A Comparison of H₂S, SO₂, and COS Poisoning on Ni/YSZ and Ni/K₂O–CaAl₂O₄ During Methane Steam and Dry Reforming

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Abstract

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.

Keywords: Methane steam reforming, methane dry reforming, CO₂ reforming, hydrogen sulfide, sulfur dioxide, Ni/YSZ, solid oxide fuel cell, SOFC, nickel catalyst, YSZ support, sulfur poisoning, carbonyl sulfide, sulfur, poisoning

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 1 and 2. SOFCs possess some internal reforming capacity and can operate on hydrocarbon-based fuels such as diesel reformat, natural gas, and biogas. Each of these fuels contains varying amounts of methane. This is beneficial since the internal reforming reactions of methane (equations 3 and 4) are endothermic and help to mitigate the heat produced by the highly exothermic electrochemical oxidation.[1–4] Many studies in the past two decades have confirmed the applicability of SOFCs for both steam [5–12] and dry (CO₂) methane reforming. [13–19]

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.[20, 21] Sulfur impurity concentrations are typically 5 - 500 ppm for natural gas [20, 21], 15 - 900 ppm for diesel [22, 23], and 200 - 20,000 ppm for biogas [24, 19]. Desulfurization processes are used to remove sulfur, and may require either hydrogenation or oxidation of the fuel stream to produce H₂S or SO₂, 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.[21, 25, 26]

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.[27] The sulfur poisoning mechanism that is generally accepted for H₂S on metallic nickel (Ni) proceeds as:

where sulfur adsorbs dissociatively and hydrogen gas is

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formed.[28, 29] Equation 5 indicates that the partial pressure of hydrogen in an operating SOFC system could influence the poisoning behavior of H₂S on Ni, however there is no consensus in the literature to confirm this. Instead, it has been demonstrated that even sub-ppm levels of H₂S increase the polarization resistance on an operating Ni/YSZ SOFC by upwards of 28% at 750°C in the presence of 0.05 ppm H₂S.[30] At similar operating temperatures, the cell voltage of an operating SOFC was observed to drop 10% in the presence of 0.1 ppm H₂S.[27] Upon removal of sulfur, some studies have speculated that the cell regenerates via equation 5 because only hydrogen and inert gases are present in the system.[27]

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. [31] examined a methane-containing simulated coal syngas and reported that 1 ppm H₂S 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 [32] examined the steam methane reforming activity of a Ni/YSZ SOFC operating with a biogas-type fuel that contained 29% CH₄, 13% H₂, and 58% H₂O doped with 2 to 25 ppm H₂S. 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. [14] found that 1 ppm H₂S 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 [33] examined the activity of methane steam reforming on Ni/YSZ in 50 ppm H₂S 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., H₂S vs SO₂) 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, SO₂ is a main product that is removed catalytically and carbonyl sulfide (COS) has been observed as an unwanted side-product.[34, 35] SO₂ and COS formation proceed as:

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.[34] It is clear that there is a possibility that H₂S is not the only sulfur impurity present in

natural gas after desulfurization by various techniques. To our knowledge, no studies have ever been performed to delineate the effects of COS or SO₂ 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/K₂O–CaAl₂O₄). Ni/K₂O–CaAl₂O₄ 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 (H₂S, SO₂, 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.

2. Experimental

2.1. Catalyst Preparation

The Ni/YSZ anode material was purchased from CoorsTek Inc. and was provided in tubular form. Details of the fabrication of similar tubular anodes made by CoorsTek are given elsewhere.[36] Ni/YSZ tubular anodes were crushed using a hammer mill and sieved to +45/-60 mesh (250 - 355 micron). A nickel-alumina based commercial naphtha reforming catalyst (Süd Chemie, C11-NK) was purchased as a 5 hole ring pellet, and was crushed and sieved in the same way as the Ni/YSZ anodes. C11-NK is a nickel loaded on CaAl₂O₄ catalyst with approximately 8.5 wt% K₂O (Ni/K₂O–CaAl₂O₄).[37]

2.2. Packed Bed Reactor Apparatus

Experiments were carried out in the packed bed reactor (PBR) system shown in Figure 1 that consists of a 11 mm i.d. (12 mm o.d.) quartz tube suspended in an electric furnace (Thermcraft). An identical tube is hung next to the reactor tube and used as a bypass. Because low concentrations of sulfur were delivered to the catalyst, it was important to prevent sulfur uptake on stainless steel tubing which could result in uncontrolled sulfur exposure to the catalyst. All sulfur containing gases, from the supply gas cylinder to the inlet of the reactor, were delivered via completely inert tubing that was either made of Teflon or stainless steel coated with a thin film of Sulfinert® (Restek). Two gas manifolds were used:

1) coated sulfur delivery manifold for nitrogen (sweep gas), hydrogen sulfide, sulfur dioxide, and carbonyl sulfide and 2) non-coated manifold for nitrogen, helium, hydrogen, carbon monoxide, carbon dioxide, methane, and air. Sulfur containing gases were delivered directly to the reactor through a Teflon tee using a 3-way Teflon solenoid valve (Valco). All other gases were fed through a five foot stainless steel capillary tube heated to 200°C. The gases were co-fed with water that was delivered at a steady rate using a high pressure liquid metering pump (Optos, Eldex). Mass flow controllers were calibrated and checked using an optical flow calibrator (Bios, Drycal). 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.

Figure 1: Schematic of the packed bed reactor (PBR) experimental apparatus.

Downstream of the catalyst bed, vapors were removed in a tube-in-tube Teflon condenser that was cooled using a recirculating chiller (Oasis, Solid State Cooling). Any remaining water was removed in a coalescing filter with a paper filter element (Parker) and non-condensable gases were 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) with a cycle time of approximately 3 minutes. Gases measured using the micro-GC include He, H₂, N₂, O₂, CH₄, CO₂, and CO. Opto 22 hardware and software (PAC Project Pro) was used to record data from thermocouples, pressure transducers, mass flow controller feedback and time every 15 seconds.

2.3. Experimental Procedure

Approximately 200 mg of quartz wool was used to keep the catalyst in position in the center of the furnace to maintain a uniform catalyst temperature. The thermocouple used to record the temperature of the reaction was placed just above the catalyst bed. Prior to reaction, NiO in both Ni/YSZ and the Ni/K₂O–CaAl₂O₄ was reduced to metallic nickel via hydrogen reduction. Temperature programmed reduction (TPR) profiles of the catalysts showed different optimal reduction temperatures possibly as a result of the different support materials, and therefore different reduction protocols were used. Ni/YSZ was reduced in 12 vol% H₂ 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/K₂O–CaAl₂O₄ was reduced in 12 vol% H₂ 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.

Methane dry and steam reforming experiments were performed following the pretreatment step. After the pretreatment step, the catalyst was cooled to the reaction temperature (650°C, 750°C, or 800°C) and purged in nitrogen. 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 $1.5 \times 10^5 \text{ h}^{-1}$ with 800 mg catalyst. To put the Ni/YSZ and Ni/K₂O–CaAl₂O₄ catalysts on the same basis, a catalyst mass was used for each such that the total nickel surface area in the system was 0.051 m². This was approximately 800 mg for Ni/YSZ and 55 mg for Ni/K₂O–CaAl₂O₄. To ensure the same GHSV in both systems, the 55 mg Ni/K₂O–CaAl₂O₄ was diluted with 745 mg pure α -Al₂O₃ since the native support was not available. The α -Al₂O₃ material was examined for methane reforming activity and it was confirmed that it has none. The composition of the reactant stream for both steam and dry reforming was: 14.3 vol% He, 8.6 vol% H₂, 34.3 vol% N₂, 14.3 vol% CH₄, and 28.5 vol% H₂O or CO₂. Hydrogen was added to the stream to ensure that metallic nickel stayed reduced during reforming. Helium was used as the tracer because the GC was calibrated very precisely for the concentration range used, and nitrogen was used as a bath gas to increase the GHSV. 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. H₂S, SO₂, and COS were examined at concentrations of 1, 3, and 5 ppm.

2.4. Catalyst Characterization

Brunauer-Emmett-Teller (BET) surface areas were calculated from nitrogen physisorption isotherms collected at 77 K using a Quantachrome Quadrasorb SI instrument using ultrahigh purity nitrogen (99.999%, Airgas). Prior to obtaining

the isotherms, the catalysts were first degassed by heating to 250°C under vacuum (30 mTorr) and held overnight. The catalysts were then cooled to room temperature under a flow of ultrahigh purity helium (99.999%, Airgas).

Hydrogen temperature programmed desorption (H_2 -TPD) was performed using a Micromeritics ASAP 2020 unit. Catalysts were first treated in the same way as described in the Section 2.3. After *in situ* pre-treatment, the catalyst was 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. From hydrogen uptake data, the catalyst dispersion was calculated using a relation given by Davis and Davis [38]:

$$d = \frac{2 \times (H_2 \text{ chemisorbed})}{\text{Total number of Ni atoms}} \quad (9)$$

Nickel crystallite growth as a function of ramp temperature during reduction was examined in a Quantachrome Autosorb-1C. Ni/YSZ was dried at 120°C in ultrahigh purity He (99.999%, Airgas) for one hour and then ramped at 1°C/min, 3°C/min, 10°C/min, and 20°C/min to 850°C and held for one hour in 100% ultrahigh purity H_2 (99.9999%, Air Liquide). It was then cooled to adsorption temperature (40°C) and H_2 was dosed for 30 minutes. The resultant pressure-volume data was used to calculate the hydrogen dispersion via the bracketing method.

Powder x-ray diffraction (XRD) spectra were taken with a Rigaku Ultima IV with Cu- K_α 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. The Scherrer equation was used to calculate the particle size of metallic nickel and nickel oxide on each catalyst. 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. ever 50°C).

3. Results

3.1. Catalyst Characterization

The nickel loading, BET surface area, hydrogen uptake from TPD data, and dispersion data are listed in Table 1. The Ni/YSZ catalyst has a much lower BET surface than the commercial catalyst (Ni/K₂O–CaAl₂O₄) indicating that it is much less porous. This is expected because YSZ is a dense and hard support capable of withstanding frequent thermal cycling. Results from the hydrogen uptake show that the commercial reforming catalyst takes up roughly 15 times more hydrogen. This agrees with the BET surface area; the

majority of the nickel is on the surface of the YSZ. Metal dispersion was calculated from the hydrogen uptake data, and Ni/K₂O–CaAl₂O₄ has a dispersion of roughly 30 times Ni/YSZ which incorporates the difference in metal loading (roughly a factor of 2) and the difference in H_2 uptake (roughly a factor of 15). Though there is more than double the nickel loaded on Ni/YSZ than Ni/K₂O–CaAl₂O₄, the dispersion results indicate it is present in a form that is difficult to access. One possibility is that there are large nickel “islands” on the surface of the YSZ that create large nickel particles which have very low active surface area.

Table 1: Metal loading, BET surface area, hydrogen uptake calculated from H_2 -TPD, and dispersion of the Ni/YSZ and Ni/K₂O–CaAl₂O₄ catalysts.

	Metal Loading, (wt%)	BET SA, (m ² /g)	H_2 uptake, $\mu\text{mol/g}$	d^a , %
Ni/K ₂ O–CaAl ₂ O ₄	20	9.7	15.2	0.892
Ni/YSZ	46	0.8	1.1	0.028

^a Dispersion (d) calculated from equation 9

The XRD spectra for both as synthesized, untreated, and undiluted catalysts are shown in Figure 2. The NiO peaks labeled in the spectra indicate a difference in particle size between Ni/YSZ and Ni/K₂O–CaAl₂O₄. Comparing the peak at approximately 44°, the Ni/YSZ peak is sharp in contrast to the Ni/K₂O–CaAl₂O₄ 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 650Å for Ni/YSZ and 250Å for Ni/K₂O–CaAl₂O₄. Other peaks in the two XRD spectra were confirmed to be from the support materials.

Figure 2: XRD spectra for fresh Ni/YSZ and Ni/K₂O–CaAl₂O₄ with labeled NiO peaks (■). All of the other peaks in the spectra are from support materials.

Reduction *in situ* was performed in a hot stage XRD and spectra were taken at varying intervals during the ramp from room temperature to the reduction temperature (800°C). The catalyst was held at the reduction temperature for two hours to determine whether crystallite growth was observed. Results from *in situ* reduction of Ni/YSZ are shown in Figure 3 for the metallic nickel peak at 51.85°. Metallic nickel is not present

below 300°C as observed in the room temperature XRD spectra of fresh catalysts shown in Figure 2. The first evidence of metallic nickel is at 300°C which is in agreement with H₂ temperature programmed reduction (TPR) spectra. As the temperature ramps, the nickel crystallite growth is linear until roughly 650°C and then grows at a slower rate to a steady size of approximately 700Å. These data shows that the metallic nickel crystallite size more than triples in size during reduction which could play a role in the activity of the catalyst. The effect of ramp rate during reduction on the Ni/YSZ crystallite size was examined by measuring the active nickel surface area using hydrogen chemisorption after reduction pretreatments with varying ramp rates. The results of this study indicate that there is no strong correlation between the ramp rate and the active nickel surface area.

Figure 3: Change in crystallite size during *in situ* reduction of Ni/YSZ in the XRD during a temperature ramp from room temperature to 800°C and held at 800°C for 2 hours (arrow).

3.2. 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 4. 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 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 10) or the Boudouard reaction (equation 11).[39, 40]

Figure 4: Methane turnover frequencies on Ni/YSZ and Ni/K₂O–CaAl₂O₄ for steam (bottom) and dry (top) methane reforming at 750°C.

There is extensive literature on the coking of nickel-based reforming catalysts.[41–44] 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/K₂O–CaAl₂O₄. In particular, step sites are more reactive than terrace sites and carbon has high stability on these step sites.[45] 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/K₂O–CaAl₂O₄. 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.[45] Unlike Ni/K₂O–CaAl₂O₄, 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.[46] Ni/K₂O–CaAl₂O₄ has very similar dry and steam methane reforming rates as shown in Figure 4, and the deactivation rates are also very similar. This indicates that carbon deposition might not come from CO₂ 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/K₂O–CaAl₂O₄, 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.[46, 47] The disparity between methane dry and steam reforming turnover frequencies is another example of the activity differences between Ni/YSZ and Ni/K₂O–CaAl₂O₄.

Figure 5: Results from the Ni/YSZ activity loss of steam (left) and dry (right) methane reforming by 1, 3, and 5 ppm H_2S (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.

3.3. Methane Reforming With Sulfur

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

$$a = \frac{(n_{\text{CH}_4,i} - n_{\text{CH}_4})_t / n_{\text{CH}_4,i}}{(n_{\text{CH}_4,i} - n_{\text{CH}_4})_o / n_{\text{CH}_4,i}} \quad (12)$$

where $n_{\text{CH}_4,i}$ 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 12 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 $\text{Ni/K}_2\text{O-CaAl}_2\text{O}_4$.

The deactivation of Ni/YSZ is given in Figure 5 for steam (left) and dry (right) methane reforming at 750°C in H_2S (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 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.

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_2S and SO_2 have similar deactivation rates for steam and dry reforming data. Bartholomew [48] describes how some qualitative information about the nature of deactivation can be gleaned from the shape of the deactivation

Figure 6: Activity loss of steam (left) and dry (right) methane reforming by 1, 3, and 5 ppm H_2S (top), SO_2 (middle), and COS (bottom) at 750°C for the $\text{Ni}/\text{K}_2\text{O}-\text{CaAl}_2\text{O}_4$ commercial catalyst.

curve. For example, the 1 ppm deactivation curve shape for both H_2S 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_2S and SO_2 cases for both steam and dry reforming.

Deactivation curves for $\text{Ni}/\text{K}_2\text{O}-\text{CaAl}_2\text{O}_4$ are given in Figure 6 for steam (left) and dry (right) methane reforming at 750°C in H_2S (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 and exhibits the same spike near minute 27 time on stream that corresponds to valves switching.

The shape of the deactivation curves for $\text{Ni}/\text{K}_2\text{O}-\text{CaAl}_2\text{O}_4$ 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.[48] 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 $\text{Ni}/\text{K}_2\text{O}-\text{CaAl}_2\text{O}_4$ (right) is shown in Figure 7 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 $\text{Ni}/\text{K}_2\text{O}-\text{CaAl}_2\text{O}_4$ 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.[28] These results suggest that the observed temperature dependence is affected by factors in addition to the adsorption/desorption equilibrium.

Table 2 summarizes the measured normalized activities at various times for all the experiments. There are substantial differences in deactivation rate behavior between

Figure 7: 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 2: Comparison of activities at various conditions between Ni/YSZ and Ni/K₂O–Al₂O₄ at different temperatures and either for steam methane reforming (SMR) or dry methane reforming (DMR).

Conditions	Sulfur Species	Temperature	Conc. (ppm)	Ni/YSZ					Ni/K ₂ O–CaAl ₂ O ₄				
				Activity ^c at time (minutes)					Activity ^c at time (minutes)				
				30	40	60	80	100	30	40	60	80	100
SMR ^a	none	650°C	0	1.00	0.98				1.00	0.86			
		750°C	0	1.00	0.99	0.99	0.99	0.99	1.00	0.90	0.87	0.85	0.82
		800°C	0	1.00	0.98				1.00	0.87			
	H ₂ S	650°C	1	0.98	0.88	0.52	0.06		0.79	0.76	0.62	0.53	0.49
		750°C	1	0.99	0.92	0.57	0.13		0.85	0.77	0.59	0.47	0.39
			3	0.94	0.65	0.11	0.03		0.78	0.57	0.38	0.29	0.24
			5	0.93	0.38	0.02	0.02		0.72	0.48	0.29	0.22	0.17
		800°C	1	0.99	0.86	0.13	0.04		0.89	0.76	0.55	0.42	0.33
	SO ₂	650°C	1	0.99	0.90	0.68	0.27	0.08	0.92	0.88	0.75	0.74	0.66
		750°C	1	0.97	0.89	0.49	0.09	0.05	0.84	0.76	0.63	0.54	0.46
			3	0.97	0.75	0.06	0.06	0.05	0.85	0.70	0.49	0.36	0.30
			5	0.93	0.29	0.06	0.07	0.06	0.78	0.57	0.35	0.26	0.21
		800°C	1	1.00	0.92	0.68	0.24	0.07	0.87	0.77	0.64	0.51	0.43
	COS	650°C	1	0.99	0.72	0.06	0.05	0.04	0.79	0.78	0.60	0.48	0.40
		750°C	1	0.89	0.57	0.06	0.05	0.06	0.78	0.61	0.42	0.27	0.24
			3	0.75	0.01	0.01	0.01	0.01	0.57	0.33	0.14	0.06	0.07
			5	0.52	0.01	0.01	0.02	0.02	0.50	0.28	0.17	0.11	0.11
		800°C	1	0.88	0.52	0.05	0.04	0.04	0.86	0.74	0.56	0.43	0.31
DMR ^b	none	650°C	0	1.00	1.00				1.00	0.95			
		750°C	0	1.00	0.99	0.99	0.99	0.99	1.00	0.95	0.93	0.91	0.90
		800°C	0	1.00	0.98				1.00	0.95			
	H ₂ S	650°C	1	0.81	0.66	0.29	0.04	0.04	0.87	0.81	0.69	0.58	0.52
		750°C	1	0.94	0.86	0.61	0.26	0.02	0.93	0.86	0.72	0.60	0.53
			3	0.88	0.50	0.04	0.06	0.05	0.87	0.68	0.47	0.35	0.25
			5	0.80	0.04	0.03	0.03	0.03	0.75	0.49	0.27	0.16	0.09
		800°C	1	0.96	0.82	0.36	0.03	0.03	0.87	0.77	0.61	0.49	0.39
	SO ₂	650°C	1	0.82	0.73	0.58	0.40	0.18	0.09	0.85	0.77	0.70	0.66
		750°C	1	0.95	0.84	0.61	0.22	0.04	0.89	0.84	0.75	0.67	0.60
			3	0.90	0.61	0.05	0.05	0.04	0.92	0.81	0.64	0.50	0.40
			5	0.85	0.23	0.08	0.04	0.04	0.95	0.79	0.52	0.34	0.24
		800°C	1	0.96	0.87	0.63	0.35	0.08					
	COS	650°C	1	0.87	0.79	0.51	0.16	0.07	0.94	0.81	0.64	0.53	0.45
		750°C	1	0.92	0.74	0.19	0.04	0.04	0.82	0.63	0.40	0.28	0.21
			3	0.82	0.17	0.06	0.05	0.05	0.72	0.36	0.18	0.14	0.12
			5	0.77	0.08	0.07	0.07	0.08	0.64	0.28	0.15	0.12	0.12
		800°C	1	0.92	0.80	0.46	0.05	0.03	0.86	0.65	0.40	0.27	0.18

^a Steam methane reforming (SMR)

^b Dry methane reforming (DMR)

^c Activity is defined in equation 12

the two catalysts. Specifically, the initial deactivation rate $\text{Ni/K}_2\text{O-CaAl}_2\text{O}_4$ 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.

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 deactivation. As seen in Table 2, Ni/YSZ is almost completely deactivated while $\text{Ni/K}_2\text{O-CaAl}_2\text{O}_4$ maintains between 10 - 60% of its initial activity depending on the sulfur species. The maximum deactivation should reflect the pseudo-equilibrium sulfur surface coverage, θ_s , which can be calculated from the maximum observed loss in activity $(1 - a)$. [49] The results for the H_2S poisoning studies are shown in Table 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, $\text{Ni/K}_2\text{O-CaAl}_2\text{O}_4$ retains some of its initial activity and the sulfur coverages are much lower.

The sulfur coverage can be estimated from the empirical relationship of Rostrup-Nielsen et al. [49] This study focused on coke-prevention during steam reforming on $\text{Ni/Al}_2\text{O}_3$ and $\text{Ni/MgAl}_2\text{O}_4$ catalysts by sulfur passivation with H_2S . The change in initial reforming rate, $r_{o,sp}$, is dependent on the sulfur coverage, θ_s as:

$$r_{sp}^0 = \frac{r_{sp}}{(1 - \theta_s)^3} \quad (13)$$

where r_{sp} is the reforming rate at sulfur coverage of θ_s . The sulfur coverage can be calculated from a relation also given by Rostrup-Nielsen [28] as:

$$\theta_s = 1.45 - 9.53 \times 10^{-5}T + 4.17 \times 10^{-5}T \cdot \ln\left(\frac{p_{\text{H}_2\text{S}}}{p_{\text{H}_2}}\right) \quad (14)$$

which is dependent on the reaction temperature, T , and the ratio of the partial pressures of H_2S and H_2 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 3. For Ni/YSZ the calculated coverages are slightly lower than the measured values, and for $\text{NiK}_2\text{O-CaAl}_2\text{O}_4$ they are significantly higher. The calculated coverages also decrease as temperature increases; this reflects a shift in the adsorption/desorption equilibrium. In contrast, for $\text{Ni/K}_2\text{O-CaAl}_2\text{O}_4$ the coverages increase with increasing temperature and this may indicate that other forms of deactivation occur. No clear trend is observed for 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 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 $\text{Ni/K}_2\text{O-CaAl}_2\text{O}_4$ 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 Ni/YSZ and $\text{Ni/K}_2\text{O-CaAl}_2\text{O}_4$ 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. [21] As shown in Figure 3, 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 $\text{Ni/K}_2\text{O-CaAl}_2\text{O}_4$ was measured to be 196 Å on post-reaction samples at both 650°C and 800°C. The low dispersion measured for 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 $\text{Ni/K}_2\text{O-CaAl}_2\text{O}_4$. One study by Zhang et al. [50] found that YSZ was the best support for rhodium dispersion when compared with Al_2O_3 , TiO_2 , SiO_2 , La_2O_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. [51]

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 $\text{Ni/K}_2\text{O-CaAl}_2\text{O}_4$.

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

Table 3: Calculated sulfur coverages, θ_s , and the maximum deactivation reached for Ni/YSZ and Ni/K₂O–CaAl₂O₄.

	650°C	750°C			800°C
	1 ppm	1 ppm	3 ppm	5 ppm	1 ppm
Calculated θ_s [49]	0.93	0.87	0.91	0.94	0.84
Ni/YSZ	0.96	0.92	0.97	0.98	0.96
Ni/K ₂ O–CaAl ₂ O ₄	0.50	0.61	0.76	0.83	0.67

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:

$$\gamma = \frac{d\theta}{dt} \frac{N_o \sqrt{2\pi m k_B T}}{p_A} \quad (15)$$

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.[21] 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 H₂S, and 0.031 for SO₂. The “sticking fractions” for H₂S and SO₂ vary by a factor of two, even though the rates of deactivation in Figure 5 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 H₂S interactions on a nickel surface.[52–54] Appari et al. [54] developed a microkinetic sub-mechanism for H₂S poisoning on nickel, which is coupled with the Detuschmann mechanism [12, 55, 56] for methane steam and dry reforming on nickel. They reported a sticking coefficient for H₂S of 0.6, which is similar to the value reported by Riegraf et al. [57] ($\gamma = 0.5$). This assignment is very high compared with other sticking coefficients used in the Deutschmann mechanism for other coadsorbates such as H₂O ($\gamma = 0.1$), H₂ ($\gamma = 0.01$), and CH₄ ($\gamma = 0.008$). It is also higher than the Appari assignment for SO₂ ($\gamma = 0.02$), 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.[21] 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 SO₂ should be closer to the value reported for H₂S.

Poisoning by COS is more prolific than it is by H₂S and SO₂. 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. [47] 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°, 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 16.

All three sulfur compounds have significantly slower deactivation rates during dry methane reforming than steam reforming (see Figure 5). 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 H₂S does not affect H₂S adsorption.[28] In the absence of sulfur after sulfidation, it has also been proposed that high partial pressures of steam can regenerate the surface via equation 17:

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 reformat for Ni/YSZ SOFCs.

Appari proposes several surface reactions that may be pathways towards surface sulfur removal and can therefore regenerate the nickel.[54] They propose that carbon monoxide (CO-Ni) can oxidize sulfur on the nickel surface (e.g., SH-Ni, S-Ni) via the following reactions:

Through this pathway, SO-Ni groups may react with surface adsorbed O to form SO₂-Ni and desorb thereby regenerating

the surface. This is one of many possible pathways for the regeneration of the nickel surface, but it 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_2S , SO_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.[27] 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. 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_2O - CaAl_2O_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_2S , SO_2 , or COS), Ni/YSZ was essentially completely deactivated at 1, 3, and 5 ppm at varying deactivation rates. Ni/ K_2O - CaAl_2O_4 was deactivated to a non-zero steady state, and the sulfur surface coverage with H_2S 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.

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References

- [1] A. Lee, R. Zabransky, Internal reforming development for solid oxide fuel cells, *Industrial & Engineering Chemistry Research* 29 (1990) 766–773.
- [2] P. Dokmaingam, S. Assabumrungrat, A. Soorritantawat, N. Laosiripojana, Modelling of tubular-designed solid oxide fuel cell with indirect internal reforming operation fed by different primary fuels, *Journal of Power Sources* 195 (2010) 69–78.
- [3] J. V. herle, F. Marechal, S. Leuenberger, Y. Membrez, O. Bucheli, D. Favrat, Process flow model of solid oxide fuel cell system supplied with sewage biogas, *Journal of Power Sources* 131 (2004) 127–141.
- [4] R. O'Hayre, S.-W. Cha, W. Colella, F. Prinz, *Fuel Cell Fundamentals*, John Wiley & Sons, Inc., 2009.
- [5] V. Belyaev, T. Politova, O. Mar'ina, V. Sobyenin, Internal steam reforming of methane over ni-based electrode in solid oxide fuel cells, *Applied Catalysis A: General* 133 (1995) 47–57.
- [6] J. Rostrup-Nielsen, L. Christiansen, Internal steam reforming in fuel cells and alkali poisoning, *Applied Catalysis A: General* 126 (1995) 381–390.
- [7] A. Dicks, Advances in catalysts for internal reforming in high temperature fuel cells, *Journal of Power Sources* 71 (1998) 111.
- [8] K. Ahmed, K. Foger, Kinetics of internal steam reforming of methane on ni/ysz-based anodes for solid oxide fuel cells, *Catalysis Today* 63 (2000) 479–487.
- [9] S. Bebelis, A. Zeritis, C. Tiropani, S. Neophytides, Intrinsic kinetics of the internal steam reforming of CH_4 over a ni-ysz-cermet catalyst-electrode, *Industrial & Engineering Chemistry Research* 39 (2000) 4920–4927.
- [10] O. Costa-Nunes, R. Gorte, J. Vohs, Comparison of the performance of cu-CeO₂-ysz and ni-ysz composite sofc anodes with H_2 , co, and syngas, *Journal of Power Sources* 141 (2005) 241–249.
- [11] V. Janardhanan, V. Heuveline, O. Deutschmann, Performance analysis of a sofc under direct internal reforming conditions, *Journal of Power Sources* 172 (2007) 296–307.
- [12] E. Hecht, G. Gupta, H. Zhu, A. Dean, R. Kee, L. Maier, O. Deutschmann, Methane reforming kinetics within a ni-ysz sofc anode support, *Applied Catalysis A: General* 295 (2005) 40–51.
- [13] Y. Shiratori, T. Oshima, K. Sasaki, Feasibility of direct-biogas sofc, *International Journal of Hydrogen Energy* 33 (2008) 6316–6321.
- [14] Y. Shiratori, T. Ijichi, T. Oshima, K. Sasaki, Internal reforming of sofc running on biogas, *International Journal of Hydrogen Energy* 35 (2010) 7905–7912.
- [15] C. Xu, J. Zondlo, M. Gong, F. Elizalde-Blancas, X. Liu, I. Celik, Tolerance tests of H_2S -laden biogas fuel on solid oxide fuel cells, *Journal of Power Sources* 195 (2010) 4583–4592.
- [16] I. Yentekakis, T. Papadam, G. Goula, Electricity production from wastewater treatment via a novel biogas-sofc aided process, *Solid State Ionics* 179 (2008) 1521–1525.
- [17] J. V. herle, Y. Membrez, O. Bucheli, Biogas as a fuel source for sofc co-generators, *Journal of Power Sources* 127 (2004) 300–312.
- [18] S. Farhad, F. Hamdullahpur, Y. Yoo, Performance evaluation of different configurations of biogas-fuelled sofc micro-chp systems for residential applications, *International Journal of Hydrogen Energy* 35 (2010) 3758–3768.
- [19] M. Ashrafi, C. Pfeifer, T. Proll, H. Hofbauer, Experimental study of model biogas catalytic steam reforming: 2. impact of sulfur on the deactivation

- and regeneration of ni-based catalysts, *Energy & Fuels* 22 (2008) 4190–4195.
- [20] T. Gardner, D. Berry, K. Lyons, S. Baer, A. Freed, Fuel processor integrated H_2S catalytic partial oxidation technology for sulfur removal in fuel cell power plants, *Fuel* 81 (2002) 2157–2166.
- [21] I. Chorkendorff, J. Niemantsverdriet, *Concepts of Modern Catalysis and Kinetics*, Wiley-VCH, 2007.
- [22] Y. Wang, J. Pasel, R. Peters, Hydrodesulfurization process with pre-saturation using reformat for application in a 5 kw fuel cell system, *Fuel Processing Technology* 127 (2014) 59–65.
- [23] H. Mei, B. Mei, T. Yen, A new method for obtaining ultra-low sulfur diesel fuel via ultrasound assisted oxidative desulfurization, *Fuel* 82 (2003) 405–414.
- [24] B. Tjaden, M. Gandiglio, A. Lanzini, M. Santarelli, M. Jarvinen, Small-scale biogas-sofc plant: Technical analysis and assessment of different fuel reforming options, *Energy & Fuels* 28 (2014) 4216–4232.
- [25] R. Larraz, Influence of fractal pore structure in claus catalyst performance, *Chemical Engineering Journal* 86 (2002) 309–317.
- [26] E. Brightman, D. Ivey, D. Brett, N. Brandon, The effect of current density on H_2S -poisoning of nickel-based solid oxide fuel cell anodes, *Journal of Power Sources* 196 (2011) 7182–7187.
- [27] Z. Cheng, J.-H. Wang, Y. Choi, L. Yang, M. Lin, M. Liu, From ni-ysz to sulfur-tolerant anode materials for sofc: electrochemical behavior, *in situ* characterization, modeling and future perspectives, *Energy & Environmental Science* 4 (2011) 4380 – 4409.
- [28] J. Hansen, J. Rostrup-Nielsen, Sulfur poisoning on Ni catalysts' and anodes, volume 6.
- [29] D. Niakolas, Sulfur poisoning of ni-based anodes for solid oxide fuel cells in h/c-based fuels, *Applied Catalysis A: General* 486 (2014) 123–142.
- [30] Y. Matsuzaki, I. Yasuda, The poisoning effect of sulfur-containing impurity gas on a sofc anode: Part i. dependence on temperature, time, and impurity concentration, *Solid State Ionics* 132 (2000) 261–269.
- [31] J. Bao, G. Krishnan, P. Jayaweera, A. Sanjurjo, Effect of various coal gas contaminants on the performance of solid oxide fuel cells: Part iii. synergistic effects, *Journal of Power Sources* 195 (2010) 1316–1324.
- [32] J. Rasmussen, A. Hagen, The effect of H_2S on the performance of sofc using methane containing fuel, *Fuel Cells* 10 (2010) 1135–1142.
- [33] N. Lakshminarayanan, U. Ozkan, Effect of H_2O on sulfur poisoning and catalytic activity of ni-ysz catalysts, *Applied Catalysis A: General* 393 (2011) 138–145.
- [34] P. Clark, N. Dowling, M. Huang, W. Svrcek, W. Monnery, Mechanisms of co and cos formation in the claus furnace, *Industrial & Engineering Chemistry Research* 40 (2001) 497–508.
- [35] K. Karan, A. Mehrotra, L. Behie, Cos-forming reaction between co and sulfur: A high-temperature intrinsic kinetics study, *Industrial & Engineering Chemistry Research* 37 (1998) 4609–4616.
- [36] D. Storjohann, J. Daggett, N. Sullivan, H. Zhu, R. Kee, S. Menzer, D. Beeaff, Fabrication and evaluation of solid-oxide fuel cell anodes employing reaction-sintered yttria-stabilized zirconia, *Journal of Power Sources* 193 (2009) 706.
- [37] P. Kechagiopoulos, S. Voutetakis, A. Lemonidou, I. Vasalos, Hydrogen production via steam reforming of the aqueous phase of bio-oil in a fixed bed reactor, *Energy & Fuels* 20 (2006) 2155.
- [38] M. Davis, R. Davis, *Fundamentals of chemical reaction engineering*, McGraw-Hill, 2003.
- [39] H. Liu, B. Wang, M. Fan, N. Henson, Y. Zhang, B. Towler, H. Harris, Study on carbon deposition associated with catalytic CH_4 reforming by using density functional theory, *Fuel* 113 (2013) 712–718.
- [40] J. Rostrup-Nielsen, K. Pedersen, Sulfur poisoning of boudouard and methanation reactions on nickel catalysts, *Journal of Catalysis* 59 (1979) 395–404.
- [41] J.-H. Koh, B.-S. Kang, H. Lim, Y.-S. Yoo, Thermodynamic analysis of carbon deposition and electrochemical oxidation of methane for sofc anodes, *Electrochemical and solid-state letters* 4 (2001) A12–A15.
- [42] J. Rostrup-Nielsen, Mechanisms of carbon formation on nickel-containing catalysts, *Journal of Catalysis* 48 (1977) 155–165.
- [43] Q. Zhang, B. Han, X. Tang, K. Heier, J. Li, J. Hoffman, M. Lin, S. Britton, A. Derecskei-Kovacs, H. Cheng, On the mechanisms of carbon formation reaction on ni(111) surface, *Journal of Physical Chemistry C* 116 (2012) 16522–16531.
- [44] J.-W. Snoeck, G. Froment, M. Fowles, Filamentous carbon formation and gasification: Thermodynamics driving force, nucleation and steady-state growth, *Journal of Catalysis* 69 (1997) 240–249.
- [45] H. Bengaard, J. Norskov, J. Sehested, B. Clausen, L. Nielsen, A. Molenbroek, J. Rostrup-Nielsen, Steam reforming and graphite formation on ni catalysts, *Journal of Catalysis* 209 (2002) 365–384.
- [46] J. Wei, E. Iglesia, Isotopic and kinetic assessment of the mechanism of reactions of CH_4 with CO_2 or H_2O to form synthesis gas and carbon on nickel catalysts, *Journal of Catalysis* 224 (2004) 370–383.
- [47] D. Blaylock, T. Ogura, W. Green, G. Beran, Computational investigation of thermochemistry and kinetics of steam methane reforming on ni(111) under realistic conditions, *Journal of Physical Chemistry C* 113 (2009) 4898–4908.
- [48] C. Bartholomew, Mechanisms of catalyst deactivation, *Applied Catalysis A: General* 212 (2001) 17.
- [49] J. Rostrup-Nielsen, Sulfur-passivated nickel catalysts for carbon-free steam reforming of methane, *Journal of Catalysis* 85 (1984) 31–43.
- [50] Z. Zhang, V. Tsipouriari, A. Efstathiou, X. Verykios, Reforming of methane with carbon dioxide to synthesis gas over supported rhodium catalysts, *Journal of Catalysis* 158 (1996) 51–63.
- [51] M. Casarin, V. Sglavo, Influence of processing conditions on the microstructure of nio-ysz supporting anode for solid oxide fuel cells, *Ceramics International* 41 (2015) 2543–2557.
- [52] V. Janardhanan, D. Monder, Sulfur poisoning of sofc: A model based explanation of polarization dependent extent of poisoning, *Journal of the Electrochemical Society* 161 (2014) F1427–F1436.
- [53] B. Prasad, V. Janardhanan, Modeling sulfur poisoning of ni-based anodes in solid oxide fuel cells, *Journal of the Electrochemical Society* 161 (2014) F208–F213.
- [54] S. Appari, V. Janardhanan, R. Bauri, S. Jayanti, O. Deutschmann, A detailed kinetic model for biogas steam reforming on ni and catalyst deactivation due to sulfur poisoning, *Applied Catalysis A: General* 471 (2014) 118–125.
- [55] V. Janardhanan, O. Deutschmann, Cfd analysis of a solid oxide fuel cell with internal reforming: Coupled interactions of transport, heterogeneous catalysis and electrochemical processes, *Journal of Power Sources* 162 (2006) 1192–1202.
- [56] L. Maier, B. Schadel, K. Delgado, S. Tischer, O. Deutschmann, Steam reforming of methane over nickel: development of a multi-step surface reaction mechanism, *Topics in Catalysis* 54 (2011) 845.
- [57] M. Riegraf, G. Schiller, R. Costa, K. Friedrich, A. Latz, V. Yurkiv, Elementary kinetic numerical simulation of ni/ysz sofc anode performance considering sulfur poisoning, *Journal of the Electrochemical Society* 162 (2015) F65–F75.