The Importance of Gas Phase Kinetics Within the Anode Channel of a Solid Oxide Fuel Cell (SOFC)

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Introduction

A complete SOFC model is very complex, requiring descriptions of kinetics in multiple phases and coupling these kinetics to multiple transport processes. [1] Chemical reactions within the SOFC occur in three regions: in the anode channel (gas-phase kinetics), on the surface of the porous anode (heterogeneous catalysis) and at the three-phase boundary layer between the anode and electrolyte (electrochemical catalysis). Thus the homogeneous and heterogeneous kinetics have the potential to substantially change the nature of the species that ultimately undergo electrochemical oxidation. It is essential to account for such kinetic modifications to properly characterize SOFC operation and predict the overall efficiency.

As a first step toward characterizing the complex kinetics, we want to make sure that we properly understand the gas-phase hydrocarbon chemistry. The effect of gas phase reactions of methane in SOFCs has previously been reported. [2] There it was shown that the electrochemical production of H_2O and CO_2 did indeed significantly impact the predictions regarding deposit formation. In this work we extend this approach to butane, which is significantly more reactive than methane and thus more representative of a range of hydrocarbon fuels.

Experimental

The experiments used n-butane as the fuel over a temperature range of 550 – 800ºC, with a nominal five second residence time through a tubular flow reactor operating at an ambient (high-altitude) pressure of ~0.8 atm. The reactor used in these experiments was a 24 cm length x 6 mm ID (12mm OD) quartz tube, which was housed within a 14.5 cm length single-zone clamshell 2.5 cm ID electric tube furnace. The product stream flowed through a water trap, and the de-humidified product stream then flowed to a Hewlett-Packard 5890 Series II+ gas chromatograph. Axial temperature profiles were measured and used in the plug flow model.

Three different fuel mixtures were used: neat n-butane (100% n-butane), a 50:50 n-butane:N_2 mixture and a 50:50 n-butane:H_2O(g) mixture. The neat n-butane case is intended to simulate the situation near the entrance of the anode channel where little CO_2 and H_2O would be present. Likewise the nC_4/H_2O mixture represents a mixture further down the channel where the products of the electrochemical reaction would be coming into the fuel stream. The nC_4/N_2 mixture was used to account for the effect of simple dilution with an inert in contrast to dilution with steam, which could possibly be a reactant.

Reaction Mechanism

The reaction mechanism that was utilized in this study consists of 291 species and 2498 elementary reactions. It is an extension of a previous mechanism[3], which included formation of C_4 hydrocarbon species. The extensions include substantially more molecular weight growth chemistry, especially involving propargyl radical pathways, and explicit inclusion of certain C_6 hydrocarbon species, including n-hexane, cyclohexane, and 2,3-dimethyl butane. The current mechanism is similar to the one recently used by Walters, *et al*.[2] in their analysis of methane kinetics under SOFC conditions.

Comparison to Model Predictions

Butane Conversion The ratio of the predicted final/initial mole fraction of butane is compared to that observed for the neat and nC_4/N_2 mixture cases in Fig. 1.

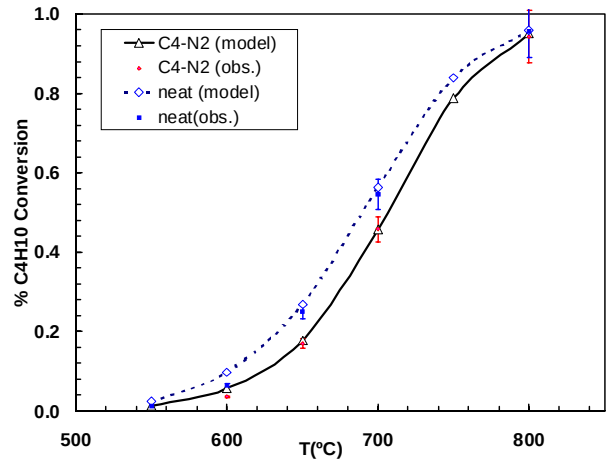

Figure 1. Comparison of predicted butane conversion to that observed for the neat butane case and for the 50% butane/50% nitrogen mixture.

The modeling predictions are in excellent agreement with the observations for both the neat and the nC_4/N_2 fuel mixture cases. The predictions clearly capture the observed temperature dependence for both the neat and nitrogen fuel mixture cases. From both the model predictions and the observed experimental data, it is also clear that the conversion for the neat n-butane case is higher than the nC_4/N_2 case. This difference is simply due to dilution in the nC_4/N_2 mixture. This good agreement, achieved without any modifications to the gas-phase kinetic mechanism, was very encouraging and suggests that the model can account for conversion of light hydrocarbons fuels under SOFC conditions.

Product Selectivity Four major products are observed: methane, ethane, ethylene, and propylene. The predicted selectivities are in reasonable agreement with those observed. For methane, the observed selectivity ranges from ~32% at 600ºC to ~38% at 800ºC, while the model predictions range from 32% to 35%. The propylene selectivity is observed to decrease with increasing temperature, from ~34% at 600ºC to ~13% at 800ºC. The predictions vary from ~32% at 600ºC to ~20% at 800ºC, not dropping off quite so rapidly with temperature as observed. The observed ethylene selectivity increases sharply from ~21% at 600ºC to ~42% at 800ºC. The predictions follow this reasonably well, ranging from ~19% at 600ºC to ~34% at 800ºC. This underprediction of the ethylene yield at 800ºC is reflected in an overprediction of the ethane yield. It was observed to vary from ~12% at 600ºC to ~5% at 800ºC, while the predictions yielded ~16% at 600ºC to ~10% at 800ºC. Thus one problem with the current model is the inability to precisely account for the distribution within the C_2 branch (ethane and ethylene) and with the C_1-C_3 branch (methane and propylene). Note that the predictions for the total C_2 branch are very consistent with the observations and properly account for the increase with temperature. Similarly, the sum of the methane and propylene selectivities show good agreement between predictions

and that observed, including the decrease in overall selectivity with temperature.

Deposit Formation One of the major concerns with the use of hydrocarbon fuels in solid oxide fuel cells is the propensity for deposit formation. In our experiments, qualitative observations of deposit formation were made by examining the quartz reactor after running a specific mixture through the reactor for 4 hours. We observed no apparent deposit formation within the reactor for any of the mixtures at 650ºC or lower temperatures. As the reactor temperature was increased to 700ºC, an obvious deposit film was observed on the inner walls of the quartz reactor with the neat butane mixture. The deposit film was noticeably less dense for the nC_4/N_2 mixture, and barely evident for the nC_4/H_2O mixture. The first inference from these qualitative observations is that dilution does play a role in minimizing deposit formation. This is to be expected, since the lower concentration of reactive species would be expected to decrease the rate of molecular weight growth leading to deposits. The marked difference in the nitrogen and steam mixtures suggests that the steam is either actively participating in inhibition of molecular weight growth or that it is participating in some type of gasification of the deposit. All three mixtures show significant deposit formation at 800ºC.

To compare to the model, we considered all species in the model predictions above C_4 (denoted as C_5^+) as potential deposit precursors. The predicted C_5^+ mole fraction is a very strong function of temperature as illustrated in Fig. 2. It is encouraging to note that the predicted rapid increase in deposit precursors near 700ºC is consistent with the experimental observations.

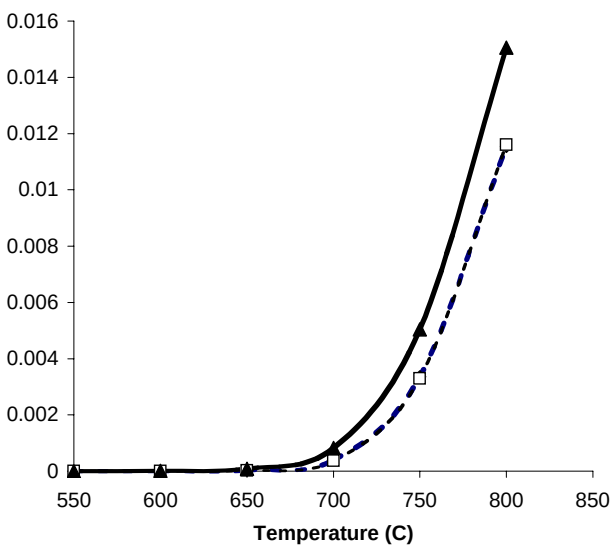

Figure 2. Predicted effect of temperature on the mole fraction of C5+ species.

The predicted C_5^+ values for the steam and nitrogen dilution cases are virtually identical. This is consistent with our observation that any gas-phase reactions of steam are very slow under these conditions, and thus steam is simply acting as a diluent, just like nitrogen. This is in contrast to the experimental observations that steam diminished deposit formation. This effect is probably due to heterogeneous reactions. The ratio of C_5^+ predicted for the neat butane case to that of the diluted mixtures decreases from approximately five at 550ºC to only slightly greater than unity at 800ºC. Thus at the higher temperatures, the predictions suggest that the inhibition of deposit formation by dilution is much less effective.

Kinetics Overview

The results from a sensitivity analysis indicate that, although the system consists of ~2500 reactions, there are only 10 reactions that dominate the formation or consumption of the five major species. These reactions suggest that butane pyrolysis can be described in terms of a simple Rice-Herzfeld mechanism. After initiation by breaking the C-C bonds in butane, the radicals formed abstract from the parent butane to form $n\text{-}C_4H_9$ and $s\text{-}C_4H_9$ radicals. The primary radicals lead to the C_2 products via beta-scission, while beta-scission of the secondary radicals lead to the C_1 and C_3 products. Thus the selectivity to these two product pairs can be traced to the selectivity of forming the two radicals in abstraction from the parent. An interesting complication is that the propylene product has an easily abstractable hydrogen, and the formation of allyl acts to inhibit conversion by modifying the nature of the free radical pool. This same allyl radical was also shown to be responsible for the small amounts of molecular weight growth observed since it can add to ethylene, forming cyclopentene. This pathway is accelerated since it is chemically-activated, and the initially energized linear adduct can directly form the cyclic species prior to collisional stabilization.

Conclusion

The butane pyrolysis experiments demonstrate that substantial gas-phase chemistry does occur under SOFC conditions, and that this must be accounted for when predicting fuel cell efficiency. These data were compared to predictions using a plug-flow model that incorporated the experimentally measured temperature profile along the reactor. Comparisons of the model predictions to the experimental data show that the model, without any modifications, captures the observed strong temperature dependence of n-butane conversion and is also able to capture the changes in product selectivity with temperature for the neat butane and the diluted butane mixtures. The model also properly predicts the observed onset of deposit formation near 700ºC. Both conversion and selectivity are shown to be sensitive to only a very small subset of the reactions in the mechanism. Comparison of the rate coefficients of this subset to literature values, where available, are generally reasonable and suggest that the kinetic model employed is adequate for describing reactions of small hydrocarbons in the anode channels of a SOFC. Thus such models should provide a useful tool to estimate the importance of gas-phase chemistry for various proposed SOFC operating conditions.

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