Numerical Investigation of the Effects of Coke on Transport Properties in an Oxidative Fuel Cell Reformer

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ABSTRACT: Experimental investigations on the technical viability of solid oxide fuel cells to replace internal combustion engines in automobiles have increased in recent years. However, the performance and stability of catalysts in the presence of carbon is key for the commercial success of fuel cell reformers. In this paper, finite element method was used to study the effect of coke deposition on heat and mass transfer during the catalytic partial oxidation of ethanol in a packed bed reactor. The properties of Ni/Al₂O₃ catalyst bed were investigated after being subjected to several hours of carbon buildup. Bed permeability, porosity, and temperature distribution were significantly affected after just 1500 s of reaction time. It was observed that void fraction and permeability became nonuniform across the bed. These two parameters decreased with axial position, and the difference became more pronounced with time. A decrease in bed porosity reduced the bed temperature due to an increase in effective thermal conductivity and ethanol conversion and hydrogen selectivity decreased as a result. Thus, it was concluded that heat transfer becomes a limiting factor in reforming reactions in the presence of carbon. Production distribution before deactivation was also studied, and it was observed that a maximum ethanol conversion of 100% was achieved at 600 °C and a C/O ratio of 1.0. Finally, results from the reactions were compared to that of a different study to validate the reaction mechanism and similar results were found in the literature.

1. INTRODUCTION

Synthesis gas production via catalytic partial oxidation (CPOX) of hydrocarbons for fuel cells has gained much attention in recent years. While many fuels including natural gas, diesel, and gasoline have been investigated, ethanol appears to be the fuel best suited for automobile applications for several reasons. First, the infrastructure for fuel-grade ethanol production already exists. Second, bioethanol is obtained from biomass which is a renewable resource and thus has a net-zero carbon footprint. Furthermore, ethanol has the least amount of C atoms per molecule among all of the possible liquid transportation fuels, making syngas selectivity high in ethanol CPOX. Due to these desirable properties, the first solid oxide fuel cell (SOFC)-powered automobile that was developed ran on bioethanol.¹

One of the major challenges faced in making ethanol-fueled SOFC motor vehicles profitable is the development of suitable catalysts for ethanol CPOX.² The reaction mechanism of partial oxidation is complex and side-products such as acetaldehyde, methane, and other lower alkanes can be formed.² This means that controlling the selectivity of carbon monoxide and hydrogen is crucial because they are the only major products that are desired. Simonov et al.³ found in their study that the aforementioned side-products are absent in the product gas when reaction temperatures are above 600 °C, and thus concluded that an increase in reaction temperature during ethanol CPOX will increase the selectivity of carbon monoxide and hydrogen. Hebben et al. in their study realized that decreasing the C/O ratio in the feed can also limit the formation of side-products.⁵

Another property of a suitable catalyst is to reduce the rate of reactions responsible for carbon formation. The presence of carbon has a detrimental effect on the rate of reaction for several reasons. Unlike other side-products, carbon is solid and thus does not flow out of the reacting medium. Thus, when soot is formed, it stays behind in the catalyst bed, blocking the active sites and/or pores of the catalysts, and limiting the rate of other reactions.⁶ Partial oxidation reactions are exothermic and thus are not limited by heat transfer but rather by reaction kinetics. The presence of soot renders the reforming reactions mass transfer-limited because good transport is required between reactants and active sites of the catalyst.⁶ The number of active sites determines the activity, and thus the presence of carbon reduces the activity of a catalyst. Depending on the rate of carbon formation, the catalyst might lose its initial activity in a matter of hours or even minutes. The primary aim of
developing novel catalysts is to maintain the initial activity for longer periods of time before the catalysts need to be replaced or regenerated. Although the kinetics of carbon deposition during ethanol CPOX has been studied in the past, a few studies have been done on coke formation on the heat and mass transfer properties of the reacting medium. The primary focus of past studies was to determine the effect of carbon on catalyst performance. Because CPOX reactions are complex, it is difficult to experimentally measure heat transfer and fluid flow.

Experiments have been performed in the past to study the general effects of soot on a packed bed in the absence of CPOX reactions. Borisova and Adler in their study of methane decomposition in a Ni bed discovered that low Damköhler numbers (less than one) resulted in a uniform change in bed porosity. That is, when the convective mass transfer rate is significantly higher than reaction rate, the change in bed porosity from carbon deposition can be estimated analytically. However, these results were in the absence of other reactions. It has been also reported that the presence of coke in a Pt/Al₂O₃ bed can significantly decrease the effective diffusivity of a porous medium. Numerically analyzed the effects of reaction rate and heat of reaction of hypothetical gas-phase reactions on several parameters including Nusselt and Sherwood Numbers and temperature and concentration distribution. However, this model was developed without considering catalyst deactivation. Tomiczek et al. studied the steam reforming of ethanol in a reformer with carbon deposition. However, ethane is not a likely hydrocarbon of choice for reforming in fuel cells because it is not a conventional transportation fuel.

Sadykov et al. conducted a detailed study of the mechanism of the partial oxidation of ethanol on Ni catalysts promoted with Ru and identified ethoxy, absorbed ethanol, acetdehyde, and acetate as surface species. They also estimated their thermal stability and reactivity using Fourier-transform infrared spectroscopy. Roychowdhury et al. studied the transfer of heat during the steam reforming of ethanol in a micro-channel reformer and observed that convection resistances across channels were much higher than conducting resistances. It was also observed that even with 100% ethanol conversion, hydrogen yield was lower at higher temperatures (>1000 K) due to the water gas shift reaction. This observation was also made by Artrith et al. when they used machine learning to predict the selectivity of the catalysts during the steam reforming of ethanol. When Zhang et al. used density functional theory (DFT) to study the kinetics of dry reforming of ethanol on Rh, they observed that the dehydrogenation of ethanol was the rate-limiting step and used this observation to estimate a reaction rate of 8.23 \times 10^3 \text{ s}^{-1}.

The primary aim of the present study is to bridge this research gap by analyzing the effect of coke on heat and mass transfer properties of a packed bed in a fuel cell reformer specifically for catalytic partial oxidation of ethanol. A Ni/Al₂O₃ catalyst bed will be modeled because this is the catalyst that is most used in the industry for reforming reactions due to its versatility and low cost. Thus, should a mobile reformer be made commercially available, it will most likely be made using nickel as the bed’s active metal. To the authors’ best knowledge, no model currently exists that predicts the product and temperature distribution as well as carbon formation in a Ni/Al₂O₃ packed bed for the oxidative reforming of ethanol.

2. PROBLEM FORMULATION

Analysis of ethanol CPOX kinetics shows that temperature is a significant factor that affects the rate of reaction. The flow of reactants and products transports both mass and energy in just one direction. The heat transfer equation calculates the temperature of the reacting gas and convective heat transfer within the catalyst bed. The temperature affects both the reaction kinetics and reacting gas properties, making the energy equation very important in this model. A fully developed laminar flow is assumed in the reactor such that the average flow field is a linear function of the pressure difference along the reactor length, which is the x-direction (Figure 1).

![Figure 1. Schematic of model geometry with boundary conditions.](https://dx.doi.org/10.1021/acs omega.0c03251)

The proposed reaction pathway for partial oxidation of ethanol on Ni/Al₂O₃ catalysts is as follows:

\[
\text{Decomposition} \\
\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_4 + \text{CO} + \text{H}_2 \\
(\text{R1})
\]

\[
\text{Combustion} \\
\text{CH}_4 + 2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{CO}_2 \\
(\text{R2})
\]

\[
\text{Steam reforming} \\
\text{CH}_4 + \text{H}_2\text{O} \Leftrightarrow 3\text{H}_2 + \text{CO} \\
(\text{R3})
\]

\[
\text{Water gas shift} \\
\text{CO} + \text{H}_2\text{O} \Leftrightarrow \text{H}_2 + \text{CO}_2 \\
(\text{R4})
\]

\[
\text{Reverse methanation} \\
\text{CH}_4 + 2\text{H}_2\text{O} \Leftrightarrow 4\text{H}_2 + \text{CO}_2 \\
(\text{R5})
\]

In this model, it is assumed that carbon formation occurs as a result of methane decomposition as shown in reaction (R6).

\[
\text{CH}_4 \rightarrow 2\text{H}_2 + \text{C} \\
(\text{R6})
\]

The decomposition of ethanol into CH₄, CO, and H₂ was proposed by Sun et al. with the following rate equation.
The mechanism of methane combustion on platinum was formulated by Ma et al.\textsuperscript{23} using the Langmuir–Hinshelwood formulation, and the rate equation (eq 7) was determined.

\[ r_1 = k_1 P_{\text{CH}_4} \]  

(1)

\[ r_2 = \frac{k_2 P_{\text{CH}_4} \sqrt{P_{\text{O}_2}}}{(1 + K_0 P_{\text{CH}_4} + K_2 \sqrt{P_{\text{O}_2}})^2} \]  

(2)

Xu and Froment\textsuperscript{24} developed a set of reactions for reforming of methane on Ni, and their rates are expressed in eqs 3–5

\[ r_3 = \frac{k_3 P_{\text{CH}_4} P_{\text{H}_2} O}{P_{\text{H}_2}^{2.5}} \text{DEN}^{-2} \]  

(3)

\[ r_4 = \frac{k_4 P_{\text{CO} P_{\text{H}_2} O}}{P_{\text{H}_2}} \text{DEN}^{-2} \]  

(4)

\[ r_5 = \frac{k_5 P_{\text{CH}_4} P_{\text{H}_2} O}{P_{\text{H}_2}^{2.5}} \text{DEN}^{-2} \]  

(5)

\[ \text{DEN} = 1 + K_{\text{CO} P_{\text{CO}} + K_{\text{H}_2} P_{\text{H}_2}} + K_{\text{CH}_2 P_{\text{CH}_4}} + \frac{K_{\text{H}_2 O P_{\text{H}_2 O}}}{P_{\text{H}_2}} \]  

(6)

Zavarukhin and Kuvshinov\textsuperscript{25} in their study of carbon formation on Ni/Al\textsubscript{2}O\textsubscript{3} developed a rate equation (eq 7) to accurately model the rate of carbon deposition. The proposed mechanism for this model assumed that the rate-limiting step was adsorption of hydrogen on an active site of the catalyst surface.

\[ r_6 = k_6 \left( \frac{P_{\text{H}_2}^{1.0 \times 10^{-5}}}{1 + K_0 \sqrt{P_{\text{H}_2}^{1.0 \times 10^{-5}}}} \right) \]  

(7)

The rate and adsorption constant for carbon formation are given in eqs 8 and 9, respectively. The Gibbs free energy of this reaction as a function of temperature is 89.53–0.11\(T\), where \(T\) is the temperature in kelvin.\textsuperscript{26}

\[ k_0 = 2.31 \times 10^{-5} e^{(20.4192 - 104.200 / RT)} \]  

(8)

\[ K_0 = e^{(163200/RT - 22.426)} \]  

(9)

The kinetic and adsorption parameters in the equations were determined using extensive experimental data. The kinetic rate (Table 1), adsorption (Table 2), and equilibrium (Table 3) constants are determined using eqs 10 and 11.

\[ k_i = k_0 e^{-E_i/RT} \]  

(10)

\[ K_i = k_0 e^{-H_{\text{ads}}/RT} \]  

(11)

Table 1. Kinetic Parameters

| reaction | \( k_0 \) | \( E_i \) (kJ/mol) | \( \Delta G^\circ \) (kJ/mol) |
|----------|------------|--------------------|------------------|
| 1        | (4.55 ± 0.1) \times 10^{-2} mol Pa^{-1} kg_{ads}^{-1} s^{-1} | (2.03 ± 0.05) | 89.37 – 0.18T |
| 2        | (3.29 ± 0.05) \times 10^{-3} mol Pa^{-1} kg_{ads}^{-1} s^{-1} | (30.8 ± 1.2) | 50.5 – 0.45T |
| 3        | (3.7 ± 0.09) \times 10^{-7} mol Pa^{-1} kg_{ads}^{-1} s^{-1} | (24.01 ± 0.1) | 249.35 – 0.23T |
| 4        | (5.43 ± 0.11) mol Pa^{-1} kg_{ads}^{-1} s^{-1} | (67.13 ± 0.05) | –32.197 + 0.03104T – 177.4/T |
| 5        | (8.96 ± 0.12) \times 10^{-10} mol Pa^{-1} kg_{ads}^{-1} s^{-1} | (24.39 ± 1.15) | 34.51 – 0.03T |

Table 2. Adsorption Constants

| parameter | value | \( \Delta H_{\text{ads}} \) (kJ/mol) |
|-----------|-------|------------------|
| \( K_{\text{CH}_4} \) | (6.65 ± 0.1) \times 10^{-9} Pa^{-1} | (−38.28 ± 1.1) |
| \( K_{\text{CO}} \) | (8.23 ± 0.1) \times 10^{-10} Pa^{-1} | (−70.65 ± 1.0) |
| \( K_{\text{H}_2} \) | (6.12 ± 0.05) \times 10^{-11} Pa^{-1} | (−82.90 ± 1.2) |
| \( K_{\text{H}_2 O} \) | (1.77 ± 0.1) \times 10^{5} | (88.68 ± 1.3) |
| \( K_1 \) | (2.02 ± 0.04) \times 10^{-3} Pa^{-1} | (−36.30 ± 1.1) |
| \( K_2 \) | (7.4 ± 0.05) \times 10^{-11} Pa^{-1} | (−57.97 ± 1.2) |

Table 3. Equilibrium Constants

| reaction | \( k_i \) | \( \Delta H \) (kJ/mol) |
|----------|------------|------------------|
| 3        | (4.707 ± 0.05) \times 10^{-2} Pa^{2} | (22.40 ± 0.9) |
| 4        | (1.142 ± 0.05) \times 10^{-2} Pa^{2} | (−37.30 ± 1.1) |
| 5        | (5.397 ± 0.1) \times 10^{-9} Pa | (18.67 ± 1.7) |
| 6        | (5.088 ± 0.1) \times 10^{1} | (91.20 ± 1.2) |

2.3. Mass Transport. The mass balance due to reaction and species transport is modeled by the steady-state diffusion-convection equation (eq 12). The mass transport equation also requires specific diffusivity values of each species, which is calculated using the Wilke–Lee equation. The coefficients used to calculate transport and thermodynamic properties are taken from Mcbride et al.\textsuperscript{27}

\[ \nabla \cdot \left( -D_i \nabla c_i \right) + u \cdot \nabla c_i = R_i \]  

(12)

The term \( R_i \) refers to the rate term for each species and is given by eq 13. It is a function of the maximum reaction rate for reactions RR1–RR6 \( (r_i) \), the stoichiometric coefficient of each reaction, \( v \), and the catalyst activity, \( a \). The activity is expected to decrease with time, and eq 14 simulates this time-dependent change in activity. The activity at any given time depends on the concentration of carbon, \( c_i \), the rate of methane decomposition, \( r_{\text{de}} \), and \( k_{\text{ad}} \) which is temperature-dependent (eq 15).

\[ R_i = r_i v a \]  

(13)

\[ \frac{da}{dt} = -k_{\text{ad}} c_i^2 a \]  

(14)

\[ k_{\text{ad}} = 8.324 \times 10^{6} \exp \left\{ \frac{135600}{R_g T} – 32.007 \right\} \]  

(15)

Since mass transport is only in the direction of the reactor length (x-axis), the diffusivity components in the y- and z-axes are set to zero. The flow driven by pressure difference is also defined only in the x-axis. Thus, a plug-flow model is assumed.
in the bed such that conversion is a function of axial coordinate (x-direction) shown in eq 16.
\[
\frac{WF_{\text{EtOH},0}}{F_{\text{EtOH},0}} = \int_0^X -r_{\text{EtOH},0} \, dX
\]  

(16)

2.4. Fluid Flow. The reacting fluids are assumed to be Newtonian with laminar flow and a low Reynold’s number. Therefore, the flow of reacting species in the reactor is modeled using Darcy’s law28 as depicted by reactions 17 and 18. The change in porosity (eq 19) is related to the rate of reaction R6, and permeability is related to porosity by eq 20, which was formulated by Borisova and Adler.14
\[
\nabla \cdot (\rho u) = 0
\]  

(17)
\[
\nu = -\frac{k \nabla p}{\mu}
\]  

(18)
\[
\frac{d\phi}{dt} = -1000\phi r_6 M_C \rho_c
\]  

(19)
\[
\kappa = k_0 \left( \frac{\phi}{\phi_0} \right)^{3.55}
\]  

(20)

2.5. Heat Transfer. The equation governing heat transfer in a packed bed reactor is given by the energy eq 21. The equivalent thermal conductivity, \( k_{eq} \), of the porous media is a function of the conductivities of both the void space and solid.
\[
(\rho C_p_{eq}) \frac{\partial T}{\partial t} + \rho C_p u \nabla T = \nabla \cdot (k_{eq} \nabla T) + Q
\]  

(21)
The heat source, \( Q \), derived from all five reactions, is determined with eq 22
\[
Q = Q_1 + Q_2 + Q_3 + Q_4 + Q_5
\]
\[
= -r_1 H_1 - r_2 H_2 + r_3 H_3 - r_4 H_4 - r_5 H_5
\]  

(22)

3. RESULTS AND DISCUSSION

3.1. Change in Bed Properties. Figure 2 shows the change in bed mass transfer properties with respect to time at different axial positions in the reactor. The decrease in porosity is a result of carbon formation from reaction R6. The solid carbon stays in the bed and blocks the pores, thereby reducing the pore volume and porosity of the bed. The rate of decrease in void fraction did not become notable until after about 1500 s on stream, at which the time rate of change in porosity becomes a function of axial coordinate. At the inlet end of the bed, the rate of change in the void fraction is exponential but changes into a more linear function as the axial position reaches the bed outlet. This is primarily because the rate of carbon formation is highest at the inlet when the concentration of fuel is highest. It can also be observed that the porosity after 12 000 s decreased with an increase in axial position. After 12 000 s on stream, the void fraction at x = 20 mm reduced from an initial value of 0.5 to 0.32.

This nonuniform distribution of porosity is undesirable because it has a significant effect on the permeability in the catalyst bed, as shown in Figure 2B. The permeability reduces exponentially to less than 1 \( \times 10^{-12} \) and 2.51 \( \times 10^{-9} \) m² at the bed entrance and exit, respectively, after 12 000 s. In addition to reduced permeability, nonuniform permeability can thus be said to be another effect of carbon formation during CPOX reactions. This is also unwanted because it significantly increases the pressure drop across the bed, leading to channeling and uneven flow rate and temperature distribution. Furthermore, the surface area of contact between the reacting gases and the catalyst is reduced. At this point of the reaction, the presence of carbon causes the reforming reactions to be mass-transfer-limited and surface area becomes an important parameter. Thus, uniform porosity and permeability are paramount to ensuring that there is adequate contact between reacting species and active sites located within the bed.

Figure 3 shows what effects carbon deposition has on the heat transfer between reacting gases and the bed. The sharp initial increase in temperature is a result of heat generated from the exothermic reactions (reactions R1, R2, R4, and R5). Due to thermal insulation on the walls of the reactor, heat transfer by conduction occurs only in the porous medium and the temperature of the bed increases as a result. The temperature increases to a maximum due to an increased reaction rate and falls when a maximum conversion has been reached. At this point, the heat of reaction is zero, and consequently, there is no heat generation term in eq 17. Therefore, bed temperature
drops as the product gas flows through the reactor. This is the general trend regardless of the value of bed porosity.

Porosity influences the maximum temperature achieved at the bed position where the heat of generation is the highest. At \( t = 400 \), where the porosity is uniform across the bed, the maximum temperature was 579 °C, while at \( t = 12,000 \) s, where porosity was lowest across the whole bed, the maximum temperature was 477 °C. The void volume at any given axial position in the bed reduced with carbon deposition, thus increasing the effective thermal conductivity. As a result, the temperature gradient reduced with a reduction in porosity. This is a reasonable explanation for why catalyst performance tends to reduce with time. The temperature profile diminishes and since the rate of reaction is dependent on temperature, the rate of conversion of ethanol into syngas decreases with time. This phenomenon has been observed in numerous experimental studies on the effects of soot formation on CPOX reactions.\(^{29−31}\) It can also be inferred that the formation of carbon leads to nonuniform thermal conductivity.

### 3.2. Product Distribution

The performance of Ni/Al\(_2\)O\(_3\) catalyst was calculated after 1000 s of reaction time. This time was chosen because the presence of carbon had not yet affected the heat and mass transfer properties of the bed, as discussed in the previous section. It is evident from Figure 4 that the O/C ratio has a significant effect on the amount of ethanol converted. A ratio of 0.25 resulted in a conversion of less than 36%, and this conversion increased with an increase in the O/C ratio until a maximum of 100% was achieved at O/C = 1.0. The effects of increasing the O/C ratio on conversion was less profound at higher values than lower values, where the oxygen concentration was a limiting factor in determining the rate of reaction. This is consistent with the results obtained by Sadykov et al.\(^{18}\) At this ratio, the product gas was rich in CO and H\(_2\), which are the desirable components of synthesis gas used for SOFC applications. Methane production was minimal at this ratio, and although there was significant CO\(_2\) production, this was primarily a result of combustion reaction, which supplied the heat necessary for the reforming reactions to occur autothermally. Production of CO\(_2\) may be minimized by increasing reaction temperature, but that will come at the expense of a higher heat duty in the preheater.

Due to the length of the reactor, it is observable that methanation and water gas shift take place in the reaction medium since the composition is at equilibrium. Roychowdhury et al.\(^{17}\) observed that a length of 10 mm was not enough for complete conversion of ethanol at low temperatures. According to their study, at shorter lengths, a higher
temperature (above 2500 K) is required to achieve a desired conversion of ethanol before the outlet of the reactor. A high residence time is also able to achieve the desired conversion. This is achieved by reducing the gas hourly space velocity of the reactants and products.

3.3. Effects of Carbon on Performance. The primary reason for the decrease in reaction rate after catalyst deactivation is reduced mass transfer due to blockage of active sites. Results from this model show that reduced heat transfer also influences catalyst performance. As previously stated, the transfer of heat should not be a limiting factor for exothermic reactions. However, it can be seen from Figure 6 that with time, the conversion of ethanol gradually reduces after a maximum of 100% is achieved. This trend correlates with a reduction in bed porosity, as can be seen in Figure 2. The solid carbon concentration in Figure 5 corresponds to the porosity profile. The solid carbon starts forming in the reactor inlet and, as time progresses, extends axially. By examining Figures 2a and 5, it can be observed that the increase in the coke corresponds to the reduction in porosity. The solid carbon particles block the pores in the catalyst bed, hence reducing the pore volume and void fraction.

Interestingly, the carbon concentration at the inlet is much higher than that of the reactor outlet. For example, after 12,000 s, the molar concentration is 4.5% at the inlet and 1.2 at the outlet. Just as previously described, the overall rate of reaction is much lower at the outlet due to the decrease in the partial pressure of ethanol and oxygen. Therefore, the rate of reaction R6 is strongly inhibited. This means that one can increase the oxygen concentration in the feed to increase the rate of reaction R2 and reduce that of reaction R6, leading to methane combustion rather than methane decomposition. By doing so, the formation of carbon will reduce appreciably and the bed properties can stay uniform for a longer period of time.

The increase in carbon concentration, and thus reduction in porosity, increases thermal conductivity, and thus the rate of

Figure 5. Distribution of mole percentages of solid carbon along reactor length at times 400 s (A), 3000 s (B), 6000 s (C), 9000 s (D), and 12,000 s (E).
reaction decreases along with the bed and reaction temperature. The reduction in conversion is comparable to values from experimental studies, and it does imply that heat transfer directly contributes to reduced reaction rate. Although the decrease in conversion is only gradual with time, the selectivity of hydrogen reduces significantly while that of steam increases. This means that while ethanol is still being converted at a moderate rate, the reactions responsible for the production of hydrogen are inhibited due to lower temperatures. Both steam reforming and reverse methanation are endothermic reactions, which form hydrogen and require high temperatures to proceed. When the temperature is too low, the reactions proceed in the backward direction, forming less hydrogen and more steam. That is how a lower heat transfer rate from carbon buildup can affect the production of syngas (Figure 6).

3.4. Model Validation and Comparison. To validate the kinetic mechanism used in the model, the boundary conditions were changed so that the reactor operated isothermally. This was done so that conversion and selectivity could be calculated as a function of temperature. The reactor dimensions were changed so that the mass of the catalyst bed without the pores was 150 mg as set up by Kraleva et al. in their experimental study of bioethanol CPOX. The conversions at temperatures between 300 and 600 °C were computed and compared to the experimental results. The model and experimental results were similar, as shown in Figure 7. Although Kraleva et al.’s results showed a 6% conversion at 300 °C, results from the model showed that there was no conversion at that temperature. This was expected because 300 °C was set as the light-off temperature and any decomposition of ethanol before it comes in contact with the catalyst is undesirable. Conversion from the experimental study and the current study were the same for higher temperatures, and both studies showed that the maximum fractional conversion of 1 was achieved at 600 °C.

The selectivity of CO, H₂, CO₂, and CH₄ at the maximum conversion on a dry basis was also computed and compared to experimental errors, as shown in Table 4. The selectivity for the first three species was similar, and the percent errors were 5.7 or less. However, the percent error for CH₄ selectivity was 100%. This was because the concentration of CH₄ was so small that any deviation from the experimental results would have resulted in a significant error value. This apparent deviation is only a concern for large CH₄ concentration in the product gas because they are undesirable. It can be inferred that the mechanism of partial oxidation in this model is able to predict the conversion and selectivity of the main products at high temperatures. However, a limitation is that it is not able to account for the formation of acetaldehyde at low temperatures. Thus, it is possible that the average deviation of selectivity values will be significant at lower reaction temperatures.

Livio et al. developed an in situ sampling technique, which composed of a temperature probe that measured the temperature across the axial length of a quartz tube reactor. The oxidative reforming of ethanol was in the presence of N₂ gas as a diluent. Thus, the thermal conductivity of the model had to be altered for validation. In addition, the total flow rate was 4 Nl/min with a C/O of 0.65. Figure 8 depicts the results of their test with that of the current model, whose parameters were changed to be the same as those of the experimental study. There is a notable difference in the temperature profile within the first 7 mm of the reactor. This is most likely due to the fact that the experimental results did not see much formation of carbon, which tends to increase the thermal diffusivity of the reactor. After 7 mm in the reactor, where the amount of carbon in this study is much lower, the two results are very similar.

Figure 6. Ethanol conversion (x), and H₂ and H₂O selectivity as a function of time (O/C =1).

Figure 7. Comparison between experimental and numerical results of ethanol conversion during CPOX at different temperatures (O/C = 1, GHSV = 35 000 h⁻¹).

Table 4. Comparison between Experimental and Numerical Results of Product Selectivity in Ethanol CPOX

| species | model | Kraleva et al.’s results | error % |
|---------|-------|-------------------------|--------|
| CO      | 75    | 77                      | -2.6   |
| H₂      | 92    | 87                      | 5.7    |
| CO₂     | 24    | 23                      | 4.3    |
| CH₄     | 1.0   | 0.5                     | 100    |

a O/C = 1, T = 600 °C, GHSV = 35 000 h⁻¹.
Palma et al.37 conducted an investigation to study the effects of operation conditions on carbon deposition of several ceria-supported, nickel-promoted catalysts during the reforming of ethanol. They carried out stability tests on the catalysts at 450 °C to see how long it would take the bed to reach a pressure drop of 500 mbar. A pressure drop in the bed is an indicator of the amount of carbon deposited in the bed. They also calculated the rate of carbon formation using eq 23.

\[
CFR = \frac{\text{mass}_{\text{coke,oxidized}}}{\text{mass}_{\text{catalyst}} \times \text{mass}_{\text{carbon,fed}} \times \text{time}_{\text{reaction}}} \tag{23}
\]

The mass of oxidized coke, \(\text{mass}_{\text{coke,oxidized}}\), was determined by thermogravimetric analysis on the spent catalyst. Table 5 depicts a comparison between the carbon formation rate for the various catalysts used in the study and that calculated from this study. The time it takes for the pressure drop to reach 500 mbar is also compared. The pressure drop in the experiments was recorded using a differential pressure sensor, and that of this study was done using the Ergun equation.38 Rh–Ni catalyst had the lowest rate of carbon formation, and the Ni catalyst from this study had the highest value. The most probable reason is the promoting effects of noble metals that reduce the propensity for carbon formation, thereby deactivation.39 Moreover, the use of ceria, a Lewis acid, instead of alumina as support is another explanation for the differences in the rate of pressure drop and carbon formation. Ceria chemisorbs \(\text{CO}_2\), which reacts with deposited carbon to form \(\text{CO}\), thereby reducing the concentration of carbon.40

## 4. CONCLUSIONS
Catalyst deactivation during the partial oxidation of ethanol on Ni/Al\(_2\)O\(_3\) in a solid oxide fuel cell reformer was analyzed numerically. The effects of the presence of carbon on the temporal and axial profile of the packed bed reactor were calculated. Ethanol conversion and product distribution were considered for various temperatures and O/C ratios. It was observed that the conversion increased with an increase in both temperature and O/C ratio, with the highest conversions calculated when the O/C ratio was 1.0. Due to the formation of coke, the properties of the packed bed were significantly altered after only a few minutes of time on stream. After 12 000 s, the molar concentration of coke was 4.5%, which resulted in a porosity of less than 0.2 at the reactor entrance. The main effect of coke buildup was a nonuniform distribution of permeability, porosity, and thermal conductivity across the bed. Thus, the axial temperature profile was always changing with time due to a decrease in porosity and permeability and an increase in thermal conductivity. These nonuniform bed properties cause the reforming reactions to become heat transfer-limited and thus contribute to lower ethanol conversion and yield of hydrogen. The conversion and selectivity results were compared to the values in the literature, and similar values were obtained for high temperatures. The rate of carbon formation was estimated to be 0.0043 \(\text{g}_{\text{oxidized coke}}/\text{g}_{\text{catalyst}} \cdot \text{h}\), which was significantly higher than the rates obtained experimentally with other catalysts. Since the formation of acetaldehyde was not considered, it is recommended that the decomposition of ethanol into acetaldehyde is incorporated in future models to predict the product distribution at lower reaction temperatures. Nonetheless, results from this model further clarify why catalyst performance decreases with time in a reformer.

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### NOMENCLATURE AND ABBREVIATIONS

#### Symbol Property Units

- \(C_i\): species concentration, mol/m\(^3\)
- \(C_p\): species heat capacity, J/(mol K)
- \(D\): diffusion coefficient, m\(^2\)/s
**F** molar flow rate, mol/s

**GHSV** gas hourly space velocity, h^{-1}

**H** heat of reaction, J/(mol K)

**k_{eq}** equivalent thermal conductivity, W/(m K)

**k** rate constant

**K** adsorption constant

**P_i** species' partial pressure, Pa

**Q** heat source, W/m²

**r** reaction rate, mol/(kg,cat, s)

**R** ideal gas constant, J/(mol K)

**R_i** species' rate expression, mol/(m³ s)

**T** temperature, K

**u** velocity field, m/s

**W** catalyst weight, kg

**X** fractional conversion

**Φ** porosity

**κ** permeability, m²

**μ** gas dynamic viscosity, Pa s

**ρ** density, kg/m³

### SUBSCRIPTS

1, 2, 3, 4, 5, 6 denotes reaction number

i denotes species

C carbon

CH₄ methane

CO₂ carbon dioxide

CO carbon monoxide

EtOH ethanol

H₂ hydrogen

H₂O water

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