A CFD model for partial oxidation of methane over self-sustained electrochemical promotion catalyst

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Abstract

A multi-physical computational fluid dynamics (CFD) model coupled with detailed chemical and electrochemical processes was developed for analyzing partial oxidation (POX) of methane (CH_4) over a self-sustained electrochemical promotion (SSEP) catalyst in a fixed-bed reformer. The model incorporates a conventional kinetics for POX of CH_4 over the Ni component and the kinetics of the SSEP effect that is dictated by a unique microstructure of the catalyst and electrochemical properties of its components. The model also incorporates the transport processes and thermal fluxes in porous media. The CFD modeling results agrees with experimental data in the entire operation temperature range. Detailed profiles of temperature and species concentration in the catalyst bed can be calculated with this model. The model is also capable of quantifying the enhancement of POX of CH_4 due to the SSEP effect. The results demonstrate that the model can be used to analyze and predict the impact of catalyst activity and operation condition on POX of CH_4 over the SSEP catalyst.

Keywords: CFD, Partial Oxidation, Methane, Syngas, Self-sustained electrochemical Promotion

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1. Introduction

Hydrogen (H_2) has been used extensively by petroleum and chemical industries for a variety of applications including hydrocracking/hydrodesulphurization of hydrocarbons [1], syntheses of ammonia, methanol, and other liquid hydrocarbons (Fischer-Tropsch synthesis) [2-4]. It is also recognized as the most promising energy carrier/fuel in a sustainable energy economy because of its high specific energy and zero emission [5]. Today, H_2 is produced primarily from conversion of natural gas [6]. Because the principal component of natural gas is methane (CH_4), conversion of CH_4 into H_2 or syngas (H_2 and CO) has been intensively studied for decades. Primary practical conversion processes are steam reforming (SR), dry reforming (DR), partial oxidation (POX), and autothermal reforming (ATR). To date only SR process has been scaled up for mass production [7]. However the SR process,

is highly endothermic. A significant heat supply is required to sustain the reaction. POX process

provides an alternative way to generate syngas. In a POX, CH_4 is partially oxidized by oxygen (O_2) to form syngas. Usually a catalyst is required to sustain a meaningful reaction rate. The process is mildly exothermic and energy economical. In addition, it does not require water storage and steam delivery resulting in less complex, more compact, and cost effective systems which are promising for mobile and portable applications [8].

The process of POX of CH_4 to produce syngas involves dissociation of a high energy CH_3 -H bond (429.3 kJ/mol) [8]. The catalyst as a key factor in the equation for economical conversion of CH_4 has been studied for more than 80 years. The first systematic investigation of catalytic POX of CH_4 was conducted by Liander [3] in 1929. Up to now, two major types of catalysts

have been widespread investigated [7, 8]: (1) supported transition metal based catalysts and (2) supported noble metal based catalysts. The transition metal based catalysts such as Ni or Co supported by a variety of metal oxides such as Al_2O_3 , CaO , La_2O_3 , MgO , CeO_2 , TiO_2 , ZrO_2 and UO_2 etc. have been proven to be highly active for POX of CH_4 at $\sim 900^\circ\text{C}$. However, carbon deposition decreases the catalytic activity of the catalysts and reduces their lifetime. Noble metal such as Ir, Pd, Pt, Rh, and Ru based catalysts have attracted a lot of attention because of their high conversion, high selectivities to CO and H_2 at relatively lower temperatures and of their low propensity of carbon deposition. However, the cost and availability of noble metals is an issue for widespread use of the noble metal based catalysts.

Inspired by Vayenas's [9-13] previous discovery on non-Faradic electrochemical modification of catalytic activity (NEMCA) or by electrochemical promotion catalyst (EPOC), Zhou [14] first designed, synthesized, and tested a self-sustained electrochemical promotion catalyst (SSEP), which did not contain any noble metal component and did not require an external power source to sustain electrochemical promotion. The experimental results demonstrate that the SSEP catalyst enables a significant electrochemical promotion, resulting in a higher conversion of CH_4 into H_2 and CO at temperature $350 - 650^\circ\text{C}$ similar to a commercial Pt based catalyst under the same operation condition. The CH_4 conversion was 29.4% at 350°C and reached 100% at above 550°C and the maximum selectivity of H_2 was on the level of 90% at $450 - 650^\circ\text{C}$ under gas hourly space velocity (GHSV) of $42,000\text{ h}^{-1}$ [15-17]. Hernandez et al. [18] studied similar catalysts for NO_x storage and reduction (NSR) in diesel engine emission control. The catalysts exhibited enhanced NO_x removal efficiency for lean burn engine exhaust compared with a standard NSR catalyst. Hibino group used another similar catalyst for oxidation of methane to produce methanol, carbon combustion and as a three-way catalyst [19-21].

Computational fluid dynamics (CFD) simulation package, a powerful tool to model and analyze mass and heat transfer, coupled with a chemical reaction kinetics has been used to predict the chemical reaction rate, species concentration and temperature profile for **catalytic reforming of hydrocarbons**. Deutschmann et al. [22], Horn et al. [23], Schwiedernoch et al. [24], Williams et al. [25], Ding et al. [26], Chaniotis et al. [27] Quiceno et al. [28] employed CFD approaches to investigate the reacting flow of POX of CH₄. Cao et al. [29], Baek et al. [30], Zhai et al. [31], Said et al. [32], Savuto et al. [33], Murphy et al. [34] and Fan et al. [35] simulated SR of methane by using CFD with chemical kinetics. Shi [36] developed a CFD model for ATR of n-hexadecane over a catalytic monolith reformer. Kim et al. [37] investigated ATR of n-heptane with CFD coupled transport and chemical kinetics. Yan et al. [38, 39] investigated ATR of methane in a spiral multi-cylinder micro reactor and in a micro premix chamber with CFD approaches. Hamed et al. [40] developed a CFD model with detailed kinetic mechanism for exhaust gas reforming of biogas to syngas. Fazeli [41] studied steam reforming of methanol with CFD approach. Xuan et al. [42] Studied ATR of biogas with CFD model integrated with chemical kinetics. Wehinger et al. [43] studied DR of methane in fixed-bed reactors with CFD **modeling**. In these researches, CFD was used to study hydrocarbons reforming over a variety of different reformers along with different catalysts resulting in a better understanding of the complex interaction between chemical reaction rates, mass/heat transfer, activity of catalyst, and operation conditions. However, none of these researches deal with a SSEP catalyst and the effect of electrochemical promotion process. Huang et al. [44] numerically analyzed POX of liquid hydrocarbon, n-pentadecane (C₁₅H₃₂), over the SSEP catalyst using a 1-D plug flow reactor model. However, based on the assumption of plug flow reactor the mass and heat transfer are not

included. Thus, radial profiles of reactants/products concentrations over the reformer could not be predicted, and temperature profile over catalyst could not be calculated neither.

In this work, a CFD model coupled with detailed chemical and electrochemical processes for POX of CH_4 over the SSEP catalyst in a fixed-bed reformer was developed. The objective of the research was to elucidate the mechanisms and roles of electrochemical promotion in POX of CH_4 over the SSEP catalyst. It is our anticipation that this study will deepen our understanding of SSEP in catalytic POX of hydrocarbons and underpin the design of the SSEP catalysts in many other interesting chemical engineering processes including catalytic reduction of NO_x from vehicle emission and production of hydrocarbon fuel from CO_2 and steam. The CFD analysis was performed using ANSYS FLUENT V14.0. The electrochemical processes and reaction rates were calculated and coupled with the FLUENT solver by using User-Defined Functions (UDFs). The CFD model was validated with the experimental data published in our earlier work [15].

2. CFD model

2.1 Geometric configuration of the reformer

POX of CH_4 experiments were conducted in a quartz tube fixed-bed reformer/reactor [15]. The geometric configuration of the reformer was schematically shown in Fig. 1. The inner diameter of the reformer was 10 mm; 0.5 g catalyst diluted with 1g quartz wool was supported in the center of the reformer and the length of the catalyst bed was around 40mm. The mixed reactants (CH_4 and air) were fed into the reformer filled with a porous catalyst through the inlet. A 2D axisymmetric CFD model was used to analyze the reacting flow of POX of CH_4 over the catalysts at steady states. It was discretized into 32,000 quadrilateral cells. Grid density was increased near the reformer inlet, outlet and wall where higher velocity and species concentration gradients existed. In order to verify that the CFD analysis results are grid-independent, the

number of the grid cells varied from 24,800 to 32,000. A maximum difference of 0.4% in CH₄ conversion was obtained.

Fig. 1 – Geometric configuration of the tubular reformer/reactor.

2.2 Governing equation and boundary conditions

The gas hourly space velocity (GHSV) was set to 42000 h⁻¹ in the experiments for POX of CH₄ over the catalysts and the particle Reynolds number is $Re_p = \frac{\rho d_p v}{\mu}$, where d_p is diameter of particles [45]. From the SEM micrographs of the catalysts [16, 44], d_p is ~500nm. The particle Reynolds number is ~ 0.003, which is lower than 1. Therefore, the reacting flow was assumed to be a laminar flow. The fundamental governing equations could be written as follows.

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{v}) = S_m \quad (3)$$

$$\frac{\partial}{\partial t} (\rho \vec{v}) + \nabla \cdot (\rho \vec{v} \vec{v}) = -\nabla P + \nabla \cdot (\vec{\tau}) + \rho \vec{g} \quad (4)$$

$$\frac{\partial}{\partial t} (\rho E) + \nabla \cdot (\vec{v} (\rho E + P)) = \nabla \cdot \left[k_{eff} \nabla T - \sum_j h_j \vec{J}_j + (\vec{\tau}_{eff} \cdot \vec{v}) \right] + S_h \quad (5)$$

$$\frac{\partial}{\partial t} (\rho Y_i) + \nabla \cdot (\rho \vec{v} Y_i) = -\nabla \cdot \vec{J}_i + R_i + S_i \quad (6)$$

$$P = \rho RT \sum \frac{Y_i}{M_i} \quad (7)$$

where ρ is the density, t is time, $\vec{v}$ is the velocity, S_m is the mass source. P is the static pressure, $\vec{\tau}$ is the stress tensor, $\rho \vec{g}$ is gravitational body force, μ is the molecular viscosity, where k_{eff} is the effective conductivity, $\vec{J}_j$ is the diffusion flux of species j , S_h includes the heat of chemical reaction. R_i is the net rate of production of species i by chemical reaction and S_i is the rate of creation by addition from the dispersed phase plus any user-defined sources. M_i is the molecular weight of species i . Darcy's law with a constant porosity and permeability and ignoring convective acceleration and diffusion is used for the porous media of the catalyst bed

$$\nabla P = -\frac{\mu}{\kappa} \vec{v} \quad (8)$$

where κ is the permeability of the medium.

The thermal conductivity and viscosity of the mixed gases were calculated based on mass-weighted-mixing-law. The inlet pressure of the reactants was set to 6 psi, and reformat gas pressure at the outlet was 0 (gauge pressure). The wall of the reformer was at constant temperature (isothermal).

2.3 Reaction kinetics

The SSEP catalyst is in form of microscopic particles with mainly four components [15, 16]. The anode is a Ni/NiO/Cu/CeO₂ particle. The support is an oxygen ion conductor yttria-stabilized zirconia (YSZ). If there is no cathode, this catalyst could be treated as conventional Ni based catalyst and the POX process could be described by using a conventional kinetic model for Ni based catalyst. However, if there are a cathode, La_{0.9}Sr_{0.1}MnO₃ (LSM), and an electronic conductor (Ni/Cu) between the anode and cathode, the four components form a microscopic electrochemical cell. Oxygen ions are continuously supplied to the anode from the cathode, forming an electrical double layer (EDL) [9, 10] at the catalyst/gas interface and resulting in an

accelerated reaction rate for POX. Therefore, the reaction rate for POX over the SSEP catalyst is a superposition of: (1) reaction rate defined by the kinetic model for POX of CH₄ over Ni based catalyst; and (2) the reaction rate enhancement by the SSEP effect [44]. A detailed discussion will be given below.

2.3.1 Kinetic model for POX of CH₄ over Ni based catalyst

Prettre et al. [46] first proposed an indirect mechanism of POX of CH₄ over a Ni based catalyst. Their experiments demonstrate that the longitudinal temperature profile of the catalyst bed is not uniform. The temperature at the front part of the catalyst bed (close to the inlet of the reformer) is significantly higher than that at the latter part of the catalyst bed and the furnace temperature. These results can be explained by a two-step reaction mechanism: the initial exothermic CH₄ total combustion followed by the endothermic steam reforming, and mild exothermic water gas shift reactions. In this indirect POX of CH₄ mechanism, the syngas is a secondary product. Many previous researches on modeling of POX of CH₄ over Ni based catalysts followed this indirect mechanism. The most accepted and cited kinetic model was proposed by following groups. In 1980, Trimm and Lam [47] proposed a kinetic model of CH₄ total combustion. In 1989, Xu and Froment [48, 49] proposed a kinetic model for steam reforming of CH₄ and water gas shift reaction. In 1996, De Groote and Froment [50] combined Trimm and Xu's assumptions and proposed a kinetic model for POX of CH₄. In general, two steps are involved in POX of CH₄ over Ni based catalysts in this kinetic model.

(1) CH₄ total combustion

(2) Followed by partial steam reforming, total steam reforming and water gas shift reaction

The reaction rates of the above four equations are expressed as

Total combustion

$$r_1 = \frac{k_{1a} P_{\text{CH}_4} P_{\text{O}_2}}{\left(1 + K_{\text{CH}_4}^c P_{\text{CH}_4} + K_{\text{O}_2}^c P_{\text{O}_2}\right)^2} + \frac{k_{1b} P_{\text{CH}_4} P_{\text{O}_2}}{1 + K_{\text{CH}_4}^c P_{\text{CH}_4} + K_{\text{O}_2}^c P_{\text{O}_2}} \quad (13)$$

Partial steam reforming

$$r_2 = \frac{k_2}{P_{\text{H}_2}^{2.5}} \left(P_{\text{CH}_4} P_{\text{H}_2\text{O}} - \frac{P_{\text{H}_2}^3 P_{\text{CO}}}{K_I} \right) \times \frac{1}{\text{DEN}^2} \quad (14)$$

Total steam reforming

$$r_3 = \frac{k_3}{P_{\text{H}_2}^{3.5}} \left(P_{\text{CH}_4} P_{\text{H}_2\text{O}}^2 - \frac{P_{\text{H}_2}^4 P_{\text{CO}_2}}{K_{II}} \right) \times \frac{1}{\text{DEN}^2} \quad (15)$$

Water gas shift

$$r_4 = \frac{k_4}{P_{\text{H}_2}} \left(P_{\text{CO}} P_{\text{H}_2\text{O}} - \frac{P_{\text{H}_2} P_{\text{CO}_2}}{K_{III}} \right) \times \frac{1}{\text{DEN}^2} \quad (16)$$

where

$$\text{DEN} = 1 + K_{\text{CO}} P_{\text{CO}} + K_{\text{H}_2} P_{\text{H}_2} + K_{\text{CH}_4} P_{\text{CH}_4} + K_{\text{H}_2\text{O}} \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} \quad (17)$$

k_i is the reaction rate constant, which expresses in Arrhenius equations

$$k_i = A_i \exp\left(-\frac{E_i}{RT}\right) \quad (18)$$

A_i is the pre-exponential factor, E_i is the activation energy, which are listed in Table 1 [48, 51].

R is the universal gas constant; T is the reaction temperature in Kelvin. P_i is the partial pressure of reactants or products, K_i is the adsorption constants of reactants or products which is written by

$$K_i = K_{oi} \exp\left(-\frac{\Delta H_i}{RT}\right) \quad (19)$$

K_{oi} and ΔH_i are listed in Table 2 [48, 51]. K_I , K_{II} , and K_{III} are reaction equilibrium constants for partial steam reforming, total steam reforming and water gas shift reactions respectively. They are listed in Table 3 [48, 51].

Table 1 – Arrhenius parameter values for combustion, reforming and water gas shift reactions.

Reaction	Pre-exponential factor A_i	Activation energy E_i (J/mol)
Total combustion	$8.11 \times 10^5 \text{ mol bar}^{-2} \text{ kg}_{\text{cat}}^{-1} \text{ s}^{-1}$	86000
	$6.82 \times 10^5 \text{ mol bar}^{-2} \text{ kg}_{\text{cat}}^{-1} \text{ s}^{-1}$	86000
Partial steam reforming	$1.17 \times 10^{15} \text{ mol bar}^{0.5} \text{ kg}_{\text{cat}}^{-1} \text{ s}^{-1}$	240100
Total steam reforming	$2.83 \times 10^{14} \text{ mol bar}^{0.5} \text{ kg}_{\text{cat}}^{-1} \text{ s}^{-1}$	243900
Water gas shift	$5.43 \times 10^5 \text{ mol bar}^{-1} \text{ kg}_{\text{cat}}^{-1} \text{ s}^{-1}$	67130

Table 2 – Van't Hoff parameter for species adsorption.

Component	K_{oi}	ΔH_i (J/mol)
CH ₄ (combustion)	$1.26 \times 10^{-1} \text{ bar}^{-1}$	-27300
O ₂ (combustion)	$7.78 \times 10^{-7} \text{ bar}^{-1}$	-92800

CH ₄	$6.65 \times 10^{-4} \text{ bar}^{-1}$	-39280
O ₂	$8.23 \times 10^{-5} \text{ bar}^{-1}$	-70650
H ₂	$6.12 \times 10^{-9} \text{ bar}^{-1}$	-82900
H ₂ O	1.77×10^5	88680

Table 3 – Equilibrium constants.

Reaction	Equilibrium constant
Partial steam reforming	$K_I = \exp\left(\frac{-26830}{T} + 30.114\right) \text{ bar}^2$
Total steam reforming	$K_{II} = K_I K_{III} \text{ bar}^2$
Water gas shift	$K_{III} = \exp\left(\frac{4400}{T} - 4.036\right)$

2.3.2 Kinetic model for reaction rate enhanced by SSEP effect

SSEP is realized via an electrochemical coupling between anode and cathode phases through an oxygen ion conductor. The constant supply of promoters, O²⁻, from cathode phases to the surface of the anode phases shifted the electrochemical potential in the positive direction. A detailed illustration can be found in Refs. [15-17, 44]. The microstructure of the catalyst was described and displayed in previous publication [16, 44]. Essentially, the YSZ is used as the oxygen ion conductor whereas the LSM is used as the cathode, Ni/NiO/Cu/CeO₂ as anode, and Ni/Cu as electron conductor. LSM and YSZ particles are jointed to form a porous support resembling clusters of micro-rods. Ni/NiO/Cu/CeO₂ particles are uniformly distributed on the surface of the micro-rods.

Based on this microscopic structure of the SSEP catalyst, a simplified geometric configuration of a SSEP catalyst unit is proposed as shown in Fig. 2. In the simplified SSEP catalyst unit, oxygen ion conductor (YSZ) and cathode (LSM) particles are in direct contact with each other and form a micro-rod. Anode particles (Ni/NiO/Cu/CeO₂) and electron conductor (Ni/Cu) are distributed evenly on the surface of the oxygen ion YSZ/LSM support [44].

Fig. 2 – Simplified geometric configuration of a unit SSEP catalyst.

The SSEP process is described with following reactions [44, 52, 53]:

On anodic catalysts (anodic phase):

On cathodic catalysts (cathodic phase):

In a general form of $\text{A} + \text{D} \rightarrow \text{products}$ (e.g. Eq. (9) CH₄ total combustion reaction), where A is the electron acceptor or oxidizing reactant and D is the electron donor or reducing reactant, the catalytic reaction rate of electrochemical promotion was [10-12]:

$$r_{pro} = k_{pro} \theta_A \theta_D \quad (24)$$

where r_{pro} was the reaction rate enhancement due to SSEP effect, k_{pro} was the SSEP reaction constant, the coverage ratios of the electron donor and acceptor, θ_D and θ_A were given by:

$$\theta_D = \frac{k_D P_D \exp(\lambda_D \Pi)}{1 + k_D P_D \exp(\lambda_D \Pi) + k_A P_A \exp(\lambda_A \Pi)} \quad (25)$$

$$\theta_A = \frac{k_A P_A \exp(\lambda_A \Pi)}{1 + k_A P_A \exp(\lambda_A \Pi) + k_D P_D \exp(\lambda_D \Pi)} \quad (26)$$

Combining Eqs. (24 – 26) gave:

$$r_{pro} = k_{pro} \theta_A \theta_D = \frac{k_{pro} k_A k_D P_A P_D \exp[(\lambda_A + \lambda_D) \Pi]}{[1 + k_D P_D \exp(\lambda_D \Pi) + k_A P_A \exp(\lambda_A \Pi)]^2} \quad (27)$$

where

$$k_{pro} = A_{pro} \exp\left(\frac{-E_{pro}}{RT}\right) \quad (28)$$

The total reaction rate is a superposition of the reaction rate defined by the kinetic model for conventional promotion over Ni based catalyst, and the reaction rate enhanced by the SSEP effect [44]. The total reaction rate is applied to CH₄ total combustion:

$$r_1^{total} = r_1 + r_{pro} \quad (29)$$

where r_1^{total} is the total reaction rate of CH₄ total combustion over the SSEP catalyst. The reaction rate of partial steam reforming r_2 , total steam reforming r_3 , and water gas shift reaction r_4 are assumed not to be affected by the SSEP, thus remain the same as in the Eqs. (14 – 16).

In the above equations, $\Pi = e\Phi_A / k_b T$, where e is the electric charge of an electron, k_b is the Boltzmann constant. Thus, the catalytic rate of electrochemical promotion can be defined by the potential of the anode, Φ_A , if other parameters are fixed. In order to calculate the anode

potential Φ_A , the potential distribution in the oxygen ion conductor is calculated. Fig. 3 shows the domain for calculation of the potential distribution in the oxygen ion conductor along with its boundary conditions based on the simplified SSEP catalyst unit as shown in Fig. 2. Boundary A is the boundary between oxygen ion conductor and anode. Boundary B is the boundary between oxygen ion conductor and electron conductor. Boundary C is the boundary between oxygen ion conductor and cathode.

Fig. 3 – Schematic of the domain of oxygen ion conductor in a unit SSEP catalyst model.

O^{2-} is driven by the electrical potential difference between the anode and cathode. The governing equation in the domain can be represented as [54]:

$$\nabla \cdot (\sigma E) = \nabla \cdot (-\sigma \nabla \Phi) = 0 \quad (30)$$

where E is the electric field intensity, Φ is the electric potential. σ is the O^{2-} conductivity of the oxygen ion conductor. Because σ is a constant at any given temperature, Eq. (30) can be simplified as:

$$\Delta \Phi = 0 \quad (31)$$

At Boundary A, anode is in contact with the oxygen ion conductor, thus the boundary condition is,

$$i_{anode} = \sigma E = -\sigma \nabla \Phi \quad (32)$$

where i_{anode} is the anode current density.

At Boundary C, cathode is in contact with the oxygen ion conductor, and the boundary condition is,

$$i_{cathode} = \sigma E = -\sigma \nabla \Phi \quad (33)$$

where $i_{cathode}$ is the cathode current density.

At Boundary B,

$$\frac{\partial \Phi}{\partial \vec{n}} = 0 \quad (34)$$

where $\vec{n}$ is the unit vector at the normal direction.

From Butler-Volmer equation [55],

$$i_{anode} = i_{anode}^0 \left[\exp \left(\frac{\alpha n F (\Phi - \Phi_{anode}^0)}{RT} \right) - \exp \left(- \frac{(1-\alpha) n F (\Phi - \Phi_{anode}^0)}{RT} \right) \right] \quad (35)$$

$$i_{cathode} = i_{cathode}^0 \left[\exp \left(\frac{\alpha n F (\Phi_{cathode}^0 - \Phi)}{RT} \right) - \exp \left(- \frac{(1-\alpha) n F (\Phi_{cathode}^0 - \Phi)}{RT} \right) \right] \quad (36)$$

Combining Eqs. (32, 33, 35 and 36) gives:

$$-\sigma \nabla \Phi = i_{anode}^0 \left[\exp \left(\frac{\alpha n F (\Phi - \Phi_{anode}^0)}{RT} \right) - \exp \left(- \frac{(1-\alpha) n F (\Phi - \Phi_{anode}^0)}{RT} \right) \right] \quad (37)$$

at Boundary A

$$-\sigma \nabla \Phi = i_{cathode}^0 \left[\exp \left(\frac{\alpha n F (\Phi_{cathode}^0 - \Phi)}{RT} \right) - \exp \left(- \frac{(1-\alpha) n F (\Phi_{cathode}^0 - \Phi)}{RT} \right) \right] \quad (38)$$

at Boundary C

where α is the charge transport coefficient, n is number of moles of electrons transferred and F is Faraday's constant. i_{anode}^0 and $i_{cathode}^0$ are anode and cathode exchange current density respectively. They can be written as [56]:

$$i_{anode}^0 = \gamma_{anode} \left(\frac{P_{H_2}}{P_{ref}} \right) \left(\frac{P_{H_2O}}{P_{ref}} \right) \exp \left(-\frac{E_{act,anode}}{RT} \right) \quad (39)$$

$$i_{cathode}^0 = \gamma_{cathode} \left(\frac{P_{O_2}}{P_{ref}} \right)^{0.25} \exp \left(-\frac{E_{act,cathode}}{RT} \right) \quad (40)$$

Φ_{anode}^0 and $\Phi_{cathode}^0$ are the equilibrium potentials of anode and cathode respectively, which can be calculated in terms of partial pressures of reactants/products according to the Nernst equation [55].

$$\Phi_{anode}^0 = 0 \quad (41)$$

$$\Phi_{cathode}^0 = \Phi_{cathode}^{STP} - \frac{RT}{nF} \ln \frac{P_{H_2O}}{P_{H_2} P_{O_2}^{0.5}} \quad (42)$$

where P_{H_2} , P_{H_2O} and P_{O_2} are partial pressures of the reactants, $\Phi_{cathode}^{STP}$ is the potential of cathode under standard temperature and pressure.

The parameters in the Eqs. (25 – 43) are given in Table 4 [11, 56]. And the oxygen ion conductivity in oxygen ion conductor (YSZ) at temperature 350 – 650 °C is given in Table 5 [57, 58]. The pre-exponential factor A_{pro} and activation energy E_{pro} in Eq. (29) are estimated from the experimental results of POX of CH₄ over the SSEP catalyst as listed in Table 6.

Table 4 – Model parameters.

Parameter	Unit	Value
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κ	m^2	1.44×10^{-12}
e	C	1.602×10^{-19}
k_b	J K^{-1}	1.381×10^{-23}
α	dimensionless	0.5
n	dimensionless	2
F	C mol^{-1}	96485
Φ_{anode}^0	V	0
$\Phi_{cathode}^{STP}$	V	1.23
R	$\text{J mol}^{-1} \text{K}^{-1}$	8.314
P_{ref}	Pa	101325
$E_{act,anode}$	J mol^{-1}	1.2×10^5
$E_{act,cathode}$	J mol^{-1}	1.2×10^5
γ_{anode}	A m^{-2}	5.5×10^{10}
$\gamma_{cathode}$	A m^{-2}	7.0×10^9
k_A	Pa^{-1}	100
k_D	Pa^{-1}	0.01
λ_A	dimensionless	-0.15
λ_D	dimensionless	0.15

Table 5 – Oxygen ion conductivity (σ) of the oxygen ion conductor (YSZ) at 350 – 650 °C.

Temperature (°C)	Conductivity (S cm^{-1})
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350	3.9×10^{-5}
400	2.0×10^{-4}
450	5.2×10^{-4}
500	1.2×10^{-3}
550	2.8×10^{-3}
600	5.5×10^{-3}
650	9.0×10^{-3}

Table 6 – Pre-exponential factor and activation energy.

Parameters	Unit	Values
A_{pro}	$\text{mol g}_{\text{cat}}^{-1} \text{s}^{-1}$	9.244×10^{-5}
E_{pro}	J mol^{-1}	1.241×10^4

A finite difference method (FDM) was used to solve Eq. (31) coupled with boundary condition Eqs. (34, 37 and 38). The FDM code was integrated into User-Defined functions (UDFs) which were connected to the ANSYS FLUENT solver.

3 Results and discussion

3.1 Model validation

The CFD model for POX of CH_4 over both Ni based catalyst and SSEP catalyst was validated with experimental data [15]. Fig. 4 shows a comparison between the CFD model prediction and the experimental data of CH_4 conversion over the Ni based catalyst. The experiments were conducted at operation temperature ranging from 350 to 650 °C. The CFD

model was proved to have a good agreement with the experimental data in the entire temperature range.

Fig. 4 – Comparison between model prediction and experimental data on CH₄ conversion over the Ni based catalyst.

Fig. 5 compares the experimentally observed CH₄ conversions over the SSEP catalyst with the computation results at temperatures ranging from 350 to 650 °C. The model prediction agrees very well with the experimental data. The maximum discrepancy between the experimental data and the corresponding CFD model prediction is 5% at 350 °C. The CFD model successfully describes the conversion of CH₄ over the SSEP catalyst. Both experimental and computational

results indicate that the SSEP catalyst is superior to the Ni based catalyst. For example, at 500°C the conversion is above 90% for the SSEP catalyst whereas at 650°C the conversion for the Ni based catalyst is little below 90%.

Fig. 5 – Comparison between model prediction and experimental data on CH₄ conversion over the SSEP catalyst.

3.2 Computational results

As mentioned in section 2.3.1, the experimental observation demonstrated a non-uniform longitudinal temperature profile over the catalyst bed. As shown in Fig. 6, the present CFD model also gives non-uniform longitudinal temperature profiles for both Ni based and SSEP

catalysts. Fig. 6(a) shows the CFD model prediction on temperature contour in the reformer loaded with the Ni based catalyst, while the operation temperature is at 550 °C, GHSV=42000h⁻¹ and CH₄/O₂ = 2. Fig. 6(b) shows the CFD model prediction on temperature contour in the reformer loaded with the SSEP catalyst at the same operation condition. Following the flow of the reactants and products, the temperature increases rapidly in the front part of the catalyst (near the reformer inlet), and decreases in the rear part of the catalyst. Since the wall of the reformer is thermally conductive, the temperature at the inner surface of the wall equals to the operation temperature, 550 °C (823 K). The sharp temperature increase in the front part is caused by heat released from exothermic CH₄ total combustion [Eq. (9)]. The endothermic partial steam reforming [Eq. (10)] and total steam reforming [Eq. (11)] cause subsequent gradual temperature reduction, because partial steam reforming and total steam reforming are much slower than total combustion [48]. The maximum temperature observed along the axis of the cylindrical reformer loaded with the Ni based catalyst is 130 K higher than the operation temperature [Fig. 6(a)]. The maximum temperature observed along the axis of the reformer loaded with the SSEP catalyst is 155 K higher than the operation temperature [Fig. 6(b)]. Similar maximum temperatures were observed for reactors loaded with Ni based catalysts [46-50]. The position, height, and width of the temperature peak are related to the operation condition and catalyst properties.

Fig. 6 – Temperature contours in (a) Ni based catalyst (b) SSEP catalyst beds, at operation

temperature 550 °C, GHSV=42000h⁻¹ and CH₄:O₂ = 2.

Fig. 7 illustrates the temperature profiles along the axis of the reformer loaded with Ni based catalyst at various operation temperatures, while GSHV = 42000h⁻¹ and CH₄/O₂ = 2. At 350 °C and 400 °C, the temperature profiles are almost flat. The reason is that the reactant enthalpy is insufficient to overcome the activation energy barrier of the POX reactions. Therefore the reaction rate of POX is low and very small amount of heat is released. When the operation temperature increases to 500 – 650 °C, the reaction rate of POX increases, leading to a greater reaction rate and rate of heat release in the front part of the reformer. The position of the temperature peak moves backward from 0.28 to 0.13 in the normalized length as operation

temperature increases from 500- 650 °C. When the operation temperature is at 650 °C (923 K), the maximum temperature is 767°C (1040 K) near the inlet of the reformer.

Fig. 7 – Temperature profile along the axis of the Ni based catalyst bed at $\text{GHSV} = 42000\text{h}^{-1}$ and $\text{CH}_4/\text{O}_2=2$.

Fig. 8 illustrates the temperature profiles along the axis of the reformer loaded with the SSEP catalyst at various operation temperature, while $\text{GSHV}=42000\text{h}^{-1}$ and $\text{CH}_4/\text{O}_2 = 2$. For all operation temperatures, the temperature along the reformer axis also increases rapidly in the

front part but decreases gradually in the rear part of the reformer. The peak temperatures in the SSEP catalyst bed are universally higher than those in the Ni based catalyst bed at the same operation temperatures. This is due to the SSEP effect. In terms of the height of the temperature peak, the SSEP effect is most significant at 350 and 400 °C or at lower temperatures. At operation temperature of 350 °C, the height of the temperature peak is 110 °C compared with the operation temperature in the SSEP catalyst bed whereas the height of the temperature peak is only 10°C in the Ni based catalyst bed. This agrees with the previous experimental observations and theoretical prediction that usually if the electrochemical promotion is enabled, a greater relative enhancement of catalytic activity appears at lower temperatures [12]. For the present cases, because of the difference of the electrochemical potentials between the anode and cathode particles, the O^{2-} ions produced at the cathode are driven to the anode through the oxygen ion conductor to form an electrical double layer (EDL) on the anode which greatly accelerates the partial oxidation of CH_4 at as low as 350 °C.

Fig. 8 – Temperature profile along the axis of the SSEP catalyst bed at $GHSV = 42000h^{-1}$ and $CH_4/O_2=2$.

Fig. 9 illustrates the CH_4 mass fraction contours in the catalyst beds at a typical operation temperature 550 °C, $GSHV = 42000h^{-1}$ and $CH_4:O_2 = 2$. Fig. 9 (a) shows the CH_4 mass fraction contour in the Ni based catalyst bed and Fig. 9 (b) shows the CH_4 mass fraction contour in the SSEP catalyst bed. Because of the SSEP enhancement, more CH_4 is converted into syngas. In both the catalyst beds, the CH_4 mass fraction gradient is greatest in the front part of the catalyst

bed correlating with the location where the temperature gradient is greatest. The CH_4 mass fraction gradient is lower near the wall of the reformer, because the catalyst temperature is lower at the wall.

Fig. 9 – CH_4 mass fraction contours in (a) Ni based catalyst (b) SSEP catalyst beds at operation temperature $550\text{ }^\circ\text{C}$, $\text{GHSV}=42000\text{h}^{-1}$ and $\text{CH}_4/\text{O}_2=2$.

Fig. 10 shows the temperature contour in the SSEP catalyst bed at various CH_4/O_2 ratios from 2 to 6, while the operation temperature is $550\text{ }^\circ\text{C}$ and $\text{GHSV}=42000\text{h}^{-1}$. The temperature increases in the front part of the catalyst and reaches a peak at 0.19 normalized distance to the entrance. Increasing CH_4/O_2 ratio in the feed gas leads to a decrease of the peak temperature since less heat is released in the POX with insufficient oxidant.

Fig. 10 – Temperature contour in the SSEP catalyst bed at operation temperature 550 °C and GHSV=42000h⁻¹, (a) CH₄/O₂ = 2, (b) CH₄/O₂ = 4, (c) CH₄/O₂ = 6.

One of the major topics in the previous discussions was that the actual temperature in the catalyst bed is generally higher than the operation temperature at the wall of the reformer or that with the non-uniformity of the temperature distribution what should be “the operation temperature” at which the catalytic activity or performance of a catalyst system is defined [46-50]. In the present case, two catalysts systems, the Ni based catalyst and SSEP catalyst are evaluated at the same set of operation temperatures. According to the simulation results, the peak

and average temperatures for the SSEP catalyst are really higher than those for the Ni based catalyst at the same operation temperatures. However, it is clear that the apparent higher activity of the SSEP catalyst can't be attributed to the higher temperatures in the catalyst bed. As an example, at an operation temperature of 550°C, the temperature in the Ni based catalyst bed is generally higher than that in SSEP catalyst bed at an operation temperature of 500°C. However, the conversion for the SSEP catalyst at 500°C is 92% whereas that for the Ni based catalyst at 550°C is only 62% revealing a large difference in performance. Similar comparisons can be made for the catalysts at other operation temperatures. The SSEP catalyst performs much better than the Ni based catalyst in terms of peak, average, and operation temperatures.

It is interesting that although the reaction rate of combustion in the SSEP catalyst is much greater than that in the Ni based catalyst, the locations of the peak temperature are almost the same (Figs. 6-8, 10). This can be explained by the details of the reaction kinetics. The reaction rate constants, k_i , can be evaluated using the parameters in Table 1 and summarized in Table 7. At 400°C, the reaction rate constants for the steam reforming reactions [Eqs. (10, 11)] are much less than those for the combustion reaction. However, when temperature increases to 650°C, the reaction rate constants for the steam reforming reaction are either similar to or greater than those for the combustion reaction. At the entrance, since there is no water, the combustion of methane is the sole reaction [Eq. (9)] that produces water and CO₂ and gives off heat resulting in increase of temperature. Thus, with the greater reaction rate constants and concentration of water, the partial, total steam reforming, and the reverse water gas shift [Eq. (12)] reactions become dominant. These endothermic reactions will bring down the temperature following proceeding of the reactions along the axis of the catalyst bed. The higher the temperature at entrance, the more water and heat will be produced. Both favor more extensive steam reforming and water gas shift

reactions, resulting in an earlier appearance of the peak temperature. The effect of SSEP mainly multiplies the reaction rate constant of combustion of methane or oxidation of methane [9-13] but does little to the other reactions. Thus, the combustion is more extensive in the SSEP catalyst bed than in the Ni based catalyst bed. The gradient of temperature distribution is greater close to the entrance for the SSEP catalysts bed. That means it will take longer time for the endothermic reactions to bring down the temperature giving a similar location of the peak temperature.

In order to enable a high conversion at a relatively lower temperature (e.g. 550°C), it is more important and effective to promote the combustion of methane than the other reactions. It can be seen from Fig. 9 that in the SSEP catalyst bed in which the combustion is promoted, the conversion reaches 90% at 0.5 normalized distance and goes further down to 98% whereas in the Ni based catalyst bed, the conversion reaches 64% at 0.5 normalized distance and remains at the same value to the end. The results indicate that in order to obtain a conversion of 90%, only half of SSEP catalyst bed is required. However, it is not sufficient even further extending the length of the Ni based catalyst bed.

Table 7 – The reaction rate constants, k_i , for Eq. (9-12) at 400, 550, and 650°C.

Reaction	k_i at 400°C	k_i at 550°C	k_i at 650°C
Total combustion, Eq. (9)	$k_{1a} = 0.171$	$k_{1a} = 2.82$	$k_{1a} = 11.0$
(mol bar ⁻² kg _{cat} ⁻¹ s ⁻¹)	$k_{1b} = 0.144$	$k_{1b} = 2.37$	$k_{1b} = 9.26$
Partial steam reforming, Eq. (10)	$k_2 = 2.71 \times 10^{-4}$	$k_2 = 0.674$	$k_2 = 30.2$
(mol bar ^{0.5} kg _{cat} ⁻¹ s ⁻¹)			

Total steam reforming, Eq. (11)	$k_3 = 3.32 \times 10^{-5}$	$k_3 = 0.0936$	$k_3 = 4.45$
(mol bar ^{0.5} kg _{cat} ⁻¹ s ⁻¹)			
Water gas shift, Eq. (12)	$k_4 = 3.34$	$k_4 = 29.8$	$k_4 = 86.2$
(mol bar ⁻¹ kg _{cat} ⁻¹ s ⁻¹)			

4. Conclusion

A multi-physical CFD model with coupled chemical and electrochemical processes for POX of CH₄ over the SSEP catalyst in a fixed-bed reformer was developed and validated with experimental results. The catalyst bed is considered as a porous media. The reaction kinetics of the model incorporates a conventional kinetics for chemical reactions over Ni based catalyst and the mechanism for the SSEP effect. The composition, microstructure, and electrochemical properties of the components of the SSEP catalysts can be explicitly considered as the input variables in the model. The mass and heat transfer partial differential equations are numerically solved using ANSYS FLUENT while the reaction rates of the chemical and electrochemical reactions are coupled with the FLUENT solver by using User-Defined functions (UDFs).

The CFD modeling results agree well with the experimental data in terms of the temperature impact in terms of the CH₄ conversion. The model is capable of describing the mass and heat transfer of reacting flow in the catalytic POX reaction reformer, giving temperature contour and species concentration contour in the catalyst bed under different operation conditions and evaluating the effect of CH₄/O₂ gas feed ratio. It provides a mechanistic relation between the electrochemical properties of the SSEP catalyst, operation conditions and the performance of POX of CH₄. More importantly, this CFD model could quantify the enhancement of POX of CH₄ due to the SSEP effect. It can be used as a tool to predict experimental results, guide the design and optimization of the future SSEP catalyst.

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