

Optimization Methods for Efficient Solution of Reformulated Microkinetic Models

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OPTIMIZATION METHODS FOR EFFICIENT SOLUTION OF REFORMULATED MICROKINETIC MODELS

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Microkinetic models, combined with experimentally measured reaction rates and orders, play a key role in elucidating detailed reaction mechanisms in heterogeneous catalysis and have typically been solved as systems of ordinary differential equations (ODEs) or differential algebraic equations (DAEs). In the present work, we demonstrate a new approach to fitting those models to experimental data. For a small model of methanol synthesis by CO/CO₂ hydrogenation over a supported-Cu catalyst in a continuous stirred tank reactor (CSTR), we achieved a 1000-fold increase in solution speed by reformulating the microkinetic model from a system of ODEs to a system of nonlinear equations (NLP). The reduced computational cost allows a more systematic search of the parameter space, leading to better fits to the available experimental data.

We applied this approach to the full methanol synthesis network and identified over 200 good fits to the experimental data. We analyzed the fits to provide insight into the nature of the active site and reaction mechanism. We took the best of the fits obtained and optimized the experimental variables (pressure, temperature, feed rate and feed composition) to identify the

conditions which predict a maximum production for methanol, the maximum production of methanol from CO_2 , or maximum conversion of CO or CO_2 to methanol. We also performed optimizations to identify the best conditions to identify reactive intermediates on the catalyst surface.

Finally we took the first steps to extend our approach to plug flow reactors (PFRs) (which are described by systems of DAEs) using collocation on finite elements to transform the DAEs into an NLP. We used our transformed model to consider the optimal conditions for the water gas shift reaction on Cu.

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Chapter 1

Introduction

1.1. Microkinetic Modeling

Catalysts play a vital role in chemical industry. Over 90% of industrial chemical processes are catalyzed and catalysts allow chemicals to be produced under less stringent conditions, thus reducing energy consumption, an essential goal in today's environmentally-conscious and highly regulated environment¹. However, for many reactions, the catalyzed reaction mechanism is still poorly understood, hindering the ability to develop improved catalysts.

Density functional theory (DFT) provides an important computational methodology for understanding catalytic reactions and for the design of new catalysts. DFT uses the principles of quantum mechanics to predict properties of materials at the atomic and molecular scale.² Specifically, an approximation of the Schrödinger equation is solved and can be used to predict the binding sites and binding energies of atoms and molecules on catalytically active surfaces and the activation energy barriers to various potential elementary reaction steps on the surface. DFT has provided us with unprecedented insights into the detailed reaction mechanism of various catalytic processes.²

To use the information derived from DFT most effectively, we need to translate our new understanding of the elementary steps into predictions of macroscopic outcomes such as the rate of production of products and byproducts. This can be accomplished using a microkinetic model.^{3,4} Microkinetic models provide a bridge between the elementary steps that occur at the molecular scale and production rates at the macroscopic scale. They depend on the assumption that adsorbates are evenly distributed across the surface, i.e., the mean field approximation (MFA) and assume an ideal reactor with no transport limitations.⁴⁻⁶ Microkinetic modeling predicts reaction rates and surface coverages at reaction conditions based on a set of elementary steps and their rate constants.⁶ This can lead us to a better understanding of what is happening on the surface of the catalyst. A priori assumptions about surface coverages, rate limiting steps or quasi-equilibration are avoided within the framework of these models. This allows the model to be very general and predictive across a wide range of reaction conditions.⁶

1.2. Parameter Estimation

While DFT provides a good starting point for parameter values for microkinetic modeling,^{6,7} production rates can be very sensitive to the binding and activation energies (BE and Ea) of the surface species and elementary steps, respectively.⁸ The DFT values are subject to computational errors on the order of 0.1-0.2 eV and may also contain inaccuracies due to the effects of surface coverage or surface reconstruction under the reaction conditions or the selection of a specific surface to model which may not be a good representation of the active

site.⁹ Therefore, parameter estimation is a necessary component of successful microkinetic modeling.

The parameter estimation problem is shown in equations 1.1-1.3. It is a nonlinear program (NLP), where we minimize a scalar objective function, $f(x)$, (eqn 1.1) subject to a set of constraints (eqns 1.2-1.3).¹⁰ Equality constraints are captured in the vector function $g(x)$, equation 1.2, and inequality constraints in the vector function $h(x)$, equation c.

$$\min f(x) \quad (1.1)$$

$$s. t. g(x) = 0 \quad (1.2)$$

$$h(x) \leq 0 \quad (1.3)$$

The constraints can be satisfied by more than one set of values for the variables. Through the solution of the NLP, we attempt to find variable values which satisfy the constraints and result in the lowest value of the objective function. When the objective function (eqn 1.1) or the feasible region is non-convex, there may be more than one local minimum. NLP algorithms may converge to local minima which may be significantly poorer than the global minimum.¹¹

For parameter estimation on microkinetic models, our objective is to minimize the difference between our model predictions and experimental data. The primary variables are BE, Ea, surface coverages and partial pressures in the gas phase.^a Additional variables, such as rate

^a In general, parameters are fixed numbers within a model, while variables are allowed to change. BE and Ea are the parameters of the microkinetic model which are estimated in the parameter estimation problem. In the optimization model which estimates them, they are variables; i.e., they are free to vary such that the error between the microkinetic model predictions and the experimental data is minimized. Thus, depending on context, we will refer to BE and Ea as both parameters and variables.

constants and reaction rates, are functions of the primary variables and parameters such as pressure, temperature and feed composition.

1.3. Optimizing Experimental Conditions

Given a set of fitted parameters (BE and E_a) describing a particular catalytic material, a microkinetic model can be used to improve our understanding of optimal operating conditions for reactors, reaction mechanisms, surface coverages and more. While we can gain some understanding of the catalyst by manually exploring the parameter space for the experimental parameters (pressure, temperature, feed rate and feed composition) and plotting trends, this is not an effective approach for identifying the optimal operating conditions or identifying conditions that would allow us to observe elusive intermediates. Instead we want to optimize the model with the material parameters (BE and E_a) fixed, the experimental variables adjustable and objective functions tailored to answer the questions which interest us most.

1.4. Methanol Synthesis

We selected methanol synthesis as a model reaction network to develop and demonstrate our approach. Worldwide, approximately 30 Mt of methanol are produced annually, primarily by steam reforming of natural gas.¹² Climate change and fossil fuel depletion makes methanol production from renewable and sustainable feedstocks highly desirable.^{13,14} In addition to its large demand as a chemical feedstock, methanol has excellent potential as liquid transportation fuel.^{15,16} Methanol-specific production vehicles were produced as early as the 1980's, producing fewer emissions and having greater fuel efficiency than gasoline fueled engines.^{17,18}

Moreover, methanol is readily converted to dimethyl ether which is an excellent alternative to diesel fuel.¹⁴

At the industrial scale, methanol is synthesized from synthesis gas (a mixture of CO, CO₂ and H₂) over a Cu/ZnO/Al₂O₃ catalysts in reaction conditions of 230-280°C and 50-120 atm.¹⁹ Despite extensive study^{6,20-48} and a hundred year history of industrial synthesis, critical questions about the reaction mechanism and the nature of the active site for methanol synthesis remain unanswered.

Since 1987,³⁰ many kinetic models of methanol synthesis have been proposed.^{21,22,25,26,28} Yet, until recently, all of the published models included, at most, one pathway each for the hydrogenation of CO and CO₂ and one side reaction. Despite good fits, these models fail to resolve questions regarding the reaction mechanism and the nature of the active site. Microkinetic modeling has the potential to help us identify new catalysts and improved reaction conditions to produce methanol from effluent streams of CO₂.

In 2011, Grabow and Mavrikakis,²⁹ published the most extensive model to date with 49 elementary steps, including most of those previously considered by other groups (figure 1.1). This was a significant advance; however the optimization approach used allowed only a limited investigation of the parameter space. Since large microkinetic models do not have a single, unique best fit to reasonably sized data sets, the limited investigation of the parameter space is a significant limitation.

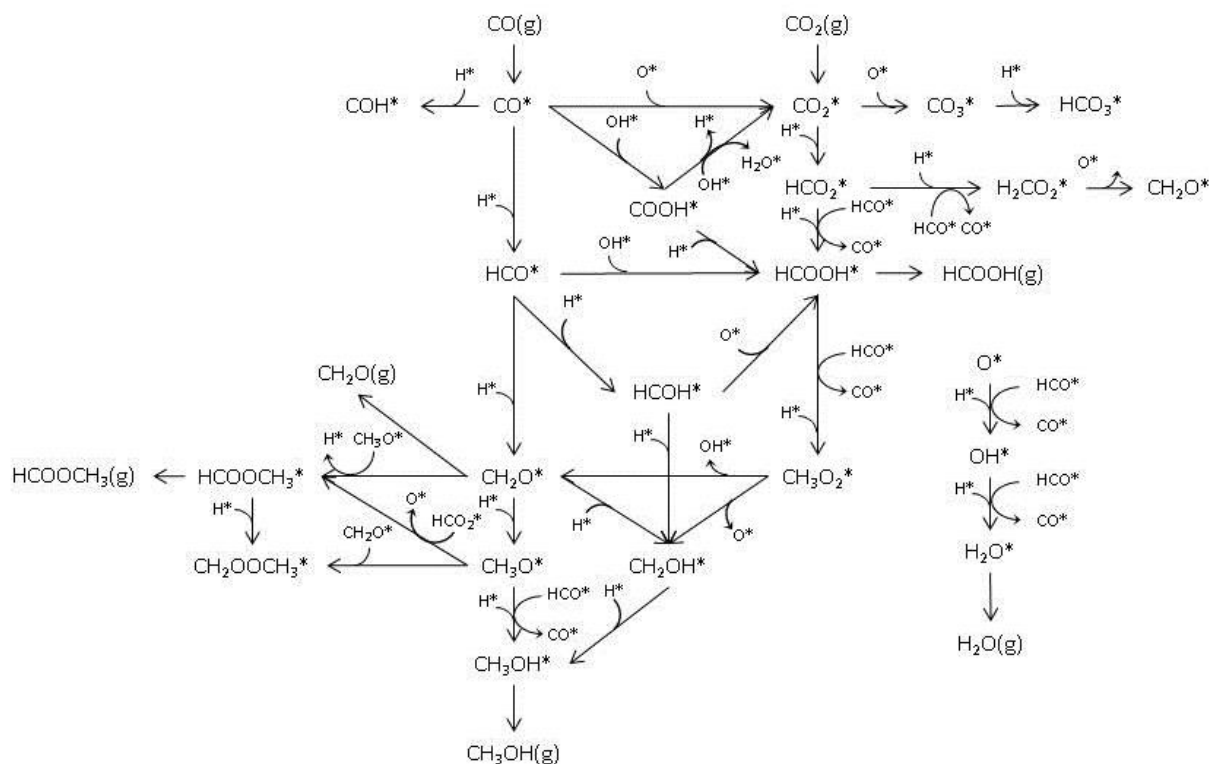


Figure 1.1: The reaction network for methanol synthesis from Grabow and Mavrikakis.²⁹ Free sites are omitted for clarity. All reactions are reversible, but are shown in the active direction for clarity. H₂(g) adsorbs dissociatively onto the surface (not shown).

In general, there are many possible sets of parameter values which would provide a good fit to the experimental data. While a given data set may provide good information about a limited number of parameters, others won't be well specified. Therefore, without thoroughly exploring the parameter space, it is impossible to know whether the predictions of the fit obtained represent the catalyst being modeled or simply the particular fit found. If the parameter space is explored more thoroughly and many fits to the experimental data are obtained, it becomes apparent what the experimental data can tell us about the actual

parameter values and their predictions for the reaction mechanism and what would require additional data to determine.

1.5. Thesis Scope

This thesis consists of four main chapters. In chapter 2, we discuss the development of an NLP optimization approach for solving the parameter estimation problem for a continuous stirred tank reactor and demonstrate the increased computational speed of the approach using a small methanol synthesis network. We apply this approach to the full methanol synthesis network from Grabow and Mavrikakis²⁹ and discuss our results in detail. In chapter 4, we formulate the experimental design problem and optimize with our fit from the full methanol synthesis model to explore the predictions of our model for optimal operating conditions, conditions for isolating reactive intermediates on the surface and more. We extend our formulation of the experimental design problem to the plug flow reactor using collocation on finite elements in chapter 5. We briefly apply our result the water gas shift reaction as an illustrative example. Finally, concluding remarks and recommendations for future work are included in chapter 6.

Chapter 2

Methods for Parameter Estimation on Microkinetic Models (CSTR)

In this chapter, we demonstrate a new approach to parameter estimation for microkinetic models. Our approach requires significantly less CPU time for optimization, allowing a more comprehensive investigation of the parameter space that is less dependent on the intuition and system-knowledge of the user.

For the sake of simplicity, and in order to demonstrate our new approach to solving microkinetic models, we consider a methanol synthesis reaction network (Figure 2.1) with 16 elementary steps and 18 distinct species (3 in the gas phase). It includes two main pathways; the synthesis of methanol from CO hydrogenation and the synthesis of methanol and water from CO₂ hydrogenation. It also includes the water gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) which connects the two pathways. This reaction network represents a subset of a more extensive model investigated by Grabow, et al.²⁹ using the standard microkinetic modeling approach.

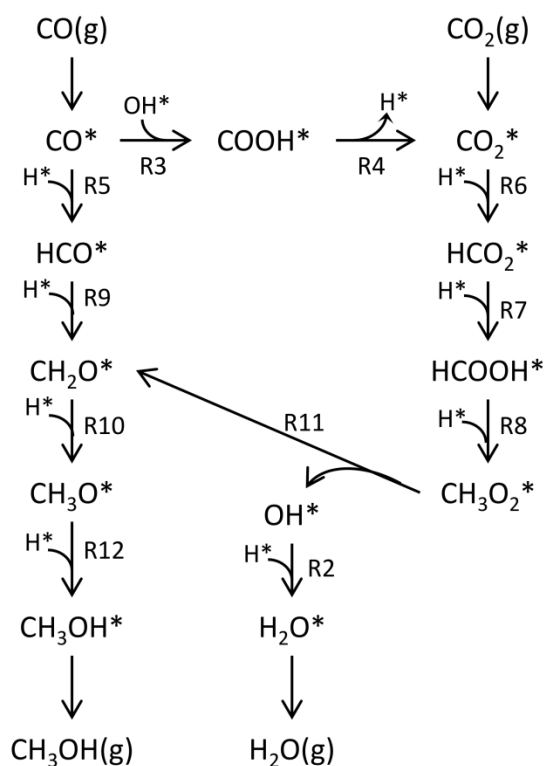


Figure 2.1: The reaction network for methanol synthesis, the example problem we have used to develop and demonstrate our approach. Free sites are omitted for clarity. The labels R# refer to the reaction numbers provided in Table 2.3 and indicate the relevant steps to convert one intermediate to another. All reactions are reversible, but are shown in the active direction for clarity. $\text{H}_2\text{(g)}$ adsorbs dissociatively onto the surface (not shown).

2.1. Basic Continuous Stirred Tank Reactor (CSTR) Microkinetic Model

Our basic microkinetic model is developed for a steady-state stirred tank reactor. The model includes the set **I** of reactions (indexed over i), the set **J** of species (indexed over j) and the set **C** of experimental conditions (indexed over c). Set **J** includes the subsets **G** (gas phase species) and **S** (surface species), with free sites (*) included in the set **S**. For each reaction, i , there exist subsets of **S** reactants ($\mathbf{R}_i$) and products ($\mathbf{P}_i$).

As shown in equation 2.1, for each species (j) and condition (c), the rate of change ($\frac{dy_{jc}}{dt}$) is equal to the difference between the flow rates into the system (F_{jc}^{in}) and out of the system (F_{jc}^{out}) plus the net generation (R_{jc}^{net}) for that species, where y_{jc} is the fractional coverage for surface species and partial pressure for gas phase species. Since we are modeling a CSTR, which is operated at steady-state, the rate of change should be equal to zero.

$$F_{jc}^{in} - F_{jc}^{out} + R_{jc}^{net} = \frac{dy_{jc}}{dt} = 0, \quad \forall j, c \quad (2.1)$$

The net generation and consumption of each species (j) is a function of rates of the reactions (r_{ic}) and the stoichiometric coefficients (ν_{ij}) of the species (j) in each reaction (i).

$$R_{jc}^{net} = \sum_i \nu_{ij} r_{ic}, \quad \forall j, c \quad (2.2)$$

There is no flow in or out of the system for surface species (eqn 2.3).

$$F_{jc}^{in} = F_{jc}^{out} = 0, \quad \forall c, j \in \mathbf{S} \quad (2.3)$$

For gas phase species, F_{jc}^{in} (the flow rate in) is a constant specific to each experimental condition. The flow rate out (F_{jc}^{out}) is proportional to the partial pressure of the species in the gas phase ($y_{jc}, j \in \mathbf{G}$) divided by the total pressure (P_c), as shown in equation 2.4. F_{jc}^{out} is equivalent to the turnover frequency (TOF) for species j in condition c (with units of s^{-1}).

$$F_{jc}^{out} = \frac{y_{jc}}{P_c} \sum_{j \in \mathbf{G}} (F_{jc}^{in} + R_{jc}^{net}), \quad \forall c, j \in \mathbf{G} \quad (2.4)$$

All surface sites must be either occupied or free, so the surface coverages ($y_{jc}, j \in \mathbf{S}$) must sum to one (eqn 2.5).

$$\sum_{j \in S} y_{jc} = 1, \forall c \quad (2.5)$$

The reaction rates (r_{ic}) are calculated using the forward (kf_{ic}) and reverse (kr_{ic}) rate constants and the concentrations (y_{jc}) and stoichiometric coefficients (v_{ij}) of the species involved in the reaction (eqn 2.6).

$$r_{ic} = kf_{ic} \prod_{j \in R_i} y_{jc}^{|v_{ij}|} - kr_{ic} \prod_{j \in P_i} y_{jc}^{|v_{ij}|}, \quad \forall i, c \quad (2.6)$$

where $R_i \subset J$ and $P_i \subset J$ are the sets of reactants and products for reaction i , respectively.

Equations 2.7-2.9 calculate the rate constants for all reactions. The forward rate constant (kf_{ic}) is calculated using the Arrhenius expression as a function of the pre-exponential factor (A_i) and activation energy (Ea_i) of the reaction (eqn 2.7). The equilibrium rate constant (Keq_{ic}) is a function of the enthalpy (ΔH_{ic}) and entropy (ΔS_{ic}) of the reaction (eqn 2.8). The reverse rate constant (kr_{ic}) is thermodynamically consistently calculated as the ratio of kf_{ic} and Keq_{ic} (eqn 2.9). The rate constants are all dependent on temperature (T_c) and include the gas constant (R).

$$kf_{ic} = A_i \exp\left(-\frac{Ea_i}{RT_c}\right), \quad \forall i, c \quad (2.7)$$

$$Keq_{ic} = \exp\left(-\frac{\Delta H_{ic}}{RT_c} + \frac{\Delta S_{ic}}{R}\right), \quad \forall i, c \quad (2.8)$$

$$kr_{ic} = \frac{kf_{ic}}{Keq_{ic}}, \quad \forall i, c \quad (2.9)$$

The enthalpy change of the reaction (ΔH_{ic}) is a function of the heats of formation (ΔHf_j) of the species in the gas phase and their binding energies (BE_j).

$$\Delta H_{ic} = \sum_j v_{ij}(\Delta H f_j + BE_j), \quad \forall i, c \quad (2.10)$$

The enthalpy may also include a correction for the temperature. In order to be thermodynamically consistent, the activation energy for each reaction must be greater than the enthalpy change of that reaction (eqn 2.11). In absence of this constraint, it would be possible for an endothermic reaction to be represented as non-activated, a scenario which is not physically possible.

$$Ea_i \geq \Delta H_{ic}, \quad \forall i, c \quad (2.11)$$

Likewise, all activation energies must be greater than zero and all binding energies less than zero.

$$Ea_i \geq 0, \quad \forall i \quad (2.12)$$

$$BE_j \leq 0, \quad j \in S \quad (2.13)$$

The parameters that we are fitting to the experimental data are BE_j and Ea_i . This gives a total of 26 fitted parameters in this work. Other parameters (e.g. A_i , ΔS_{ic}) could also be fit if desired.

2.2. ODE Formulation

Because microkinetic models are nonlinear and poorly conditioned they can be quite difficult to solve. Typically, they have been formulated as systems of ODEs.^{3,4,49-55} An initial guess is made for the surface coverage which is consistent with equation 2.5 and equation 2.5 is removed from the system, since as long as the initial point satisfies equation 2.5, so will every future time point. The initial guess will not conform to the constraint that equation 2.1 be equal to zero.

The system of ODEs is integrated from the initial guess to a steady-state solution, which then satisfies equation 2.1.

This approach is simple to set up and can be run in readily available software such as Matlab. However, the ODE version of the model is computationally intensive to solve. Furthermore, the ODE-solver operates as a black box (with respect to the optimization algorithm), making the gradient of the objective function with respect to the parameters difficult to obtain. A common solution is to use the finite difference approximation to calculate the gradient. For n parameters this requires $n+1$ solutions of the system of ODEs, a significant computational expense. Furthermore, the error in the solution to the system of ODEs compounds with the finite difference error and makes it very difficult to accurately calculate the gradient.⁵⁶ This significantly impairs the ability of most optimization algorithms to solve the problem effectively and results in the need for iterative adjustment of the parameter values by the user. Consequently, it requires considerable physical insight to obtain good fits to the experimental data.

There are more sophisticated approaches to approximating the gradient of a system of ODEs, such as adjoint equations⁵⁷⁻⁶⁰ or direct sensitivity equations,^{57,60} which give more accurate results. However, these still require multiple solutions of the system of ODEs at each iteration of the optimization and they are more difficult to implement. Overall, parameter estimation with the ODE model is expensive in both computational and user time. However, we are primarily interested in the steady-state solution rather than the transient behavior. Therefore, we can set the rate of change for all species to zero and solve the NLP instead (see eqn 2.1).

2.3. NLP Formulation

There are several advantages to solving the model (eqns 2.1-2.13) as a system of nonlinear equations. Firstly, solving a system of nonlinear equations is generally more computationally efficient than solving an equivalent system of ODEs. Secondly, when the problem is solved as a system of nonlinear equations, the gradient is directly available to the optimizer. This allows the gradients to be calculated very accurately at greatly reduced computational time, improving the performance of the optimization algorithm. Thirdly, where in the ODE formulation solving the model and performing parameter estimation are separate steps, in the NLP formulation, we are able to simultaneously solve and optimize the model. Finally, having removed the necessity of having a high-quality ODE solver available, we are able to move the problem to a platform with more powerful optimization algorithms.

Despite the advantages, formulating the problem as a system of nonlinear equations is not as straightforward as the ODE formulation. Microkinetic models are naturally ill-conditioned (where the magnitudes of the variables are very different) a major cause of difficulties in optimization.⁶¹⁻⁶³ Therefore, solving the problem as a system of nonlinear equations requires significant reformulation, but results in dramatically decreased computational time.

2.3.1. Conditioning and Scaling

Both surface coverages and rate constants naturally span many orders of magnitude. For instance, the rate constants take on values ranging from approximately 10^{-20} to 10^{20} , 40 orders of magnitude. This results in poor conditioning, where the gradient of the objective function is much steeper with respect to one variable than another, leading to poor optimization

performance. To address this, we replace our original variable (*old*) with a new variable (*new*) times a scaling constant ($old = new * scale$), where the constant, *scale*, is selected so that our new variable is on the order of 1. This rescaling is applied to variables kf_{ic} , Keq_{ic} , kr_{ic} and y_{jc} and improves the conditioning of the problem. The scaled variables are substituted into equations 2.1-2.13 to obtain a rescaled model, which no longer includes the original variables.

Another key challenge is the presence of exponential functions in the calculation of the rate constants. The gradient of the exponential function increases dramatically as the argument of the exponential increases. Consequently, for effective optimization, it is essential that the argument of the exponential remains small (approximately less than 5). However, when calculating the equilibrium constant, the heat of reaction can naturally take on a range of values that would violate this restriction. This issue cannot be addressed by using typical scaling approaches, with a multiplicative scaling factor, as the scaling factor would remain within the argument of the exponential. Instead, the equation is split in two. We replace equation 2.8 with two new equations, 2.14 and 2.15. Equation 2.14 calculates Keq_{ic} as function of a new variable, arg_{ic} , and a new constant, $argscale_{ic}$. These are related to one another and to the enthalpy of the reaction in equation 2.15. The value of the constant, $argscale_{ic}$, is selected such that the value of arg_{ic} is approximately zero at the initial point.

$$Keq_{ic} = \exp(arg_{ic}) * \exp(argscale_{ic}), \forall i, c \quad (2.14)$$

$$arg_{ic} = -\frac{\Delta H_{ic}}{RT_c} + \frac{\Delta S_{ic}}{R} - argscale_{ic}, \forall i, c \quad (2.15)$$

The heat of reaction is then bounded so that arg_{ic} remains in the acceptable range. This improves the conditioning of the equation resulting in improved optimization performance. The bound is reset at the beginning of each optimization run. This approach is not required for kf_{ic} as the argument of the exponential is always negative.

Due to the nonlinearity (and large gradient) of the exponential terms for calculating the rate constants, modest changes in BE_j and Ea_i result in large changes in the rate constants, requiring frequent rescaling. To address this, we recondition the problem automatically during optimization (see solution algorithm).

2.3.2. Objective Function

Our goal is to fit the parameters, BE_j and Ea_i , of the microkinetic model to the experimental data. We fitted our model to a comprehensive kinetic data set published by Graaf, et al.²⁸ The data was collected in a spinning basket reactor at 483 K to 547 K and 15 to 50 atm over a Cu/ZnO/Al₂O₃ catalyst with various H₂/CO₂/CO feed compositions. After removing points with relative exit mole fraction error greater than 40% (indicating that they were not obtained at steady-state) and those obtained above 518 K where diffusion limitations were observed (as discussed in previous work²⁹) we were left with 75 experimental data points.

A well-fitted model allows us to make accurate predictions about reaction rates, surface coverages, etc. under different experimental conditions (pressure, temperature, feed composition, etc.). It also provides insight into the nature of the active site and the reaction mechanism. The selection of an appropriate objective function is very important, balancing the

relative error for low-producing experimental conditions against the absolute error for high-producing experimental conditions. Equation 2.16 is a normalized sum of the squared errors (nSSR) objective function. It measures the percentage difference between the model predictions (F_{jc}^{out}) and the experimental data (E_{jc}^{out}). This objective ensures that the relative error in low-producing experimental points is not too large.

$$error = \sum_c \sum_{j \in G} \left(\frac{F_{jc}^{out}}{E_{jc}^{out}} - 1 \right)^2 \quad (2.16)$$

In contrast, the standard sum of the squared errors (SSR), shown in equation 2.17, measures the absolute difference between the model predictions and experimental data. This leads to better fitting of high-producing experimental points, but may effectively disregard low-producing experimental points.

$$error = \sum_c \sum_{j \in G} (F_{jc}^{out} - E_{jc}^{out})^2 \quad (2.17)$$

It is also possible to use heteroscedastic error functions which include aspects of both of these to better capture the structure of the experimental error.²⁴

2.3.3. Penalty Functions

To further improve optimization performance, we relax the constraint that equation 2.1 must be equal to zero, i.e.,

$$F_{jc}^{in} - F_{jc}^{out} + R_{jc}^{net} = z_{jc}, \quad \forall j, c \quad (2.1b)$$

and introduce equation 2.18.

$$d = \sum_j \sum_c |z_{jc}| \quad (2.18)$$

The sum of the deviations from steady-state, d , is added to the objective function (see eqn 2.20 below) as a penalty with a large leading coefficient ($\alpha = 10^4$), to insure that the solution remains very near steady-state. The combination provides good control of even small deviations from steady-state. The overall value of d in most solutions is 10^{-6} - 10^{-4} ; this is a small error especially when spread over 75 conditions and 18 species. Moreover, the deviation from steady-state at the individual points is generally much smaller than that obtained by solving the system of ODEs to “steady-state.”

With 26 parameters to fit 75 experimental points, there are regions of the parameter space where the response surface of the objective function is flat with respect to one or more parameters. In this case, we would like the values of the parameters to stay as close to the DFT values as possible without compromising the fit to experimental data. To that end, we have introduced a quadratic bias function, p , in equation 2.19, which acts like a prior probability in Bayesian formulation.⁶⁴

$$p = \sum_j (BE_j - BE_j^{DFT})^2 + \sum_i (Ea_i - Ea_i^{DFT})^2 \quad (2.19)$$

The quadratic form penalizes larger deviations from the DFT values more strongly than small deviations, in accordance with what we expect about the experimental error. We add p to the objective function (eqn 2.20), with a small leading coefficient ($\beta = 0.08$) to allow the

parameters to move away from their DFT values when it improves the fit to the experimental data, but keep them near DFT when the improvement is minimal.

Our final, overall objective function, *obj*, is shown below, in equation 20.

$$\min obj = error + \alpha d + \beta p \quad (2.20)$$

2.4. Solution of NLP

To solve the parameter estimation problem, we use the NLP-solver CONOPT, which is based on a generalized reduced gradient algorithm.⁶⁵ CONOPT is designed for large, sparse (where most variables are involved in only a few equations) systems and is particularly effective when the number of equations and number of variables is similar, as is the case here.⁶⁶ The optimization model is formulated and solved within the General Algebraic Modeling System (GAMS), an optimization modeling environment specifically designed to solve a wide range of optimization problems with a special emphasis on large systems of equations.⁶⁷ GAMS includes a modeling language which readily represents systems of equations, a compiler, automatic differentiation capabilities and links to powerful optimization solvers.

2.4.1. Solution Algorithm

We have developed a solution algorithm to get the best possible fits to the experimental data for our reformulated model (Figure 2.2). The algorithm is initialized by a single solution of the ODE version of the model and then the reformulated model is optimized with different subsets of parameters free (often only one) until we can obtain no further improvement. A formal statement of the algorithm is included at the end of this section.

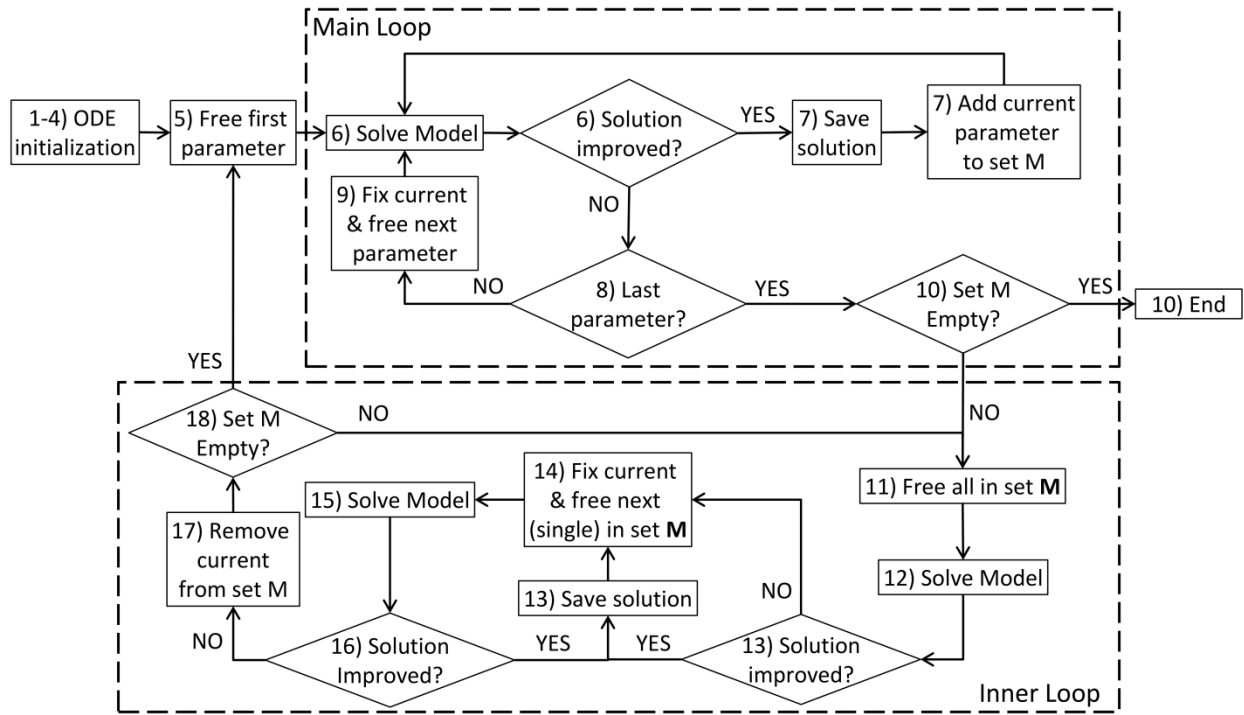


Figure 2.2: Flowchart of solution algorithm. The problem is initialized by a single solution of the ODE formulation to obtain good initial guesses for the surface coverages and gas-phase concentrations. In the main loop, the parameters are optimized one at a time, in a fixed sequence. In the inner loop, the parameters which improved the objective in the main loop (set M) are optimized as a set and then individually. Parameters which do not improve the objective are removed from set M and when set M becomes empty we return to the main loop. The algorithm terminates when the objective does not improve in the main loop.

Given a set of material parameters BE_j and Ea_i and values for y_{jc} (coverages and partial pressures) for all species and conditions, all the remaining values can be calculated. However, this means that an initial guess must be specified for the values of y_{jc} . Furthermore, due to the nonlinearity of the problem, the guess must be reasonably accurate to obtain feasible solutions. During initialization, the problem is solved once as a system of ODEs for each initial set of BE_j and Ea_i (step 1) to obtain good initial guesses for the coverages and partial pressures of all species. The results from this solution are imported into GAMS where the problem is initially solved with BE_j and Ea_i fixed to ensure that the optimization is initialized with a minimal deviation from steady-state (steps 2-4).

To minimize the size of the problem, the optimization may be performed over subsets of the parameters. The model is optimized with a subset of the parameters free, while parameters are fixed resulting in a subset of the equations becoming fixed as well (steps 5 and 9). These equations are removed from the system of equations. We have found that the best solutions are obtained by initially optimizing the model with one free parameter at a time. In the main loop, the parameters are freed in a predetermined order and the model is optimized with each parameter free until no further improvement is obtained. The specific order in which the parameters are freed may affect the final result; however we try to minimize this effect with our algorithm's inner loop. The extent of improvement for each parameter is recorded and the problem is rescaled prior to each round of optimization. Each subsequent optimization is initialized at the final point of the prior optimization, unless the solution of the prior optimization is infeasible or the objective function (fit) has deteriorated (step 6). In that case, the next optimization is initialized from the current best solution (which was stored in step 7). When the model has been optimized with each of the parameters free (step 8) we stop if there has been no improvement in the objective function. Otherwise we move on to the inner loop.

In the inner loop, the model is initially optimized with all of the parameters in set **M** (parameters which improved in the main loop) free simultaneously (steps 11-13). The model is then optimized with each of the parameters in set **M** freed one at a time, in order according to the degree of improvement in the objective function in the main loop (steps 14-16). When the fit no longer improves when the model is optimized with a particular parameter free, that parameter is removed from set **M** (step 17) and the model is optimized with all of the

parameters in the reduced set **M** free (steps 11-13). When set **M** is empty (step 18), we return to main loop at step 5 and the process repeats. Optimization stops when the model has been optimized with each of the parameters freed sequentially (main loop) without further improvement in the objective function (step 10). This gives us the best local minimum for the objective function. Therefore, we will find different solutions from different initial points.

2.4.2. Formal Statement of Parameter Estimation Algorithm

Initialization – Define **A** as the set of all parameters and establish good initial guesses for y_{jc} .

- 1) Solve the ODE model and store BE_j , Ea_i and y_{jc} .
- 2) Fix all parameters in set **A**.
- 3) Initialize and scale all variables and solve NLP model (eqns 2.1-2.20)
- 4) Store BE_j , Ea_i and y_{jc} . Set $best = obj$.

Main Loop – Optimize all parameters individually until they show no further improvement.

- 5) Free first parameter in **A** and fix all others.
- 6) Initialize and scale all variables and solve NLP model (eqns 2.1-2.20). If $obj > best$, the current best value, goto 8.
- 7) Store BE_j , Ea_i and y_{jc} . Set $best = obj$. Add the current parameter to set **M** of improved parameters. Goto 6.
- 8) If current parameter is the last in the set of all parameters, **A**, goto 10.
- 9) Fix the current parameter and free the next parameter in **A**. Goto 6.

10) If the set **M** is empty, end.

Inner Loop – Further optimize the parameters that showed improvement in main loop (set **M**).

11) Free all parameters in set **M**.

12) Initialize and scale all variables in **M** and solve NLP model (eqns 2.1-2.20).

13) If $obj < best$, store BE_j , Ea_i and y_{jc} , set $best = obj$.

14) Fix current parameter(s) and free the next parameter in set **M**.

15) Initialize and scale all variables in **M** and solve NLP model (eqns 2.1-2.20).

16) If $obj < best$, goto 13.

17) Remove the current parameter from set **M**.

18) If the set **M** is empty, goto 5. Otherwise, goto 11.

2.4.3. Performance Evaluation

The above algorithm and the reformulation of the model resulted in a dramatic decrease in the computational time required for parameter estimation. For the reaction network in Figure 2.1, on average, a single simulation of the model as a system of ODEs takes approximately 5 CPU minutes on a 3 GHz Intel Core Duo CPU. To optimize the system of ODEs, over two hours would be required just for one gradient approximation; a significant computational load which must be completed at every iteration of the optimization algorithm. In all, it would take approximately 2 weeks to complete an optimization of the ODE model with 150 optimization iterations. In contrast, solving the system with CONOPT requires an average of just 15 CPU minutes for the full optimization, a 1000-fold increase in speed. The increase in speed is

dependent on the number of parameters optimized, the size of the reaction network and the number of experimental points to be fitted. Broadly, the speed-up increases as the size of the problem increases. However, as the problem becomes very large additional improvements in the code and/or algorithm may be required to solve the problem as a NLP.

2.5. Multi-start Approach

Since microkinetic models are non-convex and have multiple local minima, the final solution of any local optimization depends on the initial guess provided for the parameter values. Because the reformulation of the model dramatically reduces solution times we can implement a multi-start approach to efficiently and systematically search the parameter space for parameter values which provide a good fit to the experimental data. However, the number of points required to sample the space on a grid grows as n^p , where p is the number of parameters and n is the number of different values for each parameter we want to test. It follows that with 26 parameters, and intervals around the DFT values of approximately 1 eV (± 0.5 eV), if we want to sample the space at 0.1 eV intervals it would require approximately 10^{26} points. If we increased our interval to 0.2 eV, we would still require approximately 10^{18} points. Therefore, our initial (stage 1) sample is necessarily low-resolution. In order to obtain better solutions, we introduce a second sampling stage (Figure 3). After solving the model from the initial points in stage 1, we identify the best solutions. Two or more of these solutions (preferably relatively close together in the parameter space) are used to define a parameter subspace, which includes parameter values intermediate between the stage 1 solutions. We sample the

subspace (stage 2) and use the new points to initialize the model. Additional sampling phases are included as needed based on the quality of the fits obtained and the stage 2 sample resolution.

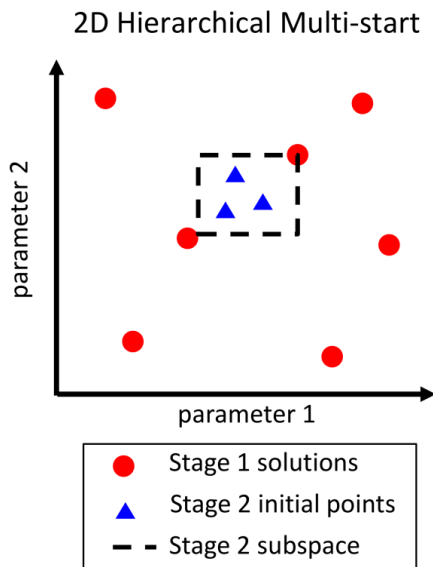


Figure 2.3: Hierarchical Multi-start Approach An initial (stage 1) sample of the parameter space is taken and the model is optimized. The best solutions in stage 1 are used to define one or more parameter subspaces for stage 2. The subspaces are sampled and the model is optimized from these points giving a higher-resolution sampling of promising parts of the parameter space.

Other groups have also combined multi-start approaches with NLP solvers in order to obtain greater reliability and improved solutions to nonlinear optimization problems. A notable example is QQNLP^{68,69} a multi-start NLP solver available in GAMS.

2.6. Application to Methanol Synthesis

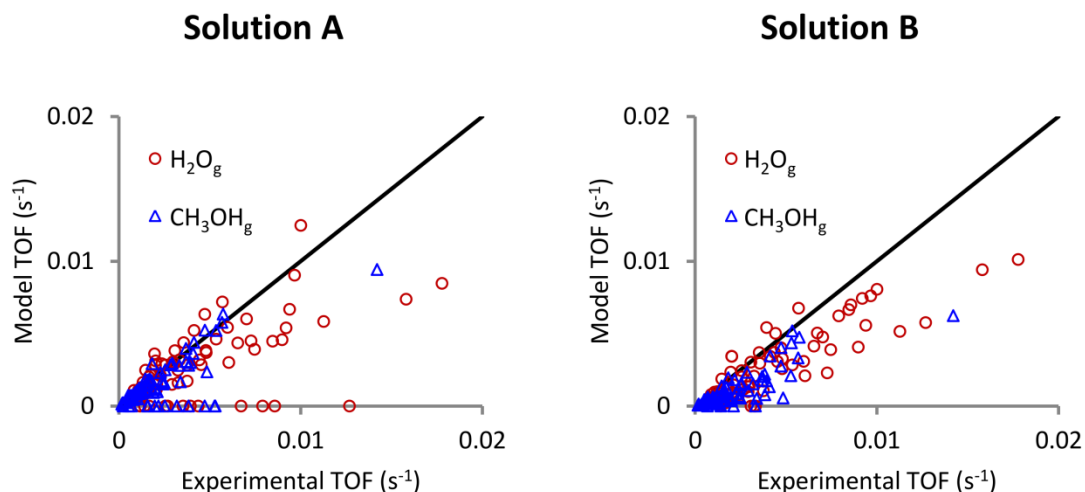


Figure 2.4: Two of the better solutions generated from the stage 1 sampling; solutions A and B have objective function values of 37 and 50 respectively. These points are used to define the parameter subspace for stage 2 sampling. Model-predicted TOF is plotted against experimentally measured TOF. Blue triangles represent methanol production rates; red circles, water production rates.

The hierarchical multi-start approach was used to provide initial points for optimization. For our methanol synthesis example, our stage 1 sample was a 10,000 point latin hypercube sample (LHS)⁷⁰ of the parameter space with bounds 0.65 eV on either side of the DFT values, or as constrained by the thermodynamics of the problem. (The activation energies must be positive and satisfy equation 2.11. The binding energies must be negative.) In stage 2, we sampled one parameter subspace defined by two of the best points from stage 1 with a smaller LHS (100 points). Each of the initial points generated was optimized using our solution algorithm to obtain our final results.

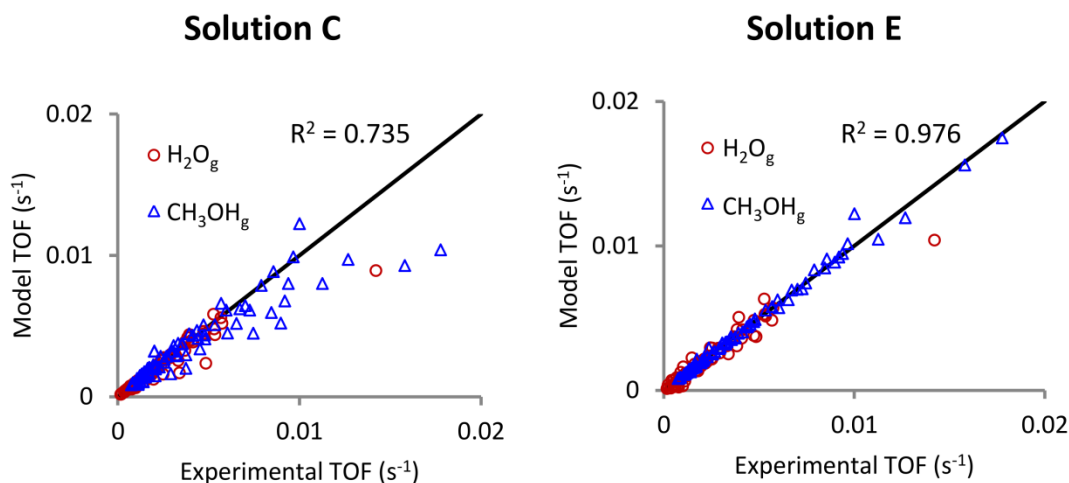


Figure 2.5: A stage 2 LHS with 100 points bounded by solutions A and B from stage 1 was generated and used as initial points for optimization. The best fits using the normalized and standard SSR in the objective function are solution C and E, respectively. As would be expected, solution C is a better fit for the data in the low-production range while solution E is a better fit in the high production. Both solutions represent an improvement over the fit obtained in Grabow and Mavrikakis²⁹ in their respective objective functions. Solution E is an improvement by all measures calculated.

With two data points (methanol and water production) at each of 75 experimental conditions, the error using nSSR at steady-state is 150 when the model predicts an inactive catalyst (no production). A perfect fit to the data would have zero (nSSR) error. In Grabow and Mavrikakis²⁹ using the ODE formulation of the same problem we found a parameter set with an error (nSSR) of 13. Using the best initial points from the stage 1 LHS, the algorithm yielded solutions A and B, with objective function (nSSR) values of 37 and 50 respectively, which are shown in Figure 4. While these fits are a dramatic improvement over the unfitted DFT parameter values (which predict no production), the fit remains poor. Solution B systematically under-predicts the production of both methanol and water. Solution A does a better job of predicting methanol production, but remains a poor predictor for water production and fails to predict any production at all for a significant number of points.

Table 2.1: A comparison of the quality fit for various solutions to the model.

	DFT	Grabow ²⁹	Stage 1 w/ nSSR		Stage 2 w/ nSSR		Stage 2 w/ SSR		
			A	B	C	D	E	F	G
Normalized SSR	149.99	13.15	37.46	50.12	5.04	5.56	6.16	6.51	10.21
Standard SSR	2.96×10^{-3}	1.38×10^{-4}	8.97×10^{-4}	6.31×10^{-4}	2.22×10^{-4}	1.55×10^{-4}	3.45×10^{-5}	5.36×10^{-5}	6.08×10^{-5}

Our stage 2 solutions fit using a standard SSR achieved improved fits to the data (compared to Grabow and Mavrikakis based on all measures. Grabow and Mavrikakis²⁹ used the standard SSR in the objective function.

We used solutions A and B to define a parameter subspace for stage 2 sampling. Of the hundred stage 2 solutions, 15 fit the data (based on nSSR) better than the fit from Grabow and Mavrikakis.²⁹ This shows that a hierarchical multi-start approach can be an effective way to investigate large parameter spaces, which will become more important for larger models with greater numbers of parameters. The best solution from stage 2 is shown in Figure 5 as solution C, which has an objective function (nSSR) value of 5.04. The fit is much better than solutions A and B; however, there is still some under-prediction of the production of methanol, especially for the higher producing experimental conditions. Meanwhile, the low-producing experimental conditions are very accurately modeled. This is partly a consequence of our selection of nSSR (equation 18) in our objective function. Since what we are minimizing is the percentage difference between the model predictions and the experimental data, the absolute deviation will naturally be larger for the higher-producing experimental conditions.

Using another starting point from the second stage LHS, we also obtained solution D from the algorithm; see Tables 2.1-2.3 for comparison. Like solution C, this solution under-predicts the production rates of high producing experimental points. For some parameters, such as the activation energy for hydrogen disassociation, the values are very similar. However, there are

differences in parameter values of up to 0.5 eV (BE of COOH), indicating these are distinct solutions.

To obtain a better fit to the high-producing points, we re-ran the optimization for the 100 point LHS, replacing equation 18 with equation 19 (the standard SSR) and scaling the leading coefficients, α and β , so that the relative influence of the penalties was unchanged. Seventeen of the resulting solutions had a standard SSR less than that found in Grabow and Mavrikakis.²⁹ The best of these solutions, with an R^2 value of 0.98, (SSR = $3.4\text{e-}5$) is shown in Figure 5 as solution E. (In comparison, Grabow and Mavrikakis²⁹ had an R^2 value of 0.88 and an SSR of $1.4\text{e-}4$.) The fit is very good, with nearly all of the data points lying on or very near the parity line. We also include solutions F and G from this set of solutions in Tables 2.1-2.3, to allow comparisons between their parameter values.

Table 2.2: BE values (eV) for DFT, best fit from Grabow and Mavrikakis, and selected fits from the present work.

	DFT	Grabow ²⁹	10 ⁴ -point LHS w/ nSSR		100-point LHS w/ nSSR		100-point LHS w/ SSR		
			A	B	C	D	E	F	G
CO	-0.9	-0.8	-0.9	-1.1	-1.0	-1.0	-1.0	-1.3	-1.0
H ₂ O	-0.2	-0.2	-0.3	-0.3	-0.2	-0.4	-0.3	-0.5	-0.4
H	-2.4	-2.5	-2.5	-2.4	-2.4	-2.5	-2.5	-2.5	-2.4
CO ₂	-0.1	-0.1	-0.1	-0.3	-0.2	-0.4	-0.3	-0.1	-0.2
OH	-2.8	-3.2	-3.1	-3.3	-3.1	-3.2	-3.3	-3.0	-3.2
COOH	-1.5	-1.8	-1.5	-1.5	-1.5	-2.0	-1.5	-1.5	-1.5
HCOOH	-0.2	-0.7	-0.9	-0.8	-0.8	-1.2	-0.9	-1.3	-1.1
HCO	-1.2	-1.7	-1.7	-2.2	-2.0	-2.0	-2.3	-1.9	-2.1
HCO ₂	-2.7	-3.3	-3.1	-3.0	-3.1	-3.2	-3.2	-3.3	-3.2
CH ₃ O ₂	-2.0	-2.6	-3.1	-2.5	-3.0	-2.9	-2.8	-3.2	-2.9
CH ₂ O	-0.0	-0.5	-0.8	-0.1	-0.6	-0.3	-0.3	-0.8	-0.4
CH ₃ O	-2.5	-3.1	-3.1	-2.5	-2.9	-2.5	-2.8	-2.7	-2.7
CH ₃ OH	-0.3	-0.5	-0.5	-0.5	-0.5	-0.3	-0.3	-0.4	-0.3

There are differences of more than 1 eV between BE values in our present work and DFT predictions (e.g. HCO). There are also differences of more than 0.5 eV between solutions from our current work (e.g. CH₂O). There are other species for which all solutions have very similar BE values (e.g. H, H₂O, CH₃OH). Solutions from Figures 4 and 5 in bold.

Table 2.1 includes the normalized and standard sum of squared errors for each, allowing us to compare and contrast the different solutions. Overall our stage 2 sampling using the standard SSR provided the best solutions. They have the highest R^2 values and the lowest values for SSR. Their nSSR values are lower than those from Grabow and Mavrikakis²⁹. The stage 2 sampling optimized with nSSR in the objective function had lower values of nSSR, but the fit is poor for high-producing experimental points (Figure 2.5).

Table 2.3: Ea values (eV) for DFT, best fit from Grabow and Mavrikakis, and selected fits from the present work.

	DFT	Prior Fit ¹⁸	10 ⁴ -point LHS w/ nSSR		100-point LHS w/ nSSR		100-point LHS w/ SSR		
			A	B	C	D	E	F	G
R1 $H_2 + 2 * \rightarrow 2 H^*$	0.5	0.4	0.5	0.5	0.5	0.5	0.5	0.5	0.5
R2 $H_2O^* + * \rightarrow H^* + OH^*$	1.1	0.7	1.0	0.6	0.9	1.1	0.9	1.0	1.0
R3 $CO^* + OH^* \rightarrow COOH^* + *$	0.5	0.5	1.0	0.9	1.0	1.0	0.9	1.0	0.9
R4 $COOH^* + * \rightarrow CO_2^* + H^*$	1.0	1.2	1.0	1.0	1.0	0.5	1.0	1.0	1.0
R5 $CO^* + H^* \rightarrow HCO^* + *$	0.9	0.5	1.1	1.1	1.1	1.1	1.1	1.4	1.1
R6 $CO_2^* + H^* \rightarrow HCO_2^*$	0.8	0.4	0.6	0.6	0.6	1.1	0.6	0.8	0.7
R7 $HCO_2^* + H^* \rightarrow HCOOH^* + *$	0.8	0.9	1.3	0.8	1.0	1.0	1.2	1.1	1.1
R8 $HCOOH^* + H^* \rightarrow CH_3O_2^* + *$	1.0	1.0	0.9	0.8	1.0	1.1	1.0	1.0	1.0
R9 $HCO^* + H^* \rightarrow CH_2O^* + *$	0.4	0.5	0.5	0.6	0.5	0.6	1.0	0.6	0.6
R10 $CH_2O^* + H^* \rightarrow CH_3O^* + *$	0.2	0.2	0.4	0.1	0.4	0.2	0.3	0.6	0.4
R11 $CH_3O_2^* + * \rightarrow CH_2O^* + OH^*$	0.6	0.4	0.9	0.6	0.8	0.8	0.6	1.0	0.8
R12 $CH_3O^* + H^* \rightarrow CH_3OH^* + *$	1.1	1.4	1.2	0.6	1.1	0.8	1.1	1.1	0.7

There are differences of more than 0.5 eV between Ea values in our present work and DFT predictions (e.g. R3, R4, R5, R9). There are also differences of more than 0.4 eV between solutions from our current work (e.g. R9, R11, R12). There are other reactions for which all solutions in our current work have very similar Ea values (e.g. R1, R2, R3). Solutions from Figures 4 and 5 in bold.

Tables 2.2 and 2.3 contain the BE and Ea values for selected fits, respectively. The fits are distinct in their parameter values. Certain parameters are fairly consistent across all solutions (such as Ea $HCOOH^* + H^* \rightarrow CH_3O_2^* + *$, and BE CO). Other parameters vary widely from solution to solution (such as the BE HCO and Ea $HCO^* + H^* \rightarrow CH_2O^* + *$). Since we have identified several solutions of similar quality, with different parameter sets, it is necessary to

consider additional factors to identify the best fit to the data. These may include considering more than one measure of fit (such as standard and normalized SSR and R^2 value), privileging solutions whose parameters most resemble DFT, and examining subsets of the data and evaluating the model's ability to accurately predict trends in production based on temperature, pressure, feed composition, reaction orders with respect to reactants and products, etc. The model may also be validated by comparing the predictions of the fitted model to a dataset not used in the fitting. We will further investigate these directions in future work.

2.7. Conclusions

Reformulating microkinetic models as systems of nonlinear equations requires careful scaling and bounding to produce meaningful results. However it pays off in dramatic improvements in computational speed; 1000-fold for our example problem. This allows more comprehensive searches of the parameter space than were previously feasible. In the past, the initial values of the parameters were adjusted manually based on intuition, knowledge of the system and the gradient at the current point. This approach was very time-consuming and yielded results that were heavily dependent upon the skill and knowledge of the user. Moreover, since the process was guided by prior assumptions about the system, the results were less likely to provide novel insights. Our improved approach allowed us to identify multiple fits to the data which are significantly better than those previously identified. This approach can be extended to reaction networks including multiple reaction pathways to identify which are feasible and most probable. We can further improve our approach by using more refined, statistically-based,

objective functions. Greater insight into the reaction on industrially relevant catalysts can help us develop better catalysts and better conditions for operating existing catalysts. Moreover, the techniques described herein can be directly extended to the problem of designing better catalysts, by allowing us to model new catalysts *in silico* much more efficiently than was previously possible.

Chapter 3

Results for Fitting of Full Methanol Network

We apply our optimization approach from chapter 2, which allows much more rapid optimization and consequently makes possible a multi-start approach which more thoroughly investigates the parameter space in an unbiased way, to the full methanol synthesis network as investigated by Grabow and Mavrikakis.²⁹ This more systematic investigation of the parameter space allows additional insight into what we can know about the parameter values and mechanism. In turn, an improved understanding of the parameter values of the active site, combined with DFT may provide additional insight into the nature of the active site.

3.1. Model Set-up and Optimization

We present an extensive microkinetic model,^{4,6} based on that used in Grabow and Mavrikakis,²⁹ including 50 elementary steps and 22 surface species. The model accounts for the possible production of byproducts such as formaldehyde, formic acid and methyl formate. No assumptions regarding the mechanism or rate-limiting steps are made. All model parameters, except sticking coefficients, are rigorously derived from DFT calculations and then fitted to reproduce published experimental data using a Cu/ZnO/Al₂O₃ catalyst under realistic conditions. Consistent with Grabow and Mavrikakis²⁹, we have chosen to model the active site

using the Cu(111) surface in our DFT calculations, since under reducing conditions, at low pressures, the Cu(111) and Cu(100) surface are predominantly exposed.³¹

The entropy was calculated directly from the vibrational frequencies and used to fit the parameters of the Shomate equation. To obtain enthalpy estimates for all intermediates, the electronic energy was corrected for zero point energy (ZPE) contributions and temperature effects using Cp. The transition state energies were corrected using ZPE and Cp in an analogous fashion. The pre-exponential factor was calculated from the entropy difference between the initial and transition state of the elementary step.⁶ For spontaneous reactions, the pre-exponential factor was assumed to be 10^{-13} s^{-1} . All DFT calculations were performed using the DACAPO total energy code on the Cu(111) surface using a 3x3 unit cell and 3 layer slab and were published in Grabow and Mavrikakis.²⁹

We fitted our model to a comprehensive kinetic data set published by Graaf, et al.^{28,71} The data was collected in a spinning basket reactor between 483 K to 547 K and 15 to 50 atm over a Cu/ZnO/Al₂O₃ catalyst with various H₂/CO₂/CO feed compositions. After removing points with relative exit mole fraction error greater than 40% (consistent with prior work^{21,29}) and those obtained above 518 K where diffusion limitations were observed²⁹ we were left with 75 experimental data points.

The microkinetic model was treated as a system of nonlinear equations and fitted to the experimental data as discussed in chapter 2. The activation energies for adsorption reactions and non-activated reactions were fixed at their DFT values. An additional 5 activation energies

and 9 binding energies which preliminary work indicated were less important to the fit were also fixed. The remaining 13 BE's and 34 Ea's were optimized starting at many different initial points which systematically varied in the values of the 47 adjustable parameters.

The parameter space to be investigated was defined as extending up to 0.5 eV in each direction away from the DFT values (or as constrained by the thermodynamic constraints). We started with a 50,000 point Latin hypercube sample of the parameter space. During optimization, the parameters were absolutely constrained to move no more than 1 eV away from the DFT value in any direction, nor were they allowed to violate the thermodynamic constraints. The points which best fit the experimental data from the initial round of optimization were used to define subspaces of the total parameter space where we expected to find better solutions. Each subspace was bounded by the parameter values of two of the first round solutions and was sampled with a 1000 point Latin hypercube sample to generate a second round of initial points. In all, 66 subspaces were sampled.

Fit was evaluated using the sum of squared errors (SSR) normalized such that a model which no production has a value of 100. The SSR is the sum (over the experimental conditions) of the squares of the differences between the model predictions and the experimental data (equation 2.17). For methanol synthesis methanol and water production were measured. The pSSR is the predicted SSR normalized relative to the SSR for the case with no production of methanol or water such that the pSSR represents a percentage of the error in the no production condition.

$$pSSR = \frac{\sum_c \sum_{j \in G} (F_{jc}^{out} - E_{jc}^{out})^2}{\sum_c \sum_{j \in G} (E_{jc}^{out})^2} \quad (3.1)$$

The unfitted values of the parameters predict nearly no production so pSSR represents the degree of improvement in the fit relative to the DFT parameters.

3.2. Set of Optimized Solutions

In total, we generated 217 solutions with $pSSR < 1.5$. All of these represent good fits to the experimental data. For comparison, the solution from Grabow and Mavrikakis had a pSSR of 4.7.²⁹ With many distinct solutions (in terms of parameter values) with similar values of the objective function, additional factors must be considered when evaluating solutions. Despite its limitations, DFT provides a rational, theoretically-sound approximation to the parameter values of the catalytic material. As such, we argue that solutions where the parameter values most resemble the DFT values are most desirable.

There are several possible measures of change from DFT; how many parameters have been changed or changed by more than a threshold value (e.g. 0.2 eV, the error in DFT predictions), the maximum change in any single parameter, the distance between the points defined by the DFT values of the parameters and the fitted values (treating the parameter space as a vector space), or how many elementary steps have had their activation energies reduced to near zero. After assessing all of these factors, we selected as our best solution the one with the smallest maximum change in any single parameter. This solution had a pSSR of 1.46 and also ranked relatively high with regards to the other measures of change from DFT.

3.3. Best Solution

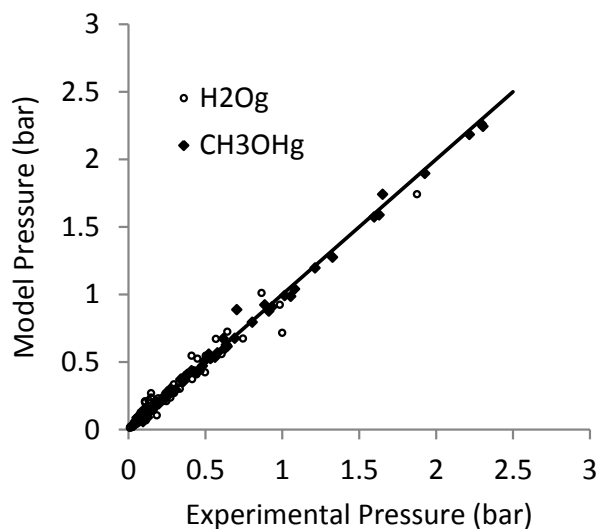


Figure 3.1: Parity Plot of Experimental and Calculated Partial Pressures. Full diamonds represent CH₃OH pressures; open circles, H₂O pressures. Experimental data is taken from references.^{28,71} Quality of fit: pSSR = 1.5.

A detailed analysis of the best solution found, looking at both the parameter changes and the predicted reaction mechanism, showed that there were significant changes in the value of parameters which, based on an understanding of the system, would not be expected to be significant. (For instance, significant reductions in the activation energy barrier for reactions that did not carry significant flux or changes in the binding energies of species which neither had a significant coverage nor were involved in the active reaction mechanism.) Since the initial points were randomly selected, it can be reasonably anticipated that some of the best fits to the experimental data may include changes in parameter values that are not essential to the fit, but rather represent artifacts of the initial point. Therefore, the values of selected parameters from our best fit were manually adjusted to their DFT values, giving a solution with a very similar fit to the data, but a greater resemblance to the DFT predictions for the

parameter values. Some parameters had to be changed from their DFT values in order to satisfy the constraint that the activation energy is greater than the enthalpy of the reaction (since the enthalpy changes with changes in binding energies). In this case, the parameter change was reduced to the minimum required. In all, 2 binding energies and 7 activation energies were manually modified by up to 0.59 eV. These modifications are summarized in table 3.1. A parity plot of the best solution's predictions (with modified parameters) vs. the experimental data is shown in figure 3.1.

	Original Best Fit	Modified Best Fit
BE O*	0.04	0
BE CH ₂ OH*	-0.12	0
Ea COOH* → CO ₂ * + H*	-0.23	0
Ea HCO ₂ * + * → HCO* + O*	0.21	0.08
Ea 2OH* → H ₂ O* + O*	0.65	0.60
Ea OH* + * → O* + H*	-0.49	0
Ea HCO ₂ * + H* → H ₂ CO ₂ * + *	-0.59	0
Ea HCOOH* + * → HCOH* + O*	-0.11	0
Ea CH ₃ O ₂ * + * → CH ₂ OH* + O*	-0.03	0

Table 3.1: Manual Parameter Modifications Parameter values from the best fitted solution were manually modified to more closely resemble the DFT values based on knowledge of the system and analysis of the reaction mechanism. The parameter values are expressed in eV of change from DFT. The modifications left the fit to the experimental data essentially unchanged.

Despite our best efforts to evaluate the solutions found, there is no definitive way to identify which solution most accurately represents the physical catalyst or even if the best solution has been found. Furthermore, the data set is insufficient to fully specify the parameter set. Specifically, based on the experimental data at hand, some of the parameters are unknown and unknowable. By statistically analyzing the solutions obtained, it is possible to assess which parameters are well-specified by the data and which are unknown. Unknown parameters may

still be important, but the dataset used does not provide enough information to know their value, therefore, DFT still provides the best estimate of the value of these parameters. An expanded data set could provide additional information about parameters which are currently unknown.

3.4. Analysis of Parameter Changes from DFT

The parameter values in the fitted solutions are summarized in tables 3.2 and 3.3. Only a limited number of parameters have consistent, significant changes from the DFT values across most or all of the fitted solutions identified. We define the most significant parameter changes as those where the average change in the parameter value for the selected solutions (with pSSR < 1.5) was at least 3 times the standard deviation of the change in the parameter value. Parameter changes are discussed from the most significant change to least significant separately for BE and Ea.

3.4.1. Binding Energy Modifications

BE OH The BE of hydroxyl was the second most consistent parameter change in the set of fitted solutions with an average -0.42 eV stabilization on the surface, 10.5 times the standard deviation of 0.04 eV. This is quite comparable to the change in the best solution of -0.4 eV and also comparable to the value of -0.41 eV in Grabow and Mavrikakis²⁹. Interestingly, an identical -0.4 eV stabilization has been observed for the Cu(211) surface, relative to the Cu(111) surface,²⁹ supporting the argument of Behrens et al⁴⁴ that Cu steps decorated with Zn atoms

are the active site for methanol synthesis. In all of the fitted solutions BE OH was stabilized by at least -0.26 eV, with a maximum stabilization of -0.48 eV.

	DFT	Grabow ²⁹	Best fit	Average	Standard Deviation	Min	Max
H	-2.43	-0.07	0.13	0.16	0.05	0.09	0.35
CO	-0.86	0.10	0.42	0.42	0.05	0.30	0.67
HCO	-1.18	-0.55	0.33	0.37	0.04	0.10	0.48
CH ₂ O	-0.04	-0.43	-0.30	-0.31	0.05	-0.49	-0.15
CH ₃ O	-2.45	-0.64	0	0	0	0	0
CH ₃ OH	-0.28	-0.23	0	0	0	-0.01	0.01
CO ₂	-0.08	0	-0.23	-0.15	0.08	-0.35	0.05
HCO ₂	-2.68	-0.6	0.04	-0.29	0.16	-0.49	0.13
HCOOH	-0.22	-0.49	-0.45	-0.01	0.14	-0.47	0.18
CH ₃ O ₂	-2.01	-0.55	-0.41	-0.26	0.12	-0.44	0.03
COOH	-1.52	-0.31	0	0	0	0	0
H ₂ O	-0.21	0	-0.20	-0.28	0.12	-0.50	0.03
OH	-2.80	-0.41	-0.40	-0.42	0.04	-0.48	-0.26
O	-4.25	0	0.04	0.18	0.21	-0.30	0.40
H ₂ CO ₂	-3.32	0	0	0	0	0	0
COH	-2.57	0	0	0	0	0	0
HCOH	-1.85	0	0	0	0	0	0
CH ₂ OH	-0.84	0	0	-0.03	0.05	-0.16	0.01
CO ₃	-3.62	0	0	0	0	0	0
HCO ₃	-2.48	0	0	0	0	0	0
HCOOCH ₃	-0.10	0	0	0	0	0	0
CH ₂ OOCH ₃	-1.96	0	0	0	0	0	0

Table 3.2: DFT Values and Changes from DFT Values for Binding Energies All parameters are expressed in eV. Average, standard deviation, min and max, refer to set of fitted solutions with pSSR < 1.5.

BE HCO Nearly as significant as the change in the BE of OH is the change in the BE of HCO. On average, the BE of HCO was destabilized by 0.37 which is 9.25 times the standard deviation of 0.04 eV. In the best solution it was destabilized it by 0.33 eV. In contrast, in Grabow and Mavrikakis,²⁹ HCO was stabilized by -0.55 eV, while Cu(211) shows a 0.3 eV stabilization relative to Cu(111).²⁹

BE CO The BE of CO was destabilized both on average and in the best solution by 0.42 eV, 8.4 times the standard deviation of 0.05 eV. With a DFT value of -0.86 eV (based on the PW91 functional), this results in a fitted value of the BE of -0.44 eV, very comparable to the prediction of -0.39 eV based on the RPBE functional in our own work or -0.41 eV in others.⁷² Furthermore, the predicted value is consistent with the experimentally observed value which has varied between -0.45 and -0.69 eV.^{73,74}

BE CH₂O Based on the DFT, formaldehyde is only physisorbed (BE = -0.04 eV) and any formaldehyde formed would be expected to desorb immediately. Since no formaldehyde production is measured experimentally, it is not surprising that the fitted solutions all predict significant stabilization of formaldehyde on the surface by, on average, -0.31 eV, 6.2 times the standard deviation of 0.05 eV. This gives us a prediction of a BE of -0.35 eV as compared to a measured value of -0.59 eV on Cu(110).⁷⁵ The change is of the same magnitude as the predicted -0.2 eV stabilization on the Cu(211) surface relative to the Cu(111) surface,²⁹ especially accounting for an additional stabilization of 0.1-0.2 eV due to Van der Waals forces which are poorly accounted for by DFT.⁷⁶

BE H The average change in the BE of H is 0.16 eV, which is relatively modest and only 3.2 times the standard deviation of 0.05 eV. The best solution has a change of 0.13 eV and the range in the fitted solutions was 0.09-0.35 eV. Despite the relatively modest change, the value of the BE of H is quite important as there are 4 or 6 H involved in the synthesis of methanol from CO or CO₂, respectively. Therefore, even modest changes in the parameter value have a large effect on the potential energy surface of the reaction. The best fitted binding energy of -

2.30 eV is quite close to recently published calculations of -2.22 eV⁷² and reasonably close to the experimentally measured value of -2.45 eV.⁷⁷

While three of the most significant parameter changes involve the destabilization of species on the surface, the majority of modified binding energies in the fitted solutions are increased, especially for closed shell species including carbon dioxide, water, formaldehyde and formic acid. Standard DFT methods do not adequately account for long-range interactions, such as Van der Waals forces,⁷⁸ which may dominate the binding interactions for stable, closed-shell molecules which show weak interactions with the Cu(111) surface. Recently, a theoretical method capable of representing van der Waals forces was presented.⁷⁶ Van der Waals forces account for approximately 0.1-0.2 eV stabilization per carbon on transient metal surfaces. This may largely account for the predicted stabilization of formaldehyde, water and carbon dioxide on the surface. It cannot completely account for the predicted stabilization of 0.45 eV (in the best solution) for formic acid; however this value is quite variable across fitted solutions.

3.4.2. Coverages

At typical conditions from the data set of Graaf et al^{28,71} ($T = 499.3$ K, $P = 29.9$ atm, $y_{\text{CO}} = 0.053$, $y_{\text{CO}_2} = 0.047$, $y_{\text{H}_2} = 0.90$), the best solution predicts that the surface is covered with 0.46 ML of HCO_3 and the complete set of fitted solutions predicts between 0 and 0.56 ML of HCO_3 with 88% of solutions predicting more than 0.01 ML of HCO_3 . However, there is no evidence in the literature that HCO_3 had ever been identified on the surface of a Cu/ZnO/ Al_2O_3 catalyst, although both CO_3 and HCO_3 have been observed on Ti and Zr promote catalysts⁷⁹ and several

groups⁷⁹⁻⁸² have documented the presence of CO₃ on the surface. Predicted coverages of HCO₃ could be reduced by destabilizing HCO₃ on the surface or increasing the barrier to its formation. More subtly, HCO₃ generation requires the generation of atomic O on the surface. Therefore, HCO₃ coverages are a function of the barrier to the disassociation of OH and the BE of O on the surface. Based on scaling relations⁸³ and the predicted stabilization of OH on the surface, significant stabilization of O on the surface would also be predicted (although it was a feature of our fitted solutions), which would increase the barrier to the formation of CO₃, a necessary precursor of HCO₃.

At the same typical conditions, the best solution predicts traces of H and OH on the surface (1.5e-3 and 2.3e-3 ML, respectively) and no other significant coverages. Considering the full fitted solution set, the greatest coverage observed (excluding HCO₃) is H₂O with up to 0.26 ML predicted and an average coverage (across solutions) of 0.024 ML, followed by OH with up to 0.069 ML predicted (average 8.1e-3 ML). The significant coverages of water and its breakdown products are interesting in light of the debate about the role of water in methanol synthesis discussed in more detail below. The full solution set also suggests the presence of traces of HCO₂, CO, and H, on the surface (8.4e-3, 5.0e-3, and 7.0e-3 ML maximum predicted, respectively). The presence of HCO₂ on the surface of the Cu catalyst is well established.^{45,84-86}

3.4.3. Activation Energy Modifications

Ea HCO* + H* → CH₂O* + * The most consistently changed parameter across all fitted solutions is the activation energy for the formation of formaldehyde. The standard deviation is only 0.01

	DFT	Grabow 29	Best Fit	Avg.	Std. Dev.	Min	Max
$\text{CO}^* + \text{H}^* \rightarrow \text{HCO}^* + *$	0.99	-0.45	-0.33	-0.20	0.11	-0.47	0.01
$\text{HCO}^* + \text{H}^* \rightarrow \text{CH}_2\text{O}^* + *$	0.47	0.01	-0.47	-0.47	0.01	-0.47	-0.41
$\text{CH}_2\text{O}^* + \text{H}^* \rightarrow \text{CH}_3\text{O}^* + *$	0.24	-0.08	-0.21	-0.22	0.03	-0.24	-0.06
$\text{CH}_3\text{O}^* + \text{H}^* \rightarrow \text{CH}_3\text{OH}^* + *$	1.17	0.20	-0.72	-0.68	0.09	-0.89	-0.48
$\text{CO}_2^* + \text{H}^* \rightarrow \text{HCO}_2^* + *$	0.87	-0.51	-0.20	-0.34	0.16	-0.76	-0.09
$\text{HCO}_2^* + \text{H}^* \rightarrow \text{HCOOH}^* + *$	0.91	0.04	-0.40	-0.20	0.18	-0.69	0.09
$\text{HCOOH}^* + \text{H}^* \rightarrow \text{CH}_3\text{O}_2^* + *$	1.04	-0.05	-0.46	-0.91	0.12	-1.04	-0.46
$\text{CH}_3\text{O}_2^* + * \rightarrow \text{CH}_2\text{O}^* + \text{OH}^*$	0.74	-0.39	-0.36	-0.54	0.12	-0.74	-0.29
$\text{CO}^* + \text{OH}^* \rightarrow \text{COOH}^* + *$	0.56	-0.02	0.43	0.39	0.07	0.17	0.44
$\text{COOH}^* + * \rightarrow \text{CO}_2^* + \text{H}^*$	1.23	-0.15	0	-0.30	0.18	-1.04	-0.23
$\text{OH}^* + * \rightarrow \text{O}^* + \text{H}^*$	1.68	-0.74	0	-0.27	0.20	-0.68	-0.03
$\text{H}_2\text{O}^* + * \rightarrow \text{OH}^* + \text{H}^*$	1.39	-0.69	-0.58	-0.54	0.11	-0.86	-0.39
$\text{HCOOH}^* + * \rightarrow \text{HCO}^* + \text{OH}^*$	1.63	-0.44	-0.10	-0.46	0.15	-0.64	0.00
$\text{HCOOH}^* + * \rightarrow \text{HCOH}^* + \text{O}^*$	2.5	0.21	0	-0.34	0.17	-0.74	-0.03
$\text{CH}_2\text{O}^* + \text{H}^* \rightarrow \text{CH}_2\text{OH}^* + *$	0.82	0.21	0	-0.06	0.10	-0.47	0.18
$\text{CH}_3\text{O}_2^* + * \rightarrow \text{CH}_2\text{OH}^* + \text{O}^*$	2.01	0.26	0	-0.20	0.24	-0.83	0.15
$\text{CH}_2\text{OH}^* + \text{H}^* \rightarrow \text{CH}_3\text{OH}^* + *$	0.51	-0.09	0	-0.11	0.15	-0.51	0.07
$\text{COOH}^* + \text{H}^* \rightarrow \text{HCOOH}^* + *$	0.73	-0.11	0	-0.01	0.05	-0.40	0.02
$\text{HCO}_2^* + * \rightarrow \text{HCO}^* + \text{O}^*$	2.36	-0.10	0.08	0.68	0.26	-0.07	1.03
$\text{CO}^* + \text{O}^* \rightarrow \text{CO}_2^* + *$	0.65	-0.06	0	-0.01	0.05	-0.59	0.04
$\text{HCO}_2^* + \text{H}^* \rightarrow \text{H}_2\text{CO}_2^* + *$	1.59	0.16	0	-0.42	0.12	-0.59	-0.24
$\text{H}_2\text{CO}_2^* + \text{H}^* \rightarrow \text{CH}_3\text{O}_2^* + *$	0.74	-0.35	0	-0.02	0.05	-0.23	0
$\text{H}_2\text{CO}_2^* + * \rightarrow \text{CH}_2\text{O}^* + \text{O}^*$	0.91	-0.46	0	0.06	0.10	-0.05	0.36
$\text{CO}^* + \text{H}^* \rightarrow \text{COH}^* + *$	2.25	-0.09	0	0	0	0	0
$\text{HCO}^* + \text{H}^* \rightarrow \text{HCOH}^* + *$	0.91	0.25	0	-0.84	0.21	-0.91	0
$\text{HCOH}^* + \text{H}^* \rightarrow \text{CH}_2\text{OH}^* + *$	0.47	0.05	0	-0.43	0.13	-0.47	0.02
$\text{CO}_2^* + \text{O}^* \rightarrow \text{CO}_3^* + *$	0.34	-0.07	0	0.02	0.06	-0.01	0.46
$\text{CO}_3^* + \text{H}^* \rightarrow \text{HCO}_3^* + *$	1	-0.02	0	0	0	0	0
$2\text{CH}_2\text{O}^* \rightarrow \text{HCOOCH}_3^* + *$	1.11	0.56	0	0	0	0	0
$\text{CH}_3\text{O}^* + \text{HCO}_2^* \rightarrow \text{HCOOCH}_3^* + \text{O}^*$	1.24	1.03	0	0.34	0.26	-0.24	0.67
$\text{HCOOCH}_3^* + \text{H}^* \rightarrow \text{CH}_2\text{OOCH}_3^* + *$	0.94	-0.03	0	0	0	0	0
$\text{CH}_3\text{O}^* + \text{CH}_2\text{O}^* \rightarrow \text{CH}_2\text{OOCH}_3^* + *$	0.13	0.53	0	0.11	0.12	-0.05	0.53
$\text{CH}_2\text{O}^* + \text{HCO}^* \rightarrow \text{CH}_3\text{O}^* + \text{CO}^*$	0	0	0	0	0	0	0
$\text{CH}_3\text{O}^* + \text{HCO}^* \rightarrow \text{CH}_3\text{OH}^* + \text{CO}^*$	0.38	0.50	0	0	0	-0.01	0.02
$\text{HCO}_2^* + \text{HCO}^* \rightarrow \text{HCOOH}^* + \text{CO}^*$	0.6	0.13	0	-0.03	0.10	-0.49	0.02
$\text{HCOOH}^* + \text{HCO}^* \rightarrow \text{CH}_3\text{O}_2^* + \text{CO}^*$	0.42	0.15	0	0	0	-0.05	0
$\text{O}^* + \text{HCO}^* \rightarrow \text{OH}^* + \text{CO}^*$	0	0	0	0	0	0	0
$\text{OH}^* + \text{HCO}^* \rightarrow \text{H}_2\text{O}^* + \text{CO}^*$	0.3	0.42	0	-0.02	0.08	-0.30	0.17
$\text{HCO}_2^* + \text{HCO}^* \rightarrow \text{H}_2\text{CO}_2^* + \text{CO}^*$	0.8	0.55	0	0	0	0	0
$\text{CH}_3\text{O}^* + \text{OH}^* \rightarrow \text{CH}_3\text{OH}^* + \text{O}^*$	0.47	NA	0.50	0.70	0.22	0.18	0.95
$\text{COOH}^* + \text{OH}^* \rightarrow \text{CO}_2^* + \text{H}_2\text{O}^*$	0	0.06	0	0	0	0	0
$2\text{OH}^* \rightarrow \text{O}^* + \text{H}_2\text{O}^*$	0.61	0.79	0.60	0.75	0.17	0.10	1.10

Table 3.3: DFT Values and Changes from DFT Values for Activation Energies All parameters are expressed in eV. Average, standard deviation, min and max, refer to set of fitted solutions with pSSR < 1.5.

eV and the barrier is reduced, on average, by -0.47 eV in the fitted solutions, making the step inactivated. This is identical to the best solution. However, while both BE HCO and $\text{Ea HCO}^* + \text{H}^* \rightarrow \text{CH}_2\text{O}^* + *$ are consistently modified across the set of fitted solutions, manual modifications of the parameters indicate that both parameters can be modified with minimal effect on the fit so long as the absolute height of the transition state for the formation of formaldehyde is kept constant. Since these parameters are moved in opposite directions in the fitted solutions, both can be brought closer to the DFT values.

$\text{Ea HCOOH}^* + \text{H}^* \rightarrow \text{CH}_3\text{O}_2^* + *$ On average the Ea for the formation of hydroxymethoxy is reduced by 0.91 eV which is 7.6 times the standard deviation of 0.12 eV. The best solution has a much smaller reduction of 0.46 eV to give an activation energy of 0.58 eV, this is consistent with the values found by Behrens et al⁴⁴ which ranged from 0.38 eV on Cu(211) to 0.55 eV on Cu(111) with intermediate values found on the proposed active site.

$\text{Ea CH}_3\text{O}^* + \text{H}^* \rightarrow \text{CH}_3\text{OH}^* + *$ In the best solution Ea for the formation of methanol is reduced by -0.72, 7.6 times the standard deviation of 0.09 eV. This is a dramatic reduction in the barrier for a step that has been argued to be the rate-limiting step in methanol synthesis.⁸⁷ All of the fitted solutions required the reduction of this activation energy by at least -0.48 eV. This dramatic reduction is not consistent with calculated barriers on a range of active sites.⁴⁴ Therefore, it is desirable to consider alternative mechanisms for this conversion. One option is the use of hydroxyl as a hydrogen donor for the conversion of methoxy to methanol ($\text{CH}_3\text{O}^* + \text{OH}^* \rightarrow \text{CH}_3\text{OH}^* + \text{O}^*$). Based on the DFT, this reaction has a barrier of only 0.47 eV, however, when hydroxyl is stabilized on the surface (as it is in all of the fitted solutions) this reaction

becomes quite endothermic and the barrier increases to 0.97 eV in the best solution with an average increase to 1.17 eV, identical to the DFT value for the simple hydrogenation. In contrast, in Grabow and Mavrikakis²⁹ the barrier to the formation of methanol by direct hydrogenation was increased in the fitted solution, although the fit was not as good.

Ea $\text{CH}_2\text{O}^* + \text{H}^* \rightarrow \text{CH}_3\text{O}^* + *$ Various groups have predicted highly variable values for the activation energy for the formation of methoxy with some groups finding it to be nearly spontaneous.⁴⁸ On average, we found the reaction to be nearly spontaneous after fitting. Overall the reduction in the barrier was relatively modest as the initial DFT value was only 0.24 eV. However, the average change is 7.33 times the standard deviation of 0.03 eV.

$\text{CO}^* + \text{OH}^* \rightarrow \text{COOH}^* + *$ The formation of carboxyl is the only barrier which was consistently increased from DFT beyond the enthalpy of reaction. On average, the barrier was increased by 0.39 eV, 5.6 times the standard deviation of 0.07 and comparable to the best solution. This step controls the conversion of CO into CO₂, along the carboxyl mediated pathway since the subsequent step of $\text{COOH}^* + \text{OH}^* \rightarrow \text{CO}_2^* + \text{H}_2\text{O}^*$ is spontaneous.

$\text{H}_2\text{O}^* + * \rightarrow \text{OH}^* + \text{H}^*$ On average, the barrier to the disassociation of water is reduced by -0.54 eV in our fitted solutions, 4.9 times the standard deviation of 0.11 eV, comparable to the best solution and similar to what was found in Grabow and Mavrikakis.²⁹ An alternate path, the disproportionation of water ($2\text{OH}^* \rightarrow \text{H}_2\text{O}^* + \text{O}^*$) has a much lower barrier based on the DFT (0.61 eV vs. 1.39 eV). However, as in the case of hydroxyl as a hydrogen donor for the formation of methanol, the stabilization of hydroxyl on the surface causes this reaction to be

significantly endothermic, leading to an average increase in the barrier of 0.75 eV with a 0.6 eV increase in our best solution.

$\text{CH}_3\text{O}_2^* + * \rightarrow \text{CH}_2\text{O}^* + \text{OH}^*$ The E_a for the disassociation of hydroxymethoxy was on average reduced by -0.54 eV, 4.5 times the standard deviation of 0.12 eV. In the best solution it was only reduced by -0.36 eV, very similar to what was found in Grabow and Mavrikakis.²⁹ Recently Behrens et al⁴⁴ calculated an activation energy on the proposed active site between 0.21 and 0.5 eV, consistent with our fitted data showing activation energies of less than 0.45 eV. This is in contrast of their finding of 0.63 eV on the Cu(111) surface.⁴⁴

$\text{HCO}^* + \text{H}^* \rightarrow \text{HCOH}^* + *$ and $\text{HCOH}^* + \text{H}^* \rightarrow \text{CH}_2\text{OH}^* + *$ In a minority of the fitted solutions, the formation of methanol from carbon monoxide passes through HCOH and CH₂OH intermediates. In these cases there is generally a very large decrease in the barrier for the reactions above, leading to an overall average decrease in the barrier of 0.84 eV and 0.43 eV for the formation of HCOH* and CH₂OH* respectively. While this mechanism is active in some of the fitted solutions found, the fact that it requires a highly activated step to be virtually spontaneous suggests that this mechanism may not be relevant on the real catalyst.

$\text{HCOOH}^* + * \rightarrow \text{HCO}^* + \text{OH}^*$ This reaction is a minor contributor to the overall rate of methanol production from carbon monoxide (running in reverse). On average it was facilitated by -0.46 eV (consistent with Grabow and Mavrikakis²⁹), but the barrier was only reduced by -0.1 eV in the best solution.

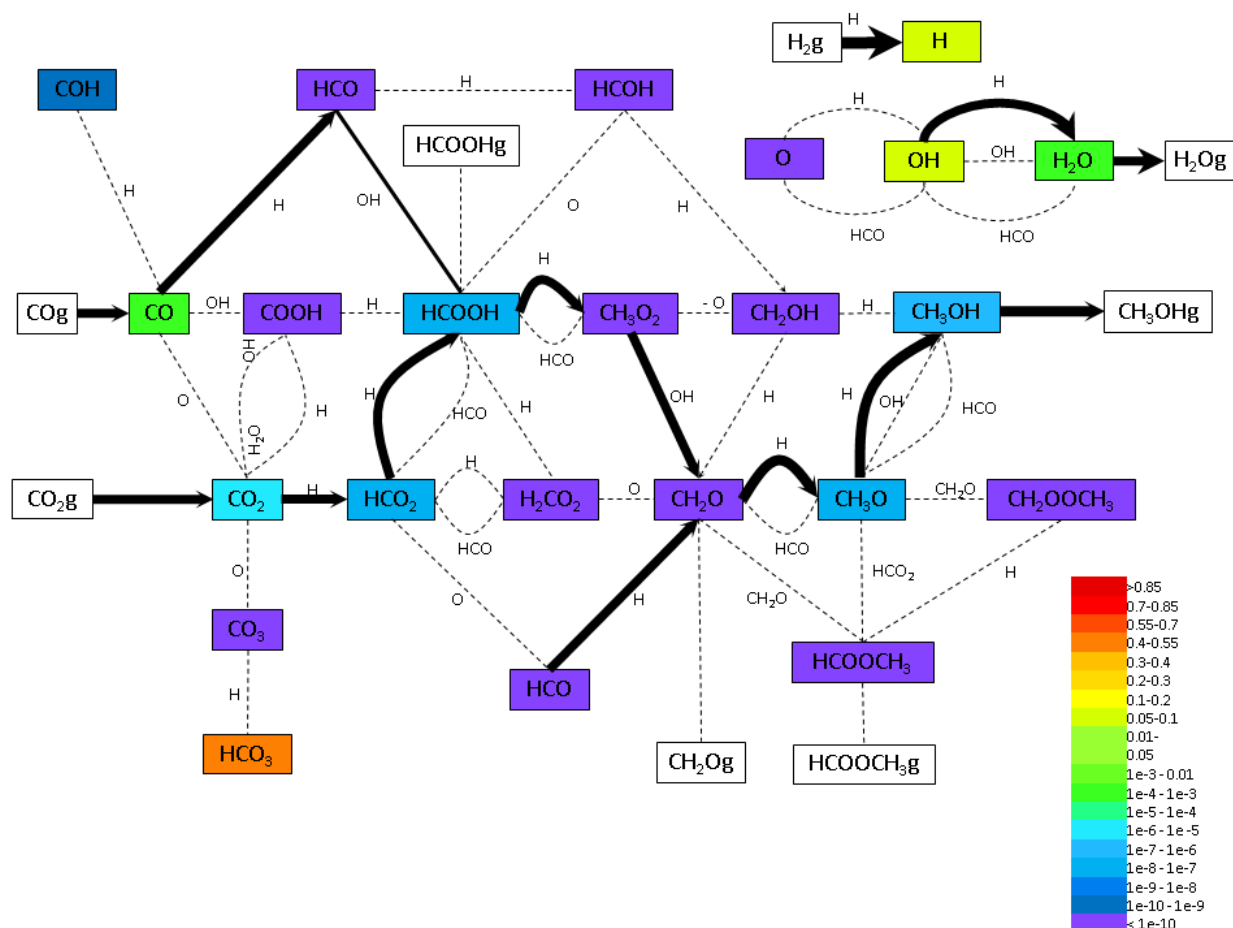


Figure 3.2: Schematic Representation of Reaction Network for Best Solution at T = 499.3 K, P = 29.9 atm, $y_{\text{CO}} = 0.053$, $y_{\text{CO}_2} = 0.047$, $y_{\text{H}_2} = 0.90$ The thickness of the arrows represents the relative flux through different pathways in the network. Dotted lines represent reactions included in the network which do not carry significant flux at steady state. The color of the boxes represents the coverage for surface species in accordance with the key at the lower right. Note that HCO is represented at both the top and bottom of the diagram to prevent crossing lines. A single mechanism accounts for all generation of methanol from CO₂ and this mechanism is observed to be consistent across all of our well-fitted solutions. The relative rates of production from CO and CO₂ are comparable. HCO₃ is predicted to be the most abundant species on the surface under these conditions.

$\text{HCO}_2^* + \text{H}^* \rightarrow \text{H}_2\text{CO}_2^* + *$ While on average this barrier was reduced by -0.42 eV, the reaction did not contribute significantly to the rate of methanol production and there was no change in the barrier in the best solution.

In the fitted solutions the activation energy barriers to all active steps in the active mechanism have been systematically reduced, increasing the predicted activity of the catalyst. This may indicate a more reactive site than the Cu(111) surface or the existence of a reaction mechanism which we have failed to include in our model.

3.5. Reaction Mechanism

Without exception, in all of the fitted solutions, as well as the solution from Grabow and Mavrikakis²⁹ methanol is synthesized from CO₂ through the following sequence of intermediates: HCO₂*, HCOOH*, CH₃O₂*, CH₂O*, and CH₃O*. All of the reactions are simple, unassisted hydrogenation reactions except the disassociation of hydroxymethoxy. This is also the most active mechanism with the DFT parameter values (although the rates predicted are much too low). Along with the identification of the same reaction mechanism on the Cu(211) surface by Behrens et al⁴⁴, this strongly suggests that this is the reaction mechanism on the physical catalyst (unless there is an alternate mechanism we have failed to include in our model).

With respect to the hydrogenation of carbon monoxide, our findings are less consistent. However, in most cases the reaction appears to proceed primarily through the series of intermediates; HCO*, CH₂O*, and CH₃O* by simple hydrogenation, which is consistent with the findings in Grabow and Mavrikakis²⁹ and the findings of Behrens et al⁴⁴ on the Cu(211) surface. We did identify a minor contribution of the reaction $\text{HCO}^* + \text{OH}^* \rightarrow \text{HCOOH}^* + *$ to the overall generation of methanol from carbon monoxide. In a minority of solutions the reaction

proceeds the intermediates HCOH^* and CH_2OH^* . However, in these solutions the changes in critical parameters are very large, leading to reactions predicted by DFT to be highly activated being characterized as spontaneous (or nearly so) by the fitted solution.

Previous modeling studies⁸⁸ have shown that carboxyl is a key intermediate in the water gas shift reaction and it is unexpected that this reaction is largely shut down in our fitted solutions by the increase in the barrier for the reaction $\text{CO}^* + \text{OH}^* \rightarrow \text{COOH}^* + *$. At the same time, the parallel reaction $\text{HCO}^* + \text{OH}^* \rightarrow \text{HCOOH}^* + *$ is significantly facilitated such that it contributes significantly to the overall reaction mechanism. It seems likely that a comparable fit could be achieved with both barriers closer to the DFT values and more of the activity proceeding through the carboxyl pathway. In fact, based on manual parameter modification it was observed that, to a limited extent, increases in the barrier for the formic acid pathway offset the deterioration in fit observed when the barrier for the carboxyl pathway was lowered towards its DFT value.

3.5.1. Role of water

As suggested by Behrens et al,⁴⁴ species which bind through O, including water and its breakdown products, appear to play a significant role in methanol synthesis. Yang et al found that dry CO/H_2 mixtures produced minimal amounts of methanol and the reactivity is significantly enhanced by small amounts of water.⁴⁷ Similarly, water produced during the production of methanol from CO_2 auto-catalytically enhances the rate of methanol synthesis.⁴⁷

There may be several mechanisms for water's promotional effect on methanol synthesis. DFT studies of various co-adsorbed species on Cu(111) have shown that O* and OH* exhibit attractive interactions with many other intermediates on the order of -0.1 to -0.2 eV, but varying with coverage.²⁹ In extreme cases, this interaction has been shown to stabilize intermediates by more than -0.7 eV.⁸⁹ Not only does the presence of oxygen species on the surface affect the strength of the binding of intermediates, it also affects how they bind, which can, in turn, affect their reactivity. Yang et al⁴⁶ studied the reactivity of HCO₂ on a Cu/SiO₂ catalyst. They found that HCO₂ adsorbed to the surface in a reducing atmosphere in a bidentate configuration and did not react significantly with H₂ gas to produce methanol. However, under a more oxidizing atmosphere including O₂ or N₂O, the HCO₂ changed to a monodentate conformation and reacted to methanol at a significant rate.

In addition to their effect on the binding of intermediates to the surface, oxide species (including OH) may directly participate in the reaction mechanism. We found that OH* catalytically promoted CO hydrogenation through the formation of formic acid from formyl (HCOOH* + * → HCO* + OH*, running in reverse), accounting for 17% of CO hydrogenation at T = 499.3 K, P = 29.9 atm, $y_{\text{CO}} = 0.053$, $y_{\text{CO}_2} = 0.047$, $y_{\text{H}_2} = 0.90$. Although it was not observed to play a significant role in the reaction mechanism in our fitted solutions, OH* could play a similar role through the water gas shift reaction with a carboxyl intermediate (CO* + OH* → COOH* + *) and dramatically facilitates the second step in WGS (COOH* + OH* → CO₂* + H₂O*), which also provides a less activated path for the formation of water.

There are two steps ($\text{CH}_3\text{O}^* + \text{H}^* \rightarrow \text{CH}_3\text{OH}^* + *$ and $\text{H}_2\text{O}^* + * \rightarrow \text{OH}^* + \text{H}^*$) which were found to require a dramatic decrease in barrier to accurately fit the experimental data and it does not appear that a simple change in active site accounts for this facilitation. In both cases, there is an alternate pathway with a much lower barrier (based on DFT) which used OH^* as a hydrogen donor. We did not find these paths to be active in our fitted solutions as the significant stabilization of OH^* on the surface observed in all fitted solutions (and consistent with the step site) lead to these alternate reactions being highly endothermic and as highly activated as the original pathways. However, universal scaling relations indicate that O^* should be stabilized on the surface by approximately twice as much as OH^* .⁸³ In this case, the automatic increase in the barrier for the hydroxyl facilitated reaction steps would be negated and these alternate paths could largely account for the needed reduction in the reaction barriers for the formation of methanol and water while also explaining the dependence of the overall reaction on the presence of water.

3.5.2. Role of CO

There has been considerable debate about the role of CO in the production of methanol from $\text{CO}/\text{CO}_2/\text{H}_2$ mixtures, with some groups arguing that its role is negligible or strictly promotional,⁹⁰⁻⁹² while others have argued that CO hydrogenation is the dominant mechanism.^{32,39} Our results show that both CO and CO_2 hydrogenation significantly contribute to CH_3OH production. In our reference condition, CO_2 hydrogenation accounts for approximately 54% of CH_3OH production (as predicted by our best solution). This varies

considerably depending on the reaction conditions, from 10-100% of methanol generated from CO_2 .

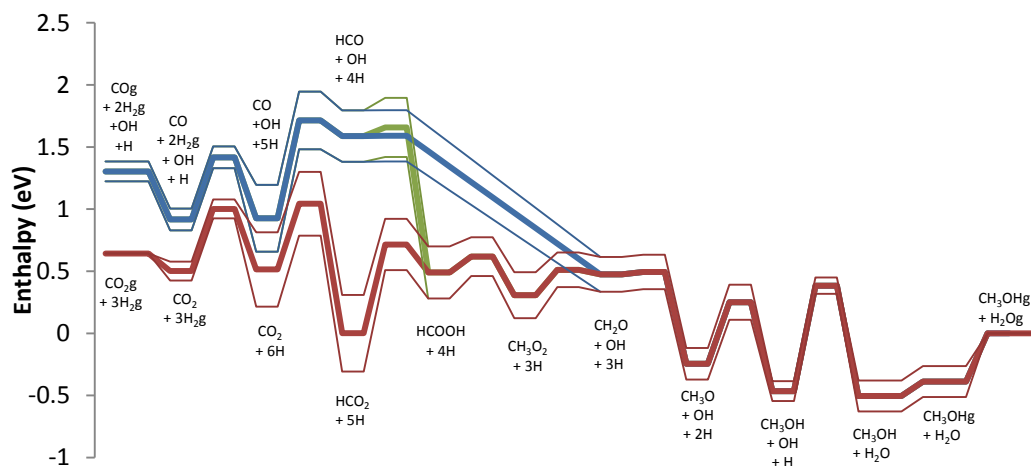


Figure 3.3: Average Fitted Potential Energy Surface with Standard Deviations Enthalpies at 499.3 K are shown and referenced to $\text{CH}_3\text{OH}(\text{g}) + \text{H}_2\text{O}(\text{g})$. The average is shown in the bold line, while the finer lines represent one standard deviation. Hydroxyl and an extra hydrogen atom are presumed to be on the surface for CO hydrogenation. The blue lines represent CO hydrogenation on the main path. The red lines represent CO_2 hydrogenation. The green lines represent CO hydrogenation with a formic acid intermediate (otherwise on the CO_2 pathway). The two main pathways converge at formaldehyde.

The most significant predictor of the contribution of CO versus CO_2 hydrogenation to methanol production is the $\text{CO}_2/(\text{CO} + \text{CO}_2)$ ratio in the feed. However, if we limit the conditions under consideration to those with approximately equal amounts of CO and CO_2 in the feed, the contribution of CO_2 hydrogenation still varies between 19 and 66%. For fixed, $\text{CO}_2/(\text{CO} + \text{CO}_2)$ ratio, the flow rate of the feed over the catalyst largely determines the relative contributions of CO and CO_2 . This behavior can be rationalized by examining the potential energy surface (figure 3.3). CO hydrogenation is significantly more endothermic than CO_2 hydrogenation. This leads to its predominance at low flow rates, where the reaction equilibrium starts to play a role. As the flow rate is increased, the extent of the reaction decreases and the relative reaction

rates are increasingly controlled by kinetic factors. The relative contribution of CO₂ hydrogenation increases until it reaches a maximum in the purely kinetically controlled regime accounting for approximately 2/3 of CH₃OH production. In this region, CO production would appear to be limited by the rate at which the highest transition state energy (CO* + H* → HCO* + *) can be surmounted. Nevertheless, it is unlikely that this behavior would have been correctly predicted by looking at the potential energy surface alone, demonstrating the value of a comprehensive microkinetic model.

At a moderate feed rate (0.25 mols/site/sec), the degrees of rate control⁹³ obtained for our model indicate that the relative contributions of CO and CO₂ hydrogenation to methanol formation are strongly influenced by the kinetics of formaldehyde formation through the steps HCO* + H* → CH₂O* + * and CH₃O₂* + * → CH₂O* + OH*. Interestingly, in our fitted solutions, HCO* + H* → CH₂O* + * is consistently predicted to be spontaneous or nearly so, so cannot reasonably be construed as a slow step. However, it is in active competition with the consumption of formyl to form formic acid (HCOOH* + * → HCO* + OH*) which has a very small barrier, as can be seen in the potential energy surface (figure 3.3).

	CH ₃ OH desorption	H ₂ O desorption	CO adsorption	CO ₂ adsorption	H ₂ adsorption
CO ₂ * + H* → HCO ₂ * + *	0.01	0.03	-0.02	0.03	0.01
HCO ₂ * + H* → HCOOH* + *	0.01	0.05	-0.04	0.05	0.01
HCOOH* + * → HCO* + OH*	0.01	-0.07	0.11	-0.07	-0.01
CH ₃ O ₂ * + * → CH ₂ O* + OH*	0.13	0.36	-0.12	0.36	0.18
HCO* + H* → CH ₂ O* + *	0.13	-0.15	0.49	-0.16	0.07
CH ₂ O* + H* → CH ₃ O* + *	0.08	0.08	0.08	0.08	0.08
CH ₃ O* + H* → CH ₃ OH* + *	0.06	0.06	0.07	0.06	0.06

Table 3.4: Degrees of Rate Control for Adsorptions and Desorption Reactions of CH₃OH, H₂O, CO, CO₂, and H₂O
Values are reported for T = 499.3 K, P = 29.9 atm, y_{CO} = 0.053, y_{CO2} = 0.047, y_{H2} = 0.90, using a CSTR model.

The above reactions also have the highest degrees of rate control for the overall formation of methanol. Close behind them are the two surface reactions common to both major reaction pathways ($\text{CH}_2\text{O}^* + \text{H}^* \rightarrow \text{CH}_3\text{O}^* + *$ and $\text{CH}_3\text{O}^* + \text{H}^* \rightarrow \text{CH}_3\text{OH}^* + *$).

3.6. Nature of Active Site

The systematic reduction in activation energies along with the general stabilization of reactants on the surface strongly suggest that Cu(111) may not accurately reflect the catalytic active site. While it has been suggested that ionic Cu^+ sites are the active catalytic centers,^{32,33} linear scaling of the catalyst activity with metallic Cu area³⁴ and experiments on single crystal Cu(100)^{24,35}, Cu(110)³⁹ and Cu films exposing primarily Cu(111) facets³⁸ provide strong evidence that metallic Cu is the active, but also demonstrate the reaction is structure-sensitive. All the DFT calculations in this study were performed on the Cu(111) surface, which is more stable, but less reactive than more open surfaces (Cu(110) and Cu(100)) and step and defect sites.

Support effects also play an important role on the industrial Cu/ZnO/ Al_2O_3 catalyst.^{94,95} ZnO has been proposed to play a role in catalysis either directly with spillover mechanisms involving the migration of H/OH ⁴¹ and formate⁴³ or indirectly by stabilizing Cu^+ ions³² or inducing shape changes in the catalyst particles.³¹ Likewise, Al has been shown to have a strong promoter effect on catalyst which modifies not only structural, but also electronic properties by changing interaction between Cu and ZnO.⁹⁶ On the other hand, Chinchin et al found that Cu supported on SiO_2 and MgO are equally active and argue that no support effect exists.³⁴

Recently, Behrens et al⁴⁴ combined experimental and theoretical techniques to argue that the active site consists of Cu steps decorated with Zn atoms and stabilized by bulk defects and partial coverage by species binding through the O, including H₂O, OH, and HCO₂. Both the presence of step sites and the alloying of Zn, increase the binding of a range of adsorbates and facilitate many reactions. Several of the most consistent parameter changes in our fitted solutions (BE OH, BE CH₂O, Ea HCOOH + H → CH₃O₂, Ea CH₃O₂ → CH₂O + OH) have fitted values that are consistent with the Cu(211) or Zn modified Cu(211) surface, providing further support for this as the active site.

3.7. Conclusions

Starting from previously published DFT data, we fitted a comprehensive, mean-field microkinetic model to published experimental methanol synthesis data collected under realistic conditions on a Cu/ZnO/Al₂O₃ catalyst, using more powerful optimization techniques than had previously been applied to microkinetic modeling. The improved optimization techniques allowed a more systematic exploration of the parameter space with no prior assumptions about the final parameter values or mechanism. Not only did the optimization approach allow a more thorough investigation of the parameter space, it also achieved a dramatically improved fit to the experimental data compared to prior work.

By analyzing a full set of fitted solutions, insight can be gained into the reaction mechanism and active site of the catalyst. Without exception, the fitted solutions predicted a single mechanism for the production of methanol from carbon dioxide with the sequence CO₂* → HCO₂* → HCOOH* → CH₃O₂* → CH₂O* → CH₃O* → CH₃OH*. We also found that CO is hydrogenated

to form methanol (accounting for 46% of methanol formation in our reference condition). The latter half of the mechanism is the same as for CO₂ hydrogenation ($\text{CH}_2\text{O}^* \rightarrow \text{CH}_3\text{O}^* \rightarrow \text{CH}_3\text{OH}^*$) and is consistent across solutions, as is the formation of formyl from CO ($\text{CO}^* \rightarrow \text{HCO}^*$) at the beginning of the mechanism. However, in between more variation was observed. In the best solution, the majority of CO hydrogenation occurs by hydrogenation of formyl to formaldehyde ($\text{HCO}^* \rightarrow \text{CH}_2\text{O}^*$), with 17% generated through a formic acid intermediate ($\text{HCO}^* + \text{OH}^* \rightarrow \text{HCOOH}^* + *$). A minority of solutions involved the sequence $\text{HCO}^* \rightarrow \text{HCOH}^* \rightarrow \text{CH}_2\text{OH}^*$, however large reductions in relevant activation energy barriers suggest that this mechanism may not accurately reflect the mechanism on the real catalyst.

In order to obtain a good fit to the experimental data, many intermediates had to be significantly stabilized on the surface and almost all active steps had to have their barriers reduced. The two largest barrier reductions in the best solution were for the steps $\text{CH}_3\text{O}^* + \text{H}^* \rightarrow \text{CH}_3\text{OH}^* + *$ and $\text{H}_2\text{O}^* + * \rightarrow \text{OH}^* + \text{H}^*$. Both of these steps have alternate mechanisms with much lower barriers (based on the DFT) using OH* as a H donor to facilitate the reaction. However, we found that neither was a viable alternative mechanism as the significant stabilization of OH* on surface, observed in all fitted solutions, caused them to be highly endothermic. However if O* was stabilized proportionately to OH* (as one might expect), these might provide a viable alternative mechanism accounting for the dramatic reduction in barrier required.

The systematic stabilization of intermediates on the surface and reduction of reaction barriers required to obtain a good fit to the experimental data suggest that Cu(111) does not accurately

reflect the active site on the commercial Cu/ZnO/Al₂O₃ catalyst. Where DFT is available, much of our fitted data is consistent with the Cu(211) surface, possibly reflecting the role of step sites in methanol synthesis. Repeating our study of the parameter space using Cu(211) surface as a starting point might produce interesting results.

While our exploration of the parameter space was extensive, due to the large number of parameters, it is impossible to fully investigate even a small area of the parameter space. Consequently, there may exist other solution sets that fit equally well that have been completely missed. Moreover, our conclusions are limited to the reaction network modeled. While we did include a large number of reactions and intermediates, other reaction mechanisms have been proposed. On the basis of this model, we cannot exclude these mechanisms and it is possible that they could contribute to accurately predicting the experimental results with smaller changes from DFT values of the parameters.

Chapter 4

Methods and Results for Experimental Design in a CSTR

With a fitted solution to the microkinetic model we can look at the details of reaction mechanism, coverages on the surface and the effects of the experimental conditions on the overall reaction rate, selectivity, conversion, surface coverages, reaction mechanism, etc. Typically, the effect of experimental conditions has been explored by plotting the response of the model to changes in the input variables. While we can observe trends with this approach, it is not possible to identify optimal conditions since changes in one variable affect the optimal value of all the others. Therefore, it is desirable to be able to optimize our model, not only by changing the values of the BE's and Ea's to maximize the fit to the experimental data, but also, given a set of BE's and Ea's fitted to the data, adjust the operating conditions of the reactor (P, T, flow rate, and feed composition) to minimize or maximize given rates, coverages or partial pressures.

Using this tool, we can identify the optimal operating conditions for a given catalyst, probe the reaction mechanism in detail, or identify the best conditions to look for a postulated reactive intermediate on the surface. Thus, our microkinetic model can guide experiments, which, in turn, can provide additional information to evaluate our fitted parameter values. However, our

model assumes perfect mixing with no transport effects, which is not the case in all experimental conditions.

In this chapter, we explore the predictions of best solution found in chapter 3 and compare it to the best solution from Grabow and Mavrikakis,²⁹ by optimizing the pressure (P), temperature (T), feed rate (F^{in}), and feed composition (x_j) with a variety of objective functions. For selected objective functions, we further explore the effects of the experimental parameters by varying them individually around the optimum.

4.1. Experimental Design Model

The experimental design problem starts with the same basic model of the CSTR as the fitting problem (equations 2.1 – 2.13) and applies the same tricks to improve the scaling (equations 2.14 – 2.15). However, where in the fitting problem BE_j and Ea_i are variables which are fitted such that the model predictions in a range of experimental conditions (set $\mathbf{C}$) are matched to experimental data, in the experimental design problem BE_j and Ea_i are fixed parameters corresponding to a particular material to be modeled (generally a solution to the fitting problem). The set $\mathbf{C}$ is dropped (since we are no longer matching the model to experimental data) and the experimental parameters (P , T , F^{in} , x_j) become variables which are optimized to minimize or maximize the desired objective. To allow a more flexible optimization, we replace the parameter F_j^{in} from chapter 2 (the feed rate of individual species) with the total feed rate (F^{in}) and the mole fractions of all gas phase species in the feed (x_j), such that

$$F_j^{in} = x_j F^{in}, \quad j \in G \quad (4.1)$$

and introduce the constraint that the mole fractions in the gas phase must sum to one.

$$\sum_{j \in G} x_j = 1 \quad (4.2)$$

Possible objectives include reaction rates, conversion of some component of the feed, coverages and partial pressures. Similar to the fitting problem, the constraint that the rate of change ($\frac{dy_{jc}}{dt}$) is equal to zero (equation 2.1) is relaxed and stiff penalty on deviations from steady state (d) is included in the objective function (equation 2.1b, 2.18 and 2.20). The penalty on changes in BE_j and Ea_i (p) is omitted since they are now fixed parameters.

The preexponential factor (A_i) is also a function of temperature and this is explicitly included in the model. Equation 4.3 shows the temperature dependence of adsorption reactions which are modeled with collision theory, while equation 4.4 shows the temperature dependence of surface reactions.

$$A_i = \frac{A_i^{root}}{\sqrt{T}}, \quad i \in A \quad (4.3)$$

$$A_i = A_i^{root} T, \quad i \in U \quad (4.4)$$

Our model of methanol synthesis includes a temperature correction for the enthalpy of formation and calculation of the entropy based on the Shomate equations.

$$\Delta Hf_j = \Delta Hf_j^o + A_j T_r + B_j \frac{T_r^2}{2} + C_j \frac{T_r^3}{3} + D_j \frac{T_r^4}{4} + \frac{E_j}{T_r} + F_j - H_j, \quad \forall j \quad (4.5)$$

$$\Delta S_j^o = A_j \ln(T_r) + B_j T_r + C_j \frac{T_r^2}{2} + D_j \frac{T_r^3}{3} - \frac{E_j}{2T_r^2} + G_j, \quad \forall j \quad (4.6)$$

where T_r is the reduced temperature:

$$T_r = \frac{T}{1000} \quad (4.7)$$

and the Shomate parameters ($A_j, B_j, C_j, D_j, E_j, F_j, G_j, H_j$) are derived from DFT.

In the fitting problem, the enthalpy and entropy could pre-calculated, and remained fixed throughout the optimization. However, with the temperature as a variable in the experimental design problem, the dependence of enthalpy and entropy on temperature needs to be incorporated into the optimization. Since the Shomate equations are nonlinear functions of temperature, to simplify the solution of the problem, we calculate the enthalpy and entropy outside of the optimization. This is valid for a limited temperature range, so we restrict the range in which the temperature can change then recalculate the enthalpy and entropy and continue the optimization with the new value. We continue to optimize the model until one of four exit criteria is reached. 1) With a feasible, steady-state solution, the updated value of the enthalpy does not significantly change the model prediction. This gives a feasible, optimized solution to the problem. 2) Too many consecutive infeasible solutions are obtained. 3) Too many consecutive solutions with minimal improvement are obtained. 4) The maximum number of iterations is reached. A formal statement of the algorithm follows.

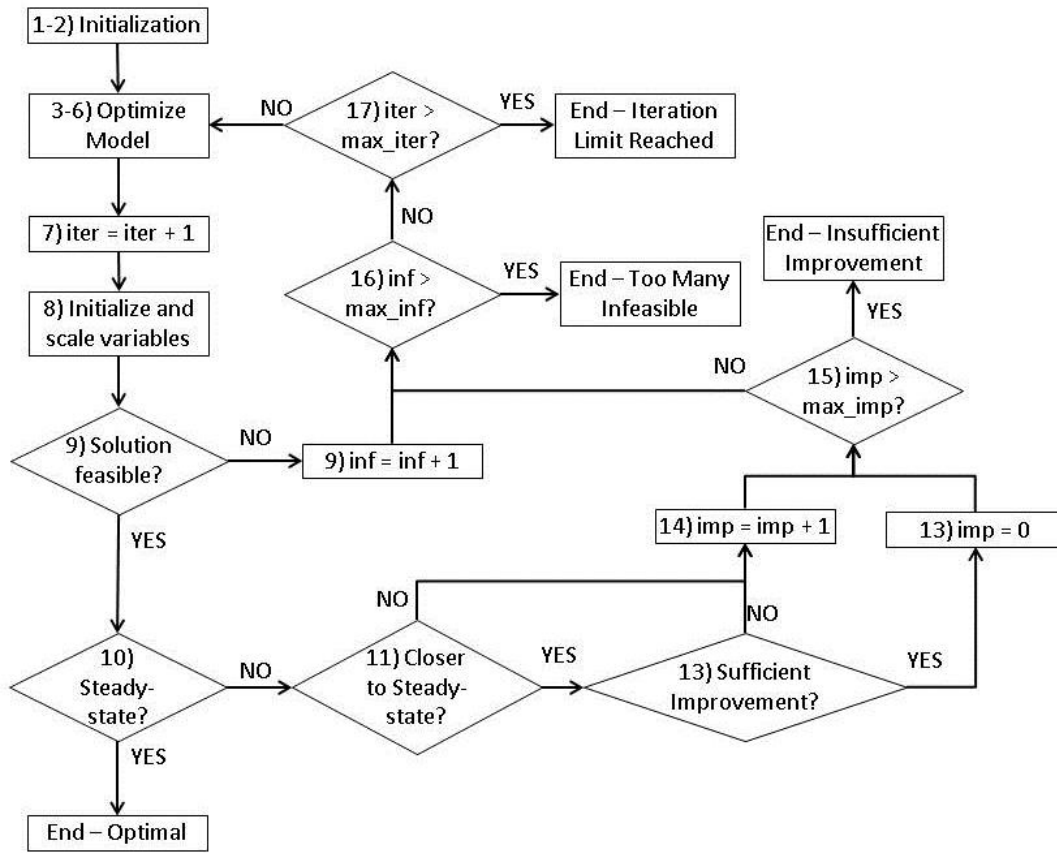


Figure 4.1: Flowchart of solution algorithm. The problem is initialized by a single solution of the ODE formulation to obtain good initial guesses for the surface coverages and gas-phase concentrations. The NLP model is optimized with strict limits on the change in temperature. The enthalpy is calculated for current value of temperature and all variables initialized and scaled. If the model prediction is significantly affected by the change in temperature, the model is reoptimized (with new limits). The process continues until steady-state is reached, the maximum iteration limit is reached, there are too many consecutive infeasible solutions to the model or too many consecutive solutions to the model with minimal improvement.

4.1.1. Formal Statement of Algorithm

Initialization – Establish good initial guesses for y_j .

- 1) Solve the ODE model.

- 2) Calculate enthalpy (ΔH_{ic}) at current temperature (T) and initialize and scale all variables.

Optimize Model – Minimize deviation from steady state and optimize experimental variables

- 3) Fix experimental variables (P, T, F^{in}, x_j) and rate constants (kf_i, Keq_i, kr_i) and scale model
- 4) Solve NLP model, minimizing deviation from steady state (d)
- 5) Free experimental variables (P, T, F^{in}, x_j) and rate constants (kf_i, Keq_i, kr_i) and set limits
- 6) Solve NLP model, minimizing objective function (obj)

Evaluate Solution – Re-optimize model or terminate optimization?

- 7) Increment iteration counter ($iter = iter + 1$)
- 8) Calculate enthalpy (ΔH_{ic}) at current temperature (T) and initialize and scale all variables
- 9) If solution from step 6 is infeasible, increment infeasibility counter (inf). Goto 16.
- 10) If deviation from steady-state is less than tolerance ($d < \delta$), end with optimal solution
- 11) If $d < best$, calculate percentage improvement (per), set $best = d$. Goto 13.
- 12) Set $per = 0$. Goto 14.
- 13) If $per > \varepsilon$, set $imp = 0$. Goto 15.
- 14) Set $imp = imp + 1$.
- 15) If $imp > max_imp$, end, insufficient improvement
- 16) If $inf > max_inf$, end, too many infeasible solutions

17) If $iter > max_iter$, end, iteration limit reached

18) Goto 3.

As for the fitting problem, we initialize the model by solving the system ODEs in Matlab to insure a good initial guess for y_j and use a multistart approach to identify multiple local optima if they exist. However, due to the lower dimensionality of the problem, many fewer initial points are required to thoroughly investigate the parameter space and a hierarchical multi-start approach is not required.

4.2. Maximal Reaction Rates

We can minimize or maximize reaction rates simply by including the reaction rate with an appropriate leading coefficient in our objective function. We can also include linear combinations of different reaction rates in our objective to address particular questions of interest. This gives us equation 4.8, which includes a penalty on deviations from steady state and a multiplier m . The set $\mathbf{M}$ is a subset of the set $\mathbf{I}$ of all reactions representing the reactions of interest to answer our question.

$$\min obj = \sum_{i \in \mathbf{M}} m_i r_i + \alpha d \quad (4.8)$$

4.2.1 Production of Methanol

To maximize the rate of production of methanol, we minimize the rate of methanol adsorption on the surface ($\mathbf{M} = [\text{CH}_3\text{OHg} + * \rightarrow \text{CH}_3\text{OH}^*]$) therefore our multiplier (m) is simply 1. The

experimental parameters were constrained such that the temperature was between 300 and 800K, the pressure was between 10^{-15} and 100 atm, and the flow rate was between 0.01 and 1 s^{-1} . Convergence for this objective function was good with 38/100 initial points converging to the same optimal solution for our best parameter set and 32/100 for the best parameter set from Grabow and Mavrikakis.²⁹

For a single, irreversible reaction with Arrhenius kinetics and fixed reactant concentrations, the reaction rate will always be maximized at the maximum temperature. However, this is not the case for reversible reactions. While the forward the reaction rate is still maximized at maximum temperature, the optimal temperature to maximize the net reaction rate will depend on the effect of the temperature on the reaction equilibrium. For a complex reaction network, this is compounded as the concentration of the intermediates will also be a function of the reaction conditions. Thus, for a full microkinetic model we cannot easily predict the optimal temperature to maximize the rate of any individual reaction or the overall flux through the network.

For our best solution, we found production of methanol was maximized at 717.6 K, a feed rate of 1 s^{-1} (the upper limit in our optimization) and a nearly stoichiometric ratio of CO and H_2 in the feed ($x_{\text{CO}} = 0.378$, $x_{\text{H}_2} = 0.622$). The turnover frequency for methanol was 0.276 s^{-1} . The best solution from Grabow and Mavrikakis²⁹ also showed maximal production with maximal feed rate and a stoichiometric ratio of CO and H_2 ($x_{\text{CO}} = 0.334$, $x_{\text{H}_2} = 0.666$). The predicted turnover

frequency is slightly higher at 0.325 s^{-1} and the optimal temperature is somewhat lower at 622.9 K. In both cases, the optimal pressure is at the upper bound of 100 atm.

In the optimal conditions, the surface for our best solution is 99.8% empty with traces of CO^* and H^* on the surface. In contrast, the best solution from Grabow and Mavrikakis predicts that the surface is 92% covered with CH_3O^* and also has traces of CH_3OH^* , CO^* and H^* . Only 7.4% of the surface is predicted to be empty.

Both solutions predict the same series of intermediates; $\text{CO}^* \rightarrow \text{HCO}^* \rightarrow \text{CH}_2\text{O}^* \rightarrow \text{CH}_3\text{O}^* \rightarrow \text{CH}_3\text{OH}^*$. For our best solution, all of the reactions are simple hydrogenations. However, for the best solution from Grabow and Mavrikakis, 44% of the formation of methanol is accounted for by the simple hydrogenation of methoxy (CH_3O^*). The other 56% of methanol formation uses HCO^* as a hydrogen donor in the hydrogenation of methoxy.

4.2.2. Production of Methanol from Carbon Dioxide

By subtracting the rate of CO consumption from the rate of methanol production, we can create an objective function which maximizes the production of methanol from CO_2 . The set **M** is composed of the reactions $\text{COg} + * \rightarrow \text{CO}^*$ and $\text{CH}_3\text{OHg} + * \rightarrow \text{CH}_3\text{OH}^*$ and the multipliers for both are 1. The experimental parameters were constrained such that the temperature was between 400 and 600K, the pressure was between 50 and 100 atm, and the flow rate was between 0.01 and 1 s^{-1} . Convergence was again good for our best fit to the data with 39/100 initial points converging to approximately the same optimal solution. Using the best fit from

Grabow and Mavrikakis²⁹ we also found an optimal solution, but only three initial points converged to the same solution.

For the production of methanol from CO₂, our overall turnover frequencies for methanol are much lower; 0.086 s⁻¹ for our best solution and 0.046 s⁻¹ for the best solution from Grabow and Mavrikakis.²⁹ We still find that methanol production is maximized when pressure and flow rate into the system go to their upper bounds of 100 atm and 1 s⁻¹, respectively. Likewise, the optimal feed composition is still essentially stoichiometric ($x_{CO_2} = 0.280$, $x_{H_2} = 0.720$ for our best solution and $x_{CO_2} = 0.247$, $x_{H_2} = 0.753$ for the best solution from Grabow and Mavrikakis²⁹), although CO has been replaced by CO₂. On the other hand, the optimal temperature for the maximal production methanol from CO₂ is much lower than the optimal temperature for the maximal production of methanol (468.2 K for our best solution and 555.6 K for the best solution from Grabow and Mavrikakis²⁹). Interestingly, this is much closer to the industrial production conditions which are typically around 523 K.⁹⁰

At the optimal conditions for our best solution, the surface is 79.7% empty, 17.1% of the surface is covered in OH*, 2.9% in H₂O* and there are traces of CO* and H* on the surface. For the best solution from Grabow and Mavrikakis,²⁹ the surface is predicted to be only 48.2% empty with 24.2% of the surface covered in CH₃O*, 11.4% covered in HCO₂*, 14.5% covered in H* and 1.8% in OH*. In both cases methanol is formed primarily via the mechanism discussed in chapter 3. In the solution from Grabow and Mavrikakis,²⁹ about 4% of CH₂O* is formed from HCO* derived from CO* formed via the reverse water gas shift mechanism.

Even at the lower optimal temperature for the production of methanol from carbon dioxide, if we instead maximize overall methanol production (keeping temperature fixed), we find that CO is the main contributor of carbon to methanol synthesis. For our best solution, at the 468.2K, the optimal feed composition is $x_{CO} = 0.300$, $x_{CO_2} = 0.092$, $x_{H_2} = 0.608$, which results in nearly a doubling of the turnover frequency of methanol to 0.159 s^{-1} . However, the consumption of CO_2 decreases 10-fold to 0.0086 s^{-1} . The results are even more dramatic for the best solution from Grabow and Mavrikakis.²⁹ At 555.6 K, the optimal feed composition is $x_{CO} = 0.429$, $x_{H_2} = 0.571$ with only traces of CO_2 in the feed. The methanol production rate increases to a level comparable to the overall optimum at 0.273 s^{-1} , but is essentially all produced from CO.

If we introduce CO into the feed, specifying that a fixed percentage of the carbon in the feed must come from CO, and optimizing the remaining variables to maximize the production of methanol from CO_2 , the overall turnover frequency for methanol is increased, but the production of methanol from CO_2 decreases. For our best solution, the mole fraction of H_2 in the feed varies only slightly as CO/C ratio is increased. It peaks when CO accounts for approximately 60% of the carbon. However, the optimal temperature drops off steadily as the amount of CO is increased. When CO accounts for 90% of carbon the optimal temperature is 445 K. The drop-off is nearly linear, but accelerates somewhat with increasing CO concentration. In contrast, the best solution from Grabow and Mavrikakis²⁹ predicts that the optimal temperature is nearly invariant as the CO concentration is increased. However, the mole fraction of H_2 in the feed steadily increases, asymptotically approaching approximately 0.94 as the CO_2 content of the feed approaches zero.

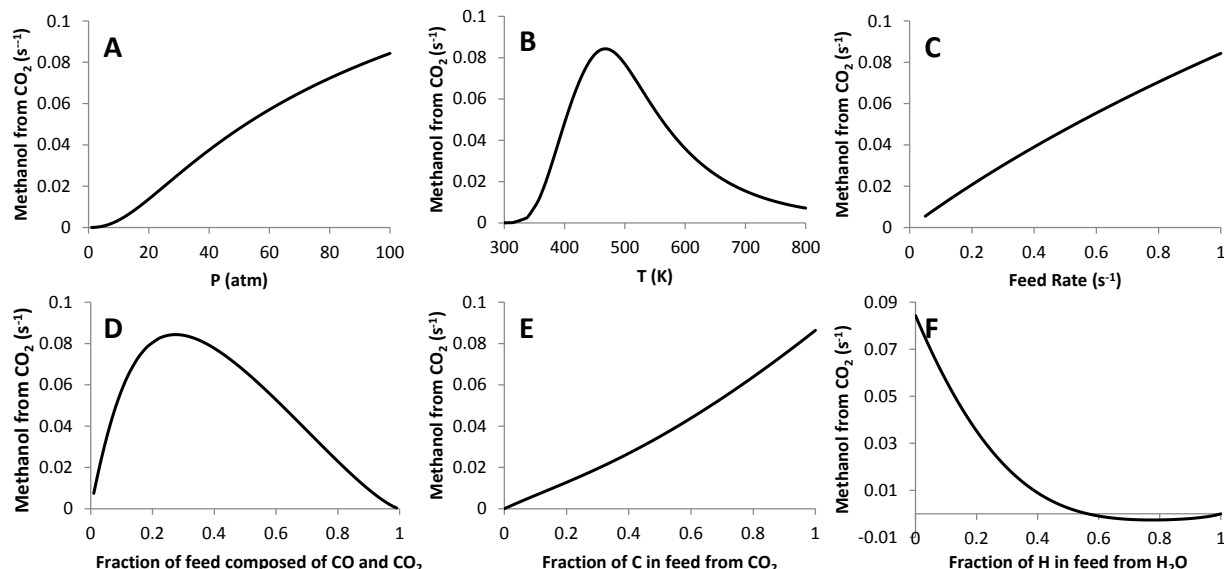


Figure 4.2: Methanol production from CO_2 as a function of changes in the experimental variables around the optimum. The variables are changed one at a time with the remaining variables fixed. Temperature and the fraction of the feed composed of CO and CO_2 show clear maxima while the effects of pressure, flow rate, and CO in the feed are monotonic. In F, the objective function becomes negative for large amounts of water in the feed as the CO is generated through the reverse water gas shift reaction. However the methanol production drops off steadily.

To further understand the response of the objective function to changes in the individual variables around the optimum point, we varied the experimental variables one at a time. We show the results graphically in figure 4.2. Methanol production has a very clear and pronounced maximum with respect to temperature that drops off abruptly as we move away from the optimum. The rate drops to zero as the temperature decreases towards room temperature and tails off with continued low-level activity at high temperatures. The rate also shows a distinct maximum as we change amount of carbon in the feed, going to zero at both extremes, as one would expect. The rate increases monotonically as the pressure, flow rate into the system or fraction of the carbon represented by CO_2 increases.

As we add water to the feed, the objective function drops off dramatically. However, our objective function stops being a good measure of methanol production from CO_2 as CO is

produced through the reverse water gas shift reaction, artificially reducing the objective function value below the production of methanol. This produces the negative values of the objective function seen in figure 4.2F and highlights the necessity of careful objective function formulation to ensure that we answer the question we are interested in. However, the objective function remains valid so long as our feed is dry.

4.3. Maximal Conversion

While we can maximize reaction rates using an objective function which is a linear function of our variables, finding the conversion requires a ratio of the rate at which a species is consumed (or a product produced) to the rate at which a reactant is fed, giving us equation 4.9.

$$\min obj = \frac{\sum_{j \in \mathbf{M}} R_j^{net}}{F^{in} \sum_{j \in \mathbf{M}} x_j} + \alpha d \quad (4.9)$$

Where j corresponds to the species for which conversion is being measured. This equation is only defined for gas phase species, but we can include more than one species in the set $\mathbf{M}$ in order to measure, for instance, the total conversion of carbon in the methanol synthesis network.

Since x_j and F^{in} are variables, the objective function can become undefined as the amount fed goes to zero. However, by placing good limits on the overall feed rate and composition of the feed we can keep the objective function within tolerable limits.

We maximized the conversion of carbon (CO and CO₂) to methanol for our best solution and found two distinct maxima corresponding to high conversion for CO and CO₂, respectively. The experimental parameters were constrained such that the temperature was between 300 and 800K, the pressure was between 10⁻¹⁵ and 100 atm, and the flow rate was between 0.01 and 1 s⁻¹. In both cases, maximal conversion was the pressure was maximal (100 atm), the feed rate was minimal (0.01 s⁻¹) and the maximum fraction of the feed was composed of H₂ (0.99). The remainder of the feed was made up of either CO or CO₂. For maximal conversion of CO the optimal temperature was 667.1K and for CO₂ it was 428.7K. These temperatures are 50K and 40K less than the optimal temperatures for a maximal rate of production from their respective feeds. The conversions achieved are 99.8% and 99.1% for CO and CO₂, respectively and the vast majority of initial points converged to one solution or the other.

In both cases, the surface is mostly free in the optimal conditions (99.5% for CO and 95.6% for CO₂). For the conversion of CO, the remaining 0.5% of the surface is covered in H*. For the conversion of CO₂, 3.2% of the surface is covered in OH*, 0.6% in H* and 0.7% in H₂O*. The mechanisms observed are the same as those found for the best solution in the conditions for maximal rate of methanol production.

To further understand how the conversion of CO₂ changes as we change the individual variables around the optimum point, we varied the experimental variables one at a time. We show the results graphically in figure 4.3. The conversion of CO₂ to methanol is relatively insensitive to the pressure, temperature and feed rate and almost completely insensitive to the fraction of the C in the feed coming from CO₂. The effect of pressure on the conversion is monotonically

increasing (the same as the effect on rate). However, the conversion asymptotically approaches 100% as the pressure increases and the bulk of the effect is seen at less than 40 atm. This means that our model predicts high conversions of CO_2 to methanol throughout the industrial pressure range of 50-100 atm (assuming very low feed rates and a high proportion of H_2 in the feed). There is a definite maximum with respect to temperature, with the conversion dropping off dramatically at very high and very low temperatures. However, the effect is relatively minimal between 350 and 533K.

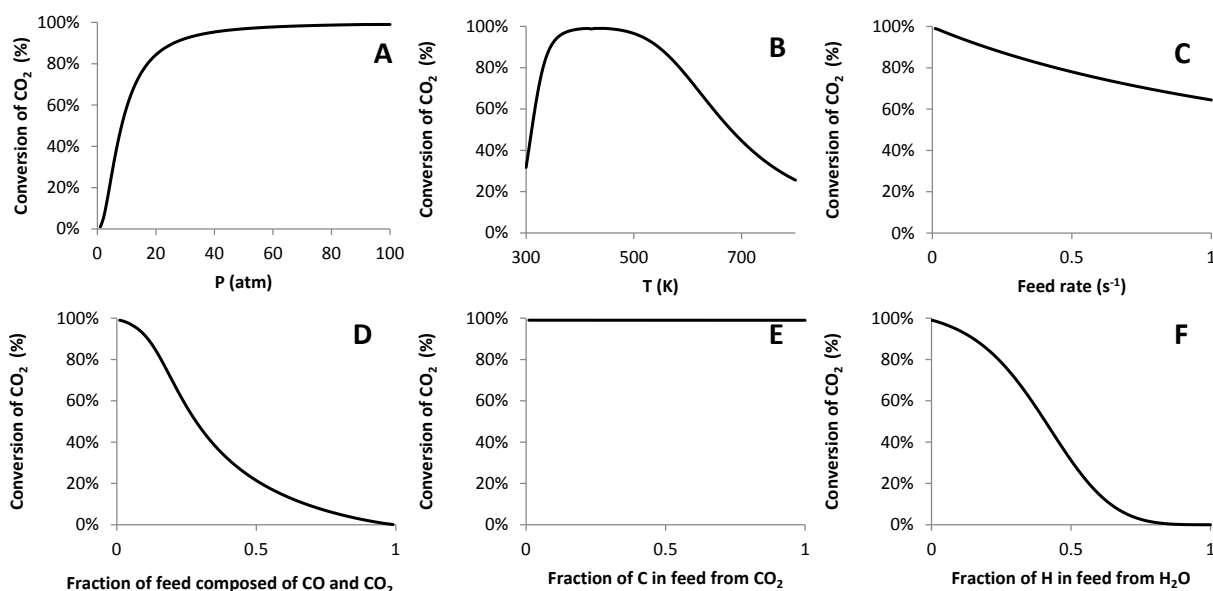


Figure 4.3. Changes in conversion of CO_2 in response to changes in the experimental variable around the optimum. The variables are changed one at a time with the remaining variables fixed. Conversion is relatively stable with respect to pressure, temperature, feed rate, and the fraction of carbon from CO_2 . In contrast, reducing the amount of H_2 in the feed by increasing the carbon content or replacing H_2 with H_2O results in a dramatic drop-off in the extent of conversion.

While the effects of pressure, temperature and feed rate on conversion of CO_2 are relatively modest, the conversion drops off dramatically when the amount of H_2 in the feed is decreased, either by increasing the carbon content of the feed or replacing some of the hydrogen with

water. Reductions in H₂ content of the feed reduce the driving force for the reaction and reduce the equilibrium extent of the reaction.

4.4. Maximal Coverage

We also considered the optimization to identify experimental conditions to maximize (or minimize) the coverage of a particular species on the surface. This objective function has the potential to provide insight into the best experimental conditions to identify elusive reactive intermediates on the catalyst surface. The objective function for minimizing and maximizing coverages (equation 4.10) is directly analogous to the objective function for minimizing and maximizing reaction rates (equation 4.8).

$$\min obj = \sum_{j \in \mathbf{M}} m_j y_j + \alpha d \quad (4.10)$$

In general, maximal coverages are likely to be achieved at very low temperature. However, we found that our model could not adequately represent the surface as the temperature dropped below room temperature. As the temperature drops, the argument of the exponential in the calculation of the equilibrium rate constant tends to become very large. Additional scaling will be required to allow the model represent the catalyst at cryogenic temperatures.

More significantly, as the temperature drops, the magnitude of the rate constants becomes progressively smaller. At some point, the magnitude of one or more rate constants can become so small that the predicted reaction rates are near zero regardless of the concentration of the reactants. If all of the reactions that consume a particular species on surface are predicted to

have very low rates, regardless of the concentration of the species on the surface, the species is 'isolated' from the reaction network and essentially frozen onto the surface. In this case, the solution to the NLP is not unique and the optimizer can adjust the coverage of the 'isolated' species independently of the coverages of other species or the values of the parameters and variable in the problem.

This corresponds to the physical case where, if the species was somehow generated on the surface, it would persist there for extended periods of time (assuming there are no other reactions occurring on the surface involving the isolated species which are not captured in the reaction network being optimized). However, it does not follow that such a coverage on the surface could be attained. Because we tolerate a small amount of deviation from steady-state, we can predict a high coverage of a species which has a much lower equilibrium coverage as long its break-down is sufficiently slow. Importantly, this phenomenon can occur at any temperature if a particular species is isolated. It is likely to happen with many species at sufficiently low temperature. In fact, as we drop the temperature, the overall reaction rate through the reaction network tends to become very small. As this happens, even small deviations from steady-state become significant in terms of the overall reaction rates. Therefore, to make meaningful predictions at low temperature we must strictly enforce the steady-state constraint.

Another challenge with the optimization of coverages is that the values of the coverages are often very small. Where the reaction rates (in the optimal range) are generally on the order of 10^{-3} - 10^{-1} , the coverages are routinely on the order of 10^{-20} - 10^{-10} . Only a few intermediates (or

byproducts) routinely have coverages in the 10^{-3} - 10^{-1} range and these are not often the intermediates we are most interested in as they easily identified on the surface without the help of optimization. Since the values are often so small, we need to introduce a much larger multiplier in our objective function than we used with the reaction rates. The exact magnitude of this multiplier will need to be determined analytically and may need to be adjusted if we identify regions of the parameter space where higher coverages are predicted.

4.4.1. CH_3O_2^*

Maximizing the coverage of CH_3O_2^* on the catalyst surface is an excellent example of both the strengths and pitfalls of the approach. To get good results from the optimization we used a multiplier of $-1\text{e}6$ and required 1000 initial points (as opposed to 100 for most of our rate optimizations). The experimental parameters were constrained such that the temperature was between 300 and 800K, the pressure was between 10^{-15} and 100 atm, and the flow rate was between 0.01 and 1 s^{-1} .

For our best solution, we identified two local optima. The first predicts that the surface is completely covered in CH_3O_2^* at a temperature of 300K (the lower limit), pressure of 100 atm (the upper limit) and a feed rate 0.01 s^{-1} (the lower limit). The feed composition varies depending on the value at the initial point and does not appear to be well-specified. The largest reaction rates are of the order 10^{-12} s^{-1} , comparable to the deviation from steady state. Moreover, the model predicts that CH_3O_2^* is slowly breaking down. Therefore, while this state

of the catalyst would persist for an extended period of time if it could be generated, it is not a true steady-state solution and is unlikely to ever be observed.

The second local optimum for our best solution is also at maximal pressure and minimal temperature. The feed rate is no longer at the lower bound, but has not increased significantly (0.0104 s^{-1}). On the other hand, the feed composition is now well defined at $x_{CO} = 0.209$, $x_{H_2} = 0.542$, $x_{H_2O} = 0.249$ and the predicted CH_3O_2^* coverage is dramatically decreased at $1.76 \cdot 10^{-7}$. Under these conditions, CO is being consumed at a rate of $5.5 \cdot 10^{-4} \text{ s}^{-1}$, primarily going to methanol with slightly less than 10% being converted to CO_2 through the water gas shift reaction.

For the best solution from Grabow and Mavrikakis²⁹ we found three local optima. The first local optimum predicts complete coverage of the surface with CH_3O_2^* under the same conditions as our best solution and with the same pitfalls. The second local optima predicts a coverage of $2.04 \cdot 10^{-9}$ at 100 atm, 523.2K, a minimal feed rate of 0.01 s^{-1} and a feed composition of $x_{CO_2} = 0.336$, $x_{H_2} = 0.561$, $x_{H_2O} = 0.104$. Under these conditions, methanol is being produced from CO_2 at a rate of $3.62 \cdot 10^{-4} \text{ s}^{-1}$.

The third local optimum predicts almost as high a coverage as the second ($1.99 \cdot 10^{-9}$), but in markedly different conditions. The optimal pressure is still predicted to be 100 atm, the temperature increased somewhat to 582.6K, the feed rate has gone to the upper bound of 1 s^{-1} and the feed composition is $x_{CO} = 0.586$, $x_{H_2O} = 0.414$. Under these conditions, CO is being

consumed at a rate of 0.413 s^{-1} to produce CO_2 at a rate of 0.296 s^{-1} and methanol at a rate of 0.117 s^{-1} .

Together these solutions suggest that, within the limits of the conditions explored by the optimization, it may not be possible to generate enough CH_3O_2^* on the surface to be detected spectroscopically. However, it also appears that CH_3O_2^* coverages are generally maximized in conditions with significant amounts of water in the feed.

4.4.2. COOH^*

Another important intermediate in methanol synthesis is COOH^* , which plays a key role in the water gas shift reaction. Like for CH_3O_2^* , we use a multiplier of $-1\text{e}6$ and use 1000 initial points to explore the parameter space and we use the same constraints on the experimental parameters.

For our best solution we find a single optimum with a coverage of COOH^* of $8.83 \cdot 10^{-12}$ at 28 atm, 800K (the maximum), a feed rate of 1 s^{-1} and a feed composition of $x_{\text{CO}} = 0.92$, $x_{\text{H}_2\text{O}} = 0.08$. At these conditions, the surface is essentially empty and CO is being consumed at a rate of 0.080 s^{-1} to produce CO_2 at a rate of 0.079 s^{-1} and methanol at a rate of 0.001 s^{-1} .

In contrast, the best solution from Grabow and Mavrikakis²⁹ predicts a significantly higher (although still very low) optimum coverage of $4.99 \cdot 10^{-8}$ at a lower temperature (499.5K) and higher pressure (100 atm). The feed rate is still 1 s^{-1} with a feed composition of $x_{\text{CO}} = 0.776$, $x_{\text{H}_2\text{O}} = 0.224$. At these conditions the surface is 23% covered in CO^* and 76% covered in CH_3O^*

and CO is consumed at a rate of 0.096 s^{-1} to produce CO_2 at a rate of 0.064 s^{-1} and methanol at a rate of 0.032 s^{-1} . The higher predicted coverage compared to our best solution is probably attributable the significant increase in the barrier to the formation of COOH^* on the surface ($\text{CO}^* + \text{OH}^* \rightarrow \text{COOH}^* + *$) in our best solution.

Reasonably, we would not expect to find significant concentrations of COOH^* on the surface of the catalyst since its hydroxyl-assisted breakdown ($\text{COOH}^* + \text{OH}^* \rightarrow \text{CO}_2^* + \text{H}_2\text{O}^*$) is spontaneous. Therefore, we ask what the effect of increasing the barrier would be on the maximal coverage of COOH^* on the surface. The effects we found were significant, but modest changes in the barrier were not sufficient to increase the coverage to anywhere near detectable levels. For our best solution, increasing the barrier by 0.1 or 0.2 eV results in a maximal coverage of 3.07×10^{-11} or 1.00×10^{-10} , respectively, with minimal changes in the values of the experimental variables. If we increase the barrier by 0.3 eV, the change in the coverage is similar (3.15×10^{-10}) but the predicted temperature changes significantly to 597.6K. For the best solution from Grabow and Mavrikakis,²⁹ increasing the barrier results in a steady increase in the predicted coverage to 6.83×10^{-6} with 0.5 eV increase in the barrier. This comes with a steady decrease in the optimal temperature to 430.6K and little to no change in the other parameters. Clearly the ease of breaking down COOH^* on the surface plays a role in its predicted low coverage. However, the low barrier does not fully account for the low coverage.

4.5. Conclusions

By changing our objective function from fitting experimental data to minimizing or maximizing rates and coverages we can gain a more complete understanding of the implications of our fitted solutions. Furthermore, the results from the experimental design problem can be used to guide experiments or reactor operation and can provide us with additional information to distinguish between different potential fits to the experimental data. However, the quality of our predictions is dependent on the quality of the fitted parameters and is subject to reactor non-ideality, such as transport limitations. Our best fit predicts that methanol is most effectively synthesized from CO, but that synthesis from CO₂ is favored at lower temperatures. Maximal conversion is predicted at minimal flow rates and is less sensitive to pressure and temperature than the production rate. Further, it predicts that neither CH₃O₂* nor COOH* accumulate on the surface at detectable levels within the range of the optimized conditions.

Chapter 5

Collocation and Optimization Applied to Plug Flow Reactors

Many industrial reactions and lab-scale experiments are conducted in plug flow reactors (PFR). It is highly desirable to be able to model reactions in a PFR as well as CSTR. However, we cannot directly extend our approach for the CSTR to the PFR.

The PFR model includes the same basic sets as the CSTR model; the set **I** of reactions (indexed over i), the set **J** of species (indexed over j) and the set **C** of experimental conditions (indexed over c). Set **J** includes the subsets **G** (gas phase species) and **S** (surface species), with free sites (*) included in the set **S**. For each reaction, i , there exist subsets of **S** reactants (**R_i**) and products (**P_i**). Like our CSTR model, our PFR model describes an ideal, isothermal reactor, assuming no transport effects.

The mathematical description of the kinetics in a PFR is identical to the description of the kinetics for a CSTR, so equations 2.1-2.10 from chapter 2 apply directly to this problem. We include these for quick reference here, but leave a full description to chapter 2. We have renumbered them for convenient inclusion as a part of the PFR model.

$$kf_{ic} = A_i \exp\left(-\frac{Ea_i}{RT_c}\right), \forall i, c \quad (5.1)$$

$$Keq_{ic} = \exp\left(-\frac{\Delta H_{ic}}{RT_c} + \frac{\Delta S_{ic}}{R}\right), \quad \forall i, c \quad (5.2)$$

$$kr_{ic} = \frac{kf_{ic}}{Keq_{ic}}, \quad \forall i, c \quad (5.3)$$

$$\Delta H_{ic} = \sum_j v_{ij}(\Delta H f_j + BE_j), \quad \forall i, c \quad (5.4)$$

The reaction rates for all reactions and the net generation and consumption of each species is calculated analogously for the PFR and CSTR. However, where the concentrations of the species and the reaction rates were a function of time in the CSTR (equation 2.6), they vary in time and space in the PFR. Therefore, even at steady-state, the reaction rates, coverages and partial pressures are a function of location along the length of the reactor.

$$r_{ic}(l) = kf_{ic} \prod_{j \in R_i} y_{jc}(l)^{|v_{ij}|} - kr_{ic} \prod_{j \in P_i} y_{jc}(l)^{|v_{ij}|}, \quad \forall i, c \quad (5.5)$$

Likewise, the net reaction rates for all species (equation 2.2 for CSTR) are now a function of location (and time when not at steady-state).

$$R_{jc}^{net}(l) = \sum_i v_{ij} r_{ic}(l), \quad \forall j, c \quad (5.6)$$

Each slice of infinitesimal length along a PFR, is essentially equivalent to a CSTR (assuming perfect mixing across the diameter of the reactor). In chapter 2, we discussed that the rate of change (with respect to time) for all species in a CSTR is given by the mass balance in equation 1,

$$F_{jc}^{in} - F_{jc}^{out} + R_{jc}^{net} = \frac{dy_{jc}}{dt} = 0, \quad \forall j, c \quad (2.1)$$

where the flow rates in and out of the reactor (F_{jc}^{in} and F_{jc}^{out}) are zero for gas phase species (equation 2.3).

For the surface species, there is still no flow through the reactor, so their concentrations may only be changed through reaction giving us:

$$R_{jc}^{net} = \frac{\partial y_{jc}(l)}{\partial t} = 0, \quad \forall c, j \in \mathcal{S} \quad (5.7)$$

At steady-state this reduces to a set of algebraic equations saying that the net generation and consumption of surface species (R_{jc}^{net}) must be equal to zero at all points along the reactor.

For the PFR, the flow rates of gas phase species (F_{jc}) are represented by partial differential equations in length and time. Over an infinitesimal segment of the reactor, the difference between the flow rates into and out of the segment is the negative partial differential of the concentration with respect to length ($-\frac{\partial F_{jc}(l)}{\partial l}$). This is equivalent to the term $F_{jc}^{in} - F_{jc}^{out}$ in equation 2.1.

$$-\frac{\partial F_{jc}(l)}{\partial l} + R_{jc}^{net} = \frac{\partial F_{jc}(l)}{\partial t} = 0, \quad \forall c, j \in \mathcal{G} \quad (5.8)$$

At steady state, the rate of change of the gas phase species with respect to location along the reactor ($\frac{dF_{jc}(l)}{dl}$) is equal to the net generation and consumption of the species the reactions (R_{jc}^{net}).

The partial pressure of the gas phase species is equal to the mole fraction of each species in the gas phase times the total pressure. In our model the pressure is constant along the length of the reactor, but a pressure drop could be specified.

$$y_{jc}(l) = P_c \frac{F_{jc}(l)}{\sum_{j \in G} F_{jc}(l)}, \quad \forall c, j \in G \quad (5.9)$$

The same constraints apply to the PFR as the CSTR (equations 2.5 and 2.11-2.13).

$$\sum_{j \in S} y_{jc} = 1, \quad \forall c \quad (5.10)$$

$$Ea_i \geq \Delta H_{ic}, \quad \forall i, c \quad (5.11)$$

$$Ea_i \geq 0, \quad \forall i \quad (5.12)$$

$$BE_j \leq 0, \quad j \in S \quad (5.13)$$

Whereas a CSTR is represented mathematically by a set of ODEs, which reduce to a NLP at steady-state, a PFR is mathematically represented by a set of partial differential equations (PDEs) (in time and along the length of the reactor) which reduces to a system of differential algebraic equations (DAEs) at steady-state where the gas phase species are represented by ODEs along the length of the reactor and the surface species are described by algebraic equations at each point in the reactor. Thus, we cannot directly translate our approach to the CSTR to the solution of the PFR.

5.1. Optimization of DAEs

The general DAE optimization problem is formulated as:

$$\min_{z(l), y(l), u(l), p} \Psi(z(l_f), y(l_f), u(l_f), p) \quad (5.14)$$

such that

$$\frac{dz(l)}{dl} = f(z(l), y(l), u(l), p, t), \quad z(l_0) = z_0 \quad (5.15)$$

$$g(z(l), y(l), u(l), p) = 0 \quad (5.16)$$

$$h(z(l), y(l), u(l), p) \leq 0 \quad (5.17)$$

$$z_L \leq z(l) \leq z_U \quad (5.18)$$

$$y_L \leq y(l) \leq y_U \quad (5.19)$$

$$u_L \leq u(l) \leq u_U \quad (5.20)$$

$$p_L \leq p \leq p_U \quad (5.21)$$

where $\mathbf{z}$ are differential state profile vectors, $\mathbf{y}$ are algebraic state profile vectors, $\mathbf{u}$ are control state profile vectors and $\mathbf{p}$ are parameters which are constant over the course of the integration. Ψ is a scalar objective function at the final time, $\mathbf{f}$ are differential constraints, $\mathbf{g}$ and $\mathbf{h}$ are algebraic and inequality constraints, respectively, and all the variables are subject to upper and lower bounds. The problem is defined over the interval $l \in [l_0, l_f]$.

5.2. Collocation over finite elements

One approach to the solution of DAE optimization problems is collocation over finite elements.

It is one of a class of solutions known as simultaneous approaches where both the state and

control profiles are fully discretized and the system of DAEs is fully transformed into a (much larger) NLP. The approach is computationally expensive and leads to large scale NLPs that require efficient optimization strategies. However, the system of DAEs is solved only once (at the optimal point), avoiding the computational expense of repeated evaluations and avoiding solving the DAEs at intermediate points where a solution may not exist.^{97,98}

5.2.1. Mathematical Formulation

For collocation, the integration interval, $l \in [l_0, l_f]$, is divided up into NE finite elements, comprising the set $\mathbf{N}$, which we index over n . Each finite element, n , covers an interval such that $l \in [\zeta_n, \zeta_{n+1}]$. On each interval, we define a set $\mathbf{K}$ of collocation points used in the approximation, where $\mathbf{K} \in [0 \dots K_c]$ which is indexed over k . There also exists a subset of collocation points which are internal to the interval $\mathbf{T} \in [1 \dots K_c]$. As the set $\mathbf{K}$ appears multiple times in several equations, we will use additional letters to index it as needed for clarity.

The state and control profiles are discretized over the finite elements and approximated using a family of polynomials. In our case, we use Lagrange polynomials, but other basis sets are possible. The approximated profiles are given by:

$$\mathbf{z}_n^{K_c}(l) = \sum_{k=0}^{K_c} \mathbf{z}_{nk} \phi_{nk}(l), \quad \phi_{nk}(l) = \prod_{m=0, k}^{K_c} \frac{(l - l_{nm})}{(l_{nk} - l_{nm})}, \quad \forall n \quad (5.22)$$

$$\mathbf{u}_n^{K_c}(l) = \sum_{k=1}^{K_c} \mathbf{u}_{nk} \theta_{nk}(l), \quad \theta_{nk}(l) = \prod_{m=1, k}^{K_c} \frac{(l - l_{nm})}{(l_{nk} - l_{nm})}, \quad \forall n \quad (5.23)$$

where $m = 0, k$ means m starting at zero, excluding k . Thus, the state profiles are approximated using a $(K_c + 1)^{\text{th}}$ degree piecewise polynomial and the control profiles are approximated using a piecewise polynomial of order K_c . The Lagrange polynomials $\phi_{nk}(l)$ and $\theta_{nk}(l)$ satisfy the condition that $\phi_{nk}(l_{nm}) = \delta_{km}$, where δ_{km} is the Kronecker delta (i.e. if $k = m$, $\delta_{km} = 1$ and if $k \neq m$, $\delta_{km} = 0$). This gives the piecewise polynomials the desirable property that

$$\mathbf{z}_n^{K_c}(l_{nk}) = \mathbf{z}_{nk}, \forall n, k \quad (5.24)$$

By replacing the variable l with $\tau \in [0,1]$ which is normalized over each element such that:

$$l_{nk} = \zeta_n + \Delta\zeta_n \tau_k, \quad (5.25)$$

the Lagrange basis functions are rendered independent of the individual intervals or their length and can be calculated in advance.

The state profiles are required to be continuous at the interval boundaries.

$$\mathbf{z}_n^{K_c}(\zeta_n) = \mathbf{z}_{n-1}^{K_c}(\zeta_n), \quad n > 1 \quad (5.26)$$

While the control profiles are allowed to have discontinuities.

For the differential state profiles, the derivatives of the piecewise polynomials are matched to the value of the original differential equations at the internal collocation points. The residual is calculated in equation 5.27, where $m \in [1, K_c]$.

$$\Delta\zeta_n \lambda(l_{nm}) = \sum_{k=0}^{K_c} \mathbf{z}_{nk} \dot{\phi}_k(\tau_m) - \Delta\zeta_n \mathbf{f}(t_{nm}, \mathbf{z}_{nm}, \mathbf{y}_{nm}, \mathbf{u}_{nm}, \mathbf{p}), \forall n, m \quad (5.27)$$

The derivatives of the basis profiles are $\dot{\phi}_k(\tau_m) = \frac{d\phi_k}{d\tau}$ and are pre-calculated along with the basis functions $\phi_n(\tau)$ and $\theta_n(\tau)$.

The residual should be equal to zero at all collocation points.

$$\lambda(l_{nm}) = 0, \forall n, m \quad (5.28)$$

The initial value of the discretized system is the same as the initial value of the original system.

$$\mathbf{z}_{10} = \mathbf{z}_0 \quad (5.29)$$

The value of the differential state variables at the final point is equal to value of the piecewise polynomial at the end of the final interval.

$$\mathbf{z}_f = \mathbf{z}_{NE}^{K_c}(l_f) \quad (5.30)$$

We add two additional constraints on the interval lengths. The sum of the lengths of the intervals must add up to the overall interval.

$$\sum_{n=1}^{NE} \Delta\zeta_n = l_f - l_0 \quad (5.31)$$

And we may enforce bounds on the lengths of the intervals.

$$\Delta\zeta_L \leq \Delta\zeta_n \leq \Delta\zeta_U, \forall n \quad (5.32)$$

The algebraic and inequality constraints are enforced at the collocation points.

$$\mathbf{g}(t_{nk}, \mathbf{z}_{nk}, \mathbf{y}_{nk}, \mathbf{u}_{nk}, \mathbf{p}) = 0, \forall n, k \quad (5.33)$$

$$\mathbf{h}(t_{nk}, \mathbf{z}_{nk}, \mathbf{y}_{nk}, \mathbf{u}_{nk}, \mathbf{p}) \leq 0, \forall n, k \quad (5.34)$$

We apply the bounds from the original system of equations at the collocation points.

$$\mathbf{z}_L \leq \mathbf{z}_{nk} \leq \mathbf{z}_U, \forall n, k \quad (5.35)$$

$$\mathbf{y}_L \leq \mathbf{y}_{nk} \leq \mathbf{y}_U, \forall n, k \quad (5.36)$$

$$\mathbf{u}_L \leq \mathbf{u}_{nk} \leq \mathbf{u}_U, \forall n, k \quad (5.37)$$

The bounds on the parameters (equation 5.21) are unchanged.

Finally, the objective function is redefined in terms of the discretized variables.

$$\min_{\mathbf{z}_{nk}, \mathbf{y}_{nk}, \mathbf{u}_{nk}, \mathbf{p}} \Psi(\mathbf{z}_f, \mathbf{y}_f, \mathbf{u}_f, \mathbf{p}) \quad (5.38)$$

5.3. Implementation

Due to the complexity and large model size of discretized ODE models, we start with the optimization of experimental conditions (reactor controls) with a fixed set of parameters (BE and Ea) describing the catalyst. This reduces the size of the problem by eliminating the set $\mathbf{C}$ of experimental conditions.

We apply collocation over finite elements to the PFR microkinetic model. The differential state variables ($\mathbf{z}$) are flow rates of the gas phase species in the system, F_{jc} . The algebraic state

variables ($\mathbf{y}$) are the partial pressures in the gas phase, coverages for surface species (y_{jc}), the reaction rates (r_{ic}) and net reaction rates (R_{jc}^{net}). The flow rate into the reactor (F_{jc}^{in}) is the initial condition for the differential variables ($\mathbf{z}_0$). The remaining variables in PFR model correspond to the parameters ($\mathbf{p}$) in the collocation formulation. If temperature or pressure were varied over the length of the reactor rather than kept fixed, they would be control variables ($\mathbf{u}$), instead of parameters.

The algebraic and inequality constraints for the PFR model are discretized in accordance with equations 5.33 and 5.34. Equations 5.1-5.4 and 5.11-5.13 are unchanged (except for dropping the set $\mathbf{C}$ for the experimental design problem) because they involve only parameters which do not vary over the length of the reactor. The remaining equations are transformed as follows.

$$r_{nki} = kf_{ic} \prod_{j \in R_i} y_{nkj}^{|v_{ij}|} - kr_{ic} \prod_{j \in P_i} y_{nkj}^{|v_{ij}|}, \quad \forall n, k, i \quad (5.39)$$

$$R_{nkj}^{net} = \sum_i v_{ij} r_{nki}, \quad \forall n, k, j \quad (5.40)$$

$$R_{nkj}^{net} = 0, \quad \forall n, k, j \in \mathcal{S} \quad (5.41)$$

$$y_{nkj} = P \frac{F_{nkj}}{\sum_{j \in G} F_{nkj}}, \quad \forall n, k, j \in \mathcal{G} \quad (5.42)$$

$$\sum_{j \in \mathcal{S}} y_{nkj} = 1, \quad \forall n, k \quad (5.43)$$

When we substitute our differential equations (equation 5.8) into the equation for the residuals (5.27) we get equation 5.44, for the residual of a PFR.

$$\Delta\zeta_n\lambda_{nmj} = \sum_{k=0}^{K_c} F_{nkj}\dot{\phi}_k(\tau_m) - \Delta\zeta_n R_{nmj}^{net}, \quad \forall n, m \in [1, K_c] \quad (5.44)$$

We take the same scaling approach from the CSTR experimental design model and apply it to the PFR model to facilitate its solution. However, unlike the CSTR model we strictly enforce all of our constraints at our final solution including the steady-state constraint on the surface species (equation 5.41) and the constraint that the residuals must be equal to zero (equation 5.44).

5.3.1. Structure of problem

In order to effectively solve the collocated model, we initialize the problem by solving the system of DAEs in Matlab and then exploit the structure of the NLP within GAMS. Rather than trying to solve the whole problem directly, we break it down and solve it from the initial point to the final point prior to performing the full optimization.

At a given point in the reactor (n,k) , if we know the value of the differential variables (F_{jc}) and the parameters, equations 5.39-5.44 form a square system (with equal numbers of equations and variables) which specifies the values of the corresponding algebraic state variables (y_{nkj} , r_{nki} , and R_{nkj}^{net}). We can ease the solution of this problem by initially relaxing the steady-state constraint that equation 5.41 be equal to zero and minimizing the deviations from steady-state (as in previous chapters) prior to explicitly solving the square system for the exact values of the algebraic state variables. Since we know the value of the differential variables at the entry to

our reactor (via our specified initial values in equation 5.29), we can find all of the state variables at the initial point which correspond to a given set of parameters.

If we add equation 5.44 (specifying the values of the residuals at our collocation points) and equation 5.28 (specifying that the residuals must be equal to zero) to our system of equations, we create a new square system which specifies the values of the differential and algebraic state variable at the collocation points on the current finite element based on our piecewise polynomial approximation of the differential state profiles. To ease the solution of this subsystem we can relax the constraint that the residuals are equal to zero (equation 5.28) and minimize the sum of the residuals prior to solving the square system.

Once we have the value of the differential state variables at all of our collocation points on the present interval, we can combine equations 5.22 and 5.30 (with pre-calculated basis functions) to find the value of the differential state variables at the final point of the current interval. Equation 5.26 specifies that the value of these variables must match at the interval boundaries. Therefore, we now have the values of the differential state variables at the initial point of the next finite element and can repeat the process above until we reach the end of the reactor. This gives us the exact feasible value of all of the variables at all of the collocation points and element boundaries for a given set of values of the parameters. All the variables are then allowed be adjustable within the model and appropriate limits are set before we optimize the full system of equations, minimizing our chosen objective function (e.g. production of methanol).

5.3.2. Selection of Number of Finite Elements and Collocation points

Two critical issues are the selection of the best number of intervals and collocation points. The number of finite elements defines how fine the mesh of the approximation is. Too few finite elements and we cannot accurately represent the state and control profiles. This will tend to result infeasible solutions as the residuals cannot be reduced to zero, particularly in areas where the second derivative of the profiles is large, or poor approximations. On the other hand, the size of the problem increases as the number of intervals is increased. As the problem becomes larger, it also becomes harder to solve. Therefore, too many finite elements can also lead to optimization failure or simply to the problem taking excessively long to solve.

The number of collocation points determines the order of the piecewise polynomial approximations of the state and control profiles. Ideally this should be well matched to the shape of the state and control profiles. The selection of an appropriate number of collocation points so that the approximation is of the same order as the actual profile can allow us to obtain good approximations to the profiles with fewer finite elements. However, like the selection of the number of finite elements, increasing the number of collocation points also increases the size of the NLP and can result in increased difficulty in the optimization.

5.3.3. Formulation of Objective Functions

Whereas for the CSTR we can easily define objective functions in terms of reaction rates and coverages, for the PFR we need to specify the location along the reactor at which we are measuring state variables (such as rates and coverages). The most common location and the

simplest in terms of formulation is the reactor exit. Furthermore, the most natural variables to measure in the objective function are the differential state variables. For the microkinetic model, these are the flow rates of the gas phase species. Objective functions including these variables allow us to maximize production and conversion, as we showed for the CSTR in chapter 4.

5.4. Case Study – Water Gas Shift

The water gas shift reaction is important for industrial hydrogen production and directly or indirectly plays an important role in a range of industrially significant reactions, including methanol synthesis.^{21,99-101} We take the fitted parameter values for the low-temperature water gas shift reaction on Cu from Gokhale et al⁸⁸ and use WGS as an example problem for experimental design with a PFR reactor.

5.4.1. Problem set-up

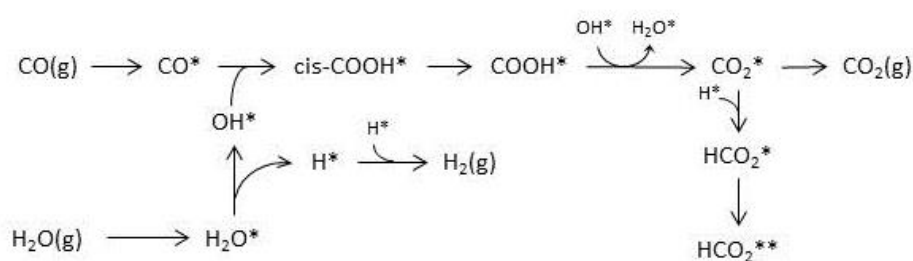


Figure 5.1: The reaction network for water gas shift, as used to demonstrate experimental design for the PFR. Free sites are omitted for clarity. All reactions are reversible, but are shown in the active direction for clarity.

The reaction network fitted in Gokhale et al⁸⁸ included 16 reactions and 14 species. To further simplify the problem, we eliminated the inactive pathways from the network for our testing.

This leaves us with 10 reactions and 13 species (figure 5.1). We specified the parameters for all reactions in the forward direction as shown in table 5.1 and table 5.2.

Species	S (J/mol*K)	BE (eV)	ΔBE (eV)
H ₂ O*	102.7	-0.18	0
CO*	85.56	-0.96	0
CO ₂ *	116.82	-0.09	0
H*	21.54	-2.55	-0.09
OH*	72.44	-2.85	-0.03
cis-COOH*	129.49	-1.68	0
COOH*	114.99	-1.88	0
HCO ₂ *	124.54	-2.32	0
HCO ₂ **	115.01	-2.77	-0.1

Table 5.1: Input parameters for species in microkinetic model of water gas shift reaction. Data derived from Gokhale, et al.⁸⁸ BE is the DFT value of the binding energy while ΔBE represents the change from DFT.

Reaction	A ^{root}	ΔH (kJ/mol)	Ea (eV)
H ₂ Og + * → H ₂ O*	6.28E+09	-17.37	0
COg + * → CO*	5.04E+09	-49.21	0
CO ₂ g + * → CO ₂ *	4.02E+09	-8.68	0
H ₂ g + 2* → 2H*	1.88E+10	-18.33	0.5
H ₂ O* + * → OH* + H*	1.59E+13	-20.26	1.14
CO* + OH* → cis-COOH* + *	2.33E+09	3.86	0.51
cis-COOH* → COOH*	2.15E+10	-22.19	0.48
COOH* + OH* → CO ₂ * + H ₂ O*	1.27E+12	-45.35	0.38
CO ₂ * + H* → HCO ₂ * + *	4.82E+10	-24.12	0.85
HCO ₂ * + * → HCO ₂ **	1.78E+10	-42.45	0.04

Table 5.2: Input parameters for reactions in microkinetic model of water gas shift reaction. Data derived from Gokhale, et al.⁸⁸

We optimize the water gas shift model using an objective function directly analogous to our coverage optimization objective (equation 4.10) from chapter 4 except that we consider gas phase species and the function is evaluated at the reactor exit.

$$\min obj = \sum_{j \in M} m_j F_j(l_f) \quad (5.45)$$

Unlike the CSTR, the PFR objective does not include a penalty on deviations from steady-state as the steady-state constraint is strictly enforced.

In order to maximize the water gas shift rate we maximize the flow rate of $\text{CO}_2(\text{g})$ at the reactor exit with a multiplier of -1, and feed that contains only $\text{CO}(\text{g})$ and $\text{H}_2(\text{g})$.

5.4.2. Selection of Number of Finite Elements and Collocation points

To assess the best number of finite elements and collocation points to solve the water gas shift problem we optimized from 10 initial points for 10, 25, 50 and 100 finite elements with K_c equal to 1, 2 or 3. We evaluated the various setups based on the success of the optimization and the quality of the approximation. In this initial phase we recognized that the model was not effectively optimizing the feed variables (feed rate and composition). This may be due to the structure of the problem. The feed variables enter into the system of equations by determining the initial state, $\mathbf{z}_0$, while the objective function is an explicit function of the state variables at reactor exit, $\mathbf{z}_f$. In between, the system of equations is composed of blocks of equations and variables corresponding to individual finite elements which are only linked at the element boundaries.

Depending on the set-up (in terms of the number of intervals and collocation points) between 0 and 6 of 10 initial points solved to optimality and up to 1 additional point ended with a feasible, non-optimal solution. One of the initial points failed to obtain a feasible solution regardless of setup while all others were solved with some set-ups but not others. In general, we found that initial points that predicted state profiles that were relatively flat (there was little change in the

states over the course of the reactor) were more likely to be solved with smaller numbers of intervals and collocation points (and were less likely to solve successfully with more) while initial points that predicted the reaction would go rapidly to completion (leading to very sharp inflection points in the state profile) were more likely to require larger numbers of intervals and collocation points to solve to optimality.

Overall, 2 collocation points were most successful leading to 6 initial points solving to optimality with 10 or 25 intervals or 3 optimal with 50 or 100 intervals. One of the two initial points with the sharpest inflection points in the state profiles was only solved with 2 collocation points (50 or 100 intervals) and the other was solved with 2 collocation point (10 or 25 intervals) or with 3 collocation points and 100 intervals. With just one collocation point 3 initial points solved to optimality, independent of the number of intervals. It was not the same 3 initial points for all numbers of intervals, but all of the state profiles predicted were quite flat. With 3 collocation points, between 0 and 4 initial points were solved to optimality. There were no initial points that were successfully solved with 3 collocation points and not with 2. Moreover, for any given number of intervals, the most initial points were solved successfully with 2 collocation points. Likewise, for any given number of collocation points, the most initial points were successfully solved with 10 intervals. Despite the higher success rate with 10 intervals and 2 collocation points, we found that the most accurate approximations of the state profiles were achieved at reasonable computational cost with 25 intervals and just 1 collocation point. Therefore, this is what we used to study the water gas shift problem.

5.4.3. *Maximum Rate of Water Gas Shift Reaction*

Although our model does not optimize the feed rate or composition, we can get insight into their effect on the rate of the water gas shift reaction by manually varying them and optimizing pressure and temperature.

With a feed rate of 1 s^{-1} and equal amounts of carbon monoxide and water in the feed we found a maximal predicted turnover frequency of 0.482 s^{-1} for CO_2 at a pressure of 10 atm and temperature of 511.7K. This is approaching the theoretical maximum of 0.5 s^{-1} corresponding to complete conversion of the reactants. We can conclude that, at this feed rate, maximal CO_2 production will be achieved with a near 1:1 ratio of CO and H_2O in the feed since a significant change from this ratio would result in a reduction in the theoretical maximum turnover frequency below our predicted turnover frequency.

If we reduce the proportion of CO in the feed to 0.4, we see very nearly complete conversion (single pass), but lower production (turnover frequency of 0.399998 s^{-1}) in our optimal conditions of 10 atm and 463.1K. If we increase the proportion of CO in the feed, we again see increased conversion of the limiting reactant, but the effect is somewhat less pronounced. When $x_{\text{CO}} = 0.6$ the best predicted turnover frequency is 0.398 s^{-1} at a temperature of 517.8K (at a pressure of 10 atm). Examining the trends we can see that the optimal pressure always goes to the upper bound of 10 atm, while the optimal temperature increases with increasing amounts of CO_2 in the feed. Unsurprisingly, as we increase the feed rate, the turnover frequency of CO_2 increases but conversion decreases. With equal amounts of CO and H_2O in

the feed and a feed rate of 5 s^{-1} our best solution predicts a turnover frequency for CO_2 or 2.29 s^{-1} at a temperature of 539.9 K and pressure of 10 atm .

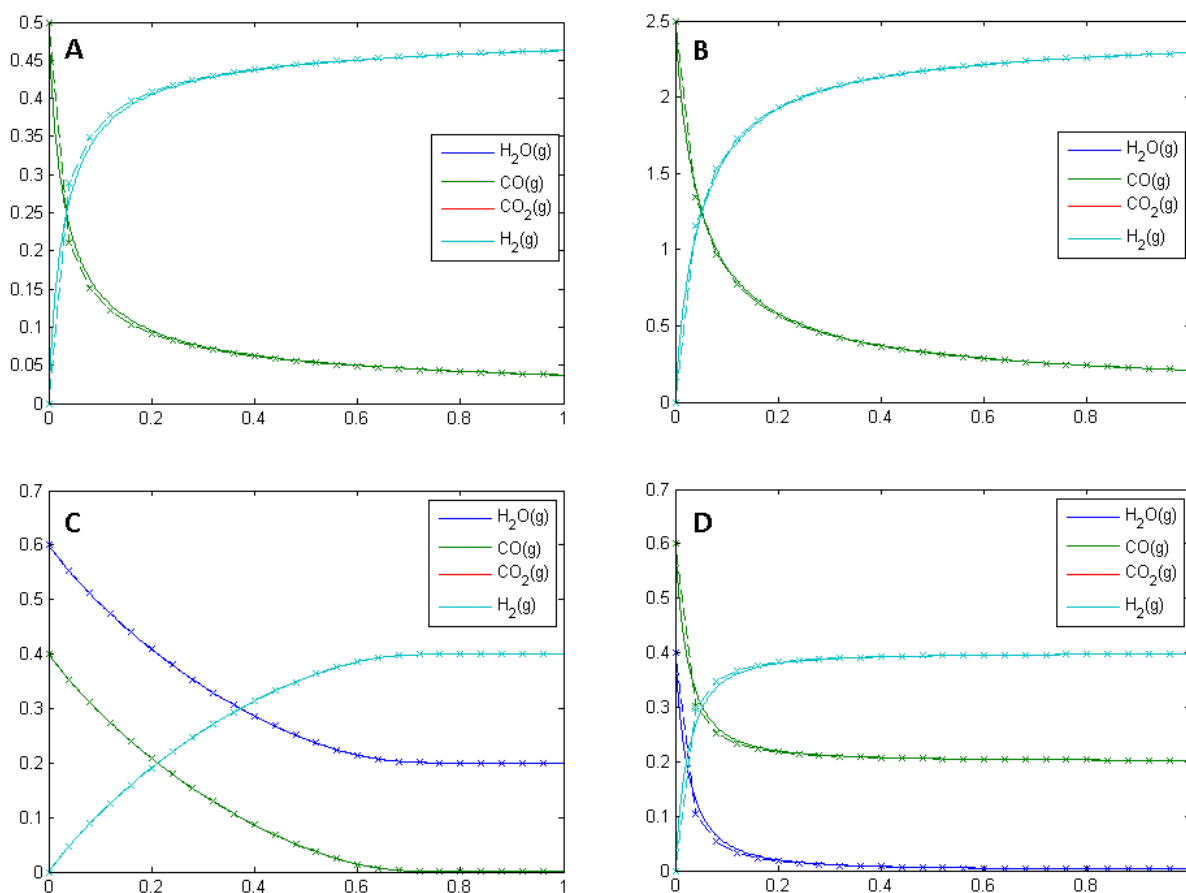


Figure 5.2: Original state profiles and piecewise polynomial approximations at optimal points. The solid lines represent the original state profile, the dotted lines represent the piecewise polynomial approximation and the x's are the element boundaries and collocation points. All calculations for these graphs were performed with 25 finite elements and 1 collocation point. (A) Profiles for $x_{\text{CO}} = 0.5$ and a feed rate 1 s^{-1} (B) Profiles for $x_{\text{CO}} = 0.5$ and a feed rate 5 s^{-1} (C) Profiles for $x_{\text{CO}} = 0.4$ and a feed rate 1 s^{-1} (D) Profiles for $x_{\text{CO}} = 0.6$ and a feed rate 1 s^{-1}

Of the four conditions we investigated, for three of them approximately 20% of initial points reached optimality (most of the remaining initial points ended in infeasible solutions. For the remaining condition (feed rate 1 s^{-1} , $x_{\text{CO}} = 0.4$), more than 55% of the initial points reached optimality. Interestingly, in all cases, all of the points which solved to optimality reached

essentially identical optimal solutions. This suggests that 1) there is likely only one local optimum in the region of the parameter space which we explored, and 2) we are effectively finding that local optimum when we manage to solve the problem successfully.

To examine the quality of the approximations generated we plotted the solution to the system of the system of DAEs (as found by Matlab) along with the collocation points and piecewise polynomials from the solution of the problem by collocation on finite elements. The results are shown in Figure 5.1. The state profiles (as found by solving the system of DAEs in Matlab) is shown as a solid line. Overlaid is the piece-wise polynomial approximation as a dotted line with the element boundaries and collocation points denoted by x's. The approximations are not perfect, especially where the state profile is changing rapidly, and would benefit from dynamic allocation of the finite elements. Nevertheless, the piecewise polynomial approximations are very close to the original state profiles and the predictions at the reactor exit are practically identical.

5.5 Conclusions

By applying collocation on finite elements to the system of DAEs representing the microkinetic model for the PFR we are able to optimize the pressure and temperature to maximize the predicted production rate of CO_2 for a given feed rate and composition. Like the transformation of the CSTR model into an NLP this has the potential to allow more efficient optimization and new insights into reacting systems. However, the technique still needs refinement to reach its maximum utility.

Chapter 6

Conclusions and Future Recommendations

6.1. Accomplishments

We developed a new approach to fitting microkinetic models of continuous stirred tank reactors to experimental data, by reformulation as a system of nonlinear equations (NLP). In our example with a reduced methanol synthesis reaction network, we achieved a 1000-fold increase in solution speed. The reduced computational cost allowed a more systematic search of the parameter space, leading to better fits to the available experimental data. We then applied this technique to the full methanol synthesis network and analyzed the resulting fitted solutions to gain additional insight into the nature of the active site, the reaction mechanism and the limits of what our experimental data set could tell us.

Using the best solution from our fitting of the full methanol synthesis network, we modified our model and optimized the experimental parameters (pressure, temperature, feed rate and composition) to identify the best conditions for the production of methanol, production of methanol for carbon dioxide, conversion of CO and CO₂ to methanol and identification of the reactive intermediates CH₃O₂* and COOH* on the surface.

Finally, we extended our experimental design optimization to the PFR by using collocation on finite elements and looked at the best conditions for the water gas shift reaction on Cu. This is a step towards being able to fit microkinetic models of PFRs to the experimental data as NLPs.

6.2. Limitations

Unfortunately, our study is subject to some significant limitations. As we discussed in chapter 4, it is possible for a species to be ‘isolated’ from the network when the rate constants for all the reactions which consume it are so small that the reaction rates are very low regardless of the concentration or coverage of the species. In this case, there exist multiple solutions to the NLP. Specifically, any concentration of the ‘isolated’ species is a valid steady-state (or near steady-state) condition. When a problem is solved as a system of ODEs, the concentration of the isolated species will remain at the initial value (or close to it). However, when solved as an NLP, the optimizer will adjust the concentration of the ‘isolated’ species to minimize the objective function. This can result in unrealistic predictions and artificially good objective function values, especially for the fitting problem. The simplest solution to the problem is to analyze the reaction network prior to optimization and remove ‘isolated’ species or constrain their concentrations to be no greater than their equilibrium value.

While the problem is readily addressed, it was not recognized prior to the fitting of the full methanol synthesis network. HCO_3^* is an ‘isolated’ species in the full methanol synthesis network. Its equilibrium coverage on the catalyst surface is very low, but our fitted solutions predict significant coverages in most experimental conditions. In this way, the optimizer

effectively reduced the amount of catalyst (independently in each reaction condition) so that the model predictions match the experimental data. If HCO_3^* is removed, the model systematically over-predicts the production of methanol and water. This fundamentally undermines the validity of the fits we obtained. This shortcoming does not apply to reduced network explored in chapter 2, as all species are actively involved in the synthesis of methanol and water.

There is one other significant failure mode for the model which we have identified. If the scaling is not sufficiently good, it is possible for tolerances within the optimizer to predict values for reactions rates and rates of change which are not consistent with the predictions of the model when the values are simply calculated based on the parameters, gas phase concentrations and coverages. Consequently, careful scaling is essential and it is strongly advised that the solutions should be check by forward calculations at the final point.

6.3. Future Work

6.3.1. Fitting Problem

While we developed an approach to the parameter estimation problem which is significantly more computationally efficient than previous methods and demonstrated its application to a large reaction network, our data was confounded by non-unique solutions with the inclusion of HCO_3^* , an 'isolated' species, in the reaction network. In order to draw clear conclusions about the reaction mechanism and the nature of the active site for methanol synthesis on supported

Cu catalysts we need to rerun our calculations with HCO_3 excluded from the reaction network or its coverage constrained so that it does not exceed its equilibrium value.

While our optimization approach has significant advantages over previous techniques, there is always room for further improvement. Ideally we would strictly enforce the steady-state constraint and improve our algorithm so that parameter values are kept closer to DFT when the change in their value does not significantly impact the fit to the experimental data. Furthermore, for a significant number of materials, the binding energies of at least some of the species are dependent on coverage. Incorporating this dependence could significantly increase the applicable range of our model. This improvement could also be incorporated into all of our experimental design models for CSTR and PFR.

6.3.2. *Experimental Design - CSTR*

We demonstrated the technique for optimizing the experimental variables to gain additional understanding of a particular fitted solution or its associated catalyst. However, the data we generated is limited by the flaws in our fit to the methanol synthesis data. These computations should be repeated with a new fit for the methanol synthesis problem and can also be extended to new reaction networks.

We could improve our technique for the experimental design by applying a global optimization solver. If implemented successfully, this would consistently provide us with information about the true best solution to problem and eliminate the need for a multi-start approach. It may

also be possible to incorporate the temperature corrections from the Shomate equation directly into the model, rather than pre-calculating and adjusting as the optimization proceeds.

6.3.3. Collocation and the PFR model

In chapter 5 we presented an approach to optimizing a microkinetic model for a PFR as system an NLP analogous to our approach for the CSTR. However, the application of collocation to experimental design problem is just a start. In our present work, we did not resolve the issue of optimization of the feed rate and composition. Addressing this issue will make this model much more powerful. The robustness of the model also needs to be increased so that the number of initial points which fail optimize successfully is significantly decreased and the model is able to handle larger and more complicated reaction networks. This could potentially allow the collocation approach to be applied to the fitting problem as well as the experimental design problem.

We initially distributed our finite elements evenly along the length of the reactor and used Lagrange polynomials in our piecewise polynomial approximation. If we used information obtained from the DAE initialization of the problem to pre-allocate the finite elements so there are more points where the state profile is changing rapidly we might be able to improve the success rate of the optimization. Moreover there are many options for representation of the state profiles. Other representations of differential and algebraic profiles (e.g. monomial basis, Hermite-Simpson collocation form) and/or different selection of collocation points (e.g. Radau) may result in improved performance.⁹⁸

There are additional model features that also would be desirable to incorporate. Unlike the CSTR model, the PFR model does not include any temperature correction for enthalpy or entropy of the reaction. This temperature dependence can have a significant influence on model predictions and should be incorporated into the model in the future. Finally, some preliminary data indicates that our sequential initialization approach exploiting the structure of the problem (combined with appropriate scaling) might allow us to omit the solution of DAEs to initialize the problem. This could result a significant savings of computational time and might be able to be applied to the CSTR models as well.

6.4. Extensions

We could extend our work by combining our experimental design model with economic model to provide greater insight into the best way to run a particular reaction. We also could combine simultaneous optimization of the material and experimental parameters to provide additional insight into the nature of the active site or the aspects of the reaction network that limit reaction rates and coverages.

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