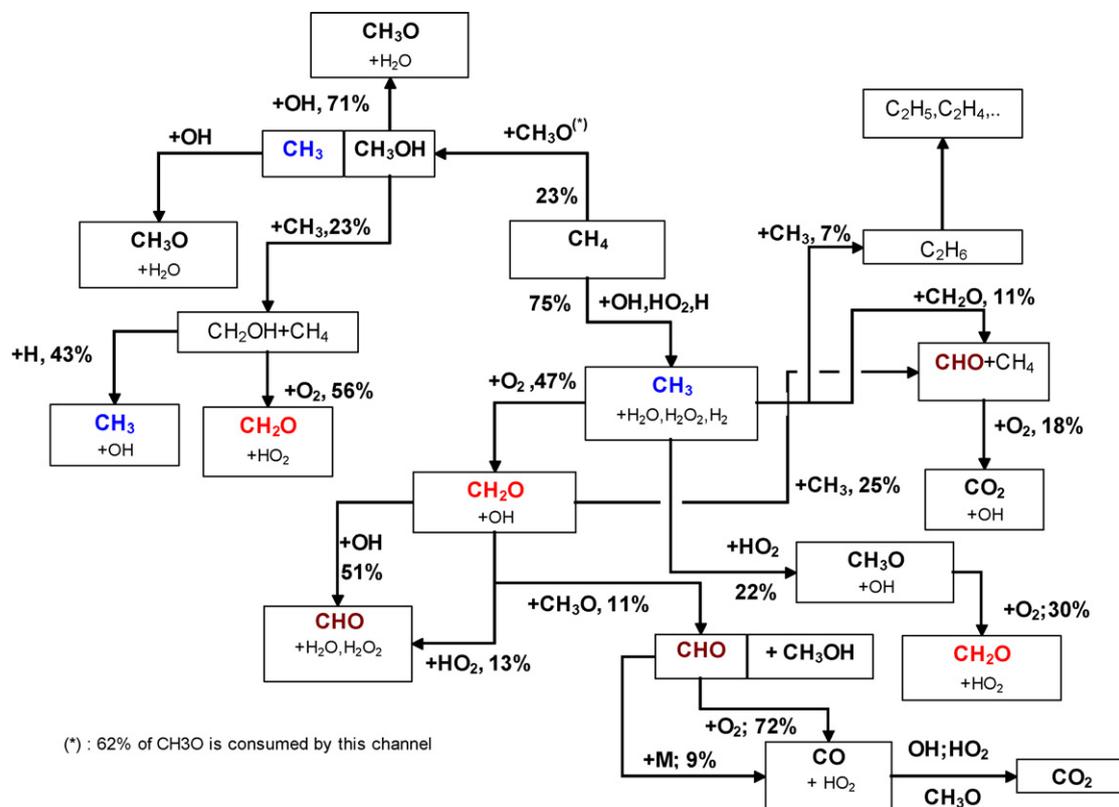


Fig. 2. Reaction path for methane oxidation in the gas-phase. Percentages in the flow analysis quantify the channel contribution to the species consumption in each elementary step. Conditions: volumetric CH_4/O_2 ratio = 2.5, $T = 1050$ K, $P = 1$ bar. The residence time was fixed in order to achieve a methane conversion of 5% (see text).

3. Results and discussion

3.1. Reaction mechanisms

In CPOM, it is often observed that increasing temperature and/or lowering the feed CH_4/O_2 ratio originate an increased methane conversion. The yield of CO_x increases with temperature and the initial O_2 mole fraction. Products of methane oxidative coupling (C_2 or higher hydrocarbons) have been observed at temperatures above 873 K [12] and particularly when the degree of methane conversion is low [13]. It is well accepted that the first step in the CPOM involves the cleavage of a C–H bond at the catalyst surface [4,12,14], leading to highly reactive CH_3 species. Heterogeneous steps at the catalyst surface are responsible for CO_x formation and it was thought they were the only responsible for methyl recombination [15]. Ito et al. [16] postulated the feasibility of the methyl radicals recombination in the gas-phase and Lunsford and co-workers [17] identified gas-phase methyl radicals during the CPOM. Accordingly, experimental evidence underlines the importance of coupling gas-phase and surface reaction mechanisms for developing robust kinetic schemes able to simulate the high-temperature catalytic partial oxidation of methane.

3.1.1. Gas-phase mechanism

Karbach [18] developed a gas-phase mechanism suitable for combustion conditions: its evaluation was performed by

comparing experiments and simulations related to ignition delay times and flame velocities. The kinetic mechanism consists of 764 reactions and involves 61 species. In the present work that mechanism was extended in order to consider processes due to occur at lower temperatures where the CPOM effectively takes place: primary and secondary oxygen additions to the parent alkyl radicals, isomerization and cycle compounds formation were included. The extended mechanism consists of 1400 reactions and 150 species [8]. In order to get a gas-phase mechanism suitable to be implemented at the present simulations, the mechanism in

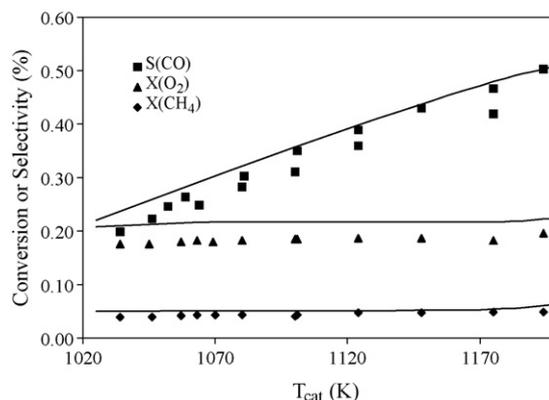


Fig. 3. Comparison of experimental results (symbols) and simulations coupling gas-phase and surface mechanisms (lines). Conditions: volumetric CH_4/O_2 ratio = 2.5, $V_0 = 10$ m/s, $T_0 = 600$ K and $P = 1.3$ bar.

ref. [8] was simplified and only the most relevant reactions were considered in the 3D simulations, the reduced mechanism consisted of 150 reactions and 30 species and it is schematically shown in Fig. 2.

3.1.2. Surface mechanism

Ignition and steady-state operation during catalytic combustion of methane over platinum was previously simulated [14]. The mechanism used in ref. [14] was completed by including additional elementary steps [19]: initial adsorption for methane with adsorbed atomic oxygen and hydroxyl species and desorption pathways for the fuel. The extended kinetic

mechanism consists of 11 species and 32 elementary reactions and can be downloaded from ref. [11].

3.2. Model evaluation with experimental results

Our model has been evaluated with the experimental results reported in refs. [5,6]. These authors reported CO, CO₂ and H₂O as the main reaction products at $T < 1270$ K. Fig. 3 displays experimental data (points) and the results from our simulations (lines). CH₄ and O₂ conversions were not temperature dependent, while the selectivity of CO is strongly influenced by the reaction temperature. Simulations coupling

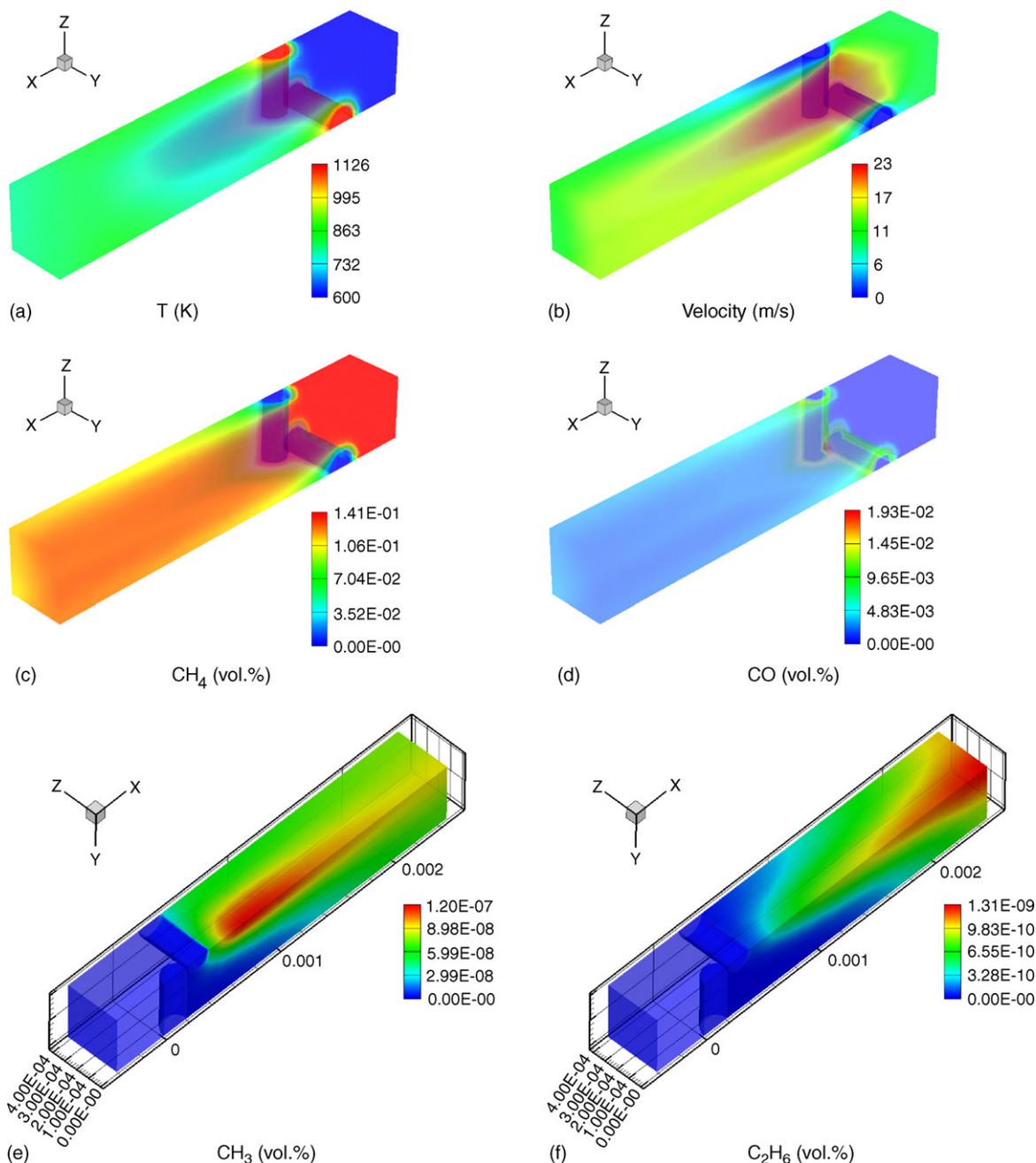


Fig. 4. (a–d) Results from the 3D simulations, including profiles of temperature, velocity and concentration of the main species. Conditions: volumetric CH₄/O₂ ratio = 2.5, $V_0 = 10$ m/s, $T_0 = 600$ K and $P = 1.3$ bar. (e and f) $V_0 = 1$ m/s.

gas-phase and surface micro-kinetics predict well the experimental performance.

Fig. 4(a–d) presents typical profiles of temperature, velocity, CH_4 and CO obtained from the simulation at the experimental conditions considered in Fig. 3. The maximum value of temperature is located at the crossing point of the wires (Fig. 4(a)). Next to the wires and nearly half of the wire diameter downstream the gas-phase temperature has a similar value as in the wires, before of being cooling down to 800 K. The velocity profiles (Fig. 4(b)) show an opposite behaviour than the temperature profiles: the maximum velocity occurs at the top of the mesh in the free path zone, approaching to zero in the zone close to the wires. The consumption of CH_4 and O_2 was maximal at the surface of the platinum wires where marked gradients of reactants and products concentration are present (Fig. 4(c and d)).

Carbon monoxide (Fig. 4(d)) and carbon dioxide are produced on the surface of the catalytic wires, with their maximal yield occurring at the crossing of the wires. Water is produced on the surface as the only H-containing product (not shown). For the conditions used in these experiments, homogeneous reactions showed not to be of relevance: simulations performed with and without the gas-phase chemistry yielded identical results.

3.3. Influence of residence time and pressure

The influence of the gas-phase chemistry in the overall process becomes significant with increasing pressure and residence time [12] and formation of oxidative coupling

products (e.g. C_2H_6) and total combustion products (CO_2 and H_2O) is expected. Fig. 4(e and f) illustrates the concentration profiles of gas-phase species CH_3 and C_2H_6 obtained after decreasing the inlet gas velocity to 1 m/s. These species were formed downstream of the gauze and the maximal production coincides with the zone with lower velocity and higher temperature. HO_2 was the first gas-phase specie formed, followed by hydroxyl radicals (OH), methyl radicals (CH_3) and ethane (C_2H_6), respectively. This result draws parallels with the reaction scheme proposed by Pollard [20] for the oxidation of hydrocarbons at intermediate temperature. The conversion of reactants was changed (from 4 to 7% for CH_4 and from 20 to 30% for O_2) as well as a higher CO_2/CO ratio at the reactor outlet (from 1 at 10 m/s to 2 at m/s). Despite this, the surface chemistry was still the main route for methane conversion.

Fig. 5 shows the calculated concentration of ethane at different pressures and inlet gas velocities. The C_2H_6 production decreases as the velocity increases (Fig. 5(a)) as it was concluded for shorter residence times (ca. five times lower concentration of ethane was obtained when going from 1 to 10 m/s). Differently, an increase in pressure favours ethane production (Fig. 5(b)) and five orders of magnitude higher of C_2H_6 yields were obtained upon increasing the pressure from 1 to 10 bar.

4. Conclusions

For the first time, the high-temperature catalytic oxidation of methane over platinum gauze has been successfully modeled using 3D numerical simulations of the flow field coupled with heat transport and detailed gas-phase and surface micro-kinetic models based on elementary steps. Model results are in perfect agreement with CPO experiments over Pt-gauzes reported in the literature. Our simulations successfully linked the interaction between the gas-phase mechanism and the surface mechanism through molecular and radical species involved in the process and the flow around the wire catalyst. For typical CPO conditions, heterogeneous steps govern the overall reactor performance. However, gas-phase reactions (e.g. producing ethane via oxidative coupling) become significant as residence time and pressure increase. Accordingly, surface (heterogeneous) and gas-phase (homogeneous) processes should be simultaneously implemented in the model in order to obtain a reliable reactor description. Our rigorous model can be used to design or optimize reactor operation during high-temperature oxidation processes.

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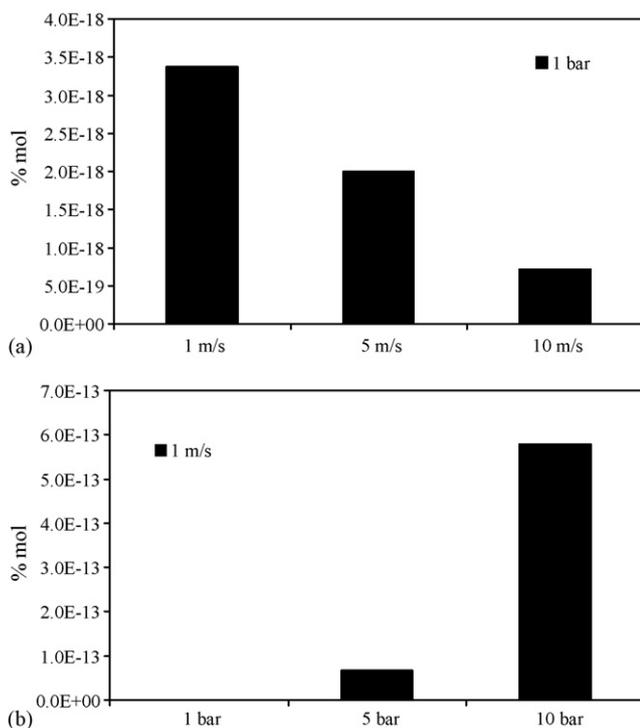


Fig. 5. Influence of (a) inlet gas velocity (at 1 bar) and (b) total pressure (at 1 m/s) on the outlet concentration of C_2H_6 . Conditions: volumetric CH_4/O_2 ratio = 2.5 and $T_0 = 600$ K.

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