INVESTIGATION OF SULFUR INTERACTIONS ON A CONVENTIONAL NICKEL-BASED SOLID OXIDE FUEL CELL ANODE DURING METHANE STEAM AND DRY REFORMING

by

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ABSTRACT

Solid oxide fuel cells (SOFC) are an attractive energy source because they do not have undesirable emissions, are scalable, and are feedstock flexible, which means they can operate using a variety of fuel mixtures containing H₂ and hydrocarbons. In terms of fuel flexibility, most potential fuel sources contain sulfur species, which severely poison the nickel-based anode. The main objective of this thesis is to systematically evaluate sulfur interactions on a conventional Ni/YSZ anode and compare sulfur poisoning during methane steam and dry reforming (SMR and DMR) to a conventional catalyst (Süd Chemie, Ni/K₂O−CaAl₂O₄).

Reforming experiments (SMR and DMR) were carried out in a packed bed reactor (PBR), and it was demonstrated that Ni/YSZ is much more sensitive to sulfur poisoning than Ni/K₂O−CaAl₂O₄ as evidenced by the decline in activity to zero in under an hour for both SMR and DMR. Adsorption and desorption of H₂S and SO₂ on both catalysts was evaluated, and despite the low amount of accessible nickel on Ni/YSZ (14 times lower than Ni/K₂O−CaAl₂O₄), it adsorbs 20 times more H₂S and 50 times more SO₂ than Ni/K₂O−CaAl₂O₄. A one-dimensional, steady state PBR model (DetchemPBED) was used to evaluate SMR and DMR under poisoning conditions using the Deutschmann mechanism and a recently published sulfur sub-mechanism[1, 2]. To fit the observed deactivation in the presence of 1 ppm H₂S, the adsorption/desorption equilibrium constant was increased by a factor 16,000 for Ni/YSZ and 96 for Ni/K₂O−CaAl₂O₄.

A tubular SAE reactor was designed and fabricated for evaluating DMR in a reactor that mimics an SOFC. Evidence of hydrogen diffusion through a supposedly impermeable layer indicated that the tubular SAE reactor has a major flaw in which gases diffuse to unintended parts of the tube. It was also found to be extremely susceptible to coking which leads to cell failure even in operating regions that mimic real biogas. These problems made it impossible to validate the tubular SAE model with experimental data, but the tubular SAE model predictions compared with predictions from an existing model agreed well for fuel channel exhaust gases.
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<td>φg</td>
<td>Porosity</td>
</tr>
<tr>
<td>ρg</td>
<td>Gas density</td>
</tr>
<tr>
<td>Yk</td>
<td>Species mass fraction</td>
</tr>
<tr>
<td>As</td>
<td>Specific active surface area</td>
</tr>
<tr>
<td>ŝk</td>
<td>Net molar production rate of species k via heterogeneous reactions</td>
</tr>
<tr>
<td>ŵk</td>
<td>Net molar production rate of species k via homogeneous reactions</td>
</tr>
<tr>
<td>Wk</td>
<td>Molar mass of species k</td>
</tr>
<tr>
<td>[Xk]</td>
<td>Molar concentration of species k</td>
</tr>
<tr>
<td>[XT]</td>
<td>Total molar concentration</td>
</tr>
<tr>
<td>Bg</td>
<td>Permeability</td>
</tr>
<tr>
<td>∇p</td>
<td>Pressure gradient</td>
</tr>
<tr>
<td>Γ</td>
<td>Surface site density</td>
</tr>
<tr>
<td>e</td>
<td>Gas internal energy</td>
</tr>
<tr>
<td>qg</td>
<td>Gas phase heat flux</td>
</tr>
<tr>
<td>qconv</td>
<td>Heat convection between the gas and solid phases</td>
</tr>
<tr>
<td>hy</td>
<td>Volumetric heat-transfer coefficient</td>
</tr>
<tr>
<td>h</td>
<td>Heat-transfer coefficient</td>
</tr>
<tr>
<td>Nu</td>
<td>Nusselt number</td>
</tr>
<tr>
<td>dp</td>
<td>Mean particle diameter</td>
</tr>
<tr>
<td>Re</td>
<td>Reynolds number</td>
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</table>
Prandtl number .................................................. $Pr$
Species specific enthalpy ........................................ $h_k$
Mixture thermal conductivity ...................................... $\lambda_g$
Gradient of the scalar temperature field ......................... $\nabla T_g$
Solid phase volume fraction ...................................... $\phi_s$
Density of the catalyst ........................................... $\rho_s$
Heat capacity of the catalyst .................................... $c_{p,s}$
Stefan-Boltzmann constant ....................................... $\sigma$
Emissivity of the catalyst ....................................... $\epsilon$
Interface area between the catalyst and the heated environment $A_{env}$
Environment temperature ........................................ $T_\infty$
Surface temperature gradient .................................... $\nabla T_s$
Thermal conductivity of the catalyst ............................... $\lambda_s$
Effective radiation conductivity of the catalyst ................... $\lambda_r$
Inlet mass flow rate ............................................. $\dot{m}_i$
Outlet mass flow rate ........................................... $\dot{m}_o$
Stirred batch volume ............................................ $V$
Source term due to net mass transport to and/or from the batch reactor $\dot{R}_k$
Universal gas constant ........................................... $R$
Specific heat at constant V ...................................... $c_{v,g}$
Specific heat at constant P ...................................... $c_{p,g}$
Gas mixture viscosity ........................................... $\mu$
Binary diffusion coefficients .................................... $D_{kl}$
Activation energy \( E \)

Pre-exponential factor \( A_i \)

Temperature dependency exponent \( n_i \)

Equilibrium constant \( K_{p,i} \)

Sticking coefficient \( \gamma \)

Rate coefficient for reaction \( i \) \( k_i \)

Total surface site concentration \( \Gamma_{\text{tot}} \)

Mean velocity \( u \)

Pressure \( p \)

Total number of gas phase species \( K_g \)

Cross-sectional flow area \( A_c \)

Anode tube diameter \( D \)

Hydraulic perimeter \( P_h \)

Wall shear stress \( \tau_w \)

Friction factor \( f \)

Specific internal energy of the gas \( e \)

Temperature at the porous anode wall \( T_m \)

Heat flux between the gas flow and anode \( q^M \)
LIST OF ABBREVIATIONS

Auxiliary power unit ................................................. APU
Colorado School of Mines ........................................... CSM
Dry methane reforming .............................................. DMR
Dusty gas model ...................................................... DGM
Gas hourly space velocity .......................................... GHSV
Liquid natural gas .................................................... LNG
Local exhaust ventilation .......................................... LEV
Low-energy electron diffraction ................................. LEED
Mass spectrometer ................................................... MS
Membrane electrode assembly ................................... MEA
Method of lines ....................................................... MOL
Monolayer .............................................................. ML
Ordinary differential equation ................................. ODE
Packed bed reactor .................................................. PBR
Partial differential equation ...................................... PDE
Secondary ion mass spectrometry ............................ SIMS
Separated anode experiment ..................................... SAE
Solid Oxide Fuel Cell ............................................... SOFC
Stainless steel ......................................................... SS
Standard temperature and pressure ......................... STP
Steam methane reforming ........................................... SMR
Temperature programmed desorption ............................ TPD
Temperature programmed reduction ............................ TPR
Tubular separated anode experiment ............................. TSAE
Ultra high vacuum .................................................... UHV
X-ray diffraction ...................................................... XRD
Yttria stabilized zirconia ............................................. YSZ
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To my family; mom, dad, brother and sister. Thank you for your support and understanding. Now I can spend vacations at home doing things with you instead of working! I love you all.

Finally, and most importantly, to my wife Kiki. You are the single most important person in my life, and you sacrificed so much to push me through school. I am so grateful to you for stretching yourself in so many directions to accommodate me. Words can’t describe my love for you.
For my wife.
Demand for renewable and locally sourced energy is rising with increasing global population and development of countries previously without extensive power needs. Political sanctions and instability can negatively affect the availability of fossil fuels to some of these nations, and others are affected by frequent power outages as a result of old or poorly maintained electrical grids. Fuel cells could offer an elegant solution to both of these problems. Conventional power plants require large scale operations that necessitate widespread distribution grids. In remote areas, areas affected frequently by natural disasters, and areas without the ability to bury electrical grids, this poses issues for access and stability. Fuel cells are highly scalable and can feasibly be used as self-contained auxiliary power units (APU) to serve at any capacity required as long as fuel is available. Solid oxide fuel cells (SOFC) are particularly applicable because they are operated at high temperatures where both hydrocarbon reforming and electrochemical conversion of hydrogen and carbon monoxide can proceed [3]. This quality makes SOFCs more fuel flexible than any other fuel cell, and they can use fuels either from existing infrastructures (e.g., natural gas) or from distributed sources (e.g., biomass-derived syngas) that are locally available and free of external political restrictions [4].

SOFCs are made up of three layers of ceramic materials that each provide an important function: the cathode dissociates oxygen to ions and transports them to the electrolyte which acts both as a barrier between the anode and cathode and as the principal ion transport media. Fuel fed to the anode reacts with O$^{2-}$ ions transported through the electrolyte to produce water, CO$_2$ and electrons that are then conducted through the anode to an external load [5]. Though the fuel flexibility and scalability of SOFCs makes them an attractive choice for non-conventional power demands, SOFC operation is not devoid of problems such as materials and operational issues. The ceramic materials that comprise the cathode, anode and electrolyte layers can be sensitive to thermal cycling. After continual thermal cycling, the structural integrity of the SOFC can weaken and cause breakage [6].
Operating the SOFC at lower temperatures to avoid severe thermal effects can impede oxygen ion transport through the electrolyte which increases polarization losses [7]. Despite these physical issues, though, possibly the most pervasive problem for SOFCs is the degradation of the active sites on the anode that facilitate electrochemistry, reforming and electron conduction. The active sites in SOFC anodes are typically metallic nickel particles supported on yttria stabilized zirconia (YSZ) to form Ni/YSZ. Nickel degradation in the SOFC is primarily the result of chemical poisoning, pore blocking (e.g., from carbon chains), and nickel sintering to form larger nickel particles [8]. Sulfur poisoning has been demonstrated by many authors to severely diminish the activity of nickel for both reforming and electrochemistry [9–12]. Ni/YSZ has been demonstrated to be highly sensitive to fuel streams containing the low amounts of sulfur remaining after sulfur removal [9, 11]. Because of this, it is advantageous to understand all aspects of sulfur poisoning on Ni/YSZ.

In this thesis, both experimental and computational methods are used to provide a deeper understanding of sulfur interactions with Ni/YSZ during steam methane reforming (SMR) and dry methane reforming (DMR). SMR is a mature technology that involves the dissociation of methane, typically from natural gas, on a nickel-based catalyst to produce hydrogen and carbon monoxide [13]. DMR is less common industrially and uses CO₂ instead of H₂O to provide oxygen on the nickel surface for subsequent formation of CO from surface adsorbed carbon. SMR is vital for SOFCs in two ways: 1) because it is the main industrial route for producing hydrogen which SOFCs need to produce electricity and 2) SOFCs can perform the endothermic SMR internally to mitigate the exothermicity of the electrochemical reaction. Concerns over the poisoning of active nickel sites from sulfur have spurred decades of research about the adsorption of sulfur on alumina or magnesium supported nickel catalysts. In Chapter 2, internal reforming (both SMR and DMR) on SOFCs is discussed, and a background of sulfur poisoning on both non-YSZ supported and YSZ supported nickel-based catalysts is given. Another aspect of evaluating catalytic properties of SOFCs is the experimental format which can either mimic a real stack, isolate a single cell (e.g., button cell), or take the form of conventional catalyst testing (e.g., fixed bed). Background information about the differences and advantages/disadvantages to the various possible SOFC
evaluation set-ups is given.

The experimental and computational methods used to evaluate sulfur interactions on Ni/YSZ are discussed in Chapter 3. Stainless steel adsorbs sulfur at room temperature, and thusly the tubing material must chosen such that it will not interact with sulfur. It is difficult to do this using a traditional button-cell or separated anode experiment that are typically used to evaluate chemistry and transport on SOFC anodes. Because of this, the work herein uses a packed bed reactor (PBR) for evaluating sulfur interactions on Ni/YSZ, and then compares model results for a tubular SOFC anode to model results from PBR that have been experimentally validated. Computational models for the PBR and tubular systems are based on work done previously, and uses the method of lines (MOL) to solve a discretized set of partial differential equations (PDE). The attempt to develop a tubular SOFC anode experimental apparatus is also discussed.

The characterization methods and results for describing catalytic properties of Ni/YSZ are described in Chapter 4. There have been very few studies in the literature that have reported the active nickel surface area, total surface area, and reduction properties of Ni/YSZ when reporting catalytic results. Measurements for these properties are reported, and the description of the calculation for the specific surface area are described and compared with previous values used in computational models that were assigned.

In Chapter 5, a comparison of the effect of different sulfur species on the deactivation of Ni/YSZ during SMR and DMR at different temperatures is described. This analysis answers the question of whether nature of the sulfur species has an effect on the extent or rate of deactivation of Ni/YSZ. Results for Ni/YSZ are juxtaposed with results from a commercially available Ni/K₂O—CaAl₂O₄ catalyst. The intent is to compare the Ni/YSZ with a commercial catalyst to put the extent of sulfur deactivation into a broader context, and not to propose this Ni/K₂O—CaAl₂O₄ catalyst as a possible anode material. Chapter 6 extends this work to probe the adsorption/desorption of H₂S and SO₂ on Ni/YSZ. Steady state results from the study done in Chapter 5 are evaluated using a steady-state PBR microkinetic model and compared with the experimentally derived sticking coefficient for H₂S and SO₂ on Ni/YSZ. In Chapter 7, the PBR and tubular computational models developed in Chapter
3 are used to describe SMR and DMR on Ni/YSZ. The final chapter summarizes conclusions from this work and discusses future research directions in areas related to work done in this thesis.
CHAPTER 2
BACKGROUND

This section provides background on steam and dry internal reforming of methane in SOFCs, nickel catalyst deactivation via sulfur poisoning, and reactor design for reforming experiments.

2.1 Internal Reforming on SOFCs

The future of most fuel cells is closely coupled with natural gas because of their dependency on hydrogen [14, 15]. Hydrogen is produced from the steam methane reforming (SMR) of natural gas. More than 50% of the 50 million tonnes of hydrogen produced annually worldwide comes from steam reforming of natural gas via equation 5.3 [14].

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO} \tag{2.1}
\]

Carbon monoxide produced during steam methane reforming is often "shifted" to convert unreacted water and CO to more hydrogen and CO\(_2\) via the water-gas-shift reaction shown in equation 2.2.

\[
\text{H}_2\text{O} + \text{CO} \rightarrow \text{H}_2 + \text{CO}_2 \tag{2.2}
\]

Unlike other fuel cells, though, the high operating temperatures of SOFCs and the presence of nickel in the anode allow some on-anode reforming of methane [5, 16]. This is advantageous for two main reasons: 1) the endothermic reforming reaction can be used to offset heat produced from the exothermic electrochemical reaction, and 2) multiple hydrocarbon containing fuels can be used with SOFCs (e.g., fuel flexibility) [4, 17, 18]. Heat integration between the exothermic electrochemical and endothermic reforming reactions can improve the overall electrical efficiency of an SOFC. Dicks states that an SOFC operating at a cell voltage of 0.78 V and under practical conditions will evolve heat that equates to 470 kJ/mol [4]. This is roughly twice the heat consumed by the reforming reaction (~ 206 kJ/mol), and therefore this reaction offsets some of the heat of the exothermic reaction. Additional cooling of the cell is achieved by flowing excess air through the
cathode [4]. It is clear, though, that there is a significant advantage if there is internal reforming in SOFC anodes.

The advantage of fuel flexibility in SOFCs has been discussed and examined in the literature over the years [19–38]. The idea of internal reforming on SOFC anodes was proposed early in the advent of SOFC research. Perhaps the best known early study was by done by Lee, Zabransky and Huber [39]. They demonstrated that in a high concentration methane stream Ni-ZrO$_2$ cermets were able to achieve complete conversion at conditions similar to SOFC operating conditions. The steam-to-methane ratio examined for this study was 2:1, but the concentration of water in the inlet stream was very high (> 62 mol %). Following this study, it became evident that it is advantageous to keep the water concentration in the inlet fuel stream to the SOFC low [5].

A study by Belyaev et al. [19] used relatively low water concentrations (< 30 mol %), and examined the reaction rate of SMR during SOFC operation. They demonstrated that though the Ni-ZrO$_2$-CeO$_2$ anode underwent significant anodic polarization during SMR with a stream containing only CH$_4$, H$_2$O, and He, the methane reforming rate was unaffected by any polarization effects. This study also demonstrated that the electrochemical activity of the anode was lower when exposed to a mixture of CH$_4$, H$_2$O, and He as compared with a mixture of H$_2$, H$_2$O, and He. In both mixtures, the H$_2$O and He concentrations were held constant and the H$_2$ and CH$_4$ concentrations were the same. This finding demonstrates the need for hydrogen in the fuel stream in addition to any hydrogen produced via reforming, and illustrates that CH$_4$ alone is not highly electrochemically active.

Results from Belyaev et al. make it clear that operating an SOFC with pure CH$_4$ is not advantageous, and instead it may be better to operate using a mixture of hydrogen, methane and steam [19]. Many studies in the literature have explored different fuel sources that contain a mixture of H$_2$, CO, CO$_2$, H$_2$O, and lower concentration of CH$_4$. Hydrogen in the inlet of the fuel stream facilitates the electrochemical reaction, and the concentration of methane dictates the magnitude of the heat balance that reforming provides. Both SMR (equation 5.3) and DMR (equation 5.4) reactions can proceed if H$_2$O and CO$_2$ are present.
\[
\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{H}_2 + 2\text{CO} \quad (2.3)
\]

Water can either be introduced in the feed to the SOFC, or it can be produced from the electrochemical H2 oxidation reaction (equation 2.4) to facilitate further methane reforming. This chemical integration is an added benefit of internal reforming in an SOFC anode.

\[
\text{H}_2 + \text{O}^{2-} \rightarrow \text{H}_2\text{O} + 2\text{e}^- \quad (2.4)
\]

There is a wide range of possible fuel sources for SOFCs including fossil-derived ones, such as natural gas reformate, diesel reformate, or coal syngas, as well as renewable-based ones such as biomass syngas or biogas. All of these potential fuel sources have been examined in the literature in the context of internal CH4 reforming on an SOFC anode. Fang et al. demonstrated good long-term performance of a 20 kW SOFC stack with 10% pre-reformed liquid natural gas (LNG) that contained approximately 28% CH4, 13% H2, and 59% H2O [40]. Janardhanan, Heuveline, and Deutschmann compared simulated natural gas and natural gas reformate streams for methane conversion on a Ni-YSZ anode [23]. They were able to demonstrate that the extent of pre-reforming of methane entering the cell strongly affected the electrical efficiency of the cell, and an improvement of 35% efficiency was observed from 0% pre-reforming to 60% pre-reforming (e.g., 60% of the inlet CH4 is reformed). This dramatic effect bolsters the argument to optimize the pre-reforming step prior to SOFC anode operation.

Diesel reformate has also been demonstrated to allow steady and stable operation of a 340 W small-scale APU stack [32]. Lindermeir et al. demonstrated that in an integrated system including a pre-reformer, SOFC stack, after-burner, and heat-exchanger fuel utilization can be improved by chemical integration when a portion of the products from the SOFC stack are recycled back to the pre-reformer. This observation builds on the notion that SOFC efficiency can be improved by optimized thermal and chemical integration.

Coal and biomass syngas can contain high concentrations of hydrogen and therefore could make attractive fuels for SOFCs. For a simulated coal syngas stream, Miao et al. demonstrated that fuel streams containing more carbon and less steam tended to degrade faster and have lower
output voltage [36]. They showed that the power density was approximately 180 mW/cm$^2$ for a stream containing 10% CH$_4$ in 90% H$_2$ compared with 275 mW/cm$^2$ for a stream containing 10% N$_2$ in 90% H$_2$. They attributed the decreased performance with the methane stream to carbon deposition on the anode surface. SOFC integration in a biomass conversion process has been studied mostly in the context of producer gas which exits the gasifier directly with no clean-up step and contains some methane [41]. Karl et al. demonstrated in a simulated combined biomass gasification-SOFC process that thermal integration between the gasifier and SOFC made for a more efficient and economical system [38]. Suwanwarangkul et al. demonstrated that for both air-blown and oxygen-blown biomass gasification product streams, there was approximately 85% fuel utilization and the water-gas shift reaction was in equilibrium at the conditions evaluated in their study [37].

Another recently popular fuel source for SOFCs is biogas, which is a mixture of CH$_4$ and CO$_2$ collected from the biological breakdown of waste [25, 28, 29, 41]. Because biogas contains a high concentration of CO$_2$ and low to no steam, it is expected that more CO would be produced and therefore may increase the possibility of coking from the Boudouard reaction (equation 5.10) [42, 43].

$$2 \text{CO} + 2 \text{Ni} \rightleftharpoons \text{CO}_2 + \text{Ni} + \text{C} + \text{Ni}$$ (2.5)

Van Herle et al. performed a thorough study on the feasibility of biogas as a fuel for SOFCs using known compositions of biogas from various sources in Europe (e.g., cattle, sewage plant) [29]. In their initial feasibility study, Van Herle et al. stated that carbon deposition could potentially be a source of deactivation but would be mitigated by oxygen fed to the SOFC. In a subsequent study where they evaluated an SOFC operating with sewage sludge-derived biogas, Van Herle et al. estimated the likelihood of carbon formation from the Boudouard reaction to be low but showed that carbon deposition may form from methane pyrolysis (equation 2.6) [44].

$$\text{CH}_4 \rightleftharpoons \text{C} + 2 \text{H}_2$$ (2.6)
Subsequent studies on the feasibility of biogas have pointed to the high concentration of sulfur in the biogas as a potential source of activity problems [25, 27, 31]. High concentration of sulfur can cause cell degradation and a decrease in cell performance [27]. This issue is not unique to biogas, and in fact all potential fuels for SOFCs contain some sulfur usually in the form of H$_2$S [45]. Typical sulfur concentrations (represented as H$_2$S) for potential SOFC fuels are reported in Table 6.1. Sulfur is found naturally in both fossil fuels and in biomass-derived fuel sources (e.g., biomass syngas). High sulfur concentrations are an impediment to internal reforming on SOFCs, and therefore must be explored in detail in order to understand the underlying mechanisms.

Table 2.1: Typical sulfur concentrations represented as H$_2$S in potential SOFC fuels.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Concentration Range (ppm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biogas</td>
<td>200 - 20,000</td>
<td>[31, 46]</td>
</tr>
<tr>
<td>Diesel</td>
<td>15 - 900</td>
<td>[47, 48]</td>
</tr>
<tr>
<td>Natural gas</td>
<td>5 - 500</td>
<td>[49, 50]</td>
</tr>
<tr>
<td>Syngas - coal</td>
<td>1000 - 15,000</td>
<td>[49, 51]</td>
</tr>
<tr>
<td>Syngas - biomass</td>
<td>30 - 800</td>
<td>[51, 52]</td>
</tr>
</tbody>
</table>

2.2 Sulfur Poisoning of Nickel

Sulfur poisoning on nickel catalysts has been evaluated extensively over the past three decades. In the literature, it is often the case that knowledge gained from sulfur adsorption studies on nickel supported on alumina and other non-YSZ supports is applied to Ni-YSZ. This section will separate the two groups of studies because it has been suggested that the catalyst support, particularly YSZ, can play a role in the sulfur poisoning process.

2.2.1 Non-YSZ Supported Ni-based Catalysts

In industry, pelletized nickel catalysts (5 - 25% Ni) are loaded into tubular reformers that operate at inlet temperatures of 450°C - 550°C [53]. Reforming catalyst support materials include γ-alumina (Al$_2$O$_3$), α-Al$_2$O$_3$, carbon, silica (SiO$_2$), ZrO$_2$, and aluminates and silicates doped with Ca, K, and
Na [53]. Rostrup-Nielsen performed pioneering work on the deactivation of nickel catalysts via coke formation, which was the principle deactivation concern early on in reforming catalysis [54, 55]. Initially, Rostrup-Nielsen observed that high concentrations of steam reduced the surface mobility of carbonaceous species thereby mitigating the effect of coking [54]. Approximately one decade after exploring coking mechanisms on nickel, Rostrup-Nielsen reported that sulfur passivated nickel catalysts demonstrated little to no carbon adsorption resulting in so-called "carbon-free steam reforming" [56]. Rostrup-Nielsen described this phenomenon as geometrical because sulfur was thought to chemisorb on nickel and at high surface coverages formed a two-dimensional surface sulfide wherein sulfur-sulfur atomic bonding was predominant [43]. The end effect of this was that carbon was prevented from polymerizing on the surface as a result of an ensemble effect from sulfides at high sulfur coverages ($\theta_s = 0.7 - 0.8$) [56].

Erley and Wagner used ultra high vacuum (UHV) diagnostic methods (e.g., LEED) and temperature programmed desorption (TPD) to evaluate the adsorption of CO on single nickel crystals in
the presence of sulfur [57]. They found that exposure on the Ni(111) surface to sulfur coverages of \( \theta_s = 0.4 \) resulted in the formation of a so-called "super structure" of well ordered sulfur atoms. It is difficult for CO to permeate this sulfur structure, and therefore increasing the sulfur coverage resulted in a decrease in CO uptake as shown in Figure 2.1. Erley estimated that nine sites active for CO adsorption were covered by one sulfur atom. This is a high estimation of the effect of sulfur poisoning when compared with other authors who estimate that four nickel sites are deactivated by one sulfur atom [43].

McCarty and Wise evaluated the sulfur poisoning of nickel catalysts supported on either \( \gamma \)-Al\(_2\)O\(_3\) or \( \alpha \)-Al\(_2\)O\(_3\), and calculated enthalpies and entropies of H\(_2\)S adsorption from adsorption data [58]. The work of McCarty and Wise is well known and validated some of the previous work on sulfur adsorption on nickel catalysts performed by Rostrup-Nielsen. They made careful measurements at equilibrium in a hydrogen and H\(_2\)S atmosphere at varying surface coverages of H\(_2\)S to calculate the heat of adsorption of sulfur on nickel. A plot of the heat of adsorption of sulfur vs the normalized
sulfur coverage normalized for CO uptake is given in Figure 2.2. With increasing sulfur coverage the heat of adsorption decreases as a result of repulsive interactions between chemisorbed sulfur atoms, but at high sulfur coverages the heat of adsorption increases possibly due to the adsorption of adspecies such as SH or H$_2$S.

McCarty and Wise also measured the sulfur capacity of the nickel catalysts and found results that agreed well with previous studies [58]. For a nickel surface site density of $11.0 \times 10^{14}$ Ni atom/cm$^2$, the sulfur saturation coverage was found to be $12.2 \times 10^{14}$ S atom/cm$^2$ [58]. This is slightly higher than the measurement made by Rostrup-Nielsen who reported $S/Ni(s) = 0.54$ ($15.4 \times 10^{14}$ Ni atom/cm$^2$ saturated by $8.3 \times 10^{14}$ S atom/cm$^2$) [58]. Pannell et al. reported sulfur saturation coverage of $11.4 \times 10^{14}$ S atom/cm$^2$ for a Ni powder and $17.6 \times 10^{14}$ S atom/cm$^2$ for a Pt-Ni/Al$_2$O$_3$ [58]. In all cases, the number of nickel atoms deactivated by one sulfur atom is greater than one as reported initially by Erley though not to the extent that Erley had estimated (e.g., $S/Ni(s) = 0.11$) [57].

The generally accepted poisoning reaction for H$_2$S on nickel is given in Equation 6.1, and most studies assume that this reaction is solely responsible for the poisoning and regeneration of nickel sites [59]. If this is the case, then it is crucially important to understand the sulfur adsorption and desorption behavior on nickel. McCarty and Wise reported the heats of adsorption at equilibrium for H$_2$S in hydrogen for Ni/$\alpha$-Al$_2$O$_3$ and Ni/$\gamma$-Al$_2$O$_3$ to be -155.2 kJ/mol and -143.5 kJ/mol, respectively [58]. They also demonstrate that the heat of adsorption is actually a function of the sulfur surface coverage. Compared with the experimental heat of adsorption measured for CO (-130 kJ/mol), the values for sulfur on nickel catalysts are higher [60]. Koningen and Sjöström evaluated sulfur chemisorption on a Ni/Mg-alumina catalyst during steam methane reforming [61]. They calculated the sulfur adsorption activation energy combined with the steam methane reforming activation energy ($\sim 110$ kJ/mol) and found that for different sulfur concentrations it was in the range of 260 - 280 kJ/mol [61]. This result, in conjunction with the equilibrium measurements of McCarty and Wise, suggest a substantial barrier, on the order of 120 kJ/mol for the adsorption step.

$$H_2S + Ni \longrightarrow Ni-S + H_2$$ (2.7)
Abild-Pedersen et al. evaluated the specific adsorption behavior of sulfur on the steps (Ni(211)) and terraces (Ni(111)) of the nickel crystal and evaluated the adsorption of methane in the presence of 0.06 ML (monolayer) - 0.33 ML sulfur using both DFT and UHV methods [62]. Results from this study suggest that sulfur adsorbs preferentially on steps, and at low surface coverages (0.06 ML) will adsorb only to steps. The energy barrier for the dissociative adsorption of methane on Ni(211) was calculated to be 88 kJ/mol, and increased to 125 kJ/mol for higher sulfur coverages. Results indicated that blocking these Ni(211) sites resulted in a significant decrease in carbon adsorption (per added sulfur) as shown in Figure 2.3. This result agrees with the work of Rostrup-Nielsen which indicated that passivating the nickel surface with sulfur resulted in carbon-free reforming [56]. It also is consistent with the desorption results of Koningen and Sjöström when combined with the equilibrium measurements of McCarty and Wise [58, 61].

![Figure 2.3: Inhibition of carbon deposition on Ni(211) in the presence of increasing monolayers of sulfur as measured and reported by Abild-Pedersen et al. [62].](image)

The effect of poisoning specific sites on the nickel crystal for carbon adsorption minimization may be applied to the minimization of sulfur poisoning. Sato and Fujimoto synthesized Ni-based
catalysts doped with 12 wt% WO$_3$ and demonstrated better than 40% improvement in methane conversion at 850°C in 300 ppm H$_2$S compared to a Ni/Al$_2$O$_3$ catalyst [63]. Though the authors did not specifically probe the crystal surface, one possible reason for the effectiveness of tungsten promotion is that it blocks step sites that are highly susceptible to sulfur adsorption. A study by Wang et al. also indicated that alloying nickel with other metals (e.g., Re) resulted in a dramatic improvement in sulfur resistance (93% improvement in C$_7$H$_{14}$ conversion) [64]. Results from this study also indicated that sulfur resistance was dramatically higher for Ni/CeZSM-5 than Ni/AAl$_2$O$_3$. The results for the different heats of H$_2$S adsorption on Ni/α-Al$_2$O$_3$ (-155.2 kJ/mol) and Ni/γ-Al$_2$O$_3$ (-143.5 kJ/mol) measured by McCarty and Wise also indicate that support materials appear to affect sulfur adsorption [58]. If the sulfur adsorption on nickel is mainly affected by the state of the step sites, then so-called support effects may be the result of a difference in the number of step sites available on one support compared with another. Like bimetallic catalysts and alkali-promoted catalysts, the structure of the nickel crystal can be affected by its conformation on the support. Because of this, it is important to understand sulfur interactions with Ni/YSZ specifically.

2.2.2 Ni-YSZ Anodes

Sulfur poisoning studies done on Ni/YSZ have focused on evaluating the effect of sulfur on the electrochemical activity, but recent work has indicated that there may be a difference in the severity of sulfur poisoning on electrochemical vs. reforming activity [65]. The first major study on the poisoning effect of sulfur on the electrochemical activity of a Ni/YSZ SOFC anode was done by Matsuzaki and Yasuda [9]. This study established the baseline for understanding the severity of sulfur poisoning on the polarization resistance of an operating SOFC, and it evaluated the effects of sulfur concentration, temperature, and poisoning time. Results from this study demonstrated that the impedance was significantly higher in the presence of 15 ppm compared with 1 ppm. This work also demonstrated that sulfur poisoning is highly dependent on temperature by showing that the overvoltage increased rapidly at 750°C with only 0.05 ppm H$_2$S in the stream compared with a much more gradual increase at 1000°C in 16 ppm H$_2$S. This study was the first to indicate that
sulfur in very low concentrations (0.05 ppm) has a strong poisoning effect on the electrochemical activity at desirable operating temperatures (750°C).

Cheng et al. further probed the effect of sulfur poisoning on electrochemical deactivation and demonstrated that the increase in cell resistance is a function of the current draw [66]. Results from this work indicated that when a Ni/YSZ SOFC was operating at higher current densities, the total cell resistance changed less for the same concentration of H₂S (10 ppm) than at lower current densities. The difference in the change in cell resistance between 391 mA/cm⁻² and 44 mA/cm⁻² was 17.5% which resulted in a dramatic improvement in cell performance. Cheng et al. suggest that the effect of current density on the reduction in sulfur poisoning severity is the result of the electrochemical oxidation of surface adsorbed sulfur to produce and desorb SO₂ gas. This is an interesting hypothesis, but it has not yet been demonstrated.

Few studies have attempted to determine the structure of sulfur or the point of adsorption on Ni/YSZ as has been done for Ni/alumina catalysts and single nickel crystals. A study by Dong et al. evaluated the formation of nickel sulﬁdes after exposure to sulfur at high temperatures (> 700°C) using ex situ Raman spectroscopy [67]. Dong et al. were able to identify Raman peaks similar to Ni₃S₂ on the sample treated with 100 ppm H₂S, but were not able to identify NiS. On samples treated in 10% H₂S for 5 days at 950°C, some NiS was observed on the Raman spectra. A subsequent study done in the same group by Cheng and Liu evaluated sulfur interactions on Ni/YSZ in situ [68]. Raman spectra taken during this study at 500°C in 50 ppm H₂S show no evidence of the formation of Ni₃S₂ or NiS unlike the ex situ sample. The authors found evidence that the bulk sulfide formed during cooling from treatment temperature to room temperature. It is interesting that no evidence of a Ni-S species was found at treatment temperatures during the in situ study, suggesting that no stable Ni-S species is formed even during severe sulfur treatment.

The lack of a stable Ni-S surface species formed during sulfur poisoning of Ni/YSZ may be responsible for the ease of regeneration of the surface upon H₂S removal as has been shown by many authors. Zha et al. demonstrated this phenomenon on an operating button cell with varying amounts of H₂S [10]. In this work it was demonstrated that for a Ni/YSZ sample treated in 50 ppm
H₂S, there was a 20.6% drop in activity which recovered approximately 92% of the original activity after sulfur flow ceased and H₂ flow continued. In a 2 ppm H₂S treatment, Zha et al. demonstrated that regeneration is time sensitive by showing full activity recovery after 4 minutes of sulfidation compared with a 1.1% drop in recovered activity after 24 hours of exposure. The regeneration of the nickel surface demonstrated in this study is facilitated by the almost pure hydrogen fuel stream. In this high concentration H₂ stream, the regeneration proceeds via equation 6.1. This works well when pure hydrogen is available for SOFC operation, but it may not be as effective when using a reformate stream.

A study by Li et al. evaluated sulfur poisoning on Ni/YSZ in a simulated coal syngas stream, and showed that regeneration after treatment with H₂S was achieved to a lesser degree in the model syngas than a H₂-N₂ stream [69]. Samples treated with H₂S in H₂-N₂ during SOFC operation recovered 100% of their initial activity, while SOFCs operated in simulated syngas achieved between 94% and 97% of their initial activity. This study did not evaluate internal reforming during SOFC operation, and the simultaneous use of nickel may reveal further issues for sulfur poisoning on Ni/YSZ.

Smith et al. studied the deactivation of a Ni/YSZ SOFC during electrochemical operation and observed a 10% drop in the cell voltage after introducing 1 ppm H₂S to a direct internal reforming stream at 750°C [70]. After removing sulfur from the feed stream, the full activity was reportedly not recovered but the authors did not report the specific loss. Secondary ion mass spectrometry (SIMS) of the post-reaction sample indicated that sulfur was present approximately 40 nm into the structure of the Ni/YSZ cell. This result implies that sulfur is not confined to the surface (< 1 nm) and instead may diffuse into the Ni/YSZ structure.

Recent reviews on sulfur poisoning on Ni/YSZ have illuminated the disparity in the literature that exists for performing consistent, comparable sulfur poisoning studies [11, 12]. Most studies describe sulfur interactions in terms of change in the exchange current density or a change in the anode polarization resistance under open circuit conditions [11]. Though these are valid indicators for cell degradation, the studies that report these values do not also report any significant catalytic
information (e.g., active metal surface) about the Ni/YSZ making it impossible for direct comparison to any other system. Further, there is no consideration between the studies for the effect of transport through the SOFC test apparatus. There is a need for examination of sulfur reactions on Ni/YSZ in a transport-independent domain with a focus on the sulfur poisoning influence on reforming activity.

2.3 Experimental Evaluation of Ni/YSZ

Evaluation of Ni/YSZ anodes has been carried out in several kinds of reactors to provide different information. Most studies focus on evaluating electrochemical aspects of SOFCs under varying conditions, and this information is important for understanding SOFC operation, materials optimization, and scale-up. For small scale, single cell testing (e.g., button cells), detailed kinetics for electrochemical oxidation reactions can be evaluated and used in coupled transport and kinetic models [71]. SOFC models combine fundamental mechanisms for electrochemical oxidation with transport models, and many groups have shown good agreement between these models and experimental data [71]. These models are important because they provide a means for probing the operation space in a way that is cost prohibitive to probe experimentally. Further, the operation of button cell type experiments can be difficult due to problems with sealing the cell at high temperatures. These materials limitations can also be evaluated in transport-kinetic models, but first fundamental catalytic information about new SOFC anode materials is needed.

The primary transport through an SOFC is gas diffusion through a porous media. According to Zhu and Kee, there are four physical processes that affect the gas transport in porous media: 1) molecular diffusion, 2) Knudsen diffusion, 3) surface diffusion, and 4) Darcy's viscous flow [72]. Molecular diffusion, Knudsen diffusion, and viscous flow are evaluated in SOFC anode models using the dusty-gas model (DGM), which is written in terms of the molar concentrations and fluxes, the concentration gradient, and the pressure gradient [72]. The range of Knudsen numbers possible for a system make it necessary to combine bulk and Knudsen diffusion so that they are both considered [72]. The Knudsen number ($Kn$) is the ratio of the mean free path length of a gas to the characteristic pore diameter [72]. For $Kn \ll 1$ bulk diffusion (molecule-molecule collisions)
dominates, for $Kn \gg 1$ Knudsen diffusion (molecule-wall collisions) dominates, and when $Kn$ is close to unity bulk and Knudsen diffusion must both be considered [71, 72]. For SOFC electrodes, $Kn$ is close to one, and the DGM combines the bulk and Knudsen diffusion in series to produce a total diffusive flux. This flux represents the diffusive transport of the gas mixture through the electrodes from the fuel channel (anode) to the electrolyte surface and vice versa [72].

At the Colorado School of Mines (CSM), an experimental apparatus was developed to evaluate internal reforming chemistry on the SOFC while maintaining an accurate transport domain [24, 73]. The separated anode experiment (SAE) decouples electrochemistry and reforming chemistry, which facilitates the study of anode materials for their hydrocarbon reforming activity while maintaining a representative cell transport domain [74]. It is important to accurately mimic the transport of an SOFC because of transport limitations which may hinder internal reforming chemistry. A one dimensional model has been developed for the SAE, and it uses the DGM for flow in porous media and assumes plug flow in the channels. This model has been shown to be very effective for predicting gas transport through both SOFC membrane assemblies and for anodes with barrier layers [24, 74].

The SAE experimental apparatus has primarily been used to evaluate steam and dry reforming chemistry in SOFC anodes. Hecht et al. evaluated dry and steam reforming on Ni/YSZ in a planar-type SAE, and demonstrated good agreement between experimental and model results [24]. They demonstrated that even for kinetically limited processes, the SAE model predictions were very close to experimental values. Another study by Richards et al. evaluated dry methane reforming on a planar-type Ni/YSZ anode using the SAE, and again demonstrated very good agreement between experimental and modeled results [74].

The good agreement between experimental and model results observed by Hecht and Richards results from the use of both an accurate transport model and a valid micro-kinetic mechanism. The micro-kinetic mechanism used in both studies was developed by the Deutschmann group, and has been validated by that group with fixed bed data [1]. Using a packed bed reactor transport model coupled with the Deutschmann micro-kinetic mechanism, Maier et al. demonstrated good
agreement between experimental SMR methane conversion and products with their PBR model [1]. These results indicate that it is possible to evaluate the heterogeneous chemistry on Ni/YSZ in a fixed bed reactor.

Transport in the SAE mimics an operating SOFC, and this means that the SAE also suffers from some of the same issues that SOFCs have. One of the major difficulties in SOFC operation is sealing the cell at the high operating temperatures (> 750°C). It is difficult to achieve an adequate seal such that the cathode and anode gases are sufficiently separated so that the only contact between the two are gases diffusing through the electrode [71]. Further, the materials of construction for the SAE used in past studies have consisted of stainless steel in regions where the temperature is above 600°C [24, 74]. Sulfur is known to passivate stainless steel tubing surfaces which causes unexpected sulfur uptake and release making it difficult to ensure uniform sulfur delivery to an experimental system, particularly for low concentrations. To avoid this effect, ”inert” tubing can be used such as Teflon or coated stainless steel. There are several commercially available coatings (e.g., Sulfinert, Dursan) for stainless steel that significantly reduce sulfur uptake, but these coatings are compromised at high temperatures (> 600°C). This means that no stainless steel tubing can be made inert to sulfur near reforming reaction temperatures.

A fixed bed reactor can be used to overcome issues with sealing and sulfur passivation. Fixed bed reactors are often tubular, and can be configured so that gases enter a quartz tube reactor in the cold zone and flow to the catalyst bed in the hot zone [75]. Using all quartz construction avoids issues with sulfur passivation, and quartz tubes can be sealed reliably at room temperature. Though this system does not accurately mimic transport through SOFCs, intrinsic information about the rates of methane reforming can be measured and applied using coupled transport-kinetic models. Both Hecht and Richards indicate that their SAE systems are in the kinetically limited region, and therefore the anode is not evaluated in the transport limited region. Therefore, a comparison between PBR and SAE results should be similar because they are both operated in non-transport limited regions.
CHAPTER 3
METHODS

In this chapter, the experimental and computational methods for this work are discussed. Detailed descriptions of the coupled transport-kinetic models developed during this work are given for two experimental apparatuses: a packed bed reactor (PBR) and a tube-in-tube separated anode experimental system (tubular SAE). Descriptions of the two experimental apparatuses built to validate the PBR and tubular SAE models are given, and implementation of the experiments is described.

3.1 Packed Bed Reactor System

Fixed or packed bed reactors (PBR) are continuously flowing systems with a stationary catalyst bed and are used on a wide range of scales because of their versatility in operating range and relatively simple design (e.g. no moving parts) [75, 76]. PBRs are primarily used for heterogeneous (gas-solid) reactions wherein the reactants are in the gas or vapor phase and the catalyst is a solid. In the context of this work, a PBR offers a convenient way to examine sulfur interactions on the Ni-YSZ anode that preserves material, minimizes transport limitations, and utilizes a simpler reaction setup that is easily reproduced. Compared with small scale stirred reactors, batch reactors and other types of catalyst reactors, mass transport and temperature in PBRs are easily controlled, making them a good candidate for obtaining intrinsic kinetic information [77]. PBRs at the laboratory scale are useful also because they can be operated at sufficiently high gas hourly space velocities (GHSV) so that transport limitations are minimized.

3.1.1 PBR Catalyst Materials

Tubular anodes were obtained from CoorsTek Inc. and synthesized via the conventional “C-based” fabrication method [78]. NiO and YSZ powders were mixed with a solvent to produce a slurry that was poured into a Plaster-of-Paris mold to form tubes. The tubes were then hang fired at
1400°C and sintered at 1550°C. The PBR system was designed to use granular catalysts in a size range of 100 - 500 micron. For use in the PBR, the anode tubes were crushed using a hammer mill and sieved to -60/+45 mesh (250 – 355 micron).

A commercially available nickel-based reforming catalyst (C11-NK, Süd Chemie) supported on \( \alpha \)-alumina was used as a reference material for comparison to the Ni/YSZ anode materials. The Süd Chemie nickel-alumina naptha reforming catalyst was provided as a 5-hole cylindrical pellet, and was crushed and sieved in the same way as the Ni/YSZ anodes. The exact composition of C11-NK is not disclosed by the manufacturer, but it has been estimated in literature to be approximately 8.5 wt% \( K_2O \) and 25 wt% NiO loaded on calcium aluminate \((CaAl_2O_4)\) [79].

### 3.1.2 PBR Experimental Apparatus

A schematic of the PBR experimental apparatus built to carry out the packed bed experiments is given in Figure 3.1. The heart of the PBR system is a 12 mm o.d. (11 mm i.d.) quartz tube reactor suspended in a furnace. An identical tube is hung next to the reactor tube and used as a bypass. A low thermal mass, quartz cylinder furnace (Thermocraft) was used to speed up furnace cool down time so experiments could be done more rapidly. The shortest furnace geometry available from the manufacturer is 12 inches, and therefore the quartz tube reactors were designed to be 18 inches long so that connections for gas and vapor flow could be made in the cool zone \((< 200°C)\). This was necessary because Teflon tee fittings were used at the top and bottom of the reactor tube to avoid sulfur uptake on tubing. All sulfur containing gases, from the supply gas cylinder to the inlet of the reactor, were delivered in tubing that was either Teflon or stainless steel coated with a thin film of Sulfinert\textsuperscript{®} (Restek) to avoid sulfur adsorption on tubing. To minimize the cost of coating the system in Sulfinert\textsuperscript{®}, the gas delivery manifold was divided into two parts: 1) coated sulfur delivery manifold that consists of mass flow controllers that deliver nitrogen (sweep gas), hydrogen sulfide, sulfur dioxide, and carbonyl sulfide and 2) non-coated manifold that consists of mass flow controllers to deliver nitrogen, helium, hydrogen, carbon monoxide, carbon dioxide, methane, and air. Gas pressures from the cylinder regulator (2-stage, Air Liquide) to the inlet of the mass flow control...
controller were controlled using a low range forward pressure regulator (SMC) labeled "R" in Figure 3.1. Check valves (labeled CV) were used to prevent backflow from the system into the mass flow controllers in the event of an over-pressurization event. Both gas manifolds have spring-type pressure safety relief valves (labeled PSV) designed to vent to the local exhaust ventilation (LEV) in the event of an over-pressurization. Water was vaporized in a five foot heated stainless steel capillary tube swept with non-sulfur reactant gases. Water was delivered to the inlet of the heated capillary tube at a steady rate using a high pressure liquid metering pump (Optos, Eldex). Switching of the gases from the non-sulfur manifold and water streams between the reactor and bypass was achieved using 316L stainless steel 3-way ball valves with pneumatic actuators controlled using electric solenoid valves (Swagelok). Sulfur containing gases were delivered to a second Teflon tee connected to the top run of the main Teflon tee. Sulfur gas switching was achieved using Teflon 3-way solenoid valves (Valco). Stainless steel thermocouples (K-type, Omega) were suspended in both the reactor and the bypass tubes in 0.125 inch o.d. quartz thermocouple sheaths to prevent reactants from interacting with them.

Downstream of the catalyst bed, condensible vapors were removed using a tube-in-tube Teflon condenser that was cooled using a recirculating chiller (Oasis, Solid State Cooling). Any remaining or overflow water was knocked out in a coalescing filter with a paper filter element (Parker) and non-condensible gases were further dried to sub-ppm levels of water in a Nafion dryer (Permapure). Analysis of the permanent gases excluding sulfur species was done using gas chromatography (Agilent 490 micro-GC). Gases measured using the micro-GC include He, H₂, N₂, O₂, CH₄, CO₂, and CO. Measurements for H₂S and SO₂ are made using a flow-through FTIR (MKS MultiGas 2030) equipped with a stainless steel gas cell coated in Dursan which makes the cell inert to sulfur uptake at high temperatures (190°C). The gas cell was kept at an elevated temperature to increase velocity through the cell and prevent condensation of any remaining moisture in the gas which can condense on the non-heated KBr windows.

Quartz tube reactors were hung vertically in the furnace, and flow over the catalyst bed was directed downwards. Approximately 200 mg of quartz wool was used to keep the catalyst in
Figure 3.1: Schematic of the packed bed reactor (PBR) experimental apparatus.
position in the center of the furnace to maintain a uniform catalyst temperature in the isothermal zone. The quartz wool plug was tamped down to ensure a flat surface for the catalyst bed to sit on, and 500 - 1000 mg catalyst was loaded on top of the quartz wool plug as shown in Figure 3.2. The thermocouple which was used to record the temperature of the reaction was placed just above the catalyst bed. After the experiment was completed, the entire quartz tube reactor was removed from the furnace and the catalyst was recovered for post-reaction characterization. The quartz wool plug was also removed and the quartz tube reactor was cleaned with methanol, rinsed with de-ionized water, and then dried at 150°C.

![Figure 3.2: Close view of the pack bed reactor catalyst bed loading structure.](image)

A supervisory control and data acquisition system was implemented for the PBR apparatus using Opto 22 hardware and software (PAC Project Pro). Data from thermocouples, pressure transducers, mass flow controller feedback and time were recorded on a 15 s interval. A control strategy was designed with temperature and pressure limitations with automatic shut-offs for safety. PID loops used to control the heat tapes and furnace were programmed in the control strategy and optimized using PID loop tuning software. The control strategy was also used to program experimental procedures that varied procedure time, water and gas flow rates, GC sample rate and reaction temperature. Because of the safety features implemented using the control system, the PBR was allowed to operate unattended for the long reaction times (12 - 24 hours).
3.1.3 Experiment Protocol

Prior to reaction, it is necessary to reduce NiO in both Ni/YSZ and the Ni/K$_2$O–CaAl$_2$O$_4$ to the active, metallic nickel form via hydrogen reduction. Ni/YSZ was reduced in 12 vol% H$_2$ in a balance of nitrogen using the protocol: i) ramp from 25°C to 650°C at 3.5 °C/min ramp rate and hold for 60 minutes and ii) ramp to 850°C at 3.5 °C/min and hold for 60 minutes. Ni/K$_2$O–CaAl$_2$O$_4$ was reduced in 12 vol% H$_2$ in a balance of nitrogen using the protocol: i) ramp from 25°C to 650°C at 5 °C/min and hold for 30 minutes and ii) ramp to 850°C at 5 °C/min and hold for 120 minutes. All reduction steps were done at a total flow rate of 250 sccm. Reduction protocols were chosen based on results from temperature programmed reduction (TPR) for each catalyst.

Methane dry and steam reforming experiments were performed following the pretreatment step. After the pretreatment step, the catalyst was cooled to the reaction temperature of interest. Experiments were performed at 650°C, 750°C, and 800°C. During the ramp down in temperature from the last reduction step at 850°C to the reaction temperature, the catalyst was purged in nitrogen at the same flow rate as the reduction step. After reaching reaction temperature, the catalyst was held in flowing nitrogen to ensure that the temperature of the catalyst bed was stable prior to the start of the reforming reaction. Experiments were done at a gas hourly space velocity (GHSV) of $1.5 \times 10^5$ with 800 mg catalyst. The composition of the reactant stream for both steam and dry reforming was: 14.3 vol% He, 8.6 vol% H$_2$, 34.3 vol% N$_2$, 14.3 vol% CH$_4$, and 28.5 vol% H$_2$O or CO$_2$. The experimental protocol was: i) 30 minutes reforming, ii) 5 minutes continued reforming with sulfur species introduced to the bypass to flush the line, iii) 90 minutes reforming with sulfur species present, and iv) purge, flush and cool in nitrogen. Three sulfur species at concentrations of 1 ppm, 3 ppm and 5 ppm were examined at three reaction temperatures (650°C, 750°C, 800°C).

Sulfur uptake experiments were performed following a hydrogen reduction step (described previously), with 800 mg catalyst and the following protocol: i) cool to 500°C, ii) bypass calibration at 500°C for 15 minutes with 480 ppm of the sulfur species of interest in 16 wt% hydrogen and nitrogen, iv) 480 ppm sulfur uptake over catalyst for 60 minutes, and v) ramp to 850°C at 10 °C/min in 16% hydrogen in nitrogen and hold for 60 minutes. A similar procedure was performed for
support materials, YSZ and $\alpha$-Al$_2$O$_3$; however they were not reduced prior to sulfur uptake. Post-reactor gases were analyzed using Fourier transform infrared spectroscopy (FTIR, MKS MultiGas 2030) which is equipped with a stainless steel cell (5m, 200 mL) coated in a Dursan film that ensures the system does not adsorb sulfur. The FTIR was used to measure the H$_2$S and SO$_2$ concentration simultaneously every 8 seconds. Measurements for H$_2$S using the FTIR had a low signal to noise ratio, and therefore a second order Savitzky-Golay filter was used to smooth the data for better readability.

3.2 Model of the Packed Bed Reactor System

Modeling the PBR system requires careful consideration of the flow dynamics in the system. A differential control volume that is representative of the PBR system is shown in Figure 3.3. The reactor is a cylindrical tube and therefore the system is posed in cylindrical coordinates which consists of an axial, radial and azimuthal coordinate. The three dimensional simulation of this system is beyond the scope of this work, and therefore simplifying assumptions are made to reduce dimensionality of the system. Changes in the azimuthal direction are considered negligible. Reactant species are introduced in the axial direction and therefore we must consider whether changes are significant in the radial direction. In a similar cylindrical system at sufficient flow rates and with no catalyst, the system might be considered plug flow which would exclude changes in the radial direction. However, it is important to note that a PBR is not a plug flow system. The velocity profile in a plug flow reactor is significantly different because the flow field in a PBR is perturbed by the catalyst particles in the bed causing temperature and pressure gradients in all directions. However, for this work, we assume that changes in the radial direction are negligible because of the relatively small reactor radius.

Neglecting changes in the radial direction and assuming that species concentration, temperature and pressure change only as a function of the axial dimension ($z$), the problem can be reduced to one-dimension which can be solved using numerical methods. The one-dimensional chemically reacting flow model for the PBR system is based on a model developed by Zhu et al. [80]. The
catalyst material is assumed to have roughly spherical geometry, but the inset picture shows that the catalyst is not a perfectly smooth sphere because it has pores with diameter $d_p$. The Ni/YSZ anode surface has few pores, so diffusion resistance into the pores is assumed to be negligible. Heterogeneous chemistry occurs on the active sites, $\theta$, represented by green islands in the pores and on the surface of the catalyst. Measurements of the abundance (number of active sites) and quality (affinity to adsorb different species) of these active sites can be translated into terms that are used in the model. Namely, the number of active sites is reflected in the site density term and the active site quality can be reflected by adding multiple surface phases to the model. The tortuosity, $\tau$, which is the ratio of the actual distance traveled between two points, represented by a red line in Figure 3.3, to the shortest distance between those two points. Porosity in the bed, $\phi_g$, is the ratio of void space to total volume (voids + catalyst). The micro-kinetic model for steam and dry methane reforming on nickel is taken from Meier et al. [1] and consists of 42 surface reactions involving 7 gas phase species and 12 surface species in the adsorbed state.
3.2.1 PBR Governing Equations

This model is developed from the equations reported by Zhu et al. [80] for one-dimensional flow in a packed bed reactor. This model is based on the principle that for a minutely small control volume, changes can be approximated using simple reductions in mathematical order. The species mass-continuity equation is given in Zhu et al. [80] as

$$\frac{\partial (\phi_g \rho_g Y_k)}{\partial t} + \nabla \cdot j_k = (\phi_g \dot{\omega}_k + A_s \dot{s}_k) W_k$$  \hspace{1cm} (3.1)

Where $\phi_g$ is the porosity or void fraction, $\rho_g$ is the gas density, $Y_k$ represents the species mass fractions, $A_s$ is the specific active surface area of the catalyst (active surface area per unit volume of catalyst), $\dot{s}_k$ is the net molar production rate of species $k$ by heterogeneous reactions, $\dot{\omega}_k$ is the net molar production rate of species $k$ by homogeneous reactions and $W_k$ is the molar mass of species $k$.

In cylindrical coordinates, the divergence of the mass flux vector is

$$\nabla \cdot j_A = \frac{\partial j_{A,z}}{\partial z} + \frac{1}{r} \frac{\partial (r j_{A,r})}{\partial r} + \frac{1}{r} \frac{\partial j_{A,\theta}}{\partial \theta}.$$  \hspace{1cm} (3.2)

The system has been assumed to be one-dimensional in the axial, $z$, direction, so the radial, $r$, and azimuthal, $\theta$, fluxes cancel. Plugging the reduced expression into the species mass-continuity equation yields

$$\frac{\partial (\phi_g \rho_g Y_k)}{\partial t} + \frac{\partial j_{A,z}}{\partial z} = (\phi_g \dot{\omega}_k + A_s \dot{s}_k) W_k$$  \hspace{1cm} (3.3)

The overall mass-continuity equation can be expanded similarly to yield

$$\frac{\partial (\phi_g \rho_g)}{\partial t} + \sum_{k=1}^{K_g} \frac{\partial j_{A,k}}{\partial z} = \sum_{k=1}^{K_g} A_s \dot{s}_k W_k$$  \hspace{1cm} (3.4)

Mass fluxes are related to the molar flux as $j_k = W_k j_k$. The Dusty-Gas model (DGM) is used to evaluate the molar fluxes of the gas-phase species. Briefly, the DGM is a transport model that describes fluid flow through a uniformly distributed, porous media [73]. The DGM requires the calculation of both the effective binary diffusion coefficients, $D_{kl}^e$, and the effective Knudsen diffusion coefficients, $D_{k,Kn}^e$. Effective binary diffusion coefficients are calculated from the ordinary
binary diffusion coefficient (determined from standard expressions) using

\[ D_{kl}^e = \frac{\phi_g}{\tau} D_{kl} \]  

(3.5)

Knudsen diffusion occurs as a result of collisions between the gas and the wall. It becomes dominant when the mean free path of the gas is restricted by the geometry of the void space. The effective Knudsen diffusion coefficient is written as

\[ D_{k,Kn}^e = \frac{4}{3} \frac{r_p \phi_g}{\pi \tau} \sqrt{\frac{8RT}{\pi W_k}} \]  

(3.6)

The overall DGM relates the molar concentrations, molar fluxes, concentration gradients and pressure gradient and is written as

\[ \sum_{l \neq k} \frac{[X_l] J_k - [X_k] J_l}{[X_T] D_{kl}^e} + \frac{J_k}{D_{k,Kn}^e} = -\nabla [X_k] - \frac{[X_k]}{D_{k,Kn}^e} \frac{B_g}{\mu} \nabla p \]  

(3.7)

Where \([X_k]\) is the molar concentration of species \(k\), \([X_T]\) is the total molar concentration \([X_T] = p/RT\), \(B_g\) is the permeability, and \(\nabla p\) is the pressure gradient. The permeability is estimated using the Kozeny-Carman relationship for closely packed spheres with diameter \(d_p\) and is written as

\[ B_g = \frac{\phi_g^3 d_p^2}{72 \tau (1 - \phi_g)^2} \]  

(3.8)

Since this is a catalytic reaction, an expression for the change in active site coverage, \(\theta_k\), is required and is written as

\[ \frac{d\theta_k}{dt} = \frac{\dot{s}_k}{\Gamma} \]  

(3.9)

Where \(\Gamma\) is the density of surface sites \((mol/m^2)\), and \(\dot{s}_k\) is the heterogeneous chemical production rate of species \(k\). The homogeneous and heterogeneous chemical production rates are functions of gas-phase and surface temperature respectively such that \(\dot{\omega}_k(T_g)\) and \(\dot{s}_k(T_s)\).

The energy balance in the system is developed from the control volume similarly to the momentum equations. The energy balance is particularly important in this system because of the endothermic steam \((\Delta H_{298}^o = 206 kJ/mol)\) and dry \((\Delta H_{298}^o = 247 kJ/mol)\) methane reforming reactions. As a result, it takes a lot of energy for the reaction to proceed which results in an initial drop in the temperature of the bed for isothermal systems and a temperature gradient along the bed.
for adiabatic systems. It is therefore important to develop the equations for modeling the energy balance. The energy balance for the gas phase is written as

$$\frac{\partial \phi_g p_g e}{\partial t} + \nabla \cdot \mathbf{q}_g = -\dot{q}_{\text{conv}} - \dot{q}_{\text{surf}}$$ (3.10)

Where $e$ is the gas internal energy described as $de = c_v g dT_g$ and $\mathbf{q}_g$ is the gas phase heat flux.

Convection of heat between the gas phase and the solid phase, $\dot{q}_{\text{conv}}$ is written as

$$\dot{q}_{\text{conv}} = h_v (T_g - T_s)$$ (3.11)

The volumetric heat-transfer coefficient, $h_v$, is written in terms of its relationship to the conventional heat-transfer coefficient, $h$, as

$$h_v = A_{\text{conv}} h$$ (3.12)

where $A_{\text{conv}}$ is the specific surface area of the catalyst material. There are several correlations available for evaluating $h_v$. Zhu et al. [80] use a correlation by Wakao and Kaguei that uses the Nusselt number, as

$$Nu = \frac{h_v d_p^2}{\lambda_g} = 2.0 + 1.1 Re^{0.6} Pr^{1/3}$$ (3.13)

where $d_p$ is the mean particle diameter and $Re$ and $Pr$ are the Reynold’s and Prandtl numbers, respectively, which are evaluated as

$$Re = \frac{\rho_g U d_p}{\mu} \quad Pr = \frac{\mu c_p g}{\lambda_g}$$ (3.14)

Heat released from heterogeneous reactions from the surface phase to the gas phase is described as a heat flux and is written as

$$\dot{q}_{\text{surf}} = -A_s \sum_{\dot{s}_k < 0} \dot{s}_k W_k h_k (T_g) - A_s \sum_{\dot{s}_k \geq 0} \dot{s}_k W_k h_k (T_s)$$ (3.15)

The gas phase heat flux, $\mathbf{q}_g$, is then written as

$$\mathbf{q}_g = -\phi_g \lambda_g \nabla T_g + \sum_{k=1}^{K_g} h_k \mathbf{j}_k$$ (3.16)

Where $h_k$ is the species specific enthalpy and $\lambda_g$ is the mixture thermal conductivity. The gradient of a scalar field (e.g. $\nabla T_g$) in cylindrical coordinates is
\[
\n\nabla T_g = \frac{\partial T}{\partial z} + \frac{\partial T}{\partial r} + \frac{1}{r} \frac{\partial T}{\partial \theta}
\]

(3.17)

Taking the divergence of the heat flux yields

\[
\nabla \cdot \mathbf{q}_g = \frac{\partial q_g}{\partial z} + \frac{1}{r} \frac{\partial rq_g}{\partial r} + \frac{1}{r} \frac{\partial q_g}{\partial \theta}
\]

(3.18)

Assuming heat flux is only in the axial, \( z \), direction, the radial and azimuthal terms are canceled. Then, combining equations 3.14 and 3.15 yields the expression for the gas-phase heat flux that can subsequently be discretized

\[
\mathbf{q}_g = -\phi_g \frac{\partial}{\partial z} \left( \frac{\partial \lambda_g T}{\partial T} \right) + \sum_{k=1}^{K_g} h_k \mathbf{j}_k
\]

(3.19)

Note that the sum term on the right-hand side of the equation does not undergo any mathematical dilation when taking the divergence of the gas-phase heat flux because only the first term contains the dependent variable, \( T_g \). The sum term contains the mass flux which we have already stated will be solved for using the Dusty-Gas model. Now, combining equation 3.19 and equation 3.10 and substituting the expression for \( e \) gives the energy balance for the gas phase

\[
\phi_g \frac{\partial \rho_g c_{v,g} T_g}{\partial t} - \phi_g \frac{\partial \lambda_g (\partial T_g)}{\partial z^2} = -\dot{q}_{\text{conv}} - \dot{q}_{\text{surf}} - \sum_{k=1}^{K_g} h_k \mathbf{j}_k
\]

(3.20)

The energy balance for the solid phase is written as

\[
\frac{\partial}{\partial t} (\phi_s \rho_s c_{p,s} T_s) + \nabla \cdot \mathbf{q}_s = \dot{q}_{\text{conv}} + \dot{q}_{\text{surf}} - \dot{q}_{\text{env}}
\]

(3.21)

Where \( \phi_s \) is the solid-phase volume fraction given as \( \phi_s = 1 - \phi_g \), \( \rho_s \) density of the solid phase (catalyst), and \( c_{p,s} \) is the heat capacity of the solid phase. Radiative heat loss from the catalyst material to the surroundings is approximated as

\[
\dot{q}_{\text{env}} = \sigma \varepsilon A_{\text{env}} (T_s^4 - T_\infty^4)
\]

(3.22)

Where \( \sigma \) is the Stefan-Boltzmann constant, \( \varepsilon \) is the emissivity of the solid material, \( A_{\text{env}} \) is the interface area between the catalyst material and the environment, and \( T_\infty \) is the temperature of the environment. The solid-phase heat flux is written as
\[ q_s = -\lambda_s^e \nabla T_s \]  

(3.23)

where the surface temperature gradient, \( \nabla T_s \), is calculated in the same way as presented in equation 3.17. The effective conductivity of the solid phase is given as

\[ \lambda_s^e = \phi_s \lambda_s + \lambda_r \]  

(3.24)

where \( \lambda_s \) is the thermal conductivity and \( \lambda_r \) is the effective radiation conductivity which is found using an expression from the literature [80]

\[ \lambda_r = 4d_p \sigma T_s^3 \{0.5756 \epsilon \tan^{-1}[1.5353(\lambda_s^e)^{0.8011} / \epsilon] + 0.1843\} \]  

(3.25)

and

\[ \lambda_s^* = \frac{\lambda_s}{(4d_p \sigma T_s^3)} \]  

(3.26)

Now, the solid-phase energy balance is written in a form specific to the model we are trying to develop

\[ \phi_s \frac{\partial}{\partial t} (\rho_s c_{p,s} T_s) - \frac{\partial \lambda_s^e}{\partial z} \left( \frac{\partial T_s}{\partial z} \right) = q_{\text{conv}} + q_{\text{surf}} - q_{\text{env}} \]  

(3.27)

Since \( \lambda_s^e \) is a \( f(T_s) \) it will be handled in a subroutine when solving this equation numerically.

This system of partial differential equations (PDE) forms an initial/boundary value problem that is too complex to be solved analytically and therefore it must be solved using numerical methods. The dependent variables in this system are the density \( \rho \), mass fractions \( Y_k \), surface coverages \( \theta_k \), gas-phase temperature \( T_g \), solid-phase temperature \( T_s \), and pressure \( p \). The independent variables are time \( t \) and the axial spatial coordinate, \( z \), along the length of the reactor. The succeeding sections will describe how these equations can be solved numerically using finite difference approximations and discretization of the system. The discretized equations are solved using Matlab and the properties of the gas and solid in the system are found using Cantera.
3.2.2 Numerical Methods for Solving PDEs

Finite difference approximations are a convenient method for solving systems of PDEs that cannot be solved analytically. The principle of finite differences is that the system can be split into discrete points along the domain and solved point by point along the domain. In this way, a mesh is formed for the spatial coordinate and grid points at either the boundary of each mesh cell or in the center are where local solutions are found. Using this method, the spatial derivative is discretized to replace the derivatives in the PDE with a series of algebraic equations that relate grid points on the mesh [81, 82]. With the spatial derivatives replaced by algebraic terms, the PDE becomes an ordinary differential equation (ODE) because only one independent variable remains [83]. A schematic of a discretized, one dimensional system with uniform mesh size, \( dz \), is given in Figure 3.4. Index points, \( i \), are given at the cell midpoints (e.g. \( i, i - 1 \)) and at the cell faces (e.g. \( i - \frac{1}{2} \)). The dependence of discretization on these face points and midpoints will be discussed further in the succeeding section.

\[
\frac{\partial j}{\partial z} \approx \frac{j_i - j_{i-1}}{\Delta z} \quad (3.28)
\]

Figure 3.4: One-dimensional mesh with grid points on the boundaries and in the center of the mesh points that are indexed with respect to the starting point, \( i \).

Applying an upwinding discretization to the overall mass continuity equation (equation 3.3) for the spatial coordinate yields

\[
\frac{\partial j}{\partial z} \approx \frac{j_i - j_{i-1}}{\Delta z}
\]

This differencing scheme generates a mesh of \( M \) ODEs in the domain \( 1 \leq i \leq M \). This conversion of PDEs to ODEs via discretization of the spatial derivative constitutes the so-called method of lines (MOL) technique [84]. To proceed in applying the MOL, it is first necessary to consider the
discretization method that is appropriate to solve the system of equations. There are three main differencing options for the simple, uniform mesh in question: backward, central, and upwind differencing. The choice of differencing method is PDE dependent, and for diffusive terms or for a second order equation, such as the energy balances, the central differencing scheme is best [84]. For the gas-phase energy equation (equation 3.20), the diffusive term is discretized with central differencing as

\[-\phi_g \frac{\partial}{\partial z} \left[ \lambda_g \frac{\partial (\rho g c v g T_g)}{\partial z} \right] \approx -\frac{2\phi_g}{z_{j+1} - z_{j-1}} \left( \frac{\lambda_{g,j+1/2} \rho_{g,j+1} c v_{g,j+1} T_{j+1} - \rho_{g,j} c v_{g,j} T_j}{z_{j+1} - z_j} \right) \]

(3.29)

Finite differencing of the time derivative can be handled similarly to the spatially dependent equations. Backward differencing in time is known as the implicit Euler method and the spatial, \(i\), and temporal, \(n\), grids are shown schematically in Figure 3.5. The gray areas show upwind differencing in \(i\) for the spatial derivative, \(dz\), and the backward differencing in \(n\) for the time derivative, \(dt\). Implicit equations are typically more stable to solve, but they are more difficult to pose because you must have information about three points at time \(t + dt\). The explicit Euler method is simpler to apply because you only have to have information at time \(t\), however it is less stable to solve [83].
The system of equations can be solved using either the explicit or implicit Euler method, but one of the advantages to using the MOL is that it does not require direct programming of the time derivative because of the multitude of solver libraries available [84]. Instead, the spatially discretized system is solved using readily available ODE integration software. The user can artificially force the system solution to march forward in time using simple programming techniques (e.g. for loop) and updating the initial conditions of the ODE. Freely available libraries that have been developed for integrating this type of system include: Sundials, DASSL, and Radau5. For this work, though, the Matlab ODE15s solver is used to integrate the system.

3.2.3 Initial and Boundary Conditions

The number of necessary boundary conditions (BC) and initial conditions (IC) can be identified by evaluating the order and type of canonical equation to be solved. Both the species mass continuity (equation 3.3) and the overall mass-continuity equations (equation 3.4) are first order, nonhomogeneous hyperbolic equations that require one initial value (first order in $t$) and one boundary condition (first order in $z$). At $t = 0$ and $z = 0$, the species mass fractions ($Y_k$) are known, the porosity is assumed to be constant, and the density of the gas is known (since the inlet temperature and pressure are specified). The energy balance equations are nonhomogeneous, parabolic equations that require one initial value (first order in $t$) and two boundary conditions (second order in $T$). At $z = 0$, the gas-phase temperature, $T_g$, is known and there is no change in temperature with respect to the spatial coordinate, $\partial T_g / \partial z = 0$. At $t = 0$, the mass flow rates of all species $k$, $\dot{m}_{k,in}$, are known. The last boundary condition is estimated by assuming that the system empties into a constant volume, continuously stirred batch reactor. This reactor has an infinitesimally small volume, and therefore does not strongly affect changes in composition in the system. The species mass continuity equation for the batch reactor is written as

$$\frac{d}{dt} (\rho V Y_k) = \dot{m}_{i,k} Y_{i,k} - \dot{m}_{o,k} Y_{o,k} + \dot{R}_k$$

(3.30)

Where $\dot{m}_i$ and $\dot{m}_o$ represent the inlet and outlet mass flow rates, respectively. The volume of the batch reactor, $V$, is held constant, and $\dot{R}_k$ is the source term that represents net mass transport into
and out of the batch reactor. This source term is written as

\[ \dot{R}_k = V W_k \dot{\omega}_k \]  \hspace{1cm} (3.31)

The overall mass continuity equation for the batch reactor is written as

\[ \frac{d}{dt} (\rho V) = \dot{m}_i - \dot{m}_o + \dot{R} \]  \hspace{1cm} (3.32)

where

\[ \dot{R}_k = \sum_{k=1}^{K_g} \dot{R}_k \] \hspace{1cm} (3.33)

The change in density in the batch reactor is estimated by assuming constant pressure and temperature and is written as

\[ \frac{d\rho}{dt} = \rho \dot{W} \sum_{k=1}^{K_g-1} \left( \frac{1}{W_k} - \frac{1}{W K_g} \right) Y_k \] \hspace{1cm} (3.34)

Heat flux to and from the batch reactor is assumed to be negligible due to the infinitesimally small volume \((1 \times 10^{-6} \text{ m}^3)\). The convenience of adding a batch reactor to the end of the system is that this boundary value can now be easily discretized in the same way as the governing equations.

### 3.2.4 Computational Methods

The discretized system of equations was solved using Matlab (version R2013b) with the Cantera (version 2.1.1) hook. Cantera is a “suite of object-oriented software tools for problems involving chemical kinetics, thermodynamics, and/or transport processes” and is open source and freely available without charge [85]. Cantera is versatile in that it can be implemented in C++, Matlab, Python, C and Fortran 90. Cantera interfaces with Matlab via a toolbox that is manually added by the user to the Matlab path and called directly from Matlab. One of the disadvantages to using Matlab, though, is that not all of the modules are available from Cantera. This is because Cantera is open source and therefore the administrators of Cantera maintain the software as a hobby and have not yet had time to implement the full Cantera to all platforms. One such example is the Dusty Gas Model which is available in C++ and Python Cantera, but not available in Matlab. Therefore, the
DGM is written as a function and called by the main driver in the PBR model.

Cantera has convenient functions and built-in values that make computing such values as heat capacity, thermal conductivity, and referencing global constants more efficient. A list of Cantera expressions for common functions and constants is given in Table 3.1. Note that these Cantera functions operate on a gas objects defined at the start of a program. The Cantera expressions given in Table 3.1 are for a gas object named \( g \) which contains an array of 7 gas species. The gas object contains the NASA polynomial parameterization necessary to calculate \( \hat{c}_p^0(T) \), \( \hat{h}_0^0(T) \), and \( \hat{s}_0^0(T) \) for each gas specie. Note that to calculate viscosity \( \mu \) and thermal conductivity \( \lambda_g \), a transport manager must be instituted for the gas object. For this system, a "Mixture" transport model has been implemented to handle the gas phase mixture. It is only under a specified transport manager that calculations for viscosity and thermal conductivity can be made. Likewise, the binary diffusion coefficient \( (B_{kl}) \) is calculated in the transport manager environment as a function of pressure and temperature. The net production rates for the gas phase species are calculated easily using Cantera.

### Table 3.1: Cantera expressions for common functions and constants.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Cantera Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stefan-Boltzmann constant (( \sigma ))</td>
<td>W/m(^2)-K(^4)</td>
<td>StefanBoltz</td>
</tr>
<tr>
<td>Universal gas constant (( R ))</td>
<td>cal/mol-K</td>
<td>gasconstcal</td>
</tr>
<tr>
<td>Gas mixture mass density (( \rho_g ))</td>
<td>kg/m(^3)</td>
<td>density(g)</td>
</tr>
<tr>
<td>Array of molecular weights (( W_k ))</td>
<td>kmol/m(^3)</td>
<td>molecularWeights(g)</td>
</tr>
<tr>
<td>Array of mass fractions (( Y_k ))</td>
<td></td>
<td>massFractions(g)</td>
</tr>
<tr>
<td>Array of mole fractions (( X_k ))</td>
<td></td>
<td>moleFractions(g)</td>
</tr>
<tr>
<td>Specific heat at constant V (( c_{v,g} ))</td>
<td>J/kg·K</td>
<td>cv_mass(g)</td>
</tr>
<tr>
<td>Specific heat at constant P (( c_{p,s} ))</td>
<td>J/kg·K</td>
<td>cp_mass(g)</td>
</tr>
<tr>
<td>Gas mixture viscosity (( \mu ))</td>
<td>Pa·s</td>
<td>viscosity(g)</td>
</tr>
<tr>
<td>Mixture thermal conductivity (( \lambda_g ))</td>
<td>W/m·K</td>
<td>thermalConductivity(g)</td>
</tr>
<tr>
<td>Binary diffusion coefficients (( D_{kl} ))</td>
<td>( 10^{-5} )m(^2)/s</td>
<td>binaryDiffCoeffs(g)</td>
</tr>
<tr>
<td>Net production rate, gas (( \dot{w} ))</td>
<td>kmol/m(^3)/s</td>
<td>netProdRates(g)</td>
</tr>
</tbody>
</table>

Similarly to the gas phase object, the surface phase object can be defined and called with Cantera expressions. Both the surface and gas phase objects are defined by the user in a .cti file that contains
all of the thermodynamic information about both the gas and surface (adsorbed) species and all of the heterogeneous and homogeneous reactions. For this work, the .cti file is comprised of the aforementioned micro-kinetic mechanism developed in the Deutschmann group by Meier et al. [1] which contains all of the pertinent adsorption, desorption and surface reactions for dry and steam methane reforming on nickel. The Deutschmann mechanism does not contain gas-phase reactions, and therefore $\omega_k = 0$.

All reactions in the mechanism are posed irreversibly meaning that a reversible reaction is given as separate forward and reverse rate equations. All reactions in the mechanism are in Arrhenius form and the rate coefficient for equation $i$ is calculated as

$$k_i = A_i T^{n_i} \exp \left( \frac{-E_i}{RT} \right)$$

(3.35)

Where $E_i$ is the activation energy, $A_i$ is the pre-exponential factor and the temperature dependency exponent is $n_i$. All parameters are defined for reaction $i$ in the micro-kinetic model from Meier et al.[1] The equilibrium constant $K_{p,i}$ is easily calculated from thermodynamic properties stored in Cantera and the conditions calculated during the execution of the model.

It is not always possible to define the Arrhenius parameters ($A$, $E$, and $n$) for a reaction. Instead, sticking coefficients are sometimes used for simple surface reactions. The sticking coefficient, $\gamma$, is defined as the probability that collisions between gas species and an active surface will result in the species remaining on the surface for some period of time. The sticking coefficient is expressed in a form analogous to that of the Arrhenius expression and is written as

$$\gamma_i = a_i T^{b_i} e^{c_i/RT}$$

(3.36)

where $a_i$ and $b_i$ are unitless and $c_i$ has units compatible with $R$. Since the sticking coefficient is a probability, it must lie between 0 and 1. Sticking coefficients are typically assumed to be relatively small ($<< 1$) such that the molecular motion of gas molecules is random near the surface and collisions are not affected by surface reactions. However, when the sticking coefficient is sufficiently high (close to one), a correction factor must be applied to account for any distortion of the molecular velocity distribution. Commonly, the Motz-Wise correction factor is applied to
the sticking coefficient to account for perturbations of the velocity field near the surface. The Motz-Wise correction can be implemented in the rate coefficient expression as

\[
k_i = \left( \frac{\gamma_i}{1 - \gamma_i/2} \right)^m \left( \frac{m}{\Gamma_\text{tot}^m} \sqrt{\frac{RT}{2\pi W}} \right)
\] (3.37)

The total surface site concentration \( \Gamma_\text{tot} \) is raised to the power \( m \) where \( m \) is the sum of all of the surface reactants’ stoichiometric coefficients [83].

User input parameters to the computational model are outlined in Table 3.2. The emissivity (\( \varepsilon \)) of Ni/YSZ is difficult to determine and there is insufficient information about this value in the literature. In a similar manner to Janardhanan and Deutschmann [86], we will assume that due to a high aspect ratio between the bed length and particle diameter (\( L/r_p \approx 100 \)) the surfaces can be treated as black bodies (\( \varepsilon = 1 \)). Properties of the catalyst including particle diameter, pore radius, porosity, tortuosity and specific catalyst area were estimated using methods that will be described in the Characterization section. The catalyst site density was taken from the value reported by the Deutschmann group [1, 86].

Table 3.2: Example user inputs to satisfy parameters in the governing equations of the PBR model.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bed length (L)</td>
<td>2.54</td>
<td>cm</td>
</tr>
<tr>
<td>Reactor radius (r)</td>
<td>1.3</td>
<td>cm</td>
</tr>
<tr>
<td>Average particle diameter (d_p)</td>
<td>300</td>
<td>( \mu m )</td>
</tr>
<tr>
<td>Pore radius (r_p)</td>
<td>250</td>
<td>( \mu m )</td>
</tr>
<tr>
<td>Porosity (( \phi_g ))</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Tortuosity (( \tau ))</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Specific catalyst area(( A_s ))</td>
<td>1080</td>
<td>( cm^{-1} )</td>
</tr>
<tr>
<td>Catalyst site density(( \Gamma ))</td>
<td>( 2.66 \times 10^{-9} )</td>
<td>mol/m²</td>
</tr>
<tr>
<td>Emissivity (( \varepsilon ))</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

A flow diagram representative of the solution algorithm for the computational model is given in Figure 3.6. An input file is first read into the model that contains the properties listed in Table 3.2, information about time start, time end and the time step, and initial values for the gas temperature, pressure, velocity, gas concentration composition, initial surface species concentrations and the
Figure 3.6: Algorithm used to take input data from the user, create solution arrays for dependent variables, and solve the system of equations.
environment temperature and area. Next, arrays for the dependent variables are initialized. The size of these arrays is equal to the number of mesh points, $n$, in the system, and each variable has its own array size $[n \times 1]$ long. The number of total dependent variables, $x$, is also calculated. An initial guess file that was written from previous solutions is then used to populate the dependent variable arrays and used as the initial value to the solver. A Jacobian matrix is generated and also fed to the solver. Iteration of the solution loop is then initiated in the range of the initial time ($t = 0$) and the final time ($t = t_{end}$) with spacing calculated from the given $\Delta t$ in the input file. The species mole fractions for the gas phase and surface coverages are then normalized to unity. The dependent variable arrays are concatenated to a single vector of size $[(n \times x) \times 1]$. This solution vector is fed to the solver (for Matlab ODE15s) which iterates within specified absolute ($1 \times 10^{-16}$) and relative ($1 \times 10^{-6}$) error tolerances. The converged solution is then written to a new "restart" file which can be fed into subsequent problems as an initial guess. The solution algorithm then restarts if the end time has not yet been reached.

### 3.3 Tubular Separated Anode System

The separated anode experiment (SAE) was designed to isolate the anode of a solid oxide fuel cell to examine the gas transport and catalytic properties without impedance from electrochemical reactions. The SAE has been described in detail in several publications where it has been implemented for a planar anode [24, 74, 87, 88]. In principle, the SAE provides a convenient, simplified system in which detailed gas transport and reforming kinetics can be modeled. In practice, implementation of the SAE can be difficult because of issues related to sealing. A schematic of the flow channels and a picture of the original SAE in the CFCC is given in Figure 3.7 [87].

The planar-type SAE shown in Figure 3.7 uses compressive force from solid, one inch diameter alumina tubes to push two halves of a gas manifold together. The compressive force is applied using a hydraulic jack that is ratcheted up after the two gas delivery plates are aligned. Each plate consists of an inlet tube, an outlet tube and a pressure tap. The design shown in Figure 3.7 has no indentation for the planar anode to sit, but as the planar SAE was developed over the years a groove for the
Figure 3.7: Picture and schematic of the original SAE in the CFCC reported by Ethan Hecht [87].
anode to sit in was implemented [74]. Mica paper was cut and placed around the anode to help sealing at high temperatures because it melts and creates a seal at reaction temperatures (700°C - 800°C). The SAE isolates a well defined geometry called a “reaction zone” that is simpler to model than the entire SOFC cell. As shown in Figure 3.8, the fuel and electrolyte diffusion through the anode is isolated to the reaction zone making the SAE a well defined system that in turn produces good results for model validation.

![Figure 3.8: Schematic of fuel and electrolyte diffusion through the SAE. (adapted from [88])](image)

The main weakness in the design of the SAE is the necessity to compress two separate plates together. This creates multiple problems including sealing the two plates together such that air does not leak into the system, cell fracture as a result of excessive compression and materials mismatch, and general difficulty with setting up an experiment. At the temperatures necessary for internal hydrocarbon reforming, air is highly reactive and can skew results. It is therefore important to seal the system against air inflow, but this was very difficult using this SAE design. Cell fracture was often incurred at the end of experiments and prevented some post-mortem analysis of the anode. Materials mismatch exacerbated the cell fracture issue because of the difference in thermal expansion between the metal gas manifold and ceramic anode. Finally, setting up an experiment added variability to the system because the mica paper had to be cut each time and may not have been cut the same every time. Further, simply aligning the anode between the plates while holding
it between the heavy alumina tubes and compressing with the hydraulic jack was unnecessarily difficult for the user.

Several modified designs of the planar SAE were proposed for this work, but none were implemented. The unused designs are shown in Figure 3.9, and are discussed briefly for posterity.

Figure 3.9: Comparison of three SAE designs: a) conventional metal SAE but using Inconel instead of stainless steel, b) conventional SAE design with alumina gas manifolds, and c) solid alumina gas delivery system.

The first design (Figure 3.9a) addresses the issue of pinhole leaks from the coupling of the gas delivery tubes (labeled “Inconel gas manifold”) and the anode holding plate. In the original SAE design, the gas delivery tubes were threaded at the end and connected to the holding plate by screwing them into tapped holes. Because of the high temperatures of the system, this design did not seal well and caused leakage of both reactants and products on both sides of the anode. The first design attempted to correct this problem by fabricating a solid gas manifold assembly with the gas delivery tubes welded onto the anode holding plate. Additionally, this solid gas delivery manifold
was made of Inconel because of issues with stainless steel (SS) degradation at reaction temperatures. Though this design in principle would work, it was never used because of the high nickel content in Inconel and SS. Because nickel was the catalyst of interest in these experiments, reactions on the gas manifold would not be delineated from reactions on the catalyst. Therefore, the metal gas manifold was scrapped in favor of an entirely ceramic design.

The second design (Figure 3.9b) mimicked the metal design, but too many added features intended to alleviate issues instead added undesired complexity. First, the single alumina pushrod was exchanged for two alumina rods on the outer part of the so-called “clamp plate”. The clamp plate acted as a stabilizer for alumina gas delivery tubes and thermocouple sheaths. The added thermocouple sheaths would have allowed temperature to be probed at two points in the gas channel on either side of the anode. However, both the alumina gas delivery tubes and the sheaths had to be connected through the clamp plate to the boron nitride gas manifold with an alumina paste. The boron nitride gas manifold was chosen because of the extremely low thermal expansion coefficient (similar to YSZ). This design was too complex and required the connection of delicate tubes to a flat surface of a non-like ceramic material.

The third and final design (Figure 3.9c) was the most promising because it reduced the complexity of the system by boring out a single piece of alumina to form the gas delivery tubes, thermocouple sheaths and the groove where the anode sits between the two manifolds. The alumina manifold was massive and would have been joined to the other manifold with an alumina paste that would have sealed well. The main issue with this design was the mass of the alumina piece which was too large to suspend in a vertical furnace. A smaller alumina manifold in a shorter furnace would have been more appropriate for this design.

Ultimately, the planar SAE design was scrapped for this work, and instead a tube-in-tube design was used to create a tubular SAE (TSAE). Tubular SOFCs have some advantages over their planar counterpart, and are possibly better suited for industrial use. Tubular cells were developed by Siemens-Westinghouse in the 1990’s and produced an advanced SOFC demonstration plant [89]. Tubular cells require less active surface area for sealing thereby reducing the number of
metal-to-ceramic seals necessary in the cell, and seal-less tubular cells have also been developed [90]. Tubular cells are less rigidly confined and therefore may suffer less thermal stress than planar cells [90, 91]. Based on these conclusions in the literature, the TSAE was developed to circumvent issues of sealing at high temperatures, cell fracture and to simplify the experimental setup.

A schematic of the tube-in-tube design for the SAE is given in Figure 3.10. The principle of the design is that an anode tube is placed in a quartz tube through a Teflon tee thereby isolating the fuel gases flowing in the anode from electrolyte gases flowing in the quartz tube. The anode is coated with non-porous electrolyte that defines a porous reaction zone in the center of the tube but is impervious to diffusion elsewhere. This creates an analogous SAE wherein only a well defined reaction zone participates in the heterogeneous reactions and gas diffusion through the anode.

![Figure 3.10: Schematic of the tubular SAE tube-in-tube design.](image)

### 3.3.1 TSAE Catalyst Materials

The method for synthesizing the tubular anodes was discussed in the PBR Catalyst Materials section, and all tubular anodes were purchased from CoorsTek Inc. To accurately mimic the planar SAE, the tubular anodes were dip coated with a thin film of non-porous electrolyte and then sintered.
at 1550°C in air. The length of the effective reaction zones created by dip coating the cell with non-porous electrolyte was varied between 0.25 inches to 2 inches in length to allow for a variety of experimental conditions. A schematic of the dip coated cells is given in Figure 3.11.

![Figure 3.11: Picture of the different reaction zone lengths achieved by dip coating Ni/YSZ tubular anodes in a non-porous electrolyte solution.](image)

### 3.3.2 TSAE Experimental Apparatus

A schematic of the TSAE is given in Figure 3.12. The TSAE system is similar to the PBR system described in the PBR Experimental Apparatus section in that the heart is the reactor suspended in a resistively heated furnace (ATS) with a bank of mass flow controllers (MKS Instruments) that deliver gas to the system. The tube-in-tube reactor consists of two custom made Teflon tees that have been bored such that the 10 mm o.d. anode can fit through them. Because the anode is sometimes not perfectly straight as a result of the hang firing, care must be taken to ensure it doesn’t fracture while connecting it to the tees. The branch of the tees is where the electrolyte gas flows through the 15 mm o.d. quartz outer tube. Electrolyte gases diffuse through the anode to react with fuel gases which flow through the anode itself through a 10 mm to 0.25 inch Teflon reducing union. Similar to the PBR experimental apparatus, all sulfur containing gases are flow to and from the reactor in either Teflon tubing, fittings and valves or in SS tubing, fittings and valves that have been coated with Sulfinert®. Steam is generated in the same was as the PBR experimental apparatus and introduced through heated stainless steel capillary tubing. Water is metered using a peristaltic pump (Instech) which has been calibrated so that the water flow rate is known for the pump tubing used. Both the
fuel-side and electrolyte-side product streams are passed through separate condensers cooled with recirculating chilled water (Solid State Cooling Inc.). The permanent gases are alternately sampled using a MKS Cirrus mass spectrometer. Argon is used as a tracer for the MS, and the peaks of the permanent gases of interest are normalized to the argon peak.

3.4 Model of the Tubular Separated Anode Experimental System

The approach for modeling the TSAE comes from work done by Zhu and Kee [73] to model the planar SAE. The principle behind the planar SAE model is that the SAE creates two well defined channels for the fuel and electrolyte streams that are in close contact with the anode on either side. Gas is transported through the anode via a combination of Fickian and Knudsen diffusion with
convective Darcy flow which are collectively modeled as so-called “dusty gas” (DGM) [73]. As the fuel gas moves through the porous anode, heterogeneous reactions between the active metal on the anode (e.g. Ni) can occur and are modeled using the same micro-kinetic mechanism used for the PBR case. The flow in each of the fuel channels is assumed to be one-dimensional, laminar and have no variation in the gas composition along the direction of flow. Since the planar anode is in Cartesian coordinates, flow is in the x-direction and diffusion through the anode is in the y-direction. The same assumptions hold for the TSAE because the annular area between the quartz tube and anode is less than 1 cm. As shown in the control volume for the TSAE in Figure 3.13, flow is the z-direction along the anode and diffusion is through the anode in the r-direction.

![Figure 3.13: Control volume for the TSAE. The fuel gas flows into the anode while the electrolyte-like gas (air or steam) flows on the outside of the anode in an annulus created by the outer quartz tube.](image)

### 3.4.1 TSAE Governing Equations

The governing equations for this system can be derived from the force and energy balances done on the control system shown in Figure 3.13. However, to ensure consistency with the planar SAE, the TSAE governing equations are adapted from the tubular implementation of an anode supported
membrane-electrode assembly (MEA) whole SOFC cell developed by Zhu and Kee [91]. The computational model is split into two main parts to simplify the numerical algorithm for solving the system: 1) gas flow in the channels or annuli and 2) transport and heterogeneous chemistry through the porous anode or MEA. As was done for the PBR, homogeneous chemistry is not included in this system because contributions from methane pyrolysis at temperatures below 900°C are negligible. Because of this, no chemistry occurs in the annuli and the model does not include a source term to account for chemistry.

3.4.1.1 Flow in the annuli

Because the gas-phase flow in the fuel and air annuli is one-dimensional, only flow in the \( z \)-direction is considered and variations in the radial direction are neglected. This is gas flow in a tube with no radial variations and therefore the plug flow approximation holds. The species mass continuity, overall mass continuity, and momentum equations, respectively, are simplified to

\[
\frac{\partial (\rho Y_k)}{\partial t} + \frac{\partial (\rho Y_k u)}{\partial z} + \frac{\partial j_k}{\partial z} = -\frac{P_h}{A_c} J^M_k W_k \tag{3.38}
\]

\[
\frac{\partial \rho}{\partial t} + \frac{\partial (\rho u)}{\partial z} = -\frac{P_h}{A_c} \sum_{k=1}^{K_g} J^M_k W_k \tag{3.39}
\]

\[
\frac{\partial (\rho u)}{\partial t} + \frac{\partial (\rho u^2)}{\partial z} = -\frac{\partial p}{\partial z} - \frac{P_h}{A_c} \tau_w \tag{3.40}
\]

Where \( u \) is the mean velocity, \( p \) is the pressure in the annulus, and \( K_g \) is the total number of gas phase species. The cross-sectional flow area, \( A_c \), is calculated using the inner tube diameter, \( D \), as \( A_c = \pi D^2/4 \). The hydraulic perimeter, \( P_h \), is calculated as \( P_h = \pi D \). The wall shear stress, \( \tau_w \), is calculated from a friction factor, \( f \), given as \( f = 2\tau_w/\rho u^2 \). For the circular anode channel, the friction factor is estimated based on laminar, fully developed flow as \( Re f = 16 \). The Reynolds number, \( Re \) is defined in equation 3.14. The gas density, \( \rho \), is determined from a perfect gas equation of state which is calculated using Cantera. Thus far, this model takes into account axial convective transport only and does not consider axial diffusion. For simplicity, it is assumed that a sufficiently large mesh and small \( dz \) is used in this case to warrant an assumption that there are no contributions...
3.4.1.2 Transport and chemistry in the porous anode

Gas molar fluxes evolved from the internal reforming occurring on the anode are represented as $j_k^M$ and are determined by calculating the flux through the anode in the radial direction. This is the variable that connects the gas-phase flow described in the previous section with the radial, porous-phase flow described in this section. Axial and azimuthal changes in temperature, pressure, velocity and species concentration within the porous anode are neglected for this model based on the assumption that $dz$ is sufficiently small and the anode is sufficiently thin ($< 1$ cm). In cylindrical coordinates, radial transport and heterogeneous chemistry are modeled in the overall and species mass continuity equations given as

$$\frac{\partial (\phi \rho Y_k)}{\partial t} + \frac{\partial j_k^M}{\partial r} = A_s \dot{s}_k W_k \tag{3.41}$$

$$\frac{\partial (\phi \rho)}{\partial t} + \sum_{k=1}^{K_g} \frac{\partial j_k^M}{\partial r} = \sum_{k=1}^{K_g} A_s \dot{s}_k W_k \tag{3.42}$$

As can be seen from the overall and species mass continuity equations for the TSAE, this system is very similar to the governing equations used in the PBR computational model. The molar mass flux, $j_k^M$, through the porous anode is calculated using the DGM presented in section PBR Governing Equations using equations 3.5 to 3.8. A detailed description of the full DGM and its implementation in a system likes this is given in an earlier paper by Zhu et al. [73].

The implementation of heterogeneous chemistry in the porous anode is identical to the PBR using a micro-kinetic mechanism from Maier et al. [1] for methane steam and dry reforming on a nickel catalyst described in section PBR Governing Equations. The net production rates for heterogeneous reactions are calculated using Cantera.

3.4.1.3 Energy balance equations for the whole system

Similarly to transport in the TSAE, separate energy balances are implemented for the gas-phase flow in the annulus and diffusion through the porous anode. The energy balance in the porous anode
is the same as presented in section PBR Governing Equations. The energy conservation equation is

$$\frac{\partial E}{\partial t} + \frac{\partial q}{\partial z} = -\frac{p_h}{A_c} (q^T + Q^M) \quad (3.43)$$

where the $E = \rho e$ and $e$ is the specific internal energy of the gas. The heat flux $q$ represents both axial heat conduction and gas-phase species transport and is written as

$$q = -\lambda_g \frac{\partial T}{\partial z} + \sum_{k=1}^{K_g} (\rho Y_k u + j_k) h_k \quad (3.44)$$

Between the tube and the porous anode, the convective heat flux can be calculated as

$$q^T = h_{conv} (T - T_m) \quad (3.45)$$

where $T_m$ is the temperature at the porous anode tube-wall. The energy transport associated with the mass transfer between the annular flow and the porous anode is represented as $q^M$ which is calculated as

$$q^M = \sum_{J_k^M > 0} J_k^M W_k h_k(T_a) + \sum_{J_k^M < 0} J_k^M W_k h_k(T_m) \quad (3.46)$$

where $T_a$ is the temperature in the porous anode. The heat-transfer coefficient in the tube, $h_{conv}$, is calculated using the Nusselt number correlation

$$Nu = \frac{h_{conv} D}{\lambda} \quad (3.47)$$

For laminar flow in a circular channel, the Nusselt number is calculated from the relation

$$Nu = 3.657 + 6.874 \left( \frac{1000}{Gz} \right)^{-0.488} \exp \left( \frac{-57.2}{Gz} \right) \quad (3.48)$$

where the Graetz number is calculated as $Gz = Re Pr D / \zeta$.

Though the energy balance for the TSAE system is presented here, care was taken to synthesize a reaction zone that is sufficiently short such that it is within the so-called “isothermal” zone of the furnace. This allows for the energy equations to be ignored for this system.
3.4.2 TSAE Numerical Algorithm

The MOL algorithm is used to solve the system of equations developed for the TSAE system, and the system is accordingly discretized. The flow diagram for the computational model is given in Figure 3.14, and it is roughly the same as the architecture given in Figure 3.6 for the PBR computational model. The input file reading, initial guess and Jacobian initiation steps are identical for both codes so they are omitted in Figure 3.14. Though the method for creating arrays for the dependent variables is the same, the solution vector for the TSAE includes contributions from both “sub-models” (gas flow and porous anode) developed in the TSAE Governing Equations section.

![Flow diagram of the TSAE computational model code.](image-url)

- **Start Iteration**
  - for \( t_{\text{beg}} \) to \( t_{\text{end}} \)
- **Normalize**
  - \( \sum Y_k = 1 \)
  - \( \sum \tilde{Y} = 1 \)
- **Move arrays to vector**
- **Begin ODE15s**
- **[CONVERGE]**
- **Write Solution**
- **[NO]** \( t = t_{\text{end}}? \)
- **[YES]** STOP

**Solution vector:**

\[
\begin{bmatrix}
(T_{m}, u, \rho, Y)_{e,1}, (T_{a}, \rho, Y, \theta)_{a,1}, \ldots,
(T_{a}, \rho, Y, \theta)_{a,M}, (T_{m}, u, \rho, Y)_{f}
\end{bmatrix}
\]

- \( e \) is the gas-phase electrolyte flow
- \( a \) is transport through the anode
- \( f \) is the gas-phase fuel flow
- \( M \) is the \( y \) grid points in the \( r \) direction.

Figure 3.14: Flow diagram of the TSAE computational model code.
The solution vector is first populated with the temperature \( T_m \), pressure, velocity and species concentrations \( Y \) from the electrolyte (air/steam) side of the anode (denoted with subscript \( e \) in Figure 3.14). Next, the anode temperature \( T_a \), the density, species compositions and site densities \( \theta \) are inserted into the solution vector for \( (1 - M) \) where \( M \) is the number of radial mesh points. Finally, the gas-phase flow properties for the fuel inside the anode are populated in the solution vector (denoted with subscript \( f \) in Figure 3.14).

After the solution vector is populated with the current values, it is fed to the stiff equation solver (ODE15s) and iterates until a solution is found. The solver steps through the functions such that the two sub-models are solved sequentially. First, the gas flow properties are “frozen” while functions for the porous anode are called and solved to produce the molar flux solution, \( j_k \). Next, the molar flux is frozen and the gas flow equations for both the electrolyte and fuel side are called and solved to produce values for the temperatures, pressures, densities, and molar composition of each gas stream. The system is solved for the entire length of the reaction zone which is provided by the user at the start of the program.

The initial and boundary conditions for transport and chemistry in the porous anode are the same as those presented in the Initial and Boundary Conditions section. For the gas-phase flow model developed here, the overall and species mass continuity equations are nonhomogenous and hyperbolic and therefore need one initial condition and one boundary condition. The initial conditions are given for the gas composition, temperature, velocity and pressure at \( t = 0 \). At the boundary between the porous anode and the external gas flow (fuel or air), the gas-phase composition is assumed to be equal to the composition inside the annulus. Additional user inputs include the number of mesh points in the radial and axial direction, the length of the reaction zone, the thickness of the anode, and relative and absolute error tolerances. All of the catalytic properties presented in Table 3.2 are the same for the TSAE anode. Time bounds and the size of the time step are also provided to the TSAE model as in the PBR model.
CHAPTER 4
EVALUATION OF THE PHYSICAL AND CHEMICAL PROPERTIES OF THE CATALYSTS

Catalyst characterization is important for understanding the fundamental physical and chemical properties of a catalyst, which can then be used to compare catalysts on a normalized basis. Because the electrochemical and catalyst communities are often disconnected, full characterization of the catalytic properties of Ni/YSZ are often unreported. This section presents characterization done as a part of this thesis, and collects and summarizes characterization of Ni/YSZ done as parts of other studies. This section also reports characterization results for the commercial steam reforming catalyst used for comparison to Ni/YSZ which was provided by Süd Chemie.

4.1 Characterization Methods

The catalyst surface area is an important measurement for comparison of catalysts, and it can either indicate the relative total surface area of the catalyst and the total active surface area. The total surface area of a catalyst is typically calculated from an isotherm produced by physical adsorption (physisorption) of well defined amounts of a probe molecule on the surface of the catalyst at liquid nitrogen temperatures (77 K). During this procedure, the catalyst is dosed with successive known volumes of the probe molecule and the equilibrium pressure is measured using a high resolution pressure transducer. The result is an adsorption isotherm that can be used to find the surface area.

One of the most widely used methods for calculating the total catalyst surface area from a physisorption isotherm is the Brunauer-Emmett-Teller (BET) surface area, which can be calculated from equation 4.1.

\[
\frac{1}{W((p/p_o) - 1)} = \frac{1}{W_mC} + \frac{C - 1}{W_mC} \left(\frac{p}{p_o}\right) \\
\]

In the BET equation, \(W\) is the weight of the gas adsorbed, \(p/p_o\) is the relative pressure, \(W_m\) is the weight of the adsorbate as a monolayer, and \(C\) is the BET constant. The left hand side of equation 4.1 is plotted against the relative pressure to find the slope of the line \((m)\) and y-intercept \((i)\). It is
necessary to evaluate the adsorption isotherm in the linear region which typically falls in the range of \(0.05 < \frac{p}{p_o} < 0.35\). The total surface area \(S_T\) of the catalyst is calculated from equation 4.2 using a parameter \(W_m\) calculated from the slope and intercept that is found from the graph of the left hand side of equation 4.1 vs the relative pressure.

\[
S_T = \frac{W_m N_A A_{cs}}{M} \quad (4.2)
\]
\[
W_m = \frac{1}{m+i} \quad (4.3)
\]

In equation 4.2, \(N_A\) is Avogadro’s number, \(M\) is the molecular weight of the adsorbate, and \(A_{cs}\) is the cross-sectional area of the adsorbate molecule. For this work, nitrogen physisorption isotherms were collected using a Quantachrome Quadrasorb SI instrument using ultrahigh purity nitrogen (99.999%, Airgas). Prior to obtaining the isotherms, the catalysts were first degassed at 250°C under vacuum (30 mTorr) for 24 hours. Catalysts are degassed in order to discharge strongly bound water and other environmental contaminants from the catalyst surface. Following degassing, the catalysts were cooled to room temperature under a flow of ultrahigh purity helium (99.999%, Airgas). Because the catalysts were degassed in the sample cell used for physisorption, there was minimal exposure of the sample to the atmosphere while transferring from the degassing unit to the Quadrasorb.

The active metal surface area can be found from chemisorption (chemical adsorption) of an adsorbate that chemically bonds to active sites on the catalyst. The number of exposed active sites can then be calculated from the total uptake of the adsorbate which is calculated from an adsorption isotherm. Physisorption is the weak, reversible binding of an adsorbate to the catalyst surface whereas chemisorption creates strong, irreversible bonds. A catalyst surface by definition consists of sites that differ in binding nature, and as a result of this the interaction between an adsorbate and different parts of the surface can result in either physisorption or chemisorption. The result of this is a combination of physisorption and chemisorption which can give inaccurate results for the active metal surface area. To avoid this, computational methods are used to differentiate so-called “weak” adsorption from “strong” adsorption parts of the combined isotherm.
The “bracketing” or dual isotherm method was used in this work to eliminate contributions of physisorption to the overall isotherm. A schematic of the bracketing method is shown in Figure 4.1 which depicts the initial “combined” (C) adsorption isotherm, the weak (W) isotherm which represents physical adsorption only, and the strong (S) isotherm which shows chemical adsorption only. The bracketing method is carried out by evacuating the sample at room temperature after measuring the initial combined isotherm at the adsorption treatment temperature (40°C). This evacuation at lower temperature will remove weakly bound molecules, but will not remove molecules that are chemically adsorbed. After removing all weakly bound molecules but retaining the strongly bound molecules, another isotherm is taken at treatment temperature. Because all of the active sites are already bound by adsorbate molecules, the change in pressure accounts only for the weakly bound molecules thereby creating a “weak” isotherm. This weak isotherm can be subtracted from the original total isotherm (which includes weak and strong interactions) to yield a “strong” isotherm. This strong isotherm only accounts for chemisorption on the catalyst, and can be used to find the total uptake of adsorbate.

Figure 4.1: Schematic of an adsorption isotherm with the combined (C) isotherm which is the sum of the weak (W) isotherm which represents physical adsorption and strong (S) isotherm which represents chemical adsorption.
Hydrogen was used as the probe molecule for measuring the active surface area on the nickel catalysts. The active surface area on nickel was measured using two different devices and protocols. The first was a Micromeritics ASAP 2020 unit. Samples were reduced to metallic nickel in situ, and then cooled to the adsorption temperature (40°C) and dosed in 100% hydrogen for 120 minutes. Samples were then ramped in argon from adsorption temperature to 850°C at 10°C/min and the desorption of hydrogen was measured using a thermal conductivity detector (TCD). The total hydrogen uptake of each catalyst was calculated from the TPD spectra by integration. The second device used to find the active nickel surface area was a Quantachrome Autosorb-1C. Prior to analysis, samples were dried at 120°C in ultrahigh purity He (99.999%, Airgas) for one hour and then ramped to 850°C and held for one hour in 100% ultrahigh purity H₂ (99.9999%, Air Liquide). It was then cooled to adsorption temperature (40°C) and dosed with H₂ for 30 minutes. Using the bracketing method to find the chemisorption isotherm, the pressure-volume data for both the combined (C) and the weak (W) isotherms are plotted. For the bracketing method to be valid, these isotherms must be parallel. If this is the case, then the difference between C and W at any pressure is \( V_m \). Using this value for the uptake volume of hydrogen, which is reported at standard temperature and pressure (STP), the molar uptake of hydrogen can be calculated from equation 4.4.

\[
N_m = \frac{PV_m}{RT} = 44.61 \times 10^{-5} V_m (cc_{STP}/g) \tag{4.4}
\]

After finding the molar uptake of hydrogen, a number of properties for the catalyst can be calculated. The active metal (nickel for this work) surface area is calculated as:

\[
SA_{Ni} = N_m A_m \tag{4.5}
\]

where \( N_m \) is the number of adsorbed hydrogen molecules, \( S \) is the number of surface atoms covered by each chemisorbed molecule, and \( A_m \) is the cross-sectional area occupied by each active site. The stoichiometry factor (\( S \)) for H₂ on nickel is taken to be 2 because H₂ dissociatively adsorbs on nickel thereby taking up two surface sites with one molecule. Because the active metal is nickel, the cross-sectional area of an active site is defined as one atom of nickel. The metallic radius of nickel is 1.24 x 10⁻¹⁰ m, and the cross-sectional area is 4.83 x 10⁻²⁰ m². Data were not collected for
Ni/K$_2$O–CaAl$_2$O$_4$ using the Quantachrome Autosorb-1C. Because of this, only data taken using the Micromeritics ASAP device is used for comparison of the active metal surface areas between Ni/YSZ and Ni/K$_2$O–CaAl$_2$O$_4$.

Also from hydrogen uptake data, the catalyst dispersion can be calculated. Davis and Davis describe the metal dispersion as the ratio of exposed metal atoms to the total metal atoms in the catalyst sample [77]. The dispersion can be calculated from equation 4.6, where the total number of Ni atoms in the sample can be found by multiplying the percent loading of the active metal by the total mass of the catalyst sample and dividing by the molecular weight of the metal.

$$d = \frac{SN_m}{\text{Total number of Ni atoms}}$$

(4.6)

An estimate of the particle size of the active metal sites can be found by taking the inverse of the dispersion. The particle size of metallic nickel can also be found from x-ray diffraction (XRD) measurements. X-ray diffraction is a technique that involves the elastic scattering of x-rays off of the surface of a sample. The scattered x-rays that are in phase give constructive interference. Bragg’s law (equation 4.7) can be used to calculate the distance between lattice spacings when the wavelength of the x-rays ($\lambda$), the distance between two lattice planes ($d$), and the angle between x-rays and the sample ($\theta$) is known [50]. In a typical XRD apparatus, the angle is changed in increments determined by the user, and the diffraction patterns are measured.

$$n\lambda = 2d\sin\theta; \ n = 1, 2, \ldots$$

(4.7)

For this work, powder x-ray diffraction (XRD) spectra were taken with a Rigaku Ultima IV with Cu-K$_\alpha$ radiation at 40 kV in the range of 20° to 80° 2θ. Crystalline peaks were matched with pure spectra of the components of each catalyst using the International Center for Diffraction Data (ICDD) database. Nickel particle sizes were found using the XRD software. Studies on the growth of Ni particles during reduction were done using the same XRD fitted with a hot stage for the sample mantle and equipped with a gas manifold for flowing reducing gases. Using this equipment, temperature programmed reduction (TPR) studies in the temperature range of 25°C to 800°C were done in situ and XRD spectra were taken during TPR at set intervals (e.g. every 50°C).
4.2 Characterization Results

Very few studies on Ni/YSZ report the total surface area, active metal surface area, hydrogen uptake and/or metal dispersion. These are important values to report because they make it possible to assess the reforming rates on a normalized basis which allows for the direct comparison of Ni/YSZ to other catalysts. Because the synthesis methods for Ni/YSZ can be dramatically different from study to study, it is especially important to report these values when assessing Ni/YSZ for hydrocarbon reforming activity. Differences in sintering temperature have been shown to play a role in Ni particle size, which can effect the active metal surface area [92]. These differences in preparation method necessitate a comparison of the physical and chemical properties between SOFC anodes and traditional Ni-based catalysts.

As mentioned in the previous section, the active nickel surface area was measured using two different instruments. The active metal surface area for Ni/YSZ was evaluated using the Quantachrome Autosorb-1C at different reduction ramp rates. The results for this study showed a clear correlation between the active metal surface area and the reduction ramp rate: at 1°C/min $SA_{Ni} = 0.19 \text{ m}^2/\text{g}$, at 3°C/min $SA_{Ni} = 0.17 \text{ m}^2/\text{g}$, and at 10°C/min $SA_{Ni} = 0.16 \text{ m}^2/\text{g}$. These numbers are different from the value obtained using the Micromeritics ASAP machine which gave $SA_{Ni} = 0.064 \text{ m}^2/\text{g}$ for a reduction ramp rate of 10°C/min. The difference between the values for $SA_{Ni}$ between the devices is the result of systematic error (constant for each device) and differences in the chemisorption protocol. Each device has some self-consistent systematic error that can contribute to differences device-to-device, but this systematic error should be relatively small. The greater source of error for these measurements stems from the differences in the methods used. For the Micromeritics, a temperature programmed desorption for H$_2$ was done and the area under the curve (of TCD data) was integrated to find the amount of hydrogen uptake. This method is fundamentally different from the Autosorb method which uses vacuum to treat the samples, high precision pressure measurements, and volume dosing to generate isotherms that are then evaluated to determine hydrogen uptake. Because we did not have the resources to measure Ni/K$_2$O—CaAl$_2$O$_4$ using the Autosorb apparatus, it is necessary to compare the active metal surface areas for both
catalysts taken from the Micromeritics apparatus. However, because the reduction ramp used to make measurements of \( \text{SA}_{\text{Ni}} \) with the Autosorb is closer to the experimental conditions, these values are used in the computational model, which does not consider \( \text{Ni/K}_2\text{O–CaAl}_2\text{O}_4 \).

The nickel loading, BET surface area, dispersion data, and active metal surface area are listed in Table 4.1 for the catalysts evaluated in this study (Ni/YSZ and Ni/\( \text{K}_2\text{O–CaAl}_2\text{O}_4 \)) and for Ni/YSZ catalysts studied in literature. The Ni/YSZ catalyst used in this work has a much lower BET surface than the commercial catalyst (Ni/\( \text{K}_2\text{O–CaAl}_2\text{O}_4 \)) indicating that it is much less porous. Somewhat surprisingly, the BET SA for the other Ni/YSZ catalysts are much higher than was measured in this work. This could be a function of the YSZ precursor, the synthesis method, or the sintering temperature. Triantafyllopoulos and Neophytides used a sol-gel method to synthesize Ni/YSZ starting from zirconium tetra-\( n \)-butoxide, yttrium nitrate hexahydrate, and nickel nitrate hexahydrate precursors [93]. After synthesis, the mixture was calcined in \( \text{O}_2/\text{He} \) at 850°C. Importantly, this catalyst was never sintered at a high temperature (e.g., 1400°C) and was never pressed into an SOFC anode-type shape. The synthesis method used here is the same as is commonly used to make Ni-based catalysts, and therefore may have effected the reactivity of the nickel particles. Bebelis et al. synthesized Ni/YSZ using Zircar YSZ powder (8% \( \text{Y}_2\text{O}_3 \)) and nickel nitrate precursors in a slurry that was then deposited onto a YSZ disk and calcined in air at 1500°C for 1 hour [94]. The reported BET SA in Table 4.1 is for the Zircar YSZ powder precursor. As can be seen from Table 4.1, even though the BET surface area of the support materials is high, the active metal surface area for the sintered samples (Bebelis and this work) is low. For catalysts calcined at low temperatures (Ni/\( \text{K}_2\text{O–CaAl}_2\text{O}_4 \) and Ni/YSZ [93]), the active metal surface is much higher than those prepared by traditional SOFC anode methods (Ni/YSZ this work and [94]). This is a clear indication that sintering at high temperatures cause significant nickel migration which results in large nickel particles that have a low active surface area. The metal dispersion is the ratio of accessible nickel to total nickel in the catalyst. Because the catalyst made by Bebelis et al. has a very high nickel loading, the dispersion is lower than any other catalyst. This is another indication of the effect of sintering which causes nickel mobility on the surface to agglomerate and form large
nickel “islands” that have very low active surface area.

Table 4.1: Metal loading, BET surface area, hydrogen uptake calculated from H_2-TPD, and dispersion of catalysts used in this work (Ni/YSZ and Ni/K_2O–CaAl_2O_4) and from literature.

<table>
<thead>
<tr>
<th>Metal Loading (wt%)</th>
<th>BET SA^a (m^2/g)</th>
<th>d^b (%)</th>
<th>Active SA (m^2/g)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/K_2O–CaAl_2O_4</td>
<td>20</td>
<td>9.7</td>
<td>0.892</td>
<td>0.878</td>
</tr>
<tr>
<td>Ni/YSZ</td>
<td>46</td>
<td>0.8</td>
<td>0.028</td>
<td>0.064</td>
</tr>
<tr>
<td>Ni/YSZ</td>
<td>50</td>
<td>11.6</td>
<td>0.683</td>
<td>1.693</td>
</tr>
<tr>
<td>Ni/YSZ</td>
<td>70</td>
<td>14^c</td>
<td>0.0012</td>
<td>0.0025</td>
</tr>
</tbody>
</table>

^a Surface area (SA)
^b Dispersion (d) calculated from equation 4.6
^c BET SA reported for the YSZ precursor not the whole anode

The XRD spectra for the fresh, untreated and unreduced catalysts evaluated in this work are shown in Figure 4.2. The NiO peaks labeled in the spectra indicate a difference in particle size between Ni/YSZ and Ni/K_2O–CaAl_2O_4. Comparing the peak at approximately 44°, the Ni/YSZ peak is sharp in contrast to the Ni/K_2O–CaAl_2O_4 peak which is wider at the base. Sharp peaks indicate larger particles and this is confirmed by calculation of the particle size using the Scherrer equation which shows the NiO particle size to be approximately 65 nm for Ni/YSZ and 25 nm for Ni/K_2O–CaAl_2O_4. Other peaks in the two XRD spectra were confirmed to be from the support. Note that no metallic nickel is present in these samples because they are unreduced and therefore all of the nickel is in the form NiO as a result of the calcination treatment.

A comparison of particle diameters of nickel oxide for catalysts from this work and catalysts from other studies is given in Table 4.2 for multiple measurement methods. The particle size of Ni supported on YSZ is often estimated in the literature to be 1-4 µm, and the values shown in Table 4.2 agree fairly well [67, 92, 95, 96]. There is a large discrepancy for catalysts from this work and from Triantafyllopoulos between the particle sizes measured from XRD and the dispersion. This may be caused by the limitation of inherent instrumental broadening in the diffractometer for the large particle sizes (> 1 µm) present in these samples [97]. Because of this, it is important to
Figure 4.2: XRD spectra for fresh Ni/YSZ and Ni\(_2\)O\(_{-}\)CaAl\(_2\)O\(_4\) with labeled NiO peaks (■). All of the other peaks in the spectra are from support materials.

be careful when comparing Ni/YSZ particle sizes and ensure that the measurement methods are comparable. This discrepancy is further evidence that more careful measurements of the Ni/YSZ catalytic properties should be measured and reported.

Table 4.2: Particle diameter (\(\mu m\)) of NiO particles on fresh Ni/YSZ measured either by XRD, SEM or dispersion.

<table>
<thead>
<tr>
<th>Diameter of NiO Particles ((\mu m))</th>
<th>XRD</th>
<th>SEM/TEM</th>
<th>Dispersion (a)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(<em>2)O(</em>{-})CaAl(_2)O(_4)</td>
<td>0.025</td>
<td>0.11</td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td>Ni/YSZ</td>
<td>0.065</td>
<td>3.57</td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td>Ni/YSZ</td>
<td>0.019</td>
<td>0.15</td>
<td>Triantafyllopoulos [93]</td>
<td></td>
</tr>
<tr>
<td>Ni/YSZ</td>
<td>1</td>
<td>83.33</td>
<td>Bebelis [94]</td>
<td></td>
</tr>
</tbody>
</table>

\(a\) Reciprocal of dispersion gives an estimation for the particle size.

A study by Ribeiro et al evaluated the change in NiO particle size as a result of calcination temperature (600\(^{\circ}\)C, 800\(^{\circ}\)C, 1000\(^{\circ}\)C) [98]. The results for the change in NiO crystallite size as measured by XRD is shown in Figure 4.3, and measurements were taken on samples made either by co-precipitation or a combustion method which heated the sample to 650\(^{\circ}\)C in the presence of
urea. The results show a clear relationship for both synthesis methods between the NiO crystallite site and the calcination temperature. TPR results of the catalysts evaluated in this study showed that the reduction features changed shape and the reduction temperature changed with increasing calcination temperature. The authors did not provide data on the area under the TPR curves, which would have been useful for comparison of the catalytic activity.

![Figure 4.3: Change in NiO particle size with respect to the calcination temperature (600°C, 800°C, 1000°C) for two preparation methods for Ni/YSZ reported by Ribeiro et al [98].](image)

The change in particle size of NiO and metallic Ni during hydrogen reduction was evaluated using *in situ* XRD. Though the particle size for XRD is not always comparable to particle sizes reported from SEM imaging or dispersion calculations, when compared with other XRD particle sizes this tool is useful for determining how strongly reduction effects the particle size. For the *in situ* XRD, the temperature was ramped at a rate of 10°C/min and spectra were taken every 100°C. The XRD spectra from the *in situ* reduction are shown in Figure 4.4 and demonstrate that the onset of reduction is between 300°C and 400°C. This was confirmed by a temperature programmed reduction study (TPR) that demonstrated that there are two main reduction features for the Ni/YSZ catalyst used for this study: the first, smallled feature at 280°C and the second much larger feature at 380°C. Results shown in Figure 4.4 indicate that even at 800°C, the 37.25 reflection indicates that
NiO is not completely reduced under these conditions. A longer reduction (4 hours) under these conditions was found to completely eliminate the NiO peak.

Figure 4.4: XRD spectra for the *in situ* reduction of Ni/YSZ in hydrogen from room temperature to 800°C.

The effect of reduction on the metallic nickel particle size was evaluated from the data shown in Figure 4.4. Results from the estimation of the particle size growth during *in situ* reduction of Ni/YSZ are shown in Figure 4.5 for the metallic nickel peak at 51.85° and the NiO peak at 37.25°. The NiO particle size is constant from room temperature up to approximately 600°C where a shift seems to occur between the NiO and Ni particles. At this temperature the particle size of
NiO remains large, but becomes unstable. The metallic nickel particle grows in size linearly from 300°C to 600°C, and then jumps to greater than 600 Å with 200°C. At 800°C, the metallic Ni particle reaches a stable size of approximately 700Å and does not grow during the remainder of the reduction. This indicates that reduction itself is probably not the driving factor for metallic nickel particle size growth or sintering. Instead, the change in temperature drives the increase in particle size.

![Particle sizes of NiO and Ni](image)

Figure 4.5: Particle sizes of NiO and Ni that were measured using *in situ* XRD reduction spectra from room temperature to 800°C.

The effect of ramp rate during reduction on the Ni/YSZ crystallite size was examined by evaluating ramp rates of 1°C/min, 3°C/min and 10°C/min during reduction. The results are shown in Figure 4.6 and indicate that high ramp rates produce higher nickel particle sizes. An order of magnitude increase in the ramp rate (1°C/min to 10°C/min) increases the final nickel particle size by more than 23%. This indicates that the reduction of the Ni/YSZ catalyst should be very slow in order to maintain as low of a nickel particle size as possible. As a result of this, prior to reforming experiments, Ni/YSZ was ramped a 1°C/min and held at 650°C and then 800°C to ensure the
complete reduction of NiO. This reduction protocol was repeated prior to all analyses of Ni/YSZ to ensure that the catalyst was in the same physical state. The reduction profiles with respect to temperature were evaluated prior to each reforming experiment, and they confirmed that the catalyst hydrogen consumption was similar in all cases.

Figure 4.6: Increasing the ramp rate during reduction increases the final nickel particle size.

Results from the characterization of Ni/YSZ demonstrate the strong correlation between synthesis method and the activity for reforming on Ni/YSZ. The catalysts used in this work are a tubular Ni/YSZ anode that has been calcined at a high temperature (> 1400°C) and a commercially available nickel-based catalyst that has been made by typical catalyst synthesis methods which do not typically involve high temperature treatment. Though Ni/YSZ has a higher nickel loading, it has about 14 times lower active nickel surface area than the commercial catalyst which has nearly half the total nickel. This could be the result of a large difference in the nickel particle size between the catalysts. Comparison to data for Ni/YSZ in the literature confirms that the synthesis method affects the particle size, and that larger nickel particles tend to have hydrogen uptake which indicates that they have lower active nickel surface area.
CHAPTER 5
COMPARISON OF H₂S, SO₂, AND COS POISONING ON Ni/YSZ AND Ni/K₂O–CaAl₂O₄
DURING SMR AND DMR

A systematic comparison of sulfur poisoning on Ni/YSZ and Ni/K₂O–CaAl₂O₄, a commercially available reforming catalyst, demonstrated the heightened and rapid degradation of Ni/YSZ methane reforming activity. Ni/K₂O–CaAl₂O₄ has nearly 15 times the hydrogen uptake capacity of Ni/YSZ which implies a difference in active nickel area. Because of this difference in active nickel surface area, Ni/K₂O–CaAl₂O₄ was diluted in pure α-Al₂O₃ to achieve the same active nickel surface area as Ni/YSZ. The turnover frequencies (TOF) for steam methane reforming without sulfur on Ni/YSZ and Ni/K₂O–CaAl₂O₄ were similar, although there was some deactivation on Ni/K₂O–CaAl₂O₄ possibly as a result of coking which was observed visually. Sulfur deactivation on both catalysts was examined for H₂S, SO₂, and COS at concentrations of 1, 3, and 5 ppm. Ni/YSZ deactivated rapidly to an activity close to zero. Ni/K₂O–CaAl₂O₄ deactivated quickly in the first 20 minutes, but then reached a non-zero steady state activity. The relative deactivation rates for the sulfur species examined were COS > SO₂ ≥ H₂S. Reaction temperatures of 650°C, 750°C, and 800°C were evaluated, but temperature did not strongly affect deactivation rates strongly for either catalyst. The overarching result of this study is that Ni/YSZ methane reforming activity is more sensitive to sulfur deactivation than a commercial reforming catalyst. The effect is so strong, that the use of Ni/YSZ with any hydrocarbon fuel may require removal of sulfur to sub-ppm levels.

The work presented in this chapter was published in Applied Catalysis A in July 2015 [99].

5.1 Introduction

Solid oxide fuel cells (SOFCs) efficiently convert chemical energy directly into electricity. In this process, hydrogen and carbon monoxide are electrochemically oxidized via equations 5.1 and 5.2. SOFCs possess some internal reforming capacity and can operate on hydrocarbon-based fuels such as diesel reformate, natural gas, and biogas. Each of these fuels contains varying amounts of
methane. This is beneficial since the internal reforming reactions of methane (equations 5.3 and 5.4) are endothermic and help to mitigate the heat produced by the highly exothermic electrochemical oxidation [5, 39, 44, 100]. Many studies in the past two decades have confirmed the applicability of SOFCs for both steam [4, 19–24, 94] and dry (CO$_2$) methane reforming [25–31].

\[
\begin{align*}
H_2 + O^{2-} & \rightarrow H_2O + 2e^- \quad (5.1) \\
CO + O^{2-} & \rightarrow CO_2 + 2e^- \quad (5.2) \\
CH_4 + H_2O & \rightarrow 3H_2 + CO \quad (5.3) \\
CH_4 + CO_2 & \rightarrow 2H_2 + 2CO \quad (5.4)
\end{align*}
\]

Reforming reactions occur on the SOFC anode which is typically made of nickel loaded onto yttria stabilized zirconia (Ni/YSZ). The use of nickel as a reforming and electrochemical catalyst imposes an important and unavoidable constraint that the inlet fuel must have minimal sulfur. This is problematic because hydrocarbon-based fuels typically contain sulfur impurities in the form of thiols, thiophenes or COS.\[49, 50\] Sulfur impurity concentrations are typically 5 - 500 ppm for natural gas \[49, 50\], 15 - 900 ppm for diesel \[47, 48\], and 200 - 20,000 ppm for biogas \[31, 46\]. Desulfurization processes are used to remove sulfur, and may require either hydrogenation or oxidation of the fuel stream to produce H$_2$S or SO$_2$, respectively. The efficacy of sulfur removal strategies depends on the initial sulfur concentration and the efficiency of the strategy. Typically, sulfur removal strategies can reduce sulfur concentrations to a range of less than 10 ppm \[50, 101, 102\].

The efficiencies of conventional sulfur removal processes are sufficient for industrial nickel reforming catalysts, but studies on the effect of sulfur on power output and polarization resistance during SOFC operation suggest that even low sulfur concentrations (< 10 ppm) can have extremely detrimental effects. The majority of the work done to characterize sulfur effects on Ni/YSZ have been on operating cells in a hydrogen atmosphere [11]. The sulfur poisoning mechanism that is generally accepted for H$_2$S on metallic nickel (Ni) proceeds as:

\[
H_2S + Ni \rightleftharpoons Ni-S + H_2 
\] (5.5)
where sulfur adsorbs dissociatively and hydrogen gas is formed [12, 59]. Equation 5.5 indicates that the partial pressure of hydrogen in an operating SOFC system could influence the poisoning behavior of H$_2$S on Ni, however there is no consensus in the literature to confirm this. Instead, it has been demonstrated that even sub-ppm levels of H$_2$S increase the polarization resistance on an operating Ni/YSZ SOFC by upwards of 28% at 750°C in the presence of 0.05 ppm H$_2$S [9]. At similar operating temperatures, the cell voltage of an operating SOFC was observed to drop 10% in the presence of 0.1 ppm H$_2$S [11]. Upon removal of sulfur, some studies have speculated that the cell regenerates via equation 5.5 because only hydrogen and inert gases are present in the system [11].

Sulfur poisoning on an operating SOFC during methane reforming has also been explored in the literature. Many studies consider the effect of sulfur on the electrochemical activity only. For example, Bao et al. [103] examined a methane-containing simulated coal syngas and reported that 1 ppm H$_2$S reduced the power density by only 3.5% initially, but subsequent regeneration resulted in a less than 2% deactivation. However, they did not report the effect of sulfur poisoning on the reforming activity. Rasmussen and Hagen [65] examined the steam methane reforming activity of a Ni/YSZ SOFC operating with a biogas-type fuel that contained 29% CH$_4$, 13% H$_2$, and 58% H$_2$O doped with 2 to 25 ppm H$_2$S. They found that the methane reforming activity is affected more strongly than the electrochemical activity in the presence of sulfur. For dry methane reforming, Shiratori et al. [26] found that 1 ppm H$_2$S deactivated the methane conversion by 40% and resulted in a voltage drop of 9% of the initial voltage. A catalytic study by Lakshminarayanan and Ozkan [104] examined the activity of methane steam reforming on Ni/YSZ in 50 ppm H$_2$S and observed a 60% loss in activity at 700°C. The methane reforming activity on Ni/YSZ appears to be a strong function of sulfur concentration, and the deactivation of an internal reforming SOFC is not completely described by the loss in electrochemical activity. These results demonstrate that it is important to consider the Ni/YSZ reforming activity because it can be more strongly deactivated than the electrochemical activity.
The impact of sulfur species (e.g., H$_2$S vs SO$_2$) on the extent of sulfur poisoning has not yet been explored in the literature, but may be an important factor since the type of sulfur removal process may change the nature of the sulfur species present in the fuel stream. For oxidative sulfur removal such as the Claus Process, SO$_2$ is a main product that is removed catalytically and carbonyl sulfide (COS) has been observed as an unwanted side-product [105, 106]. SO$_2$ and COS formation proceed as:

$$2\text{H}_2\text{S} + 3\text{O}_2 \rightarrow 2\text{SO}_2 + 2\text{H}_2\text{O} \quad (5.6)$$
$$\text{CO} + \text{S}_2 \rightleftharpoons \text{COS} + \text{S} \quad (5.7)$$
$$\text{CO} + \text{S} \rightleftharpoons \text{COS} \quad (5.8)$$

The exact mechanism for COS formation in a Claus furnace is not well understood, but COS is observed in low concentrations in product gases from the process [105]. It is clear that there is a possibility that H$_2$S is not the only sulfur impurity present in natural gas after desulfization by various techniques. To our knowledge, no studies have ever been performed to delineate the effects of COS or SO$_2$ on Ni/YSZ.

In this work we address the relationship between methane reforming activity on Ni/YSZ and sulfur poisoning from a catalytic standpoint. To facilitate this, we compare sulfur deactivation of methane steam and dry reforming reactions on Ni/YSZ with a commercially available, nickel-based reforming catalyst (Ni/K$_2$O–CaAl$_2$O$_4$). Ni/K$_2$O–CaAl$_2$O$_4$ is used as a point of reference so that deactivation rates from sulfur poisoning on Ni/YSZ can be put into a broader context to determine if it is realistic to use as a reforming catalyst. Experiments are carried out in differential operating conditions deliberately kept below 100% methane conversion and intended to accelerate deactivation so that short time scales can be used. Three sulfur species are evaluated (H$_2$S, SO$_2$, and COS), and the effect of sulfur concentration (1, 3, and 5 ppm) and reforming temperature (650°C, 750°C, and 800°C) are explored. This study is not meant to directly compare all aspects of Ni/YSZ to the commercial catalyst, which has a proprietary support material and composition. Rather, the objective is to perform well-defined catalytic experiments that decouple the impact of
sulfur poisoning on the reforming capability of Ni/YSZ from the electrochemical and gas transport effects that are present in an SOFC anode, and to compare these results with those obtained with a commercial reforming catalyst.

5.2 Experimental

The catalyst synthesis, PBR experimental apparatus, reforming experimental protocol, and catalyst characterization methods used for this work are described in Chapters 3 and 4.

5.3 Results

This section summarizes the experimental results that were obtained from this work.

5.3.1 Methane Reforming Without Sulfur

The turnover frequencies calculated from the sulfur-free operation of Ni/YSZ and Ni/K₂O–CaAl₂O₄ during steam methane reforming (bottom) and dry methane reforming (top) at 750°C are given in Figure 5.1. The commercial Ni/K₂O–CaAl₂O₄ catalyst was diluted in pure α-Al₂O₃ so that it had the same active nickel surface area to Ni/YSZ. The active nickel surface area was found using the hydrogen uptake (given in Table 4.1) measured from H₂-chemisorption. The initial turnover frequencies for steam methane reforming are similar for both catalysts, but Ni/K₂O–CaAl₂O₄ deactivates to a nearly steady state at approximately 26% less than its initial activity while Ni/YSZ maintains roughly the same activity. The deactivation of Ni/K₂O–CaAl₂O₄ appeared to be a result of coking based on visual inspection of the post-reaction catalyst. Catalyst coking is a common problem in industry, and is caused by carbon deposition which proceeds either through methane dissociative adsorption on the catalyst (equation 5.9) or the Boudouard reaction (equation 5.10) [42, 43].

\[
\begin{align*}
\text{CH}_4 + \text{Ni} & \rightarrow \text{C} - \text{Ni} + 2\text{H}_2 \\
2\text{CO} + 2\text{Ni} & \rightleftharpoons \text{CO}_2 - \text{Ni} + \text{C} - \text{Ni}
\end{align*}
\]  

(5.9)  
(5.10)
Figure 5.1: Methane turnover frequencies on Ni/YSZ and Ni/K$_2$O–CaAl$_2$O$_4$ for steam (bottom) and dry (top) methane reforming at 750°C.
There is extensive literature on the coking of nickel-based reforming catalysts [55, 107–109]. Carbon deposition on nickel has been demonstrated to be sensitive to the structure of nickel, and this could be one reason for the loss in activity for Ni/K$_2$O–CaAl$_2$O$_4$. In particular, step sites are more reactive than terrace sites and carbon has high stability on these step sites [13]. The dramatic difference in active nickel surface area versus the actual amount of nickel between the catalysts indicates that there could be a higher concentration of step sites on Ni/K$_2$O–CaAl$_2$O$_4$. Conversely, there might be more terrace sites on Ni/YSZ. Since terrace sites are less stable for carbon adsorption, this could explain why Ni/YSZ is observed to have low coking [13]. Unlike Ni/K$_2$O–CaAl$_2$O$_4$, no coke was observed on the Ni/YSZ after any of the experiments.

It has previously been experimentally demonstrated that the rates of methane decomposition for both steam and dry reforming are similar [110]. Ni/K$_2$O–CaAl$_2$O$_4$ has very similar dry and steam methane reforming rates as shown in Figure 5.1, and the deactivation rates are also very similar. This indicates that carbon deposition might not come from CO$_2$ adsorption on nickel and instead results from the adsorption of methane. Ni/YSZ undergoes approximately 10% deactivation during dry methane reforming, and approximately 2% during steam methane reforming. However, unlike Ni/K$_2$O–CaAl$_2$O$_4$, the turnover frequencies for steam and dry methane reforming on Ni/YSZ are different. This could be due to support effects from YSZ that inhibit methane adsorption, which has been proposed to be the rate determining step for methane dry reforming [60, 110]. The disparity between methane dry and steam reforming turnover frequencies is another example of the activity differences between Ni/YSZ and Ni/K$_2$O–CaAl$_2$O$_4$.

### 5.3.2 Methane Reforming With Sulfur

For rigorous comparison of the deactivation of Ni/YSZ with the commercial Ni/K$_2$O–CaAl$_2$O$_4$ catalyst, the activity, $a$, was used to relate the initial methane conversion to the deactivated methane conversion. The activity was calculated as:

$$a = \frac{(n_{CH_4,i} - n_{CH_4})_{t}/n_{CH_4,i}}{(n_{CH_4,i} - n_{CH_4})_{o}/n_{CH_4,i}}$$

(5.11)
where $n_{CH_4,i}$ is the inlet methane molar flow and $n_{CH_4}$ is the methane molar flow at time $t$ calculated from GC data and the helium tracer volumetric flow rate. Equation 5.11 is effectively the normalized change in activity from initial activity in the absence of sulfur which allows for the direct comparison of the deactivation of Ni/YSZ and Ni/K$_2$O–CaAl$_2$O$_4$.

![Diagram of methane reforming with sulfur concentrations](image)

Figure 5.2: Results from the Ni/YSZ activity loss of steam (left) and dry (right) methane reforming by 1, 3, and 5 ppm H$_2$S (top), SO$_2$ (middle) and COS (bottom) at 750°C. The “spike” near minute 27 corresponds to valves switching to introduce sulfur into the system.

The deactivation of Ni/YSZ is given in Figure 5.2 for steam (left) and dry (right) methane reforming at 750°C in H$_2$S (top), SO$_2$ (middle), and COS (bottom) at concentrations of 1, 3, and 5 ppm. The data is presented as collected, and therefore it contains a “spike” near minute 27 time on stream which corresponds to valves switching to introduce sulfur into the system. The experiments were programmed and operated using control software, and therefore the time of the valve switching

75
is the same for all experiments. Some experiments do not contain the spike because of a few seconds offset on GC cycle time. Because of the valve switching event, we were unable to record the initial point of activity loss. However, because the initial activity was measured before introducing sulfur, the initial loss in activity can be interpolated.

![Figure 5.3: Activity loss of steam (left) and dry (right) methane reforming by 1, 3, and 5 ppm H$_2$S (top), SO$_2$ (middle), and COS (bottom) at 750°C for the Ni/K$_2$O–CaAl$_2$O$_4$ commercial catalyst.](image)

For Ni/YSZ, the activity at longer times approaches zero for 1, 3, and 5 ppm for all sulfur species. In terms of the deactivation rate, H$_2$S and SO$_2$ have similar deactivation rates for steam and dry reforming data. Bartholomew [8] describes how some qualitative information about the nature of deactivation can be gleaned from the shape of the deactivation curve. For example, the 1 ppm deactivation curve shape for both H$_2$S and SO$_2$ are similar to the “antiselective” poisoning
curve identified by Bartholomew. Antiselectivity is defined as the deactivation of weakly active sites prior to the deactivation of strongly active sites. This antiselectivity is evident in the slower initial deactivation for the 1 ppm H$_2$S and SO$_2$ cases for both steam and dry reforming.

Deactivation curves for Ni/K$_2$O–CaAl$_2$O$_4$ are given in Figure 5.3 for steam (left) and dry (right) methane reforming at 750°C in H$_2$S (top), SO$_2$ (middle), and COS (bottom) at concentrations of 1, 3, and 5 ppm. This data set was collected in the same way as the Ni/YSZ set shown in Figure 5.2 and exhibits the same spike near minute 27 time on stream that corresponds to valves switching.

The shape of the deactivation curves for Ni/K$_2$O–CaAl$_2$O$_4$ are concave upward. As described by Bartholomew, these are selective which means that the sharp, immediate drop in activity corresponds with highly active sites being poisoned first.[8] The importance of the shape of the deactivation curves will be discussed further in the following section.

The effect of temperature on deactivation rates for Ni/YSZ (left) and Ni/K$_2$O–CaAl$_2$O$_4$ (right) is shown in Figure 5.4 for steam methane reforming (SMR) in the top three panels and dry methane reforming (DMR) in the bottom three panels. No data was collected for SO$_2$ poisoning on Ni/K$_2$O–CaAl$_2$O$_4$ at 800°C. For both catalysts, the rates of deactivation do not appear to be strong functions of temperature. Generally, an increase in temperature should result in decreased sulfur adsorption on nickel [59]. These results suggest that the observed temperature dependence is affected by factors in addition to the adsorption/desorption equilibrium.

Table 5.1 and Table 5.2 summarize the measured normalized activities at various times for all steam and dry methane reforming experiments. There are substantial differences in deactivation rate behavior between the two catalysts. Specifically, the initial deactivation rate Ni/K$_2$O–CaAl$_2$O$_4$ is much faster than for Ni/YSZ, but the ultimate extent of deactivation is greater for Ni/YSZ. This will be discussed in greater detail in the next section.

5.4 Discussion

The purpose of this study is to compare the impact of sulfur poisoning on Ni/YSZ to a commercial reforming catalyst. A major difference between the two catalysts is the maximum extent of de-
Figure 5.4: Comparison of the deactivation rates for Ni/YSZ at 650°C, 750°C, and 800°C for steam methane reforming (SMR) in the upper three panels and dry methane reforming (DMR) in the lower three panels. Deactivation as a result of H₂S, SO₂ and COS is shown. No data was collected for SO₂ poisoning on Ni/K₂O–CaAl₂O₄ at 800°C.
Table 5.1: Comparison of activities at various conditions between Ni/YSZ and Ni/K$_2$O–Al$_2$O$_4$ at different temperatures for steam methane reforming.

<table>
<thead>
<tr>
<th>Sulfur Species</th>
<th>Temperature</th>
<th>Conc. (ppm)</th>
<th>Ni/YSZ Activity$^a$ at time (minutes)</th>
<th>Ni/K$_2$O–CaAl$_2$O$_4$ Activity$^a$ at time (minutes)</th>
</tr>
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<tbody>
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<td>650°C</td>
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<td>750°C</td>
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<tr>
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<td>800°C</td>
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<td>1.00 0.87</td>
</tr>
<tr>
<td>H$_2$S</td>
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<td>0.98 0.88 0.52 0.06</td>
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</tr>
<tr>
<td></td>
<td>750°C</td>
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</tr>
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<td>0.94 0.65 0.11 0.03</td>
<td>0.78 0.57 0.38 0.29 0.24</td>
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$^a$ Activity is defined in equation 5.11
Table 5.2: Comparison of activities at various conditions between Ni/YSZ and Ni/K$_2$O–Al$_2$O$_4$ at different temperatures for dry methane reforming.

<table>
<thead>
<tr>
<th>Sulfur Species</th>
<th>Temperature</th>
<th>Conc. (ppm)</th>
<th>Ni/YSZ Activity$^a$ at time (minutes)</th>
<th>Ni/K$_2$O–CaAl$_2$O$_4$ Activity$^a$ at time (minutes)</th>
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<td>800°C</td>
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<td>1.00 0.98</td>
<td>1.00 0.95</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>650°C</td>
<td>1</td>
<td>0.81 0.66 0.29 0.04 0.04</td>
<td>0.87 0.81 0.69 0.58 0.52</td>
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<td>0.94 0.86 0.61 0.26 0.02</td>
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<td></td>
<td>3</td>
<td>0.90 0.61 0.05 0.05 0.04</td>
<td>0.92 0.81 0.64 0.50 0.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>0.85 0.23 0.08 0.04 0.04</td>
<td>0.95 0.79 0.52 0.34 0.24</td>
</tr>
<tr>
<td></td>
<td>800°C</td>
<td>1</td>
<td>0.96 0.87 0.63 0.35 0.08</td>
<td></td>
</tr>
<tr>
<td>COS</td>
<td>650°C</td>
<td>1</td>
<td>0.87 0.79 0.51 0.16 0.07</td>
<td>0.94 0.81 0.64 0.53 0.45</td>
</tr>
<tr>
<td></td>
<td>750°C</td>
<td>1</td>
<td>0.92 0.74 0.19 0.04 0.04</td>
<td>0.82 0.63 0.40 0.28 0.21</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>0.82 0.17 0.06 0.05 0.05</td>
<td>0.72 0.36 0.18 0.14 0.12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>0.77 0.08 0.07 0.07 0.08</td>
<td>0.64 0.28 0.15 0.12 0.12</td>
</tr>
<tr>
<td></td>
<td>800°C</td>
<td>1</td>
<td>0.92 0.80 0.46 0.05 0.03</td>
<td>0.86 0.65 0.40 0.27 0.18</td>
</tr>
</tbody>
</table>

$^a$ Activity is defined in equation 5.11
activation. As seen in Table 5.1, Ni/YSZ is almost completely deactivated while Ni/K₂O−CaAl₂O₄ maintains between 10 - 60% of its initial activity depending on the sulfur species. The maximum deactivation should reflect the pseudo-equilibrium sulfur surface coverage, θₛ, which can be calculated from the maximum observed loss in activity (1 − a) [56]. The results for the H₂S poisoning studies are shown in Table 5.3. The nearly complete deactivation of Ni/YSZ indicates that the surface is almost saturated with sulfur, and indeed the measured surface coverages are close to 1. In contrast, Ni/K₂O−CaAl₂O₄ retains some of its initial activity and the sulfur coverages are much lower.

Table 5.3: Calculated sulfur coverages, θₛ, and the maximum deactivation reached for Ni/YSZ and Ni/K₂O−CaAl₂O₄.

<table>
<thead>
<tr>
<th></th>
<th>650°C</th>
<th></th>
<th>750°C</th>
<th></th>
<th>800°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 ppm</td>
<td>3 ppm</td>
<td>5 ppm</td>
<td>1 ppm</td>
<td></td>
</tr>
<tr>
<td>Calculated θₛ [56]</td>
<td>0.93</td>
<td>0.91</td>
<td>0.94</td>
<td>0.84</td>
<td></td>
</tr>
<tr>
<td>Ni/YSZ</td>
<td>0.96</td>
<td>0.97</td>
<td>0.98</td>
<td>0.96</td>
<td></td>
</tr>
<tr>
<td>Ni/K₂O−CaAl₂O₄</td>
<td>0.50</td>
<td>0.76</td>
<td>0.83</td>
<td>0.67</td>
<td></td>
</tr>
</tbody>
</table>

The sulfur coverage can be estimated from the empirical relationship of Rostrup-Nielsen et al. [56]. This study focused on coke-prevention during steam reforming on Ni/Al₂O₃ and Ni/MgAl₂O₄ catalysts by sulfur passivation with H₂S. The change in initial reforming rate, r₀,sp, is dependent on the sulfur coverage, θₛ as:

\[ r₀^{sp} = \frac{r_{sp}}{(1 - θₛ)^3} \]  \hspace{1cm} (5.12)

where \( r_{sp} \) is the reforming rate at sulfur coverage of θₛ. The sulfur coverage can be calculated from a relation also given by Rostrup-Nielsen [59] as:

\[ θₛ = 1.45 - 9.53 \times 10^{-5}T + 4.17 \times 10^{-5}T \cdot \ln \left( \frac{P_{H₂S}}{P_{H₂}} \right) \]  \hspace{1cm} (5.13)

which is dependent on the reaction temperature, \( T \), and the ratio of the partial pressures of H₂S and H₂ in the system.

Using this relation, sulfur surface coverages were calculated for the conditions used in this work and they are compared to the experimental values in Table 5.3. For Ni/YSZ the calculated coverages
are slightly lower than the measured values, and for \( \text{NiK}_2\text{O}_4\) they are significantly higher. The calculated coverages also decrease as temperature increases; this reflects a shift in the adsorption/desorption equilibrium. In contrast, for \( \text{Ni/}\text{K}_2\text{O}_4\) the coverages increase with increasing temperature and this may indicate that other forms of deactivation occur. No clear trend is observed for \( \text{Ni/YSZ} \). The disparity between the calculated and measured coverages show that one should use caution when applying the empirical relationship outside of the conditions for which it was developed.

Another difference in the two catalysts is the shape of the deactivation curves. Since the experiments were designed so that the two catalysts have the same number of active nickel sites, the different shapes of the deactivation curves may be interpreted as a difference in nickel accessibility. For \( \text{Ni/YSZ} \) the initial deactivation is slow, but then it increases before the activity drops to close to zero. This indicates that there is an abundance of weakly active sites that are deactivated first because they are more readily available. For \( \text{Ni/K}_2\text{O}_4\) the initial deactivation rate is fast, but then it tapers off as the activity reaches steady state indicating that the commercial catalyst has more highly active sites. These sites are likely edge sites that are available and might be deactivated first.

The support material is the main difference between \( \text{Ni/YSZ} \) and \( \text{Ni/K}_2\text{O}_4\) and is likely a root cause of the differences in deactivation rates. The role of the support material in a typical reforming catalyst is to disperse the active metal so that smaller crystals are available for reaction. At high temperatures, particles become mobile on the surface and can agglomerate or sinter to produce larger particles [50]. As shown in Figure 4.4, the nickel particles on YSZ grow from 416 Å at 600°C to 670 Å at 800°C which indicates that sintering occurs during reduction. The nickel particle size on \( \text{Ni/K}_2\text{O}_4\) was measured to be 196 Å on post-reaction samples at both 650°C and 800°C. The low dispersion measured for \( \text{Ni/YSZ} \) may be in part due to the sintering of nickel which reduces the number of exposed surface nickel atoms.

There are very few studies in the literature that examine the effects of metal dispersion on YSZ, and this value is rarely reported in SOFC studies. This makes it difficult to compare the
numbers measured in this study for nickel dispersion on YSZ, but the dispersion is much lower than Ni/K$_2$O–CaAl$_2$O$_4$. One study by Zhang et al. [111] found that YSZ was the best support for rhodium dispersion when compared with Al$_2$O$_3$, TiO$_2$, SiO$_2$, La$_2$O$_3$, and MgO. This study also reported that the YSZ-supported catalyst had a much higher turnover frequency. The main difference between this study and conventional Ni/YSZ SOFC studies was the calcination temperature which was done in hydrogen at 200°C unlike normal Ni/YSZ catalysts done at 1400°C to 1500°C. Though some studies report beneficial effects of using dispersants and pore formers to produce Ni/YSZ, it is important to note how critical the control of metal dispersion is when synthesizing catalysts [112].

Results from this study make it clear that sulfur deactivation is much more severe on Ni/YSZ than it is on a commercial reforming catalysts, and therefore knowledge about Ni/YSZ should not be based on information gathered using conventional reforming catalyst. The effect of the support material is much more important than has previously been considered for Ni/YSZ, and affects the catalytic surface area which is much lower for Ni/YSZ than Ni/K$_2$O–CaAl$_2$O$_4$.

The experimental results presented here were collected under well-defined conditions and therefore they can be used to validate micro-kinetic models. While such efforts are beyond the scope of this current study, the data on initial deactivation rates can provide useful insights into the relative adsorption kinetics of the three species. At longer times the measured deactivation rate reflects a balance between adsorption and desorption rate and should approach equilibrium. Assuming that the desorption rate is slow at short reaction times, the initial deactivation rate can be normalized by the surface collisional frequency to obtain the fraction of collisions that stick to the surface:

$$\gamma = \frac{\frac{d\theta}{dt} N_o \sqrt{2\pi mk_B T}}{pA}$$  \hspace{1cm} (5.14)

Here $N_o$ is the number of nickel sites per area, $m$ is the molecular mass, $k_B$ is the Boltzmann constant, and $T$ is the reaction temperature [50]. The fraction of collisions that stick onto the Ni/YSZ surface at 750°C was found to be approximately 0.27 for COS, 0.015 for H$_2$S, and 0.031 for SO$_2$. The “sticking fractions” for H$_2$S and SO$_2$ vary by a factor of two, even though the rates of deactivation in Figure 5.2 are similar. For COS the fraction is significantly higher, reflecting the much higher
rate of deactivation.

Recently, there has been significant work done on the development of a microkinetic model for H$_2$S interactions on a nickel surface [2, 113, 114]. Appari et al. [2] developed a microkinetic sub-mechanism for H$_2$S poisoning on nickel, which is coupled with the Detuschmann mechanism [1, 24, 115] for methane steam and dry reforming on nickel. They reported a sticking coefficient for H$_2$S of 0.6, which is similar to the value reported by Riegraf et al. [116] ($\gamma = 0.5$). This assignment is very high compared with other sticking coefficients used in the Deutschmann mechanism for other coadsorbates such as H$_2$O ($\gamma = 0.1$), H$_2$ ($\gamma = 0.01$), and CH$_4$ ($\gamma = 0.008$). It is also higher than the Appari assignment for SO$_2$ ($\gamma = 0.02$), which can be readsorbed following sulfur oxidation.

It is important to keep in mind that the “sticking fractions” determined here are measured in an environment that contains other adsorbents. Because of this they should not be directly compared to absolute sticking coefficients. Absolute sticking coefficients are typically determined from studies done at ultra-high vacuum (UHV) and with care taken to avoid other forms of deactivation [50]. The measured fraction determined here may be considered a lower limit to the actual sticking coefficient. Not only does it assume that there is no desorption, but it also accounts for competitive adsorption by the other species present in the gas phase at much higher concentrations. These values can provide insight into the relative assignments. The results presented here suggest that the sticking coefficient assignment for SO$_2$ should be closer to the value reported for H$_2$S.

Poisoning by COS is more prolific than it is by H$_2$S and SO$_2$. The presence of a CO group in COS may contribute to the significantly faster deactivation rates. Assuming that the heat of adsorption of COS on nickel is roughly equivalent to CO, then several microkinetic mechanisms for steam and dry methane reforming in the literature can be used to probe the effect of COS adsorption. Blaylock et al. [60] reported that the heat of adsorption for CO on nickel is -121 kJ/mol at 800°C. Compared with the heats of adsorption of hydrogen and water (-92 kJ/mol and -18 kJ/mol at 800°C, respectively), CO is more strongly bound than any other surface species except for atomic H and O (-269 kJ/mol and -469 kJ/mol at 800°C, respectively). CO is not typically fed to a steam or dry reforming system, but it is formed as a product during reforming so the effect of COS is
likely not due to CO adsorption alone. Instead, the combination of the strong adsorption of CO and the presumably strong adsorption of sulfur may cause a summative effect which results in fast deactivation. One way for COS to result in such fast deactivation is via dissociative adsorption on nickel to form two surface species: Ni-S and Ni-CO as shown in equation 5.15.

$$\text{COS} + 2\text{Ni} \rightleftharpoons \text{S}−\text{Ni} + \text{CO}−\text{Ni} \quad (5.15)$$

All three sulfur compounds have significantly slower deactivation rates during dry methane reforming than steam reforming (see Figure 5.2). This indicates that either the dry reforming atmosphere slows adsorption or speeds desorption. Alternatively, the steam reforming reaction may accelerate deactivation. This may be unlikely, though, when considering that some work has demonstrated that competitive adsorption between water and H$_2$S does not affect H$_2$S adsorption [59]. In the absence of sulfur after sulfidation, it has also been proposed that high partial pressures of steam can regenerate the surface via equation 5.16:

$$\text{Ni}−\text{S} + \text{H}_2\text{O} \rightleftharpoons \text{NiO} + \text{H}_2\text{S} \quad (5.16)$$

The reason for slower deactivation during dry reforming is not well understood, but this result indicates that the use of biogas is likely more advantageous than reformate for Ni/YSZ SOFCs.

Appari proposes several surface reactions that may be pathways towards surface sulfur removal and can therefore regenerate the nickel [2]. They propose that carbon monoxide (CO-Ni) can oxidize sulfur on the nickel surface (e.g., SH-Ni, S-Ni) via the following reactions:

$$\text{SH}−\text{Ni} + \text{CO}−\text{Ni} \rightleftharpoons \text{S}−\text{Ni} + \text{HCO}−\text{Ni} \quad (5.17)$$
$$\text{SH}−\text{Ni} + \text{CO}−\text{Ni} \rightleftharpoons \text{SO}−\text{Ni} + \text{CH}−\text{Ni} \quad (5.18)$$
$$\text{S}−\text{Ni} + \text{CO}−\text{Ni} \rightleftharpoons \text{SO}−\text{Ni} + \text{C}−\text{Ni} \quad (5.19)$$

Through this pathway, SO-Ni groups may react with surface adsorbed O to form SO$_2$-Ni and desorb thereby regenerating the surface. This is one of many possible pathways for the regeneration of the nickel surface, but does not explain why sulfur poisoning is slower during dry methane reforming than steam methane reforming. More investigation on the regeneration of nickel surfaces is needed
to identify which regeneration pathways are dominant for the different sulfur species.

The results presented here show the severe impact that sulfur impurities (H\textsubscript{2}S, SO\textsubscript{2}, and COS) have on the reforming capabilities of Ni/YSZ. In an operating SOFC, transport and electrochemical effects must also be considered to evaluate the impact of sulfur. For example, if the loss of reforming capability in an operating SOFC is less severe than observed in this study, it may suggest that the electrochemical oxidation of sulfur may be a way to regenerate the surface. Interestingly, this pathway has been suggested as a means to regeneration of the electrochemical activity [11]. Another alternative may be that the variation in species concentrations across the anode width may affect competitive adsorption, thereby somewhat offsetting the impact of sulfur poisoning. In order to understand how sulfur affects SOFC operation, it is important to develop coupled kinetic/transport models that systematically account for the impact of sulfur on both reforming and electrochemical capabilities. The data presented in this paper provides valuable information that can assist in the development of such SOFC models.

5.5 Conclusions

The overarching result from this study is that Ni/YSZ has less catalytic activity than a conventional Ni-based reforming catalyst and is significantly more sensitive to sulfur poisoning. The rates of deactivation from sulfur poisoning on Ni/YSZ are faster than Ni/K\textsubscript{2}O−CaAl\textsubscript{2}O\textsubscript{4} and deactivate the catalyst activity to zero. Because of this, information about sulfur deactivation on non-YSZ supported, nickel-based catalysts may not be appropriate to apply to systems using Ni/YSZ as a reforming catalyst. Though it has been demonstrated in the literature that electrochemical reactions are more tolerant to sulfur, this work confirms that the reforming reactions on Ni/YSZ are readily poisoned by very low concentrations of sulfur.

Results from this study show that regardless of sulfur species (H\textsubscript{2}S, SO\textsubscript{2}, or COS), Ni/YSZ was essentially completely deactivated at 1, 3, and 5 ppm at varying deactivation rates. Ni/K\textsubscript{2}O−CaAl\textsubscript{2}O\textsubscript{4} was deactivated to a non-zero steady state, and the sulfur surface coverage with H\textsubscript{2}S was much lower than the calculated values using the Rostrup-Nielsen correlation. The rates of deactivation...
for the sulfur species on both catalysts was: \( \text{COS} > \text{SO}_2 \geq \text{H}_2\text{S} \). This indicates that even trace amounts of COS and SO\(_2\), products of oxidative sulfur removal processes, can significantly degrade Ni/YSZ reforming activity. The effect of sulfur poisoning is so strong, that the use of Ni/YSZ with any hydrocarbon fuel requires removal of sulfur to sub-ppm levels which may be cost prohibitive.
CHAPTER 6

ADSORPTION OF H₂S AND SO₂ ON Ni/YSZ AND Ni/K₂O−CaAl₂O₄

The adsorption and desorption behavior of H₂S and SO₂ on Ni/YSZ is compared with a conventional nickel catalyst (Ni/K₂O−CaAl₂O₄). This study demonstrates that Ni/YSZ adsorbs 21 times more H₂S and 49 times more SO₂ per accessible nickel site than Ni/K₂O−CaAl₂O₄ at 500°C. Comparison of desorbed H₂S during a temperature ramp from 500°C to 850°C in 16 mol% hydrogen indicates that Ni/YSZ retains almost half of the adsorbed sulfur after both H₂S and SO₂ treatments. Adsorption and desorption of both H₂S and SO₂ on the support material YSZ (yttria-stabilized zirconia) were compared with a conventional steam reforming catalyst support (α-Al₂O₃). YSZ appeared to adsorb almost twice as much H₂S and 5.8 times as much SO₂ than α-Al₂O₃ indicating that YSZ may indeed play a role in sulfur retention on Ni/YSZ. After desorption from the H₂S treated samples, YSZ retained ~75% of the adsorbed sulfur, whereas α-Al₂O₃ retained less than half.

Sulfur poisoning during steam and dry methane reforming was evaluated using a micro-kinetic mechanism developed in the Deutschmann group coupled with a sulfur poisoning sub-mechanism developed by Appari et al. and applied to a packed bed reactor model. Sulfur-free steam and dry reforming experimental results were compared with the predictions and showed quite good agreement for methane conversion and CO and H₂ molar compositions on both catalysts. To fit the observed deactivation in the presence of 1 ppm H₂S the adsorption/desorption equilibrium constant was increased by a factor of 16,000 for Ni/YSZ and 96 for Ni/K₂O−CaAl₂O₄. The results suggest that, for both catalysts, the barrier for desorption is higher than that employed in the model.

The work presented in this chapter was submitted for review to ACS Catalysis in October 2015.

6.1 Introduction

Solid oxide fuel cells (SOFC) oxidize hydrogen and carbon monoxide (syngas) to produce electricity, but their ability to simultaneously convert syngas to electricity and reform hydrocarbons
to syngas sets them apart from other processes [16]. Fuels containing both syngas and hydrocarbons can be fed to SOFCs because of their high operating temperature and metallic anode, typically nickel, which can reform hydrocarbons to produce more syngas [17, 39, 83]. Reforming at the anode is also beneficial because it is endothermic and can therefore help to balance the exothermic electrochemical oxidation reaction [117]. As a result of their fuel flexibility, SOFCs have been proposed for use with natural gas and natural gas reformate [19–24], biogas [25–31], diesel reformate [32–34] and syngas from coal or biomass [35, 49, 51, 52]. The primary hydrocarbon in most of these fuels is methane, and this study focuses on steam and dry methane reforming.

Most of the fuels that have been proposed for use with SOFCs contain sulfur, typically in the form of hydrogen sulfide (H₂S), but some fuels contain other sulfur species such as mercaptans [45, 118]. A range of sulfur concentrations found in potential SOFC fuels is given in Table 6.1. Sulfur is naturally occurring in both fossil fuels and in biomass-derived intermediates (e.g., syngas), and has been demonstrated to be the most detrimental poison to nickel catalysts [9, 11]. Sulfur species removal can be achieved by physical absorption either in the solid or liquid phase [45, 119]. Depending on the starting concentration of sulfur, though, the efficiency of sulfur removal processes can vary and leave several parts per million of sulfur in the fuel [119]. Previous work from this group has demonstrated that even extremely low sulfur concentrations (e.g., 1 ppm) can severely poison the nickel-based SOFC anode and deplete nearly all of its reforming activity [99]. Because of the extreme sulfur sensitivity of SOFCs, it is helpful to explore the adsorption-desorption behavior of sulfur species.

Adsorption of sulfur species on nickel has long been a focus of research on nickel-based steam reforming catalysts. Rostrup-Nielsen observed that sulfur passivated nickel catalysts to such an extent that “carbon-free steam reforming” was possible because sulfur covered active sites that typically became coked during operation [56]. A study by Abild-Pedersen et al. confirmed Rostrup-Nielsen’s findings, but demonstrated that sulfur preferentially adsorbs on step sites which mitigates the majority of coking [62]. Careful control of the sulfur coverage will therefore result in coke reduction on the step sites while leaving the terrace sites open for steam reforming [62]. This can
Table 6.1: Typical sulfur concentrations in potential SOFC fuels.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Concentration Range (ppm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biogas</td>
<td>200 - 20,000</td>
<td>[31, 46]</td>
</tr>
<tr>
<td>Diesel</td>
<td>15 - 900</td>
<td>[47, 48]</td>
</tr>
<tr>
<td>Jet</td>
<td>1400 - 3000</td>
<td>[120, 121]</td>
</tr>
<tr>
<td>Natural gas</td>
<td>5 - 500</td>
<td>[49, 50]</td>
</tr>
<tr>
<td>Syngas - coal</td>
<td>1000 - 15,000</td>
<td>[49, 51]</td>
</tr>
<tr>
<td>Syngas - biomass</td>
<td>30 - 800</td>
<td>[51, 52]</td>
</tr>
</tbody>
</table>

be achieved by depositing small amounts of sulfur (< 0.06 ML) onto a nickel catalyst.

Single crystal work on nickel surfaces (e.g., Ni(111) and Ni(100)) demonstrated that a single sulfur atom could take up as many as 9 active sites [57]. This phenomenon was studied by Erley and Wagner who posited that sulfur adsorbed on nickel to a certain coverage threshold, and then subsequent adsorption contributed to the formation of a so-called sulfur “super-structure” in a 2 x 2 matrix of sulfur atoms [57]. Work by Rostrup-Nielsen supported the notion that a 2-dimensional sulfur structure was formed [43]. McCarty and Wise calculated the thermodynamics of sulfur adsorption at varying coverages, and found that up to a certain sulfur surface coverage the heat of adsorption decreased with increasing sulfur surface concentration as a result of repulsion between adsorbed sulfur atoms. At very high surface coverages, they found that the heat of adsorption increases possibly as the result of adsorption of adspecies (e.g., SH) and molecular adsorption of H₂S as evidenced by a large change in the entropy compared with lower coverages [58]. The summation of results from these studies indicates that sulfur adsorption does not simply poison nickel but sulfur atoms combine to form a physical structure that blocks other species from adsorbing on the surface. The result is an impermeable barrier on the nickel surface that does not allow steam reforming to proceed under high sulfur conditions.

Studies on sulfur poisoning of Ni/YSZ have, for the most part, examined the effect of sulfur poisoning on the electrochemical activity [11]. More recent studies have suggested that there may be a distinction between nickel sites active for electrochemistry and reforming chemistry,
which may result in different degrees of deactivation of the two reactions [12]. Rasmussen and Hagen reported a 60% drop in the reforming activity of a Ni/YSZ anode at open circuit voltage (OCV) in a methane atmosphere containing 4 ppm H\textsubscript{2}S [65]. Alternatively, a sulfur concentration of 7 ppm was acceptable for stable electrochemical reaction at 1 A/cm\textsuperscript{2} current load [65]. The authors proposed that the better sulfur tolerance for electrochemical reactions may be due to their insensitivity to nickel site structure. Contrarily, reforming occurs primarily on step sites, which is also where sulfur atoms are thought to adsorb [65]. Studies such as those done by Rasmussen and Hagen indicate that sulfur adsorption on Ni/YSZ is as aggressive as has been shown previously by Rostrup-Nielsen and McCarty and Wise for Ni/alumina catalysts [43, 58]. However, very few studies examine the adsorption and desorption properties of sulfur on Ni/YSZ as has been done previously for nickel-based catalysts on conventional supports (e.g., \( \alpha\)-Al\textsubscript{2}O\textsubscript{3}, \( \gamma\)-Al\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2}, MgO) [43, 56, 58, 122].

Sulfur adsorption on Ni/YSZ has been evaluated using density functional theory (DFT) for both H\textsubscript{2}S and SO\textsubscript{2}. A study by Zhang et al. [123] evaluated Ni/YSZ and Ni/YSZ-O\textsubscript{v} (with an oxygen vacancy) to determine the role of the oxygen vacancy. They postulated that repulsive forces between adsorbed sulfur and lattice oxygen caused sulfur to be less likely to be adsorbed than when a vacancy was present. Their results indicated that sulfur was able to diffuse into the vacancy position on the Ni/YSZ-O\textsubscript{v} structure. A similar study by Chu et al. [124] found that DFT predicts a strong interaction between SO\textsubscript{2} and YSZ that leads to the formation of surface stabilized sulfates. Both of these studies present interesting results that implicate the support material in sulfur poisoning.

Work previously done in this group demonstrated that Ni/YSZ deactivated more quickly and to zero activity under the same reforming and sulfur conditions as a commercially available Ni/K\textsubscript{2}O—CaAl\textsubscript{2}O\textsubscript{4} catalyst [99]. The work presented herein expands on that work by probing the adsorption and desorption behavior of H\textsubscript{2}S and SO\textsubscript{2} on Ni/YSZ compared with Ni/K\textsubscript{2}O—CaAl\textsubscript{2}O\textsubscript{4}. The absorption-desorption behavior of the support material, YSZ, was also investigated and compared to a conventional catalyst support material, \( \alpha\)-Al\textsubscript{2}O\textsubscript{3}. Next, the impact of sulfur poisoning during steam and dry methane reforming on Ni/YSZ is evaluated using a packed bed reactor model.
and micro-kinetic mechanisms for the reforming reactions coupled with a sulfur sub-mechanism [1, 2]. The results presented here indicate that Ni/YSZ has an unexpectedly high capacity for sulfur adsorption and to model sulfur poisoning during methane reforming the rate of desorption had to be substantially decreased.

6.2 Experimental Section

Catalyst samples were prepared and pretreated as described in Chapter 3. The steam and dry methane reforming experimental protocols and the protocol for sulfur adsorption-desorption measurements are also described in detail in Chapter 3.

Measurements of x-ray absorption near-edge structure (XANES) of the sulfur in the Ni/YSZ samples and sulfur-containing reference materials were performed at beam line 4-3 of the Stanford Synchrotron Radiation Lightsource (SSRL). Photon energies were selected using a double-crystal Si(111) monochromator. Finely ground samples were dispersed as thinly as possible on sulfur-free Kapton tape, which was mounted across the window of an aluminum sample holder. The sample chamber was continuously flushed with helium during data collection.

The spectra were collected in the energy range of 2440 - 2600 eV using a four-element Si drift detector. Step size was 0.1 eV for the XANES region (2460 - 2483 eV), 2.0 eV in the pre-edge region, and 0.2 - 0.5 eV in the post-XANES region. Energy calibration was conducted using the first inflection of sodium thiosulfate, with the first white line of thiosulfate accurately determined as 2472.02 eV in a previous study [125]. Merging of individual scans, spectra normalization, and linear combination fitting of the data were performed with Sam’s Interface for XAS Package (SIXPACK) [126]. Detailed information and spectra of the sulfur reference compounds with different oxidation states and coordination environments are in the Supporting Information section of Cheah et al. [127].

6.3 Results and discussion

This section discusses results from the adsorption and desorption study and the evaluation of sulfur poisoning in a steady state packed bed reactor transport-kinetic model.
6.3.1 Sulfur Adsorption and Desorption

In this section the adsorption-desorption behavior of sulfur on Ni/YSZ and a commercially available catalyst (Ni/K₂O–CaAl₂O₄) are compared. This work expands on our earlier study that examined the impact of sulfur poisoning of methane dry and steam reforming on both catalysts. As a reference point we also examine sulfur adsorption on the YSZ support material and compare it with a conventional steam reforming catalyst support, α-Al₂O₃. The adsorption behavior of the commercial catalyst support material was not investigated because it was not available.

Figure 6.1: H₂S and SO₂ uptake on YSZ and α-alumina support materials at 500°C.

Sulfur breakthrough curves for H₂S and SO₂ uptake on YSZ and α-Al₂O₃ support materials at 500°C are shown in Figure 6.1. SO₂ breakthrough on α-Al₂O₃ is rapid and reaches more than 80% in approximately 2.5 minutes. YSZ reaches 80% SO₂ breakthrough after 30 minutes, but there is significant uptake during the first 6 minutes, demonstrating that YSZ does have some capacity.
for \(\text{SO}_2\) adsorption. This \(\text{SO}_2\) uptake behavior is consistent with work done by Chu et al. who suggested that there are several adsorption sites for \(\text{SO}_2\) on YSZ and that after adsorption \(\text{SO}_2\) can be oxidized to \(\text{SO}_x\) \((x = 3 - 4)\) by lattice oxygen [124]. The measured \(\text{SO}_2\) uptake for YSZ is 118 \(\mu\text{mol}\) and for \(\alpha\)-\(\text{Al}_2\text{O}_3\) it is 21 \(\mu\text{mol}\). Results from \(\text{H}_2\text{S}\) uptake experiments indicate that both support materials adsorb more \(\text{H}_2\text{S}\) than \(\text{SO}_2\); YSZ adsorbed 148 \(\mu\text{mol}\) \(\text{H}_2\text{S}\), and \(\alpha\)-\(\text{Al}_2\text{O}_3\) adsorbed 83 \(\mu\text{mol}\). This may be an indication that the sulfur adsorption activity on Ni/YSZ is not a function of the oxygen vacancy in the lattice but instead some activity of the yttria or zirconia for sulfur adsorption. The \(\text{H}_2\text{S}\) uptake curve for YSZ is similar to \(\alpha\)-\(\text{Al}_2\text{O}_3\), and both supports appear to reach a time independent sulfur breakthrough at approximately 25 minutes on stream that is less than unity. This apparent continued adsorption is surprising; the expected uncertainty in the FTIR reading is on the order of 5%, not enough to account for the difference.

After sulfur uptake, sulfur desorption from YSZ and \(\alpha\)-\(\text{Al}_2\text{O}_3\) was evaluated in a temperature range of 500\(^\circ\text{C}\) – 850\(^\circ\text{C}\) with a hydrogen-nitrogen mixture as the sweep gas. Hydrogen was used to facilitate sulfur desorption as \(\text{H}_2\text{S}\), although the \(\text{SO}_2\) signal was also monitored. Under these conditions, no desorption from either of the \(\text{SO}_2\) treated support materials was observed. In this case, the amount of adsorbed sulfur was below the FTIR detection limit of 100 ppm for \(\text{H}_2\text{S}\) and 5 ppm for \(\text{SO}_2\). Thus, if the sulfur were desorbed as \(\text{H}_2\text{S}\), the amount desorbed was less than 31 \(\mu\text{mol}\). Since the alumina support adsorbed only 21 \(\mu\text{mol}\), we can draw no conclusion as to the amount of sulfur that might have stayed on the support. However for the YSZ support, which had adsorbed 118 \(\mu\text{mol}\), it is clear that at least 75\% of the adsorbed sulfur is still bound to the surface at 850\(^\circ\text{C}\). Conversely, if sulfur were desorbed as \(\text{SO}_2\), the amount was less than 2 \(\mu\text{mol}\). In this case, both YSZ and \(\alpha\)-\(\text{Al}_2\text{O}_3\) retain almost all of the adsorbed sulfur. Characterization of the sulfur-treated support with highly sensitive sulfur detection methods (e.g., inductively couple plasma (ICP) spectroscopy) could be used to reveal whether sulfur is still bound in the solid; however those methods were not available for this study.

Figure 6.2 shows the desorption curves for \(\text{H}_2\text{S}\) treated YSZ and \(\alpha\)-\(\text{Al}_2\text{O}_3\) as the temperature ramps from 500\(^\circ\text{C}\) to 850\(^\circ\text{C}\). Both supports begin to desorb sulfur below 500\(^\circ\text{C}\) and have two
apparent desorption features: the first is at $\sim 570^\circ C$ and the second at $\sim 655^\circ C$. The similarity in the desorption features indicates that the two support materials have sulfur surface species that have similar adsorption bond strengths. The integrated area under the desorption curves indicate that YSZ desorbed approximately $39 \, \mu$mol sulfur and $\alpha$-Al$_2$O$_3$ desorbed approximately $46 \, \mu$mol. The sulfur balance for YSZ indicates that the support retains up to $109 \, \mu$mol, whereas $\alpha$-Al$_2$O$_3$ retains roughly $37 \, \mu$mol H$_2$S. Increasing the temperature beyond $850^\circ C$ may further facilitate the sulfur desorption. Nevertheless, the results indicate that, under these conditions, YSZ has a higher capacity for sulfur compared with $\alpha$-Al$_2$O$_3$, which may mean that YSZ adsorbs some sulfur when it is incorporated into a Ni/YSZ catalyst. In any case, this finding indicates that YSZ may not behave similarly to a conventional catalyst support material and may have some enhanced activity for sulfur adsorption.

![H$_2$S Desorption](image)

Figure 6.2: Desorption of sulfur from support materials after treatment in 480 ppm H$_2$S at 500°C.

Uptake of SO$_2$ and H$_2$S on the Ni/YSZ and Ni/K$_2$O–CaAl$_2$O$_4$ catalysts is shown in Figure 6.3. Ni/YSZ shows no breakthrough for either SO$_2$ or H$_2$S, indicating that it adsorbs all of the sulfur during the one hour exposure period (318 $\mu$mol). Ni/K$_2$O–CaAl$_2$O$_4$ showed greater than 80% breakthrough for SO$_2$ after approximately 25 minutes on stream, and a total calculated adsorption
of 90 µmol. For this catalyst there appeared to be immediate SO$_2$ breakthrough which then declined to a minimum before increasing to a steady state. This feature is different for this catalyst, and may be due to diffusional resistance in the catalyst wherein sulfur took more time to diffuse to less accessible nickel in pores. Significantly more sulfur from H$_2$S was adsorbed on Ni/K$_2$O–CaAl$_2$O$_4$ (211 µmol), and stable breakthrough was 20% after 15 minutes on stream with a noticeable increase in adsorption at ~50 min. The net result of the uptake study is that, despite an active nickel surface area 14 times smaller than Ni/K$_2$O–CaAl$_2$O$_4$, Ni/YSZ appears to adsorb significantly more sulfur when exposed to either H$_2$S or SO$_2$.  

![SO$_2$ Uptake](image1)

![H$_2$S Uptake](image2)

Figure 6.3: Comparison of uptake of H$_2$S and SO$_2$ on Ni/YSZ and Ni/K$_2$O–CaAl$_2$O$_4$ at 500°C.
The \( \text{H}_2\text{S} \) desorption curves upon the ramp in temperature for \( \text{Ni/YSZ} \) and \( \text{Ni/K}_2\text{O–CaAl}_2\text{O}_4 \) are shown in Figure 6.4. Sulfur desorption from \( \text{Ni/YSZ} \) begins at approximately 600\(^\circ\)C and rises sharply until approximately 700\(^\circ\)C where it reaches a steady level as the temperature continues to ramp to 850\(^\circ\)C where it is held for an hour. Sulfur desorption drops off sharply after 1.1 hours, and the area under the desorption curves indicate that 146 \( \mu \text{mol} \) \( \text{H}_2\text{S} \) and 156 \( \mu \text{mol} \) \( \text{SO}_2 \) are desorbed. The shape of desorption curves for \( \text{H}_2\text{S} \) and \( \text{SO}_2 \) on \( \text{Ni/YSZ} \) are similar and indicate that the sulfur surface species are likely independent of the sulfur source. \( \text{Ni/K}_2\text{O–CaAl}_2\text{O}_4 \) desorption curves for \( \text{SO}_2 \) and \( \text{H}_2\text{S} \) are similar to one another, and the area under the curve indicates that both samples desorb similar amounts of sulfur; 45 \( \mu \text{mol} \) for the \( \text{SO}_2 \) treated sample and 30 \( \mu \text{mol} \) for the \( \text{H}_2\text{S} \) treated sample. For \( \text{Ni/K}_2\text{O–CaAl}_2\text{O}_4 \), there is significant desorption starting at 500\(^\circ\)C directly following the purge step. Because this desorption is so immediate, the entire curve is not captured and therefore some sulfur that was desorbed is not measured. This initial desorption may be the result of non-surface bound sulfur that is part of a 2-dimensional sulfur matrix that desorbs rapidly before hydrogen is introduced. This initial desorption stops at a temperature of approximately 675\(^\circ\)C, and is followed by a secondary desorption which starts at 750\(^\circ\)C for \( \text{SO}_2 \) and 800\(^\circ\)C for \( \text{H}_2\text{S} \) treated catalyst. Desorption significantly decreases after approximately 1.5 hours on stream and appears to trend towards zero. The two main desorption features for \( \text{Ni/K}_2\text{O–CaAl}_2\text{O}_4 \) are different from the single desorption feature for \( \text{Ni/YSZ} \), and this indicates that sulfur is bound on the surface in a different way.

The overall sulfur balances from the adsorption and desorption of \( \text{H}_2\text{S} \) and \( \text{SO}_2 \) for each material that was examined are given in Table 6.2 for the 1 hour exposure. The differences between the adsorbed and the desorbed sulfur either represents sulfur that is retained on the samples or sulfur not measured because it was below the FTIR detection limit. Based on the information reported in Table 6.2, it is likely that all of the samples retain some sulfur. The support materials retain much less than the catalysts, and YSZ retains almost three times more sulfur than a conventional support material. The commercial catalyst appears to retain a similar amount of sulfur as \( \text{Ni/YSZ} \) after \( \text{H}_2\text{S} \) treatment. Because the low temperature desorption was not entirely captured, the amount
of sulfur desorbed (and thus the amount retained) for Ni/K₂O–CaAl₂O₄ are listed as inequalities. The amount of sulfur desorbed from Ni/YSZ for both H₂S and SO₂ treatments is very similar, and implies that sulfur retention is independent of the sulfur species. There is evidence in the literature that treatment at much higher temperatures will fully remove sulfur from the nickel-based catalysts [31, 59]. The goal of the study was to compare sulfur adsorption and desorption for both catalysts, and not to optimize sulfur removal from the catalysts.

![H₂S Desorption](image1.png)
![SO₂ Desorption](image2.png)

Figure 6.4: Desorption of H₂S from SO₂ and H₂S treated catalysts Ni/YSZ and Ni/K₂O–CaAl₂O₄.

The amount of sulfur adsorbed by Ni/YSZ and Ni/K₂O–CaAl₂O₄ is reported in terms of the sulfur per nickel mole ratio in Table 6.2. There is significantly more accessible nickel on
Ni/K$_2$O–CaAl$_2$O$_4$ than Ni/YSZ (about 14 times more), and therefore the sulfur per surface nickel site is much higher for Ni/YSZ. The S/Ni ratio reported for Ni/K$_2$O–CaAl$_2$O$_4$ in Table 6.2 (11) is much higher than values for H$_2$S on Ni-alumina reported by Rostrup-Nielsen (0.54) and McCarty and Wise (1.11) [56, 58]. In terms of the number of sulfur atoms per nickel surface area, Rostrup-Nielsen reports 8.3 x 10$^{14}$ S atom/cm$^2$, which is much lower than the values reported in this study for Ni/K$_2$O–CaAl$_2$O$_4$ (1.9 x 10$^{16}$ S atom/cm$^2$) [53]. The unusually high sulfur coverage for both catalysts is likely a function of the high treatment concentration, which was intended to overcome the relatively high detection limit on the FTIR. The experiment is designed to evaluate sulfur uptake and compare it between Ni/YSZ and a conventional catalyst, and therefore the amount of sulfur adsorbed was not controlled as was done in studies by Rostrup-Nielsen and McCarty and Wise [56, 58]. Work by Hansen and Rostrup-Nielsen suggests that hydrogen and sulfur chemisorption on active nickel sites should be roughly equal [59]. Results reported in Table 6.2 indicate that this is not the case for either catalyst, but particularly not for Ni/YSZ wherein the sulfur uptake was two orders of magnitude more than the measured accessible nickel. These high numbers for sulfur adsorption on the Ni/YSZ catalyst imply that some physical event occurs when the catalyst is treated with high concentrations of sulfur. One possibility is that sulfur diffuses into the Ni/YSZ structure and possibly exchanges with oxygen vacancies in the lattice as proposed by Zhang et al. [123] Another possibility is that sulfur atoms bind together to create a large physical structure similar to those described by Erley [57]. The necessary analytical techniques to validate either of these scenarios were not available for this study. However, it is clear from this work that Ni/YSZ adsorbs much more sulfur per accessible nickel site than a greater than a conventional nickel-based catalyst: ~20 times more for H$_2$S and almost 50 times for SO$_2$.

An analysis of Ni/YSZ samples treated in 1000 ppm H$_2$S and 1000 ppm SO$_2$ was completed using XANES spectroscopy. As the oxidation state of sulfur in the molecule or crystal increases, the white line or absorption edge of the sulfur increases, in addition, the scattering environment in different structures also provide unique signatures to determine oxidation sates and structure environment of sulfur in a wide variety of samples [128]. The samples were prepared in the same
Table 6.2: Total sulfur adsorbed during uptake, sulfur desorbed, sulfur not desorbed, accessible nickel in catalysts, moles of sulfur per mole accessible nickel, and sulfur coverage in terms of the accessible nickel surface area.

<table>
<thead>
<tr>
<th></th>
<th>Sulfur Adsorbed (µmol)</th>
<th>Sulfur Desorbed (µmol)</th>
<th>Difference (µmol)</th>
<th>Accessible nickel&lt;sup&gt;a&lt;/sup&gt; (µmol)</th>
<th>mol S per mol Ni&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Sulfur coverage&lt;sup&gt;c&lt;/sup&gt; (S atom/cm&lt;sup&gt;2&lt;/sup&gt;)</th>
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<tr>
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<td>39</td>
<td>110</td>
<td></td>
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<tr>
<td>Ni/YSZ</td>
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<td>146</td>
<td>172</td>
<td>1.35</td>
<td>236</td>
<td>3.8 x 10&lt;sup&gt;17&lt;/sup&gt;</td>
</tr>
<tr>
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<td>1.9 x 10&lt;sup&gt;16&lt;/sup&gt;</td>
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<tr>
<td>Ni/YSZ</td>
<td>318</td>
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<td>162</td>
<td>1.35</td>
<td>236</td>
<td>3.8 x 10&lt;sup&gt;17&lt;/sup&gt;</td>
</tr>
<tr>
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<td>&gt; 45</td>
<td>&lt; 45</td>
<td>18.7</td>
<td>5</td>
<td>7.7 x 10&lt;sup&gt;15&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Amount of accessible nickel is calculated from hydrogen chemisorption measurements [99]

<sup>b</sup> Moles of accessible nickel

<sup>c</sup> Number of sulfur atoms per accessible nickel in units of surface area

<sup>d</sup> Assuming desorption as H<sub>2</sub>S
way as the adsorption-desorption experiments, but sulfur was not desorbed from the surface and instead the catalyst was cooled at 3°C/minute in nitrogen to room temperature. The samples were collected with care taken to minimize exposure to air so that the nature of adsorbed sulfur species would not change as a result of oxidation.

The normalized XANES spectra for two samples treated in H₂S and SO₂ are shown in Figure 6.5. A 10X magnified spectra of the raw S K-edge XANES spectrum of unreacted Ni/YSZ is also shown. We were not able to normalize this spectrum because the sulfur signal in this sample is very small and the Zr L-I edge (2531.6 eV) interferes with the post-edge S spectrum. A small sulfate peak near 2482 eV can be seen for this sample; given the 10X magnification the actual S intensity in this sample is very small. The sulfate in the unreacted sample is probably derived from sulfur in sulfated zirconia.

Analysis and fitting of the S K-edge XANES with reference compounds show that the main sulfur surface structure for the H₂S and SO₂ treated samples is a sulfide (e.g., NiS or Ni₃S₂). In fitting the data, we had used both Ni₃S₂ and NiS as references and found that NiS provides better fit results through the differences between the Ni₃S₂ and NiS references are small [127]. The fits (dotted lines) shown in Figure 6.5 are derived from fitting each of the two samples with 100% sulfide. We have also attempted to determine the fraction of sulfate in these two samples and the contribution from sulfate was found to be statistically insignificant. In other words, under the conditions of treatment, very little formation of sulfate layer over the YSZ was detected. A previous study by Chu et al. [124] used DFT calculations to demonstrate the possibility of sulfate formation on YSZ. The XANES result does not necessarily contradict this DFT prediction, rather, the XANES data suggests that in the two samples studied, sulfur prefers to react with Ni to form a sulfide rather than with YSZ to form a sulfate. This is evident when comparing the relative amounts of sulfide and sulfate; there is significantly more sulfide while sulfate is negligible. The XANES result of sulfide formation in treatment gas containing H₂S aligns with the results of Cheng and Liu, where Raman spectroscopic measurements during and after Ni/YSZ sulfidation in H₂S indicated formation of bulk sulfide in ex situ conditions [68].
The S XANES method only determines S speciation, so the question arises as to whether the sulfide formed is NiS or ZrS$_2$. In the literature, ZrO$_2$ only transforms to ZrS$_2$ in the presence of carbon disulfide at a temperature $> 1,300^\circ$C [129]. Therefore, the sulfide phase is most likely tied to nickel. The formation of the same main sulfur-containing phase helps to explain the similar (very slightly different) sulfur desorption from Ni/YSZ after it was treated with H$_2$S or SO$_2$.

![Figure 6.5: Normalized experimental (solid line) and fitted (dotted line) XANES spectra of Ni/YSZ treated in H$_2$S (top spectra) and SO$_2$ (middle spectra). Both are fitted with 100% sulfide. The red (at 2471.4 eV) and the blue (2482.3 eV) dashed lines indicate sulfide and sulfate X-ray absorption white lines, respectively. The 10X magnified non-normalized spectrum of unreacted Ni/YSZ is also shown, indicating the presence of small amounts of sulfate in the support.](image-url)
6.3.2 Methane Steam and Dry Reforming Sulfur Deactivation

Results from the adsorption-desorption study indicate that the interactions of sulfur on the surface of Ni/YSZ and Ni/K2O–CaAl2O4 are different, and therefore they may affect the steam and dry methane reforming activity of the catalysts differently. A previous study by this group evaluated the methane steam and dry reforming activity in the presence and absence of sulfur for both of these catalysts [99]. Results from this study indicated that extent of deactivation was greater for Ni/YSZ than the conventional nickel catalyst when exposed to H2S, SO2, and COS, as might be expected based on results from the adsorption-desorption study. The extent of deactivation during sulfur exposure measured during our previous study indicated that the sulfur poisoning mechanism for Ni/YSZ is particularly troublesome. This section explores the effect of the adsorption and desorption of sulfur on both nickel catalysts during methane reforming using micro-kinetic modeling.

To gain some insight into the adsorption/desorption behavior, we used a micro-kinetic mechanism and compared its predictions to the experimental results from our previous study. The micro-kinetic model for methane reforming on nickel catalysts was developed by the Deutschmann group, and they have validated it against experimental results for a variety of nickel-based catalysts including Ni/YSZ [1, 24]. A recent report by Appari et al. expanded on the Deutschmann micro-kinetic mechanism for methane reforming by adding a 26 reaction sub-mechanism to describe H2S poisoning on Ni-based catalysts; the mechanism was validated against data for dry and steam reforming of biogas [2]. Both mechanisms are developed using data derived from unity bond index-quadratic exponential potential (UBI-QEP) calculations to obtain the heats of adsorption, reaction enthalpies and activation barriers. The Appari sub-mechanism was further refined by adjusting the pre-exponential factors so that the predictions best matched the experimental data. A freely available software package for modeling steady state systems using a packed bed reactor (PBR) coupled kinetic and transport model (DETCHEM\textsuperscript{PBED}) is employed [68].

Prior to attempting to model the sulfur deactivation, the transport-kinetic model and methane reforming micro-kinetic mechanism were first validated against methane steam and dry reforming experimental results evaluated with no sulfur present. A comparison of computational results with
the observed methane conversions for steam and dry reforming in our previous study are shown for Ni/YSZ and Ni/K\textsubscript{2}O–CaAl\textsubscript{2}O\textsubscript{4} in Figure 6.6 [99]. There is generally very good agreement for both steam and dry reforming for both Ni/YSZ and Ni/K\textsubscript{2}O–CaAl\textsubscript{2}O\textsubscript{4}. The predicted and observed product distributions are shown in Figure 6.7, and the agreement is very good for both CO and H\textsubscript{2}. There is a slight discrepancy for hydrogen at lower temperatures for steam methane reforming; the Deutschmann group also reported a similar discrepancy [1]. The hydrogen produced during dry methane reforming is slightly under predicted by the model for Ni/YSZ. Overall, this micro-kinetic mechanism predicts the experimental results quite well under non-sulfur deactivated conditions. This good agreement is particularly impressive since the system is far from equilibrium (predictions shown by black lines) and thus is kinetically controlled.

Figure 6.6: Comparison of experimental and computational results for steady state steam and dry methane reforming in a packed bed reactor for Ni/YSZ and Ni/K\textsubscript{2}O–CaAl\textsubscript{2}O\textsubscript{4}.

The combined Deutschmann and Appari mechanisms were used to predict deactivation of methane conversion during steam and dry methane reforming by H\textsubscript{2}S using Ni/YSZ and Ni/K\textsubscript{2}O–CaAl\textsubscript{2}O\textsubscript{4} catalysts [99]. The predictions using the original mechanism are compared with our experimental results for steam methane reforming at 750°C and 1 ppm H\textsubscript{2}S in Table 6.3 (case 1). For both catalysts, the model predicts virtually no sulfur deactivation, while the experimental values were 93\% and 61\%, respectively. This discrepancy indicates that the model requires modifications to
Figure 6.7: Comparison of CO and H$_2$ mole fractions between computational results (model) and experimental results (symbols) for both dry and steam methane reforming.
describe the observed sulfur poisoning. One possible reason for such modifications is that the Appari sub-mechanism had been validated under different conditions. Appari et al. evaluated methane reforming with a Ni/Al₂O₃ catalyst in an atmosphere containing both CO₂ and H₂O at system velocities 10 times lower than our system [2, 130].

In the mechanism, sulfur adsorption on nickel is considered to be associative as shown in equation 6.1.

\[ \text{H}_2\text{S} + \text{Ni} \rightleftharpoons \text{Ni--H}_2\text{S} \quad (6.1) \]

Appari et al. performed a sensitivity analysis on the reactions in the sulfur poisoning sub-mechanism and concluded that the predictions are most sensitive to the \( \text{H}_2\text{S} \) adsorption and desorption reactions shown in equation 6.1 [2]. The magnitude of the sensitivity coefficients suggested that the reaction is partially equilibrated. If this is the case, it suggests that the equilibrium constant needs to be significantly higher. This can be accomplished by decreasing the desorption rate constant, increasing the adsorption rate constant, or some combination of both changes. In the Appari mechanism, the adsorption rate constant is calculated from a sticking coefficient \( \gamma = 0.6 \) that describes \( \text{H}_2\text{S} \) adsorption on Ni [2]. This value was chosen based on findings by Hegde and White for \( \text{H}_2\text{S} \) chemisorption on Rh(100), which reported a sticking coefficient of > 0.5 [131]. Thus the adsorption rate constant is already very close to the upper limit of \( \gamma = 1 \), so we first considered decreasing the desorption rate constant. For the first modification to the mechanism (Table 6.3, case 2), the desorption rate constant was reduced by a factor of close to 16,000 for Ni/YSZ and 96 for Ni/K₂O–CaAl₂O₄ to match the experimentally observed deactivation measurements. This reduction could be accomplished by either reducing the pre-exponential factor, increasing the activation energy, or a combination of both. The desorption reaction rate constant given by Appari et al. is \( 1.108 \times 10^{10} \text{ s}^{-1} \times T^{-0.8} \times \exp(-69.47\text{kJ/RT}) \). This can be expressed in simple Arrhenius form at 750°C as \( 1.9 \times 10^7 \times \exp(-62.7\text{kJ/RT}) \). We chose to increase the activation energy because the pre-exponential factor reported by Appari et al. to fit their data is already much lower than a typical simple desorption pre-exponential factor that is on the order of \( \sim 10^{13–16} \text{ s}^{-1} \) [2, 50]. The adjusted activation energy (in simple Arrhenius form) to fit the Ni/YSZ data was 145 kJ/mol, and
for Ni/K$_2$O–CaAl$_2$O$_4$ an adjustment to 101 kJ/mol was required.

Even though the adjusted barriers are higher than the value employed by Appari, they are still lower than expected based on literature measurements. McCarty and Wise measured the enthalpies of adsorption to be -143.1 kJ/mol (± 16.3 kJ/mol) for Ni/γ-Al$_2$O$_3$ and -155.2 kJ/mol (± 17.7 kJ/mol) for Ni/α-Al$_2$O$_3$ from equilibrium measurements for Ni/Al$_2$O$_3$ catalysts [58]. These measurements suggest that the desorption rate constant for the commercial catalyst should have a barrier of at least $\sim$150 kJ/mol, assuming that the support materials in this study are similar to the aluminas. Koningen and Sjöström measured the apparent activation energy for sulfur adsorption to be $\sim$120 kJ/mol on Ni/alumina catalysts during steam methane reforming [61]. This value, combined with the adsorption enthalpy measured by McCarty and Wise, results in a desorption barrier of $\sim$270 kJ/mol. Based on earlier work, Koningen and Sjöström estimated the desorption barrier would be $\sim$220 kJ/mol.

Table 6.3: Predicted deactivation by 1 ppm H$_2$S at 750°C on Ni/YSZ and Ni/K$_2$O–CaAl$_2$O$_4$ using the original Appari sulfur sub-mechanism and various changes to fit the experimental data.

<table>
<thead>
<tr>
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<th>Ni/YSZ</th>
<th>Ni/K$_2$O–CaAl$_2$O$_4$</th>
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<tbody>
<tr>
<td></td>
<td>$k_{ads}/k_{des}$ (cm$^3$/mol)</td>
<td>$k^{a}_{des}$ (s$^{-1}$)</td>
</tr>
<tr>
<td>Case 1$^b$</td>
<td>3.7 x 10$^8$</td>
<td>1.2 x 10$^4$</td>
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<tr>
<td>Case 2$^c$</td>
<td>5.9 x 10$^{12}$</td>
<td>7.5 x 10$^{-1}$</td>
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<tr>
<td>Case 3$^d$</td>
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<tr>
<td>Case 2$^c$</td>
<td>3.4 x 10$^{10}$</td>
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<tr>
<td>Case 3$^d$</td>
<td>4.0 x 10$^{10}$</td>
<td>2.0 x 10$^1$</td>
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</table>

$^a$ Desorption rate coefficient

$^b$ Original Appari mechanism (not adjusted) [2]

$^c$ Adjusted desorption activation energy ($E_{a,des}$) and Appari sticking coefficient (0.6)

$^d$ Adjusted desorption activation energy ($E_{a,des}$) and experimental sticking coefficient
These results suggest that an even higher barrier than the ones employed for case 2 should be considered. One way to accommodate a higher desorption barrier is to consider a lower adsorption rate coefficient than was used by Appari et al. [2]. We can estimate this value from the slopes of the deactivation curves \((d\theta_s/dt)\) reported in our previous work [99]. The deactivation curves are given in terms of the activity, which is calculated from the ratio of the deactivated activity to the initial activity. Rostrup-Nielsen postulated that the activity is equivalent to \(1 - \theta_s\), and therefore the change in sulfur coverage with respect to time can be found by taking the slope of the deactivation curve in the first several minutes of deactivation assuming that the reverse reaction is negligible. Using this value, the sticking fraction \((S_o)\) was calculated using equation 6.2 [50].

\[
\frac{d\theta_s}{dt} = \frac{p_{H_2S}}{N_A\sqrt{2\pi nk_bT}}S_o(T)
\]  

(6.2)

In this relation, \(k_b\) is the Boltzmann constant, \(T\) is the experimental temperature, \(m\) is the molecular mass of \(H_2S\), and \(N_A\) is Avogadro’s number. The partial pressure of \(H_2S\) was calculated for 1 ppm, 3 ppm, and 5 ppm at the experimental pressure (0.8 – 1 atm) and for the three temperatures that were evaluated (923 K, 1023 K, and 1073 K). The sticking fractions evaluated from the experimental data are reported in Table 6.4. Because they were not measured using the traditional ultra-high vacuum methods, the sticking fractions given in Table 6.4 are not absolute sticking coefficients. Instead, these are estimates that are meant to provide a measure of the initial sulfur adsorption rate on Ni/YSZ relative to the conventional catalyst as well as a “ballpark estimate” of the actual sticking coefficient.

The reported values for the commercial catalyst at higher \(H_2S\) concentrations might be lower limits; the steep initial drop in activity was followed by more gradual deactivation, making it difficult to properly capture the initial slope. For the 1 ppm dry reforming case, the initial deactivation rates are comparable for the two catalysts; note for Ni/YSZ that this rate is significantly faster than the steam reforming case. This could be due to the presence of more CO in the stream which is known to adsorb very strongly on Ni [60]. This is another reason to use the reported sticking fractions in Table 6.3 carefully, because other potential sources of deactivation were present. Despite the scatter, there appears to be an increase in the sticking probability on Ni/YSZ for both steam
Table 6.4: Sticking fractions evaluated from experimental data during steam and dry methane reforming at 750°C for 1 ppm, 3 ppm, and 5 ppm H₂S

<table>
<thead>
<tr>
<th></th>
<th>Steam Methane Reforming</th>
<th>Dry Methane Reforming</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni/YSZ</td>
<td>Ni/K₂O–CaAl₂O₄</td>
</tr>
<tr>
<td>1 ppm⁸</td>
<td>0.015</td>
<td>0.109</td>
</tr>
<tr>
<td>3 ppm⁹</td>
<td>0.094</td>
<td>0.059</td>
</tr>
<tr>
<td>5 ppm⁹</td>
<td>0.092</td>
<td>0.049</td>
</tr>
<tr>
<td>650°C⁽⁴⁾</td>
<td>0.018</td>
<td>0.026</td>
</tr>
<tr>
<td>750°C⁽⁴⁾</td>
<td>0.015</td>
<td>0.109</td>
</tr>
<tr>
<td>800°C⁽⁴⁾</td>
<td>0.144</td>
<td>0.143</td>
</tr>
</tbody>
</table>

⁸ Sticking fraction measured at 750°C  
⁹ Sticking fraction measured with 1 ppm H₂S

and dry reforming as the concentration of H₂S increases, whereas there is not much change for the commercial catalyst. For steam and dry reforming the sticking probability for both catalysts increases with the temperature in most cases, suggesting that the adsorption step is activated and not a simple molecular adsorption on the nickel surface. This observation is consistent with the measurements of Koningen and Sjöström [61] and Rostrup-Nielsen [56].

The sticking fractions calculated from the deactivation of the methane reforming reactions are much lower than the sticking coefficient used by Appari. This is perhaps the most important point to take away from these data because the lower sticking coefficients indicate that a lower desorption rate constant is appropriate. For the 1 ppm H₂S poisoning case during steam methane reforming, the sticking fraction is estimated to be a factor of 40 lower, meaning that the desorption rate would be a factor of 40 lower as well. To evaluate this, the experimentally evaluated sticking fractions (0.015 for Ni/YSZ and 0.109 for Ni/K₂O–CaAl₂O₄) were used in place of the Appari value of 0.6 and the desorption barriers were adjusted to fit the deactivation data for 1 ppm H₂S at 750°C (case 3). This resulted in a desorption activation energy for Ni/YSZ of 176 kJ/mol and 117 kJ/mol for Ni/K₂O–CaAl₂O₄. The desorption rate for Ni/YSZ case 3 is 6 x 10⁵ times lower than the desorption rate for the unadjusted model (case 1).
The experimental and predicted results at 1 ppm, 3 ppm, and 5 ppm H\textsubscript{2}S for steam and dry methane reforming at 750\textdegree C are compared in Figure 6.8. Predicted results were evaluated using the experimental sticking fractions from Table 6.4 in place of the sticking coefficient (SC) in the mechanism (solid lines) as well as the average of the experimentally based sticking fractions (dashed lines). All predicted results were found using the adjusted desorption barriers: 176 kJ/mol for Ni/YSZ and 117 kJ/mol for Ni/K\textsubscript{2}O–CaAl\textsubscript{2}O\textsubscript{4}. Given the uncertainties in estimating the sticking fractions, the agreement observed is encouraging, and demonstrate that the predictions are not unduly sensitive to their assignments. The difference for the dry reforming case for Ni/YSZ at 1 ppm H\textsubscript{2}S might well be due to experimental error, as one expects less deactivation at this lower concentration of H\textsubscript{2}S. The agreement between experimental and predicted results is quite good for Ni/K\textsubscript{2}O–CaAl\textsubscript{2}O\textsubscript{4}. Overall these results demonstrate that at 750\textdegree C, the adjusted model does a good job of modeling experimental deactivation for varying H\textsubscript{2}S concentrations.

![Figure 6.8: Comparison of experimental (symbols) and predicted (lines) results for steam and dry methane reforming at different H\textsubscript{2}S concentrations at 750\textdegree C for Ni/YSZ and Ni/K\textsubscript{2}O–CaAl\textsubscript{2}O\textsubscript{4}. Results were modeled using the experimentally-based sticking fractions (solid lines) and average sticking fraction (dashed lines).](image)

The current temperature dependent data were not adequate to properly evaluate the temperature dependence of H\textsubscript{2}S poisoning on either catalyst. Nevertheless, it is helpful to discuss this tem-
perature dependence in terms of the adjusted model parameters. The adjusted activation energies
(176 kJ/mol for Ni/YSZ and 117 kJ/mol for Ni/K$_2$O–CaAl$_2$O$_4$) are still lower than the previously
reported values (220-270 kJ/mol) [58, 61]. The fitted barriers could be increased by selecting a
higher pre-exponential factor for the desorption rate constant. To evaluate this, the pre-exponential
factor was evaluated using the inferred desorption activation energy of 270 kJ/mol for the com-
mercial catalyst based on the combination of the equilibrium measurements of McCarty and Wise
[58] and the 120 kJ/mol adsorption barrier measured by Koningen and Sjöström [61]. We chose
this catalyst since its support material is more similar to the alumina supports in the measurements.
For Ni/K$_2$O–CaAl$_2$O$_4$, the adjusted pre-exponential factor is $1.3 \times 10^{15}$ s$^{-1}$. This value is in the
range expected for desorption barriers [50]. Using this pre-exponential factor, the activation energy
for Ni/YSZ was evaluated and found to be 328 kJ/mol. This higher value could reflect the tighter
binding of H$_2$S to the YSZ support. It must be emphasized that our data cannot be used to determine
a definitive activation energy for desorption, but only to point out that it is not inconsistent with
earlier measurements. In this sense the corresponding pre-exponential term is reasonable. In any
event, more definitive statements regarding the temperature dependencies of the desorption rate
constant will require additional experiments.

Another way to check for consistency is to consider the temperature dependence of the measured
sticking fractions. As discussed above, the measured barrier for adsorption was $\sim$120 kJ/mol for
steam reforming using the alumina support material [2]. Given the scatter in our measured sticking
fractions in the steam reforming experiments, at best we can obtain approximate values of the
adsorption barriers from an Arrhenius plot of these values at the three temperatures. We focus on
the Ni/YSZ data since the initial slope measurements that determine the sticking fractions are better
defined here. This plot yields an adsorption barrier of $\sim$91 kJ/mol, lower than the earlier work, but
still suggesting that the adsorption is an activated process.

The results presented in this section demonstrate that the Appari et al. sulfur micro-kinetic
mechanism significantly underestimates the impact of very low concentrations of H$_2$S on reducing
the rate of steam and dry reforming of methane on both Ni/YSZ and Ni/K$_2$O–CaAl$_2$O$_4$. We
have shown that the sulfur poisoning is significantly more severe for Ni/YSZ than a conventional steam reforming catalyst. This difference demonstrates the importance of explicit consideration of the catalyst support in development of models for sulfur poisoning of nickel catalysts. There is indirect evidence that both the Appari desorption pre-exponential and activation energy are too low. Our data can be satisfactorily rationalized by using a desorption barrier based on earlier literature measurements. This in turn requires a much higher pre-exponential factor.

6.4 Conclusions

In this study, we measured the adsorption and desorption behavior of H$_2$S and SO$_2$ on Ni/YSZ and compared those measurements with analogous measurements on Ni/K$_2$O–CaAl$_2$O$_4$, a commercial reforming catalyst. The support for Ni/YSZ, (8% yttria stabilized zirconia), was evaluated for H$_2$S and SO$_2$ adsorption and desorption and compared to a conventional support material (α-Al$_2$O$_3$). H$_2$S retention on the YSZ support was approximately three times more than on the α-Al$_2$O$_3$ support, indicating that YSZ is likely to have significantly enhanced sulfur adsorption compared with conventional steam reforming catalyst supports, assuming these are similar to α-Al$_2$O$_3$. Ni/YSZ was observed to adsorb dramatically more sulfur (both H$_2$S and SO$_2$) than the conventional Ni/K$_2$O–CaAl$_2$O$_4$ steam reforming catalyst, despite having 14 times less accessible nickel surface area. The Ni/YSZ adsorbed ~20 times more H$_2$S and ~50 times more SO$_2$. More H$_2$S desorbed from the Ni/YSZ catalyst than from Ni/K$_2$O–CaAl$_2$O$_4$, and both catalysts retained similar amount of sulfur. For SO$_2$, Approximately 50% of the adsorbed sulfur desorbed from both catalysts at 850°C. Characterization of sulfur treated Ni/YSZ catalysts using XANES revealed that more SO$_2$ is desorbed than H$_2$S; implying that H$_2$S treated samples retain more sulfur. XANES characterization also showed that the main sulfur surface structure resulting from either H$_2$S or SO$_2$ adsorption is a nickel sulfate (e.g., NiSO$_4$), and that no bulk sulfide (Ni$_3$S$_2$) is formed.

The steam and dry reforming data for both catalysts with no added sulfur were compared to a micro-kinetic mechanism taken from the literature. Predictions with this mechanism, with no adjustments, were in good agreement for both methane conversion and product distributions for
both catalysts over the full range of experiments. We then compared an expanded version of this mechanism that included a sub-mechanism to describe H$_2$S poisoning on Ni-based catalysts to our data with added H$_2$S. The initial mechanism predicted much less deactivation than observed. Adequate fits to the observed deactivation data for Ni/YSZ required a factor of 16,000 increase in the adsorption/desorption equilibrium constant, suggesting that the desorption rate constants are significantly lower. For Ni/K$_2$O–CaAl$_2$O$_4$, a factor of 96 higher equilibrium constant was required to fit experimental data. Although it was not possible to properly characterize the temperature dependence of the desorption rate constant, the data for 1, 3, and 5 ppm added H$_2$S could be fit by using a desorption barrier consistent with literature measurements and a plausible pre-exponential factor ($\sim 10^{15}$ s$^{-1}$). The initial slopes of the time-dependent deactivation data were analyzed to obtain approximate adsorption sticking coefficients. Their temperature dependence suggested that the adsorption is an activated process, with a barrier similar to a literature measurement ($\sim$91 kJ/mol).

Results from this study characterize the severe impact of H$_2$S on Ni/YSZ, and point towards a very slow desorption rate as the reason. This is particularly a concern for SOFC applications where sulfur poisoning of the Ni/YSZ could inhibit the desired endothermic on-anode methane reforming as an approach to offset the exothermic electrochemical oxidation of the fuel.
CHAPTER 7
TRANSIENT TRANSPORT-KINETIC NUMERICAL SIMULATION OF STEAM AND DRY METHANE REFORMING OVER NI/YSZ

Packed bed reactor and tubular SAE results are compared with model predictions for methane steam and dry reforming on Ni/YSZ.

7.1 Introduction

In the previous chapter, the effect of sulfur on Ni/YSZ was modeled using a steady state packed bed reactor model. This chapter considers a transient packed bed reactor model. The steady PBR model is appropriate for validating steady state data such as for methane steam and dry reforming, but a transient model is better suited for time-dependent reactions like sulfur deactivation. As discussed in Chapter 5, the shape of the sulfur deactivation curve can be interpreted to understand certain aspects of the deactivation mechanism such as when different types of active sites are deactivated. A transient PBR model can be used to interrogate the sulfur deactivation sub-mechanism to determine if the observed shape of the deactivation curve is consistent with the modeling predictions. The differences between the model and experiment can then be evaluated for further improvement to the sulfur deactivation sub-mechanism. Attempts to model the transient sulfur deactivation on Ni/YSZ at the low concentrations (1 – 5 ppm $H_2S$) used in this study were unsuccessful. Personal communications with Professor Vinod Janardhanan, the original developer of the sulfur sub-mechanism, revealed that he and his students also had great difficulty in modeling concentrations of sulfur below 20 ppm using their sulfur sub-mechanism [132]. Attempts to model the simple adsorption and desorption of $H_2S$ on Ni/YSZ at 1 ppm were also unsuccessful.

Though attempts at transient sulfur deactivation modeling were unsuccessful, steady state results from the transient PBR experiments were compared with the steady state results obtained from Detchem in Chapter 6. The transient packed bed reactor model that is used in this work was previously used to model catalytic methane partial oxidation on substituted hexaaluminates
The development and implementation of this model was described in detail in Chapter 3. A micro-kinetic model that was developed by the Deutschmann group is used in conjunction with the packed bed reactor transport model [1]. The most recent version of this micro-kinetic model uses 42 elementary reactions, 7 gas phase species and 14 surface species in a micro-kinetic mechanism to describe methane steam and dry reforming and oxidation. In the mechanism, methane adsorbs associatively and reacts with either surface adsorbed oxygen or hydrogen to produce carbon species $\text{CH}_x$ ($x = 3, 2, 1$) adsorbed on the surface. Surface reactions between the intermediate carbon, hydrocarbon and oxygen species produce $\text{H}_2$, $\text{H}_2\text{O}$, CO, and $\text{CO}_2$ adsorbed on the surface which can then desorb. Likewise, unconverted $\text{CH}_4$, $\text{H}_2\text{O}$, and $\text{CO}_2$ also desorb from the surface. Heats of adsorption, reaction enthalpies, and activation barriers were found using the unity bond index-quadratic exponential potential (UBI-QEP) approach [1]. Some rate parameters were validated against experimental measurements.

The Deutschmann micro-kinetic mechanism has been validated for both dry and steam methane reforming in multiple reactor geometries including for channel flow such as a monolith [1, 23], for a button cell [133], in a packed bed reactor [80], and in the separated anode experiment (SAE) [24, 74]. The Deutschmann mechanism was evaluated in the steady state PBR Detchem model in Chapter 6, and model predictions were found to match experimental data very well. In this chapter, the Deutschmann micro-kinetic mechanism is used with the Zhu PBR model and a separated anode experimental reactor model for predicting steam and dry methane reforming results. The steady state PBR model results are compared with the transient PBR model predictions that have been run to steady state. Steady state for the transient PBR model is defined as a computational time off 60 seconds, or until the results are within 2% standard deviation of one another. Very small (0.001 second) time steps are taken in the 60 second computational time interval. The results from the PBR and the SAE are then compared for steam and dry methane reforming at similar conditions. The purpose of this comparison is to build a platform for studying catalytic aspects of Ni/YSZ, such as deactivation rates, in an environment that is free of transport effects associated with button cell experiments. Further, the rigorous validation of the methane steam and dry reforming
micro-kinetic mechanism for Ni/YSZ in a packed bed reactor allows for the subsequent addition of sub-mechanisms that can account for sulfur poisoning.

7.2 Evaluation of Methane Steam and Dry Reforming on Ni/YSZ in a Packed Bed Reactor

In this section, the packed bed reactor model with the Deutschmann micro-kinetic methane steam and dry reforming mechanism are used to predict experimental data. Where possible, experimental values for catalyst properties needed for the model are used.

7.2.1 Computational Parameters

The packed bed reactor model used for this work was described in Chapter 3 in detail. For the purpose of comparison of catalytic properties between Ni/YSZ and other catalysts presented in this chapter, a brief description of the necessary computational parameters for the model is given. Changes in mass and momentum in the system are assumed to be negligible in the radial and azimuthal direction, and are considered only in the axial direction. The catalyst bed is made up of many particles, but this model does not attempt to simulate chemistry on individual particles. Instead, the packed bed is posed as a porous foam structure. The porous foam has physical properties including porosity or void fraction, tortuosity, and the specific active surface area of the catalyst. These properties can be difficult to assign for modeling purposes either because they are difficult to measure or because they have not been reported by the authors. The origin of these properties and all other computational parameters for the packed bed reactor model are discussed in this section.

Tortuosity is the ratio of the distance traveled by a gas molecule through porous media to the distance traveled if the molecule traveled in a straight line. This value is difficult to characterize experimentally, and is therefore often used as a fitting parameter [134]. Al Juaied et al. [135] rearranged parameters in the Dusty Gas Model so that they were able to evaluate the porosity-to-tortuosity ratio numerically for flow through a stainless-steel membrane. Keyser et al. [134] experimentally evaluated the tortuosity of HNO$_3$-H$_2$O ices by measuring diffusion through the ices of varying thickness and fitting a curve to find the tortuosity from the Knudsen diffusion equation. They found an experimental value of 3.3, which is within the range commonly measured for solid
particles (2 – 6). For this study, the tortuosity was chosen based on this experimental work and on work done by Zhu et al. in packed bed reactors [80, 136].

It is possible to calculate porosity in the packed bed reactor, but assumptions must be made about particle geometry. The Ni/YSZ particles are assumed to be jagged but roughly spherical with a sphericity similar to sand (0.86). The catalyst particles were sieved to a size range of 300 – 355 micron particles. For packed beds with spherical particles in this size range, the porosity is on the order of 0.42 [137]. To maintain similarity with the most current implementation of the PBR transport model, a value of 0.45 was chosen for the porosity for both Ni/YSZ and Ni/K₂O—CaAl₂O₄ [136]. The specific catalytic surface area is the ratio of the active surface area to the volume of the catalytic bed [136]. The active surface area for both Ni/YSZ and Ni/K₂O—CaAl₂O₄ was measured and reported in Chapter 4. A lower value (2000 cm⁻¹) for the surface-to-volume ratio was calculated from the measured active nickel surface area after using a hydrogen reduction ramp rate of 10°C/min. A higher value (4200 cm⁻¹) was calculated when using a reduction ramp rate of 1°C/min. The higher value is used for modeling because the preparation of the catalyst sample for that analysis was similar to the preparation prior to PBR experiments. The same catalyst particle size fractions were used for Ni/YSZ and Ni/K₂O—CaAl₂O₄, and therefore the bed height and size fraction are assumed to be the same. The catalyst site density was reported by Maier et al. [1] after the development of the methane steam and dry reforming micro-kinetic mechanism (Γ = 2.60 x 10⁻⁹ mol cm⁻²).

For this study, three catalysts were evaluated in the packed bed reactor model: Ni/YSZ, Ni/K₂O—CaAl₂O₄, and Ni/MgAl₂O₄. The computational parameters for these catalysts are reported in Table 7.1. The nickel magnesium-spinel (Ni/MgAl₂O₄) material was used by Xu and Froment in their study to develop methane steam reforming kinetics [138]. They reported a great amount of detail about the catalyst and measured the active metal surface area, porosity and gave detailed descriptions about the experimental conditions. This made it possible to evaluate their catalyst using the packed bed reactor model.
Table 7.1: Computational parameters used in the packed bed reactor model for the catalysts used in this study (Ni/YSZ and Ni/K$_2$O–CaAl$_2$O$_4$) and a catalyst used in the work of Xu and Froment (Ni/MgAl$_2$O$_4$).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Ni/YSZ</th>
<th>Ni/K$_2$O–CaAl$_2$O$_4$</th>
<th>Ni/MgAl$_2$O$_4$ [138]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, °C</td>
<td>650 - 800</td>
<td>650 - 800</td>
<td>500-550</td>
</tr>
<tr>
<td>Pressure, atm</td>
<td>0.9 - 1</td>
<td>0.9 - 1</td>
<td>10</td>
</tr>
<tr>
<td>Bed length, mm</td>
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<td>7.62</td>
<td>10</td>
</tr>
<tr>
<td>Porosity</td>
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<td>0.45</td>
<td>0.528</td>
</tr>
<tr>
<td>Tortuosity</td>
<td>3.5</td>
<td>3.5</td>
<td>3.5</td>
</tr>
<tr>
<td>Particle diameter, μm</td>
<td>3.5</td>
<td>0.2</td>
<td>0.35</td>
</tr>
<tr>
<td>Pore radius, μm</td>
<td>1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Specific catalyst area, cm$^2$/cm$^3$</td>
<td>4,200</td>
<td>10,000</td>
<td>87,600</td>
</tr>
</tbody>
</table>

7.2.2 Evaluation of Homogeneous Chemistry

The absence of homogeneous chemistry was confirmed by predictions using a reaction mechanism developed at the Colorado School of Mines. The mechanism was based on updated version of C$_6$ pyrolysis and C$_3$ oxidation [139] mechanisms that have been validated against n-hexane pyrolysis randolph and ethane oxidation [139] data as well as several unpublished data sets [140]. This mechanism was evaluated between 873 K and 2073 K using a plug flow reactor (PFR) model in Chemkin-Pro. The inlet conditions to the PFR match those of the PBR, and both steam and dry methane reforming were evaluated. Results for the hydrogen, carbon monoxide, carbon dioxide and water mole fractions in the gas phase are shown with respect to temperature in Figure 7.1. No gas phase chemistry is observed in the operating region of interest (923 K - 1073 K) as evidenced by the constant mole fractions of reactants (H$_2$, H$_2$O, CO$_2$). No gas phase chemistry is observed until approximately 1400 K for both SMR and DMR. This is an important finding because it validates the assumption that no homogeneous chemistry is occurring in the temperature region of interest.

7.2.3 Steam and Dry Methane Reforming in a Packed Bed Reactor

The packed bed reactor model was used to evaluate the steam methane reforming experimental conditions reported by Xu and Froment [138]. A comparison of the model predictions with
Figure 7.1: Gas phase chemistry in the temperature range 873 K – 2073 K for the reactants of SMR and DMR in a plug flow reactor.

Experimental results from this study are shown in Figure 7.2. This experimental system is fairly close to equilibrium, but it is likely kinetically controlled. The packed bed reactor model predictions match the experimental results well, and are all slightly higher. Xu and Froment did not report the product concentrations for this study, and we were therefore not able to compare their results with the predicted results. This good agreement indicates that both the packed bed reactor model and the micro-kinetic mechanism from Deutschmann can be used to predict steam methane reforming activity on nickel-based catalysts in a packed bed reactor.

A comparison of experimental and modeling results for the steam and dry methane reforming on Ni/YSZ is shown in Figure 7.3. Model predictions for the steady state PBR model Detchem are shown along with results from the transient PBR model at steady state. For steam methane reforming, the Detchem model matches experimental data quite well, whereas the transient PBR model under predicts methane conversion particularly at lower temperatures. Both models use the same governing equations, but the Detchem model does not have a time dependent term. The authors
of Detchem give details about the governing equations, method for solution and the solver and language used to develop the software. However, they do not explicitly discuss the implementation of the model. Differences between the modeling results could be caused by differences in the modeling implantation or differences in the solvers (e.g., Limex vs. ODE15s). Both PBR models give good predictions of methane conversion for the dry methane reforming. Both model predictions are within the error bars of the experimental results indicating that either model would be appropriate for prediction of the steam and dry methane reforming on YSZ over this temperature range.

A comparison of the \( \text{H}_2 \) and CO molar fractions produced from steam (left) and dry (right) methane reforming is given in Figure 7.4. Again, the results from the Detchem steady state model and the PBR transient model ran to steady state are compared. For the Detchem model, there is generally very good agreement with experimentally measured CO and \( \text{H}_2 \). Only the hydrogen concentration for dry methane reforming is under predicted. The PBR model under predicts

Figure 7.2: Comparison of experimental results from Xu and Fromment with model results and equilibrium [138].
hydrogen for both steam and dry methane reforming, and appears to have a greater discrepancy than the Detchem model. This could result from not running the transient model long enough to reach steady state. Alternatively, this could be caused in part by the Deutschmann model itself. Maier et al. [2] observed a similar discrepancy in the hydrogen model predictions when compared with methane steam reforming experimental results. They were also using the Deutschmann microkinetic mechanism, and this evidence may point to some under prediction inherent in the model. The CO model predictions from the PBR model agree well with the experimental results. The good agreement between the model prediction and experimental results for CO may indicate that the discrepancy between hydrogen model and experimental results is not caused by reactions tied to CO such as the water-gas shift.

A comparison of the model predictions for methane conversion from the Detchem and the transient PBR models are compared with experimental results from Ni/K₂O−CaAl₂O₄ shown in Figure 7.5. Predictions from both the Detchem and the transient PBR are very good. For steam methane reforming, there is a jump from the 1023 K to 1073 K case that is not linear. This may be due to a change in velocity that was higher at 1073 K than 1023 K. The experimental velocities were
Figure 7.4: Experimental $\text{H}_2$ and CO molar concentration during methane steam and dry reforming compared with model predictions and equilibrium for Ni/YSZ. Model predictions were made using a steady state model (blue line) and a transient PBR model (red line).
used where possible. Experimental velocities were calculated from the standard volumetric flow rates, measured system pressure and measured system temperature. The results shown in Figure 7.5 help to bolster the argument that the Deutschmann mechanism can be used to reliably predict methane conversion in either steam or dry methane reforming if the appropriate transport model is used.

![Figure 7.5: Comparison of experimental results (symbols) with model predictions from a steady state PBR model (red line) and a transient PBR model (blue line) for Ni/K_{2}O−CaAl_{2}O_{4}.](image)

Predictions for the major product species, CO and H\textsubscript{2}, are compared with experimental measurements in Figure 7.6. As was the case for Ni/YSZ, the concentrations of H\textsubscript{2} and CO for both dry and steam methane reforming are well predicted by the Detchem model. Again, the transient PBR model under predicts hydrogen for both SMR and DMR. Unlike Ni/YSZ, the transient PBR model over predicts CO for both SMR and DMR. The main different between Ni/YSZ and Ni/K_{2}O−CaAl_{2}O_{4} is the difference in particle size and pore size. Because of this, it could be possible that the calculation of diffusion through the catalyst causes some over prediction in the CO. Presumably, running the PBR transient model to steady state should eliminate this effect. The PBR model was operated for 100 computational seconds, which equates to one day of running time. The extensive time needed to reach steady state with this transient PBR model may be prohibitive, particularly when compared with the quick computational time for Detchem.
Figure 7.6: Comparison of CO and H$_2$ product concentrations for experimental measurements (symbols) and model predictions from the steady state PBR model (blue line) and the transient model (red line) for Ni/K$_2$O–CaAl$_2$O$_4$. 
7.2.4 Sulfur Poisoning

The original intent of using a transient PBR model was to add a sulfur sub-mechanism to the Deutschmann steam and dry methane reforming mechanism to evaluate the transient sulfur poisoning on Ni/YSZ. The sulfur sub-mechanism was developed by Appari et al. and consists of 26 reactions that describe $\text{H}_2\text{S}$ adsorption, desorption and subsequent sulfur surface reactions with other adsorbed species such as $\text{OH}^*$, $\text{H}^*$, and $\text{CO}^*$ [2]. Evaluation of the original Appari sulfur sub-mechanism using the transient PBR model quickly revealed several limitations associated with both the transient PBR model and the sulfur sub-mechanism. These limitations are evident when comparing model predictions for the transient $\text{H}_2\text{S}$ poisoning of Ni/YSZ during steam methane reforming at $750^\circ\text{C}$ with experimental results shown in Figure 7.7. For 1 ppm $\text{H}_2\text{S}$ poisoning, the model predicts a much slower decline in the methane reforming activity than was observed experimentally. As discussed previously in this chapter, the group that developed the sulfur sub-mechanism also observed similar behavior at sulfur concentrations lower than 20 ppm. Their work was done at higher sulfur concentrations (> 20 ppm), and focused on the transient deactivation of Ni/alumina catalysts. As discussed in Chapter 5, the adsorption and desorption parameters for $\text{H}_2\text{S}$ poisoning on Ni/YSZ need to be substantially different than what was reported by Appari et al. [2]. Using the original Appari sulfur sub-mechanism, the steady state model prediction for the activity of sulfur poisoned Ni/YSZ during steam and dry methane reforming was much higher than the experimentally observed value. The model prediction for the deactivation rate at 10 ppm $\text{H}_2\text{S}$ is closest to the experimentally observed rate for 1 ppm $\text{H}_2\text{S}$. It was demonstrated in Chapter 6 that the desorption rate used by Appari et al. was orders of magnitude too large to account for the observed deactivation at longer times in the current data on a conventional catalyst and especially for Ni/YSZ. In that context, the predicted decreased rate of deactivation is not surprising. A conversation with the developers of the sulfur sub-mechanism led me to understand that they validated the model for 20 ppm and higher concentrations of $\text{H}_2\text{S}$. While this may be an appropriate range for biogas which was their original modeling intent, it is not appropriate for a theoretically desulfurized stream with a low concentration of $\text{H}_2\text{S}$. 
Figure 7.7: Comparison of H$_2$S poisoning using the original Appari sulfur sub-mechanism for different H$_2$S concentrations compared with the experimental results taken at 750°C in steam methane reforming on Ni/YSZ.

The transient PBR model had some inherent limitations. Because the model was developed in Matlab, the speed of calculation was very slow. For example, it took several days and up to one week to calculate comparatively short experimental times. To obtain one data set shown in Figure 7.7 (∼14 - 20 minutes real time), it took 4 days of computational time. This prohibitively long computational time can be remedied by converting the PBR code into a compiled language (e.g., C++), but that was beyond the scope of this work.

A comparison of the 10 ppm H$_2$S deactivation curves during steam methane reforming at 750°C on Ni/YSZ for the original sulfur sub-mechanism with the adjusted mechanism using the desorption rate parameters developed in Chapter 6 ($A = 1.3 \times 10^{15} \text{ s}^{-1}$, $E_{a,des} = 328 \text{ kJ/mol}$) is shown in Figure 7.8. Due to time constraints, the model predictions for the original mechanism were not calculated past 20 minutes. Based on results from the steady state model, though, it would be expected that the 10 ppm case would deactivate Ni/YSZ to a value of greater than 90%. However, the adjusted deactivation curve model predictions were run to the point where 100% sulfur deactivation was
achieved; as would have been observed for 10 ppm H₂S poisoning under these conditions based on the near 100% deactivation observed for 1, 3, and 5 ppm H₂S. Though the model is deactivated to total completion, it deactivates much more slowly than would have been expected based on experimental results with 1, 3, and 5 ppm H₂S poisoning on Ni/YSZ. This could be the result of a shift in the total active surface area during poisoning which Appari et al. accounted for in their transient deactivation model [2, 130]. Regardless, these results are promising and indicate that the adjusted rate parameters deactivate the system more rapidly than the original sulfur mechanism when used with the transient PBR model.

Figure 7.8: Comparison of the adjusted sulfur desorption rate modeling results with the original sulfur sub-mechanism for 10 ppm H₂S on Ni/YSZ during steam methane reforming at 750°C. Time constraints did not allow for the entire time-span of the original model to be calculated.

7.3 Evaluation of Methane Dry Reforming on Ni/YSZ in the Tubular Separated Anode Experiment

The tubular SAE is a realistic physical design for SOFC implementation in industry. Tubular SOFCs are reminiscent of industrial reformers which are long tubes that are loaded with catalytic material and heated together in a furnace house with manifold inlet and outlet of reactants and products. Unlike industrial reformer tubes, tubular SOFCs must have separation between the inlet fuel and inlet air streams which diffuse through the SOFC membrane prior to reaction. This
difference makes it necessary to model both the kinetics on SOFC membranes (e.g., anodes and cathodes) and the transport because transport can affect SOFC performance. Because of this, the tubular SAE model uses the micro-kinetic model validated using packed bed experiments along with a transport model developed for predicting flow through porous media.

### 7.3.1 Computational Parameters

User defined input parameters to the tubular SAE model (this study) are compared with previously reported parameters for planar SAE models in Table 7.2 [24, 72, 74, 141, 142]. For this study, the values for bed porosity and tortuosity were taken from the previous studies as it was not possible to measure these values [24, 74]. The nickel particle size and pore radius were the same as used for the packed bed reactor reported in Table 7.1. These values were found to be higher than had previously been reported for Ni/YSZ as shown in Table 7.2. The discrepancy between previous studies and this one stems from the fact that none of the five previous studies listed in Table 7.2 used the same Ni/YSZ tubular material that was used for this study. As discussed in Chapter 4, differences in synthesis methods can cause sometimes large differences in the nickel particle size. Because of this, it is important that this value is measured for each catalyst batch. The calculated specific catalyst area that is used in this study is very close to values that were previously used for Ni/YSZ. Unlike other studies, the tubular SAE was designed to accommodate a variable reaction zone length as was discussed in Chapter 3. This allows flexibility in attempting to maintain a relatively isothermal reaction zone. Because of this, the reaction zones used in this study are quite a bit shorter than those used in previous studies. Further, a range of reaction zones (reaction channel lengths) are evaluated.

### 7.3.2 Dry Methane Reforming on Ni/YSZ in the Tubular SAE

Dry methane reforming was performed on the tubular SAE that was developed for this work. The tubular anodes are very sensitive, and loading the tubes in the experimental apparatus was done with extreme care. Reducing the anode is a slow process and was done over an 18 hour period. Once loaded, the anode was ramped to 650°C at a rate of 1°C/min and held for 2 hours. The anode
Table 7.2: User defined parameters for the PBR and tubular SAE models.

<table>
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<tr>
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<td>1</td>
</tr>
<tr>
<td>Pore radius, µm</td>
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<td>0.5</td>
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</tr>
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<td>Specific catalyst area, cm²/cm³</td>
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<td>5000</td>
<td>2080</td>
<td>500</td>
<td>1500</td>
</tr>
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was then ramped to 800°C at 1°C/min and held for another 2 hours. A comparison of XRD spectra for the fresh and post-reaction Ni/YSZ tubular anode are shown in Figure 7.9 and confirm that the anode is reduced and does not re-oxidize during reaction. This is evident from the disappearance of the NiO peaks in the fresh sample and the appearance of metallic nickel peaks in the post-reaction sample. Both XRD spectra shown in Figure 7.9 are done on the so-called “reaction zone”; the variable length zone on the anode defined by area that is not coated in electrolyte.

Dry methane reforming was carried out on the tubular SAE anode, and demonstrated the very low coking tolerance on Ni/YSZ under aggressive reforming conditions. Molar concentrations for the major reactants (CO₂, CH₄) and products (H₂, CO) measured in the fuel and electrolyte exhaust streams are shown in Figure 7.10. As can be seen in the fuel exhaust stream, the change in methane concentration from zero to > 20 mol% is rapid and indicates a rapid decline in the Ni/YSZ anode activity. This experiment was run at 800°C and at a CO₂:CH₄ ratio of 0.5 with a reaction zone length of 2 inches. The composition of this reactant stream was chosen because it mimics the biogas compositions of real sewage plants that were evaluated and reported by Van Herle et al. [44] All of the biogas compositions measured from these sewage plants exhibit a CO₂:CH₄ ratio of very close to 0.5. These aggressive experimental conditions caused significant coking on the anode surface and eventual cell failure as shown in Figure 7.11. The tubular anode broke while in the reactor,
Figure 7.9: XRD spectra for the fresh and post-reaction “reaction zone” of the tubular Ni/YSZ anode.

and this may explain why the composition in the electrolyte exhaust is mainly H₂. The measured flow rate in the electrolyte exhaust was very low (< 20 sccm), and this indicates that most of the gases in the system were exiting through the much larger annulus of the fuel tube (9 mm vs. 2 mm). These results are applicable for use in designing tubular SOFC systems, particularly those for use with biogas, because they demonstrate the physical limitations of tubular SOFCs under coking conditions. Because biogas is a popular new fuel for SOFCs, it is important to understand the limitations of Ni/YSZ SOFC operation in methane and carbon dioxide mixtures. These results make it clear that coking can be extremely detrimental for Ni/YSZ anodes and lead to cell failure.

The photograph of the post-reaction anode shown in Figure 7.11 demonstrates several other aspects of the configuration of the tubular SAE. First, it is confirmation that chemistry proceeds primarily on the reaction zone portion of the dipped tubular Ni/YSZ anodes. As can be seen in Figure 7.11, coking occurs primarily on the reaction zone. Another aspect of the tubular SAE that is evident from Figure 7.11 is that the dipped parts of the anode turn from green to gray during
Figure 7.10: Experimental results from dry methane reforming on Ni/YSZ tubular anode in the tubular SAE at 800°C and CO₂:CH₄ = 0.5. Results are for the molar concentrations of CO₂, CH₄, H₂, and CO in the fuel and electrolyte exhaust streams.
reduction. This color change is likely an indicator for the conversion of NiO to metallic nickel, and it is also apparent from the crushed catalysts used in the PBR work. This means that hydrogen is somehow accessing the underlying Ni/YSZ beneath the dip coat. Hydrogen could be diffusing directly through the electrolyte dip coat or it could be diffusing through the 1 mm thickness of the anode tube. If this is the case, then once gases enter the reaction zone, they can diffuse both radially and axially while traveling through the anode tube. The model for the tubular SAE assumes radial transport only. This apparent discrepancy between the actual transport in the experiment and the assumed transport mechanism in the model creates a problem when attempting to model the tubular SAE. Because of this, the tubular SAE experimental apparatus that was designed for this work appears to be inappropriate for use with the tubular SAE model.

7.3.3 Modeling Dry Methane Reforming on Tubular SAE

Despite difficulties with the experimental design for the tubular SAE, the tubular SAE model was developed in Matlab as described in Chapter 3. The model developed for the tubular SAE was similar to previous models for the planar SAE system, but this model was developed in Matlab
which imposed calculation restraints. Because Matlab is an interpreted language, the functions are operated sequentially rather than compiled first. The planar SAE models were written in either C++ or Fortran, which are both compiled languages. This allows for the model to solve the plug flow problem in the fuel and electrolyte channels which provides the flux into the anode which is then solved with both the inlet and outlet fluxes into the anode. In Matlab, the implementation of the plug flow problem and the porous anode requires the problems to run separately and then the fluxes are stored. The fluxes are then recalled by the porous anode program and used in the calculation. The net result is that the implementation of the tubular SAE model in Matlab requires prohibitively long calculation times.

The tubular SAE model developed in Matlab was used to predict dry methane reforming results across a temperature range of 923 – 1073 K as shown in Figure 7.12. The experimental results (symbols) were taken for a tubular anode with a reaction zone length of 0.25 inches. The experimental hydrogen results in the electrolyte are much higher than the model predictions. This could be the result of breakdown of the SOFC anode cell during experiments. The CO is also under predicted by the model. The model under predictions for CO and H$_2$ and the over prediction of methane indicate that the methane conversion is low. In the electrolyte, the CO$_2$ concentration is over predicted whereas in the fuel stream the CO$_2$ prediction is good. The poor agreement between model predictions and experimental results is probably primarily caused by difficulties in collecting steady state data using the tubular SAE reactor. Even at the higher CO$_2$:CH$_4$ ratio, there was significant coking observed on the post-reaction anode. This coking reaction is transient and causes a non-constant change in the dry methane reforming reaction rate. It is therefore very difficult to obtain steady state data that is free from deactivation.

The Matlab implementation of the SAE is severely hindered by its inability to compile and calculate the plug flow and porous gas transport simultaneously. Because of this, the planar SAE model written in C++ was converted to a tubular model by multiplying the species and total fluxes by the ratio of the hydraulic perimeter to the tube area as detailed in Chapter 3. Model predictions from the resultant tubular SAE model implemented in C++ were compared with predictions for the Matlab
Figure 7.12: Comparison of tubular SAE model predictions with experimental results at 800°C for CO₂:CH₄ = 2 for dry methane reforming.
Figure 7.13: Comparison of model predictions for the tubular SAE system made using the Matlab model and the C++ model.
model in Figure 7.13. Though it wasn’t possible to directly validate the Matlab implementation of the tubular SAE model, the comparison with an already developed and validated model (the C++ model) lends credibility to the Matlab model. The model predictions for the fuel side of the anode match well with the exception of the predictions done at 923 K. For CO in the fuel stream, the model predictions at 923 K match well but veer away from one another at 1073 K. The electrolyte model predictions are reasonably close for H\(_2\) and CH\(_4\), but very poor for CO\(_2\) and CO. This indicates that the Matlab model does not capture the flux from the anode back into the electrolyte channel.

Though the C++ model is faster, the advantage of using a Matlab-based model is that it is easier to interpret, understand, and manipulate; particularly for those inexperienced in computer programming. The Matlab programming language is relatively easy to read and interpret, whereas C++ requires some basic programming knowledge to decipher. Another advantage of using Matlab is that the ODE15s solver appears to be more robust when compared with the Cantera implementation of the CVODES solver. I glean this information from the difficulty with which the Cantera CVODES solver changes array sizes and input parameters. For example, the Cantera CVODES solver had significant difficulty when I attempted to add the sulfur species to the model. This was not the case for the Matlab model which can be easily adapted to accommodate almost any input parameters. Because of this, it may be worthwhile to evaluate the issues associated with the electrolyte channel predictions made in Matlab so that the tubular model implementation can be used more widely. Care should be taken, though, to accommodate for the extra time needed to obtain Matlab modeling results since it takes several orders of magnitude longer to complete calculations than the C++ model does.

### 7.4 Conclusions

A transient packed bed reactor model was developed for the purpose of evaluating transient sulfur poisoning of nickel. The packed bed reactor model was shown to match well with experimental results from Xu and Froment, which validated both the transport and kinetic aspects of the model. Steady state results for methane conversion from the transient PBR model matched the steady state
Detchem model results well for both steam and methane reforming for Ni/K$_2$O–CaAl$_2$O$_4$. For Ni/YSZ, the steady state PBR model results were slightly lower than the Detchem model results. For both the transient and steady state models, the products matched well to experimental data. However, for the transient PBR model, the hydrogen was under predicted indicating a possible variance in the model that causes hydrogen to be under predicted. This is confirmed by results from Maier et al. who observed similar results for the Deutschmann mechanism.

The purpose of developing the transient PBR model was to evaluate transient sulfur deactivation on Ni/YSZ. However, it was not possible to evaluate sulfur deactivation at the low concentration of H$_2$S that was used. This appeared to be the result of some computational limitation that was also observed in the Janardhanan group who developed the sulfur sub-mechanism. Results for sulfur deactivation at different sulfur concentrations were evaluated in the transient model to demonstrate the poor agreement between experimental results and model predictions. However, when comparing the unadjusted and adjusted models for the 10 ppm case, it was found that the adjusted rate parameters for H$_2$S desorption lead to faster and complete deactivation of Ni/YSZ.

The tubular SAE experimental design suffers from uncontrollable hydrogen transport within the anode tube. This is evident from a color change of the purportedly coated Ni/YSZ anode from green to gray which is likely the result of hydrogen reduction of NiO to metallic nickel. The tubular SAE experimental design was further hindered by significant and detrimental coking of the anode tube which caused cell failure. Because of this, it was difficult to evaluate the cell at steady state and compare with model predictions. The tubular SAE model was implemented in Matlab which is an interpreted language that inherently requires sequential calculation of the plug flow in channels followed by flux in the porous anode. When compared with the C++ tubular model, though, model predictions for the fuel channel matched well between the Matlab and C++ models. However, electrolyte channel predictions, particularly for CO$_2$ and CO, did not agree between the two models. This indicates that there is room for improvement in the Matlab model.
CHAPTER 8
SUMMARY AND FUTURE WORK

This section presents a summary of findings from the studies presented in this thesis, and proposes future work that might be done as a result of these findings.

8.1 Summary

The work in this thesis has contributed to the overall understanding of sulfur poisoning on Ni/YSZ and has put this into context by comparing with a commercially available nickel-based catalyst. A packed bed reactor experimental system was designed and constructed with care taken to ensure that no tubing would adsorb sulfur prior to experiments. Experiments were performed using different sulfur species (H\textsubscript{2}S, SO\textsubscript{2}, COS) in different concentrations (1 ppm, 3 ppm, 5 ppm) and at different temperatures (650°C, 750°C, 800°C). The comparison of these parameters offered a better insight into the magnitude of sulfur poisoning on Ni/YSZ during methane steam and dry reforming. When comparing the extent of deactivation of Ni/YSZ with a commercially available catalyst (Ni/K\textsubscript{2}O–CaAl\textsubscript{2}O\textsubscript{4}), it is clear that Ni/YSZ is significantly more sensitive to sulfur poisoning. The rates of deactivation for Ni/YSZ are much faster than for Ni/K\textsubscript{2}O–CaAl\textsubscript{2}O\textsubscript{4}. Previous experimental work that probes sulfur deactivation on Ni/YSZ has focused on electrochemical deactivation. The work presented in this thesis confirms that both the methane and dry methane reforming rates on Ni/YSZ are strongly affected by even small amounts of sulfur. Previous studies have not demonstrated this strong effect in the context of industrial reforming catalysts, and this finding is one of the overarching results of this thesis.

Results from this study also showed that Ni/YSZ was completely deactivated (zero activity) by all sulfur species that were studied (H\textsubscript{2}S, SO\textsubscript{2}, COS). Contrarily, the commercial catalyst was deactivated to a non-zero steady state activity for all sulfur species. The rates of deactivation for the sulfur species on both catalysts was: COS > SO\textsubscript{2} ≥ H\textsubscript{2}S. The rate of deactivation by COS poisoning was much faster than for SO\textsubscript{2} and H\textsubscript{2}S, indicating that even trace amounts of COS will
severely and rapidly poison a nickel-based catalyst and in particular the Ni/YSZ active sites. This is the first study that has examined COS poisoning on Ni/YSZ, and this finding is important because COS is a likely side-product of some sulfur removal processes that may be used to reduce sulfur content in fuels to be fed to an SOFC.

The adsorption and desorption behavior of H$_2$S and SO$_2$ on Ni/YSZ were compared with measurements made on Ni/K$_2$O–CaAl$_2$O$_4$. Ni/YSZ adsorbed ~20 times more H$_2$S and ~50 times more SO$_2$ than Ni/K$_2$O–CaAl$_2$O$_4$ despite having 14 times less active nickel. During temperature programmed desorption, Ni/YSZ appeared to desorb about 50% of the sulfur from both SO$_2$ and H$_2$S treatments. Ni/K$_2$O–CaAl$_2$O$_4$ exhibited similar sulfur retention (~50%) for SO$_2$, but most of the H$_2$S that was adsorbed by the sample did not desorb. Sulfur adsorption and desorption on the support materials was also examined, and it was found that YSZ retains three times more adsorbed sulfur from H$_2$S treatment than a conventional α-Al$_2$O$_3$ support material. The support material for the commercial catalyst was not available, and therefore a very common reforming support material (α-Al$_2$O$_3$) was used to compare with the YSZ support material. Results that demonstrated that YSZ has an enhanced sulfur capacity compared with α-Al$_2$O$_3$ support DFT studies in the literature that postulate that YSZ is active for sulfur adsorption and stabilization of sulfur in the lattice. XANES characterization of two Ni/YSZ samples treated with H$_2$S and SO$_2$ at 800°C showed the presence of nickel sulfide (e.g., NiS), but very little evidence of sulfate was found. This confirms that though oxygen is present during SO$_2$ poisoning, there is not enough to form a surface sulfate. Instead, the primary species formed during sulfidation appears to be nickel sulfide.

Methane steam and dry reforming experimental data was compared with model predictions from freely available software (Detchem) which models a steady state packed bed reactor. There was very good agreement between experimental data and model predictions for methane conversion and H$_2$ and CO molar compositions for steam and dry methane reforming between 923 K – 1073 K using the Deutschmann micro-kinetic mechanism. It is important to note that the experiments were done in the kinetically controlled regime far from equilibrium, and the developers of this micro-kinetic mechanism evaluated it near equilibrium. Therefore, this work is a valuable contribution to
the body of work pertaining to the Deutschmann mechanism because it validates the model in a non-equilibrium operating region.

The sulfur sub-mechanism was combined with the Deutschmann methane steam and dry reforming micro-kinetic mechanism and evaluated using the steady state PBR model. The original sulfur sub-mechanism predicted far less deactivation than was observed experimentally. To fit the experimental deactivation observed on Ni/YSZ, the \( \text{H}_2\text{S} \) adsorption/desorption equilibrium constant had to be adjusted by a factor 16,000. This fitting suggested that the desorption rate constant was significantly lower than was reported by Appari et al. (authors of the sulfur sub-mechanism) \[2\]. This may be unsurprising considering that Appari et al. developed their sulfur sub-mechanism for use with nickel-based catalysts supported on conventional materials such as alumina which was shown in work done as part of this thesis to have far less capacity for sulfur adsorption than YSZ. Despite this, it was also found that the commercial catalyst examined in this work required a factor of 96 increase in the equilibrium constant to fit experimental deactivation data. It was not possible to properly characterize the temperature dependence of the desorption rate constant. However, the experimental deactivation data obtained for 1, 3, and 5 ppm \( \text{H}_2\text{S} \) were fit using the adjusted desorption barrier that is consistent with literature measurements and a plausible pre-exponential factor (\( \sim 10^{15} \text{ s}^{-1} \)). This work also illuminated that the Appari pre-exponential factor used for the \( \text{H}_2\text{S} \) desorption rate is much lower (\( 10^{10} \text{ s}^{-1} \)) than might be expected for the dissociative desorption of a relatively immobile molecule from a surface (\( 10^{13} – 10^{16} \text{ s}^{-1} \)).

Initial slopes of deactivation data were analyzed to obtain approximate adsorption sticking coefficients for \( \text{H}_2\text{S} \) on Ni/YSZ and Ni/K\(_2\)O–CaAl\(_2\)O\(_4\). The experimentally measured sticking coefficients are by no means to be taken as absolute values, but they are good indicators for the temperature dependence of \( \text{H}_2\text{S} \) adsorption which appears to have a barrier similar to literature measurements (\( \sim 91 \text{ kJ/mol} \)). This work is the first to attempt to evaluate the adsorption of \( \text{H}_2\text{S} \) on Ni/YSZ in terms of an experimental sticking fraction. Results indicate that the sticking coefficient proposed by Appari et al. (0.6) may be higher than the actual value, which was measured to be approximately 0.015 at 750°C during steam methane reforming. Though the experimentally
measured sticking fractions are not to be taken as absolute, they also indicate that the adsorption rate is a function of temperature which is not reflected in the Appari sulfur sub-mechanism.

A transient packed bed reactor model that is based on work done by Zhu et al. [80] was developed for use in evaluating the transient deactivation as a result of sulfur poisoning on Ni/YSZ. Model predictions calculated using this transient PBR model were in good agreement with a data set for methane steam reforming published by Xu and Froment [138]. The transient PBR model was run to steady state (60 computational seconds or ± 2% standard deviation) and compared with the steady state model predictions obtained using the Detchem PBR software. There was good agreement between the transient and steady state model for methane dry reforming on Ni/YSZ. The transient PBR model appeared to slightly under predict methane conversion for steam methane reforming. This under prediction also affected the product model predictions which were low for both hydrogen and carbon monoxide for steam methane reforming. The model predictions for hydrogen during dry methane reforming were as low as low, and this may be the result of the micro-kinetic mechanism itself because these are similar to results obtained by Maier et al. [1]. For Ni/K_2O–CaAl_2O_4, the model predictions for the transient PBR and SS PBR matched very well with only slight discrepancies between the catalysts. A similar under prediction in the hydrogen concentration was observed, but the CO concentrations were closer to experimental data.

The purpose of using a transient PBR model was to evaluate the sulfur deactivation with respect to time. However, the low concentrations that were used to evaluate sulfur poisoning on Ni/YSZ (1, 3, 5 ppm) proved to be too low to evaluate in the transient PBR. This could have been caused by some numerical difficulties in the program itself. Communications with the group that developed the sulfur sub-mechanism confirmed that they too had difficulty modeling transient sulfur deactivation at H_2S concentrations lower than 20 ppm. To evaluate the adjusted desorption rate parameters developed in Chapter 6, an H_2S concentration of 10 ppm was used and compared with the original sulfur sub-mechanism. Results showed that the adjusted rate parameters did indeed deactivate the system more quickly and to complete deactivation as would be expected for the 10 ppm case based on the results for the 1, 3, and 5 ppm case.
Finally, a tubular SAE reactor was designed and constructed to attempt to overcome some of the sealing difficulties associated with the planar SAE. The design incorporates two custom made Teflon tees that connect the inner Ni/YSZ anode and an outer quartz tube. Fuel gases flow to the inside of the anode and the electrolyte gases (e.g., CO$_2$) are fed to the outer tube. A tubular SAE model was developed in Matlab and compared with results from an adapted tubular SAE model developed in C++. Experimental results from the tubular SAE reactor indicated that the reactor design suffered from significant coking which lead in every case to cell fracture. Because of this severe coking, it was not possible to obtain steady state methane dry reforming results that might be compared with model predictions. Upon reducing the cell in situ, it was evident that there was hydrogen diffusion to Ni/YSZ in spite of the fact that a thin electrolyte film was employed to prevent this diffusion. A color change in the Ni/YSZ that was coated indicated that the nickel was being reduced. This is probably the result of hydrogen diffusion either through the thin film or through the anode itself after gases entered the reaction zone. The tubular SAE model implementation in Matlab agreed relatively well with the C++ tubular model for the species in the fuel channel exhaust. There was poor agreement between the two models for the electrolyte exhaust. This could result from an incomplete calculation of the fluxes from the anode to the electrolyte channel in the Matlab implementation. Regardless, good fuel channel predictions appear to be obtained using the Matlab model.

8.2 Future Work and Recommendations

In Chapter 5, the sulfur poisoning effect on Ni/YSZ was evaluated at relatively low sulfur concentrations. These concentrations were chosen because they closely mimic sulfur concentrations of post-sulfur removal fuel streams. These low concentrations made it difficult to model the sulfur deactivation using the transient model presumably because of computational difficulty. More experiments at higher sulfur concentration are needed to validate the proposed changes to the sulfur sub-mechanism in the transient PBR model.
Characterization of two sulfur treated samples was done using XANES which is a powerful technique for delineating surface species. It would be interesting to evaluate the change in the sulfur surface species with different coadsorbates in the stream. This may also lead to some better understanding of the comparatively low sulfur sticking fractions that were observed experimentally. These experimentally measured sulfur sticking fractions are by no means to be used as absolute sticking coefficients, but they do indicate the need for an improvement in absolute sticking coefficients for sulfur species on Ni/YSZ. These measurements must be done under careful conditions, and are often difficult to do because of the tendency for sulfur to adsorb on stainless steel. The trend towards 3D printing could pose an interesting solution for this because some parts of the ultrahigh vacuum systems needed to evaluate these sticking coefficients could be printed using Teflon which would eliminate sulfur adsorption. New and innovative methods for fabricating analytical equipment with less reactive materials will significantly enhance our ability in the future to measure these once difficult to obtain values.

It is important to evaluate the temperature dependence of the sulfur deactivation in a more controlled atmosphere possibly at lower gas hourly space velocities. I was unable in this study to evaluate the temperature dependence of the adjusted sulfur sub-mechanism, and therefore I would recommend that these values be evaluated and verified experimentally. Further, the interesting observation that the sulfur adsorption reaction is activated will contribute to understanding the sulfur poisoning reaction equilibria. Studies to understand the temperature dependence specifically of the adsorption reaction on Ni/YSZ would enhance the body of work in this area greatly. Finally, the computational modeling done in this thesis was significantly hindered by the simple question of whether to use an interpreted or compiled language for modeling. It is not a simple choice between the two because the solvers available in C++ (e.g., CVODES) are not nearly as robust or easily applied as the ODE15s solver and other Matlab solvers. One potential solution for this problem may be combination of the two approaches. This can be done by using a relatively simple and freely available program to convert Matlab files to so-called “.mex” files which can then be compiled like C++ files. This could be done to pass Matlab arrays in a fashion similar to the way
C++ data arrays (e.g., hash tables) are passed and changed in C++ programs. One requirement for using .mex files is that the data type for each variable must be defined. Native Matlab programs do not require that data types are defined and this is part of the reason Matlab programs run slowly. Though a fully characterized Matlab program that is compiled using a C++ compiler may not run as quickly as a C++ program, it may be faster than the original Matlab program and could gain valuable computational time. This could provide some improvement over the existing packed bed program used in this work in which a single computation can span days.

Alternatively, more toolboxes are available now for scientific computation using C++. There are better solvers available, and they are improving all the time. Students in the future may attempt to write the program in C++ using some of the newly improved solved and possibly some combination of Python programming with C++. Python and C++ are more readily compatible than C++ and Matlab, and Python is almost as simple to use and has many add-ins available for scientific computing.
REFERENCES CITED


