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Microkinetic Modeling and Analysis of Ethanol Partial Oxidation and Reforming Reaction Pathways on Platinum at Short Contact Times

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Microkinetic Modeling and Analysis of Ethanol Partial Oxidation and Reforming Reaction
Pathways on Platinum at Short Contact Times

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B.S., Chemical Engineering, University of Pittsburgh, 2010

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Microkinetic Modeling and Analysis of Ethanol Partial Oxidation and Reforming Reaction
Pathways on Platinum at Short Contact Times

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NOMENCLATURE

A	s^{-1}	Pre-exponential factor
A_c/V_R	cm^{-1}	Catalyst area per unit reaction volume
d	cm	Pore or tube diameter
E	kcal/mol	Activation energy
G	$mol/cm^3 \cdot s$	Rate of gas phase species
M	g/mol	Molecular weight of species
Q	kcal/mol	Binding energy
R	erg/mol/K	Universal gas constant
s	unitless	Sticking coefficient
S	$mol/cm^2 \cdot s$	Rate of surface species
ΔS	erg/mol/K	Entropy of reaction
T	K	Temperature
u	cm/s	Velocity
Y	unitless	Mass fraction of species
z	cm	Length
α	kcal/mol/ML	Coverage dependence coefficient
β	unitless	Modified Arrhenius equation temperature exponent
γ	unitless	Temperature dependence coefficient for binding energies
θ	unitless	Coverage of species
ρ	g/cm^3	Mass density
σ	mol/cm^2	Site density
Subscript k		Species number

Subscript f

Forward reaction

Subscript b

Backward reaction

ABBREVIATIONS AND ACRONYMS

DFT	Density Functional Theory
MARI	Most Abundant Reaction Intermediate
Pt	Platinum
RPA	Reaction Pathway Analysis
RWGS	Reverse Water Gas Shift
UBI-QEP	Unity Bond Index-Quadratic Exponential Potential
WGS	Water Gas Shift

ABSTRACT

Catalytic reforming of biomass-derived ethanol is a promising pathway for essentially carbon-neutral hydrogen production. The feasibility and performance of this process has been demonstrated over the last several years, especially at short contact times. Despite the extensive experimental work conducted in this area, there remains a need for a comprehensive kinetic model for ethanol reforming that will facilitate detailed reactor design, rational catalyst design, and process development. In this work, a novel microkinetic model for ethanol partial oxidation and reforming on Platinum (Pt), consisting of 100 irreversible elementary steps, is developed and validated using experimental data at short contact times. Kinetic parameters are taken from quantum mechanical Density Functional Theory (DFT) calculations reported in literature, extracted from surface science experimental data, or estimated using semi-empirical and first-principles methods. The microkinetic model is thermodynamically consistent at both the enthalpic and entropic levels. Depending on the chosen gas phase reaction mechanism and as guided by sensitivity and reaction path analyses, seven kinetic parameters are adjusted to improve the model performance against literature experimental data for ethanol reforming. Species coverage and mole fraction profiles as well as reaction pathways and overall rates are analyzed to gain a fundamental understanding of the variations in the dominant catalytic chemistry on Pt with changing temperature. Our analysis indicates the presence of up to 4 reaction zones over the length of the catalyst, viz., (i) dehydration and complete oxidation of ethanol, (ii) transition between oxidation and dry reforming of ethanol, (iii) dry reforming of ethanol, and (iv) steam and dry reforming of methane. As the majority of the catalytic zones are dominated by dry reforming conditions, additional validation of the microkinetic model is carried out with methane dry reforming

experiments on Pt/Al₂O₃. The proposed microkinetic model for ethanol partial oxidation and reforming is able to predict the dry reforming data without any further adjustment of the kinetic parameters.

Keywords: Ethanol, oxygenates, partial oxidation, reforming, platinum, microkinetic model, reaction pathways

CHAPTER 1: INTRODUCTION

1.1 Objectives

The purpose of this work was to develop and validate a microkinetic model for ethanol partial oxidation and reforming on Platinum. Such a model allows for reaction pathway analysis and detailed understanding of the chemistry on the catalytic surface.

1.2 Motivation

Success of the hydrogen (H_2) economy and widespread implementation of H_2 as the fuel of the future requires significant technological advances in H_2 production, transportation, storage, utilization, and carbon dioxide (CO_2) capture. Processing of conventional fuels (e.g., reforming of natural gas) for H_2 production is associated with net CO_2 emissions, which is a potent greenhouse gas. Fuel processing at a centralized location may allow CO_2 capture and sequestration (CCS), provided cost-effective technologies are developed for CCS. Alternatively, H_2 could be obtained from renewable and sustainable sources such as biomass, in order to reduce net CO_2 emissions. During the growth of biomass, plants consume CO_2 from the atmosphere and convert it into carbohydrates via photosynthesis. It is then released back into the atmosphere via reforming of biomass-derived chemicals (e.g. oxygenates such as ethanol, glycerol, biodiesel, and bio-oil), thereby resulting in a closed carbon cycle [1].

Biomass-derived ethanol is a promising renewable energy source that has been developed and implemented in several countries, such as the United States and Brazil, in the latter with great success. A major drawback of bio-ethanol fuel, however, is its high water content, which must be separated using expensive distillation and zeolite adsorption

processes [1]. An alternative to using bio-ethanol directly as a fuel is to reform it to yield hydrogen. Bio-ethanol may also be reformed in a variety of ways, including reaction with water (steam reforming), oxygen (partial oxidation), carbon dioxide (dry reforming), or combinations of the three [2]. Such reforming can also yield syngas, which can be used in fuel cells or upgraded through the Fischer-Tropsch process to produce synthetic fuels and high value chemicals. Syngas production is likely to be a more immediate application of bio-ethanol reforming.

Extensive research has been carried out in the field of biomass-derived oxygenates reforming, especially in the discovery, design, and testing of suitable catalytic materials as well as process development (e.g., see review papers [2-12]). However, a comprehensive understanding of the underlying chemical kinetics is still lacking at an elementary reaction level, due to the complexity of oxygenates reforming chemistry. The generation of reliable, predictive, and comprehensive kinetic models will assist in chemical reactor design, process optimization, and systematic assessment of chemical processes that utilize such oxygenates.

In this work, we propose a novel and comprehensive microkinetic model for ethanol partial oxidation and reforming on Platinum (Pt) that provides a fundamental understanding of the catalytic reaction chemistry. To our knowledge, this is the first time that a comprehensive reaction mechanism has been developed for ethanol partial oxidation and reforming on Pt, using a hierarchical multiscale modeling approach[13-17]. The manuscript is organized as follows. Chapter 2 provides a brief background of the experimental and computational mechanistic studies for ethanol partial oxidation and reforming. The approach for microkinetic model development is described in Chapter 3.

Chapter 4 focuses on the identification and optimization of kinetic parameters, and model performance against experimental data. Mechanistic analysis of species profiles, reaction zones, and reaction order is presented in Chapter 5. Additional validation of the microkinetic model against experiments for dry reforming of methane is presented in Chapter 6, followed by conclusions and a discussion of future work.

CHAPTER 2: Mechanistic Investigations for Ethanol Reforming

2.1 Experimental Studies

Ethanol reforming processes, such as steam reforming, partial oxidation, and dry reforming, have been studied experimentally on various transition metal catalysts such as Pt [18-22], Rh [22-27], Ru [28], Co [29-31], and Ni [32], as well as bimetallics such as Rh-Ru [22] and Rh-Pt [23]. Noble metals are well studied as they are not as susceptible to deactivation, but less expensive catalysts such as Ni and Co are also studied in the interest of economy. The Deutschmann and Schmidt research groups have demonstrated the feasibility of catalytic partial oxidation and reforming of ethanol at short contact times [1,22,27,33]. The Chen and Barteau research groups have used Temperature Programmed Desorption (TPD) experiments to identify the gas phase products of reforming (H_2 , CO, unreacted oxygenates, and CH_4) on various catalysts (Pt, PtNiPt, NiPtPt, and Ni) [34]. Using TPD and Temperature Programmed Reaction (TPR) experiments, the Verykios research group has explored the dominant pathways for ethanol steam reforming on Ni, such as dehydration, dehydrogenation, Water-Gas Shift (WGS), reforming, methanation, and carbon deposition [32]. Using ultra-high vacuum TPD experiments, Vesselli *et al.* have explored the role of oxygen in ethanol decomposition and hydrogen formation on Rh [35] and suggested that an oxidizing environment is required to promote decomposition of C_2 -molecules and to avoid coking. TPD and TPR investigations of Benito *et al.* for ethanol on Co have provided valuable insights regarding the mechanistic pathways of oxygenates reforming [36]. These studies highlighted ethanol decomposition pathway dependence on support (i.e. dehydration on alumina) as well as surface coverage (i.e. water formation with high oxygen surface coverage). Main reaction products for ethanol partial oxidation on Pt are H_2 , CO, CH_4 , CO_2 , and H_2O , while

acetaldehyde, ethylene, and methanol have been identified as minor side products [22,27,37,38]. At high temperatures, ethanol conversion and H₂ yield are found to increase with temperature for partial oxidation on Pt [38]. Based on the products and intermediate species, hypotheses for ethanol decomposition chemistry on Pt have been proposed, including dehydrogenation of ethanol to ethoxy [37,39], dissociative adsorption of ethanol to acetaldehyde [26], or ethanol dehydration to ethylene [18,40]. These findings were taken into account when developing the elementary reaction pathways in the microkinetic model for ethanol partial oxidation and reforming on Pt.

2.2 Computational Studies

On the modeling front, a number of studies have focused on understanding the thermodynamic, mechanistic, and kinetic aspects of ethanol reforming. Thermodynamic analysis for ethanol reforming has been carried out to understand the effect of operating conditions on product selectivities and yields [41-43]. A number of studies have focused on developing Langmuir-Hinshelwood-Hougen-Watson (LHHW) or Eley-Rideal rate expressions followed by data fitting of the kinetic parameters [44-47].

In more fundamental first-principles computational investigations, Density Functional Theory (DFT) has been used to determine species stability and reaction pathways with the lowest activation energy on various catalyst surfaces. Mavrikakis and colleagues have studied ethanol decomposition on various transition metals and proposed Bronsted-Evans-Polanyi (BEP) relationships [48]. They developed potential energy surfaces for C-O and C-C bond breaking in ethanol, which lead to hydrogen production and alkane production, respectively. Vlachos and colleagues have proposed a group additivity approach for predicting the oxygenate stability on metal catalysts[49]. Wang *et*

al. have reported dissociation barriers and heats of reactions for ethanol decomposition on a number of metal surfaces and also correlated the dissociation barriers with d-band centers[50]. Barteau and Chen research groups have reported DFT-based binding energies for some key species, such as ethanol and ethoxy, adsorbed on the Ni/Pt(111) bimetallic surface, and have also correlated reforming reaction yields and selectivities with the surface d-band center for various catalysts (PtNiPt, Pt, Ni, and NiPt) [34,51]. The Neurock research group has reported DFT-based binding energies for a number of key species participating in C₂ chemistry on Pd and Re [52]. In another DFT study of various pathways for ethanol decomposition on Pt (111), Dumesic and colleagues have reported energetics for the C-C and C-O bond cleavage in surface species [53]. Such quantum mechanical parameter estimation studies and correlations with experimental data are critical for developing detailed kinetic models and have been used as inputs in this work, as explained later.

It is also important to note that a comprehensive gas phase reaction mechanism has been developed by Marinov for high temperature ethanol oxidation [54]. This mechanism has been validated against non-catalytic empty tube experimental data for ethanol partial oxidation in the 600-900°C temperature range. Even though Christensen *et al.* found qualitative, but not quantitative, agreement with experimental data using the Marinov mechanism[55], Salge *et al.* found that the mechanism predicts most product selectivities within 2% [22]. We have combined the surface mechanism developed in this work with the Marinov mechanism, to accurately capture the homogeneous and heterogeneous reaction chemistry.

CHAPTER 3: Surface Reaction Mechanism Development

The overall approach for surface reaction mechanism development was derived from microkinetic modeling concepts proposed by Dumesic and colleagues in the early 1990s [56], which was further extended by various researchers through hierarchical multiscale modeling [13-17]. Microkinetic modeling has been applied in the past for a variety of chemical processes such as methane partial oxidation and reforming [14,57,58], selective catalytic reduction of NO_x [59,60], NO oxidation [61], ammonia decomposition [13,62], ethylene hydrogenation [63], and Water-Gas Shift [64-66], to name a few recent applications.

3.1 Steps in the Mechanism Development

Steps in the mechanism development are shown in Figure 3.1 and briefly summarized here. Specific details for ethanol reforming on Pt are discussed in the next sub-sections. The approach starts with a detailed mechanism composed of anticipated surface reactions for the considered chemical process. Kinetic parameters associated with the species and reactions are estimated using a combination of surface science experiments, semi-empirical methods, and first-principles calculations. Thermodynamic consistency is ensured at the individual reaction level as well as at the overall mechanism level using the approach described in [67]. Reactor modeling consistent with the experimental details is carried out to predict the typically measured responses, such as reactant conversion, product selectivity, species concentrations, and temperature. At this level, the predictions of the microkinetic model are typically qualitative, but may not show quantitative comparison with integral data. Such discrepancy is quite common and may arise from various uncertainties and assumptions including those related to the choice of

reactions and species (mechanism complexity vs. practical usability), choice of kinetic parameters (accuracy of estimation methods, pressure and materials gap), experimental methods (product and intermediate species identification, availability of temperature and species concentration profiles, measurement of small values), and choice of reactor model (role of diffusion vs. kinetics). This uncertainty is inherent to model development, but provides justification for some parameter adjustment.

Figure 3.1: Steps in surface reaction mechanism development

Recently developed approaches in reaction kinetics, such as first-principles methods to determine all kinetic parameters [68], universal Brønsted-Evans-Polanyi relations for various reaction classes [69], semi-empirical rate constant assessment and refinement [49,70], and group additivity and linear scaling methods[49] may also be

utilized for reducing parameter uncertainty. The mechanism predictions are analyzed using spatial profiles of species mole/mass fractions and coverages, sensitivity analysis (SA), reaction path analysis (RPA), and reaction rate ratios, to identify the most important reaction pathways and kinetic parameters that control the model responses. Few kinetic parameters are then adjusted to improve the agreement with the experimental data. Further validation of the reaction mechanism is also carried out without adjusting any kinetic parameters. Next, we describe the application of this approach to ethanol reforming on Pt.

3.2 Network of Species and Elementary Surface Reactions

We have considered the following 16 species in our surface reaction mechanism: $\text{C}_2\text{H}_5\text{OH}$ (ethanol), $\text{C}_2\text{H}_5\text{O}$ (ethoxy), CH_3CHO (acetaldehyde), CH_3CO (acetyl), CHCH_3 (ethylidene), C_2H_4 (ethylene), CH_3 , CH_2 , CH , C , CO , CO_2 , O , H , OH , and H_2O . In the proposed surface reaction mechanism, we have considered various adsorption/desorption steps along with the steps for thermal dehydrogenation, O^* -assisted dehydrogenation, OH^* -assisted dehydrogenation, C-C scission, and C-O scission. Other reaction subsets such as, CO oxidation, H_2 oxidation, and the coupling between the CO and H_2 oxidation chemistries are considered as well. Reactions are chosen based on known reactants, products, and intermediates, as well as previously explored reaction pathways determined via first-principles calculations [50,53]. As non-elementary reactions and multiple competing pathways may be detrimental to the model performance [71], only elementary reactions are considered in this work. The mechanism primarily contains series, rather than parallel, reactions and only the sequential steps that are relevant to the species formation/destruction are considered to minimize the number of total reactions. Figure 3.2 shows an overall schematic of the C-containing species chemistry, exclusive of the side

chemistries. The proposed mechanism consists of only 100 irreversible (50 reversible) elementary step reactions, as listed in **Table 1**.

Figure 3.2: General Ethanol Reforming Reaction Mechanism

Table 1: A 100-step surface reaction mechanism for ethanol reforming on Pt. Pre-exponential factor values in the parentheses correspond to the adjusted kinetic parameters in mechanism optimization.

Number	Reaction	Sticking coefficient s (-) or Pre-exponential factor A (s ⁻¹)	Temperature Exponent β (-)	Activation Energy E (kcal/mol) at 300 K
1	$O_2 + 2* \rightarrow 2O^*$	$s=2.29 \times 10^{-2}$	-0.05627	0.0
2	$2O^* \rightarrow O_2 + 2*$	4.37×10^{12}	0.05627	$52.9-32\theta_O+f(T)$
3	$O + * \rightarrow O^*$	$s=3.16 \times 10^{-2}$	-0.16990	0.0
4	$O^* \rightarrow O + *$	1.00×10^{13}	0.16990	$86.0-16\theta_O+f(T)$
5	$CO + * \rightarrow CO^*$	$s=5.00 \times 10^{-1}$	0.16640	0.0
6	$CO^* \rightarrow CO + *$	7.11×10^{13}	-0.16640	$42.0-15\theta_{CO}+f(T)$
7	$CO_2 + * \rightarrow CO_2^*$	$s=2.89 \times 10^{-1}$	-0.07339	0.0
8	$CO_2^* \rightarrow CO_2 + *$	1.09×10^{12}	0.07339	$4.5+f(T)$
9	$H_2 + 2* \rightarrow 2H^*$	$s=2.22 \times 10^{-2}$ (2.22×10^{-4})	-0.14198	0.0
10	$2H^* \rightarrow H_2 + 2*$	1.43×10^{13} (1.43×10^{11})	0.14198	$20.8-6\theta_H+f(T)$
11	$H + * \rightarrow H^*$	$s=2.90 \times 10^{-2}$	-0.28732	0.0
12	$H^* \rightarrow H + *$	1.09×10^{13}	0.28732	$62.5-3\theta_H+f(T)$
13	$OH + * \rightarrow OH^*$	$s=1.34 \times 10^{-2}$	-0.05663	0.0
14	$OH^* \rightarrow OH + *$	2.36×10^{13}	0.05663	$60.0-33\theta_O+f(T)$

15	$\text{H}_2\text{O} + * \rightarrow \text{H}_2\text{O}^*$	$s=1.52 \times 10^{-2}$	0.12717	0.0
16	$\text{H}_2\text{O}^* \rightarrow \text{H}_2\text{O} + *$	2.08×10^{13}	-0.12717	$10.2+f(T)$
17	$\text{C} + * \rightarrow \text{C}^*$	$s=3.33 \times 10^{-2}$	-0.00417	0.0
18	$\text{C}^* \rightarrow \text{C} + *$	9.48×10^{12}	0.00417	$162.6+f(T)$
19	$\text{CH} + * \rightarrow \text{CH}^*$	$s=1.36 \times 10^{-2}$	0.04146	0.0
20	$\text{CH}^* \rightarrow \text{CH} + *$	2.32×10^{13}	-0.04146	$163.3+f(T)$
21	$\text{CH}_2 + * \rightarrow \text{CH}_2^*$	$s=1.20 \times 10^{-2}$	0.09401	0.0
22	$\text{CH}_2^* \rightarrow \text{CH}_2 + *$	2.64×10^{13}	-0.09401	$95.0+f(T)$
23	$\text{CH}_3 + * \rightarrow \text{CH}_3^*$	$s=1.92 \times 10^{-2}$	0.02960	0.0
24	$\text{CH}_3^* \rightarrow \text{CH}_3 + *$	1.65×10^{13}	-0.02960	$49.8+f(T)$
25	$\text{CH}_4 + 2* \rightarrow \text{CH}_3^* + \text{H}^*$	$s=5.96 \times 10^{-2}$ (4.77×10^{-3})	0.15146	$7.2+f(T, \theta_H)$
26	$\text{CH}_3^* + \text{H}^* \rightarrow \text{CH}_4 + 2*$	5.31×10^{12} (4.25×10^{11})	-0.15146	$14.5+f(T, \theta_H)$
27	$\text{C}_2\text{H}_4 + * \rightarrow \text{C}_2\text{H}_4^*$	$s=4.62 \times 10^{-2}$	0.10634	0.0
28	$\text{C}_2\text{H}_4^* \rightarrow \text{C}_2\text{H}_4 + *$	6.84×10^{12}	-0.10634	$17.5+f(T)$
29	$\text{CHCH}_3 + * \rightarrow \text{CHCH}_3^*$	$s=4.37 \times 10^{-2}$	-0.02472	0.0
30	$\text{CHCH}_3^* \rightarrow \text{CHCH}_3 + *$	7.24×10^{12}	0.02472	$102.0+f(T)$
31	$\text{C}_2\text{H}_5\text{OH} + * \rightarrow \text{C}_2\text{H}_5\text{OH}^*$	$s=4.58 \times 10^{-2}$	-0.06642	0.0
32	$\text{C}_2\text{H}_5\text{OH}^* \rightarrow \text{C}_2\text{H}_5\text{OH} + *$	6.90×10^{12}	0.06642	$9.2+f(T)$
33	$\text{C}_2\text{H}_5\text{O} + * \rightarrow \text{C}_2\text{H}_5\text{O}^*$	$s=8.25 \times 10^{-2}$	-0.06995	0.0
34	$\text{C}_2\text{H}_5\text{O}^* \rightarrow \text{C}_2\text{H}_5\text{O} + *$	3.83×10^{12}	0.06995	$36.1+f(T)$
35	$\text{CH}_3\text{CHO} + * \rightarrow \text{CH}_3\text{CHO}^*$	$s=5.32 \times 10^{-2}$	0.03235	0.0
36	$\text{CH}_3\text{CHO}^* \rightarrow \text{CH}_3\text{CHO} + *$	5.94×10^{12}	-0.03235	$11.2+f(T)$
37	$\text{CH}_3\text{CO} + * \rightarrow \text{CH}_3\text{CO}^*$	$s=3.87 \times 10^{-2}$	0.11413	0.0

38	$\text{CH}_3\text{CO}^* \rightarrow \text{CH}_3\text{CO} + ^*$	8.18×10^{12}	-0.11413	$57.8 + f(T)$
39	$\text{CO}^* + ^* \rightarrow \text{C}^* + \text{O}^*$	1.23×10^{11}	0.00726	$53.4 + f(T, \theta_{\text{O}}, \theta_{\text{CO}})$
40	$\text{C}^* + \text{O}^* \rightarrow \text{CO}^* + ^*$	8.12×10^{10}	-0.00726	$2.8 + f(T, \theta_{\text{O}}, \theta_{\text{CO}})$
41	$\text{CO}_2^* + ^* \rightarrow \text{CO}^* + \text{O}^*$	1.10×10^{11} (1.10×10^{10})	-0.00225	$16.0 + f(T, \theta_{\text{O}}, \theta_{\text{CO}})$
42	$\text{CO}^* + \text{O}^* \rightarrow \text{CO}_2^* + ^*$	9.07×10^{10} (9.07×10^9)	0.00225	$12.3 + f(T, \theta_{\text{O}}, \theta_{\text{CO}})$
43	$2\text{CO}^* \rightarrow \text{C}^* + \text{CO}_2^*$	1.09×10^{11}	0.03277	$46.9 + f(T, \theta_{\text{CO}})$
44	$\text{C}^* + \text{CO}_2^* \rightarrow 2\text{CO}^*$	9.21×10^{10}	-0.03277	$0.0 + f(T, \theta_{\text{CO}})$
45	$\text{OH}^* + ^* \rightarrow \text{H}^* + \text{O}^*$	1.03×10^{11} (5.16×10^{12})	0.02585	$25.0 + f(T, \theta_{\text{O}}, \theta_{\text{H}})$
46	$\text{H}^* + \text{O}^* \rightarrow \text{OH}^* + ^*$	9.69×10^{10} (4.84×10^{12})	-0.02585	$11.2 + f(T, \theta_{\text{O}}, \theta_{\text{H}})$
47	$\text{H}_2\text{O}^* + ^* \rightarrow \text{H}^* + \text{OH}^*$	1.15×10^{11}	-0.01035	$18.8 + f(T, \theta_{\text{O}}, \theta_{\text{H}})$
48	$\text{H}^* + \text{OH}^* \rightarrow \text{H}_2\text{O}^* + ^*$	8.67×10^{10}	0.01035	$11.8 + f(T, \theta_{\text{O}}, \theta_{\text{H}})$
49	$\text{H}_2\text{O}^* + \text{O}^* \rightarrow 2\text{OH}^*$	1.12×10^{11}	-0.04019	$11.6 + f(T, \theta_{\text{O}})$
50	$2\text{OH}^* \rightarrow \text{H}_2\text{O}^* + \text{O}^*$	8.93×10^{10}	0.04019	$18.4 + f(T, \theta_{\text{O}})$
51	$\text{CO}_2^* + \text{H}^* \rightarrow \text{CO}^* + \text{OH}^*$	1.08×10^{11}	-0.04181	$7.3 + f(T, \theta_{\text{O}}, \theta_{\text{H}}, \theta_{\text{CO}})$
52	$\text{CO}^* + \text{OH}^* \rightarrow \text{CO}_2^* + \text{H}^*$	9.22×10^{10}	0.04181	$17.4 + f(T, \theta_{\text{O}}, \theta_{\text{H}}, \theta_{\text{CO}})$
53	$\text{CO}^* + \text{H}^* \rightarrow \text{CH}^* + \text{O}^*$	1.28×10^{11}	-0.00285	$44.1 + f(T, \theta_{\text{O}}, \theta_{\text{H}}, \theta_{\text{CO}})$
54	$\text{CH}^* + \text{O}^* \rightarrow \text{CO}^* + \text{H}^*$	7.79×10^{10}	0.00285	$12.3 + f(T, \theta_{\text{O}}, \theta_{\text{H}}, \theta_{\text{CO}})$
55	$\text{CO}^* + \text{H}^* \rightarrow \text{C}^* + \text{OH}^*$	1.20×10^{11}	-0.02030	$40.4 + f(T, \theta_{\text{O}}, \theta_{\text{H}}, \theta_{\text{CO}})$
56	$\text{C}^* + \text{OH}^* \rightarrow \text{CO}^* + \text{H}^*$	8.36×10^{10}	0.02030	$3.5 + f(T, \theta_{\text{O}}, \theta_{\text{H}}, \theta_{\text{CO}})$
57	$\text{CH}^* + ^* \rightarrow \text{C}^* + \text{H}^*$	9.56×10^{10}	0.01239	$32.0 + f(T, \theta_{\text{H}})$
58	$\text{C}^* + \text{H}^* \rightarrow \text{CH}^* + ^*$	1.05×10^{11}	-0.01239	$13.2 + f(T, \theta_{\text{H}})$

59	$\text{CH}_2^* + * \rightarrow \text{CH}^* + \text{H}^*$	1.01×10^{11}	0.02257	$7.8 + f(T, \theta_H)$
60	$\text{CH}^* + \text{H}^* \rightarrow \text{CH}_2^* + *$	9.94×10^{10}	-0.02257	$37.4 + f(T, \theta_H)$
61	$\text{CH}_3^* + * \rightarrow \text{CH}_2^* + \text{H}^*$	1.17×10^{11} (1.17×10^{10})	0.08395	$20.4 + f(T, \theta_H)$
62	$\text{CH}_2^* + \text{H}^* \rightarrow \text{CH}_3^* + *$	8.52×10^{10} (8.52×10^9)	-0.08395	$17.3 + f(T, \theta_H)$
63	$\text{C}^* + \text{H}_2\text{O}^* \rightarrow \text{CH}^* + \text{OH}^*$	1.21×10^{11}	-0.02281	$16.0 + f(T, \theta_O)$
64	$\text{CH}^* + \text{OH}^* \rightarrow \text{C}^* + \text{H}_2\text{O}^*$	8.29×10^{10}	0.02281	$27.8 + f(T, \theta_O)$
65	$\text{C}^* + \text{OH}^* \rightarrow \text{CH}^* + \text{O}^*$	1.09×10^{11}	0.00106	$25.6 + f(T, \theta_O)$
66	$\text{CH}^* + \text{O}^* \rightarrow \text{C}^* + \text{OH}^*$	9.20×10^{10}	-0.00106	$30.7 + f(T, \theta_O)$
67	$\text{CH}^* + \text{H}_2\text{O}^* \rightarrow \text{CH}_2^* + \text{OH}^*$	1.14×10^{11}	-0.03068	$36.7 + f(T, \theta_O)$
68	$\text{CH}_2^* + \text{OH}^* \rightarrow \text{CH}^* + \text{H}_2\text{O}^*$	8.77×10^{10}	0.03068	$0.0 + f(T, \theta_O)$
69	$\text{CH}^* + \text{OH}^* \rightarrow \text{CH}_2^* + \text{O}^*$	1.02×10^{11}	0.00651	$44.3 + f(T, \theta_O)$
70	$\text{CH}_2^* + \text{O}^* \rightarrow \text{CH}^* + \text{OH}^*$	9.78×10^{10}	-0.00651	$0.9 + f(T, \theta_O)$
71	$\text{CH}_2^* + \text{H}_2\text{O}^* \rightarrow \text{CH}_3^* + \text{OH}^*$	9.37×10^{10}	-0.05611	$15.6 + f(T, \theta_O)$
72	$\text{CH}_3^* + \text{OH}^* \rightarrow \text{CH}_2^* + \text{H}_2\text{O}^*$	1.07×10^{11}	0.05611	$11.6 + f(T, \theta_O)$
73	$\text{CH}_3^* + \text{O}^* \rightarrow \text{CH}_2^* + \text{OH}^*$	1.15×10^{11}	0.04137	$13.1 + f(T, \theta_O)$
74	$\text{CH}_2^* + \text{OH}^* \rightarrow \text{CH}_3^* + \text{O}^*$	8.67×10^{10}	-0.04137	$23.7 + f(T, \theta_O)$
75	$\text{CHCH}_3^* + * \rightarrow \text{CH}_3^* + \text{CH}^*$	1.25×10^{11}	-0.06387	$9.1 + f(T)$
76	$\text{CH}_3^* + \text{CH}^* \rightarrow \text{CHCH}_3^* + *$	8.02×10^{10}	0.06387	$29.0 + f(T)$
77	$\text{C}_2\text{H}_5\text{O}^* + \text{H}_2\text{O}^* \rightarrow \text{C}_2\text{H}_5\text{OH}^* + \text{OH}^*$	1.22×10^{11}	-0.00714	$0.1 + f(T, \theta_O)$
78	$\text{C}_2\text{H}_5\text{OH}^* + \text{OH}^* \rightarrow \text{C}_2\text{H}_5\text{O}^* + \text{H}_2\text{O}^*$	8.17×10^{10}	0.00714	$7.9 + f(T, \theta_O)$
79	$\text{C}_2\text{H}_5\text{OH}^* + \text{O}^* \rightarrow \text{C}_2\text{H}_5\text{O}^* + \text{OH}^*$	9.58×10^{10}	-0.04738	$11.8 + f(T, \theta_O)$
80	$\text{C}_2\text{H}_5\text{O}^* + \text{OH}^* \rightarrow \text{C}_2\text{H}_5\text{OH}^* + \text{O}^*$	1.04×10^{11}	0.04738	$10.8 + f(T, \theta_O)$
81	$\text{C}_2\text{H}_5\text{OH}^* + * \rightarrow \text{C}_2\text{H}_5\text{O}^* + \text{H}^*$	9.44×10^{10}	-0.00527	$18.8 + f(T, \theta_H)$

82	$\text{C}_2\text{H}_5\text{O}^* + \text{H}^* \rightarrow \text{C}_2\text{H}_5\text{OH}^* + *$	1.06×10^{11}	0.00527	$4.1 + f(T, \theta_{\text{H}})$
83	$\text{C}_2\text{H}_5\text{OH}^* + * \rightarrow \text{C}_2\text{H}_4^* + \text{H}_2\text{O}^*$	1.16×10^{11} (4.64×10^{10})	-0.10634	$0.0 + f(T)$
84	$\text{C}_2\text{H}_4^* + \text{H}_2\text{O}^* \rightarrow \text{C}_2\text{H}_5\text{OH}^* + *$	8.62×10^{10} (3.45×10^{10})	0.10634	$7.6 + f(T)$
85	$\text{C}_2\text{H}_5\text{OH}^* + * \rightarrow \text{CHCH}_3^* + \text{H}_2\text{O}^*$	2.93×10^{11} (6.44×10^{11})	-0.06413	$0.0 + f(T)$
86	$\text{CHCH}_3^* + \text{H}_2\text{O}^* \rightarrow \text{C}_2\text{H}_5\text{OH}^* + *$	3.41×10^{10} (7.51×10^{10})	0.06413	$17.9 + f(T)$
87	$\text{CH}_3\text{CHO}^* + \text{H}_2\text{O}^* \rightarrow \text{C}_2\text{H}_5\text{O}^* + \text{OH}^*$	9.00×10^{10}	-0.07331	$28.1 + f(T, \theta_{\text{O}})$
88	$\text{C}_2\text{H}_5\text{O}^* + \text{OH}^* \rightarrow \text{CH}_3\text{CHO}^* + \text{H}_2\text{O}^*$	1.11×10^{11}	0.07331	$0.0 + f(T, \theta_{\text{O}})$
89	$\text{CH}_3\text{CHO}^* + \text{OH}^* \rightarrow \text{C}_2\text{H}_5\text{O}^* + \text{O}^*$	7.12×10^{10}	0.04173	$34.8 + f(T, \theta_{\text{O}})$
90	$\text{C}_2\text{H}_5\text{O}^* + \text{O}^* \rightarrow \text{CH}_3\text{CHO}^* + \text{OH}^*$	1.40×10^{11}	-0.04173	$0.0 + f(T, \theta_{\text{O}})$
91	$\text{C}_2\text{H}_5\text{O}^* + * \rightarrow \text{CH}_3\text{CHO}^* + \text{H}^*$	1.43×10^{11}	-0.00219	$0.0 + f(T, \theta_{\text{H}})$
92	$\text{CH}_3\text{CHO}^* + \text{H}^* \rightarrow \text{C}_2\text{H}_5\text{O}^* + *$	7.00×10^{10}	0.00219	$21.1 + f(T, \theta_{\text{H}})$
93	$\text{CH}_3\text{CO}^* + \text{H}_2\text{O}^* \rightarrow \text{CH}_3\text{CHO}^* + \text{OH}^*$	6.93×10^{10}	0.01204	$29.7 + f(T, \theta_{\text{O}})$
94	$\text{CH}_3\text{CHO}^* + \text{OH}^* \rightarrow \text{CH}_3\text{CO}^* + \text{H}_2\text{O}^*$	1.44×10^{11}	-0.01204	$0.0 + f(T, \theta_{\text{O}})$
95	$\text{CH}_3\text{CO}^* + \text{OH}^* \rightarrow \text{CH}_3\text{CHO}^* + \text{O}^*$	6.46×10^{10}	0.02464	$36.4 + f(T, \theta_{\text{O}})$
96	$\text{CH}_3\text{CHO}^* + \text{O}^* \rightarrow \text{CH}_3\text{CO}^* + \text{OH}^*$	1.55×10^{11}	-0.02464	$0.0 + f(T, \theta_{\text{O}})$
97	$\text{CH}_3\text{CHO}^* + * \rightarrow \text{CH}_3\text{CO}^* + \text{H}^*$	1.57×10^{11}	0.02335	$3.7 + f(T, \theta_{\text{H}})$
98	$\text{CH}_3\text{CO}^* + \text{H}^* \rightarrow \text{CH}_3\text{CHO}^* + *$	6.39×10^{10}	-0.02335	$26.4 + f(T, \theta_{\text{H}})$
99	$\text{CH}_3\text{CO}^* + * \rightarrow \text{CH}_3^* + \text{CO}^*$	1.59×10^{11}	-0.11616	$1.4 + f(T, \theta_{\text{CO}})$
100	$\text{CH}_3^* + \text{CO}^* \rightarrow \text{CH}_3\text{CO}^* + *$	6.31×10^{10}	0.11616	$21.3 + f(T, \theta_{\text{CO}})$

3.3 Kinetic Parameter Estimation

Each elementary reaction in the mechanism is associated with three kinetic parameters: (i) pre-exponential factor A , or sticking coefficient s , (ii) temperature exponent β , and (iii) activation energy E , which can be found for each reaction in Table 1. Sticking coefficients for the adsorption reactions are taken from values reported in literature, or otherwise taken as unity. Pre-exponential factors are taken from typical estimates based on Transition State Theory (e.g., 10^{13} s^{-1} for desorption and 10^{11} s^{-1} for Langmuir-Hinshelwood type surface reaction) [56]. Site density σ , is taken as $1.5 \times 10^{15} \text{ sites/cm}^2$ ($2.5 \times 10^{-9} \text{ mol/cm}^2$) based on the typical estimate for a Pt(111) facet. Species binding energies are based on experimental or DFT values reported in literature and are listed in Table 2. Binding energies are coverage (θ) and temperature (T) dependent, as shown in Eq. 1.

$$Q(T) = Q(T_0) - \alpha\theta - \gamma R(T - T_0) \quad (1)$$

Coverage dependence (adsorbate-adsorbate interactions) is taken from values reported in literature [72]. The temperature dependence from statistical mechanics is rooted in the degrees of freedom lost and gained by the species upon adsorption, and are treated as described in [67]. The coverage and temperature dependence coefficients (α and γ) are listed in Table 2. This results in coverage and temperature dependent activation energies, which are calculated on-the-fly using the semi-empirical Unity Bond Index-Quadratic Exponential Potential (UBI-QEP) theory [73], and are reported in Table 1 at 300 K. Bond index values in the UBI-QEP formalism are taken as 0.5 [73].

3.4 Thermodynamic Consistency

Thermodynamic consistency is an often overlooked, but important aspect in mechanism development [13,57,63,67]. Especially at or near equilibrium conditions, this may result in the calculation of incorrect reaction rates. UBI-QEP formalism utilizes thermodynamic loops to determine the activation energies using binding energies and hence inherently provides enthalpic consistency at the reaction and overall mechanism level. However, such a reaction mechanism still violates entropic consistency, as pre-exponentials are taken from approximate transition state theory estimates without any thermodynamic constraints. We have ensured entropic consistency in our surface reaction mechanism, at both the reaction and overall mechanism level, through the temperature exponent, β , in the modified Arrhenius equation [67]. Eq. 2 shows the relationship between the temperature dependent entropy and the modified pre-exponential factor. Here, T_o is taken as 300 K.

$$\frac{\Delta S}{R} = \ln\left(\frac{A_f}{A_b}\right) + (\beta_f - \beta_b)\ln\left(\frac{T}{T_o}\right) \quad (2)$$

In the same manner as [67], we have optimized the β values and the A_f/A_b ratios to ensure entropic consistency over a large temperature range of interest (300-2100 K). It is important to note that this parameter optimization is not against any particular experimental data set, but rather is to ensure that Hess's law is satisfied over a large temperature range. Figure 3.3 shows the ratios of equilibrium constants calculated using gas phase parameters vs. those using the surface reaction parameters. This ratio must be close to unity for a thermodynamically consistent surface reaction mechanism, thereby satisfying Hess's law. On the other hand, reactions in the thermodynamically inconsistent mechanism show a large disparity (e.g., as high as three orders of magnitude) in the

equilibrium constant values. Kinetic parameters (A and β) for the thermodynamically consistent reaction mechanism are listed in Table 2.

Figure 3.3.: K_{eq} ratio ($K_{eq}^{surface} / K_{eq}^{gas}$) for reactions in the thermodynamically consistent and thermodynamically inconsistent surface reaction mechanisms

Table 2: Species Binding Energies, Coverage and Temperature Dependence Coefficients

Species	Chosen binding energy Q (kcal/mol) and selected references	Coverage dependence $\alpha\theta$ (kcal/mol)	Temperature dependence γ (-)
O [*]	86.0 DFT [66]	160 _O [72]	1.5
H [*]	62.5 DFT [74]	30 _H [72]	1.5
OH [*]	60.0 Experiments [75]	330 _O [72]	2.0
H ₂ O [*]	10.2 DFT [76]	-	2.5
CO [*]	42.0 DFT [74]	150 _{CO} [72]	2.0
CO ₂ [*]	4.5 DFT [77]	-	2.0
C [*]	162.6 DFT [78]	-	1.5
CH [*]	163.3 DFT [79,80]	-	2.0
CH ₂ [*]	95.0 DFT [78]	-	2.5
CH ₃ [*]	49.8 DFT [78]	-	2.5
C ₂ H ₄ [*]	17.5 Experiments [81]	-	3.0
CHCH ₃ [*]	102.0 DFT [63,82]	-	3.0
C ₂ H ₅ OH [*]	9.2 DFT [49]	-	3.0
C ₂ H ₅ O [*]	36.1 DFT [49]	-	3.0
CH ₃ CHO [*]	11.2 DFT [49]	-	3.0
CH ₃ CO [*]	57.8 DFT [49]	-	3.0

3.5 Reactor Modeling

Fixed bed and washcoated foam experiments are modeled as a steady state isothermal plug flow reactor. The governing equations are shown below.

$$\frac{dY_k}{dz} = \frac{G_k M_k}{\rho u} + \left(\frac{A_c}{V_R} \right) \frac{S_k M_k}{\rho u}, \quad k = \text{gas species} \quad (3)$$

$$S_k = 0, \quad k = \text{surface species excluding empty sites} \quad (4)$$

$$\sum \theta_k = 1, \quad k = \text{surface species including empty sites} \quad (5)$$

As the surface species coverages at the reactor inlet are unknown, they are estimated using a transient simulation at the inlet, until steady state is reached. Subsequently, the set of differential-algebraic equations (DAEs) is solved using the DDASPK solver [83]. Mass transfer limitations, the importance of which has been highlighted by [84], are considered throughout the reactor length, even though mass transfer was found to be significant only in the entrance region of the reactor.

3.6 Model Assumptions and Limitations

Prior to discussing the results from this work, here we acknowledge the major assumptions/limitations related to the overall modeling approach.

- **Parameter uncertainty:**
 - Uncertainty in the kinetic parameters arises from the use of various estimation methods and their accuracy. Species binding energies extracted from experiments vs. estimated from first-principles calculations vary significantly in some cases.
 - As DFT-based activation energies are not available for all elementary reactions, they are calculated using the semi-empirical UBI-QEP method. Even though

the UBI-QEP method is highly convenient in accounting for coverage effects and ensuring enthalpic consistency, the calculated activation energies need to be verified with first-principles DFT calculations.

- Pt site density of 1.5×10^{15} sites/cm² is calculated from one facet (111) of the Pt crystal, whereas the actually utilized catalysts are polycrystalline in nature.
- Through the adjustment of kinetic parameters, uncertainty in the experimental measurements (if any) may be translated to the surface reaction mechanism.

- ***Mechanistic limitations:***

- Coking and regeneration kinetics are not a significant issue on Pt and are not included in the surface reaction mechanism, but these chemistries will be important for other catalysts, such as Ni and Co.
- The surface reaction mechanism does not include propanol and methanol species that are present, albeit in small amounts, in bio-ethanol derived from biomass sources.
- The mechanism developed in this work is not exhaustive, and does not consider all possible species and reactions in the interest of practical implementation in reactor design. The omission of some reactions may result in cancellation of errors, which may lead to translation of uncertainty to the kinetic parameters.

- ***Modeling limitations:***

- Given the uncertainty in the Marinov mechanism, as discussed earlier, a more reliable and rigorously validated gas phase reaction mechanism for C₂ and C₂₊ oxygenate species needs to be developed.

- As the temperature profile is not reported in the ethanol partial oxidation experimental data [22], the reactor modeling assumes isothermal operation at the reported temperature. Even though this may adequately represent the average reactor temperature, it is known that the typical partial oxidation reactors show a hot spot due to a combination of complete oxidation (exothermic) followed by reforming (endothermic).
- The model performance for ethanol oxidation/reforming is limited by optimization against one set of experimental data [22], which may activate only a few dominant pathways. Monte Carlo-based methods have been used by Vlachos and colleagues to identify the operating conditions which may activate different types of pathways [85,86]. Along the same lines, additional methane dry reforming experiments were conducted (with different important pathways than the ethanol oxidation/reforming chemistry) to validate the surface reaction mechanism developed in this work.

CHAPTER 4: Performance and Optimization of the Surface Reaction Mechanism

Reactor simulations were carried out to model the experimental data for partial oxidation of ethanol on Pt [22]. The experimental data reports ethanol conversion and product (C_2H_4 , CH_4 , CO , H_2 , and H_2O) selectivities as a function of C:O ratio, and corresponding reactor temperature, as shown in Figure 4.1. Figure 4.1A shows the model predictions using the thermodynamically consistent surface reaction mechanism of Table 2. The operating conditions are listed in the caption of Figure 4.1. The catalyst area per unit volume is calculated from the diameter of the pores in the foam ($\frac{A_c}{V_R} = \frac{4}{d}$). The thermodynamically consistent reaction mechanism has superior predictions for C_2H_4 , CH_4 , CO , and H_2O selectivities, compared to the initial thermodynamically inconsistent mechanism (not shown). However, the overall agreement with the experimental data is poor. Therefore, the mechanism predictions are analyzed using a variety of approaches including sensitivity analysis and spatial profile analysis for species coverages and mole fractions, as discussed next.

Figure 4.1 Comparison of the microkinetic model simulations from this work and the experimental data of [22]. Panels A and B represent the initial and optimized surface reaction mechanism, respectively. Symbols represent data from quartz tube reactor ethanol partial oxidation experiments. The operating conditions are as follows: inlet composition = ethanol and air supplied at various C:O ratios (and temperatures) of 1.1 (922 °C), 1.0 (985 °C), 0.9 (1035 °C), 0.8 (1061 °C), 0.75 (1079 °C), and 0.7 (1135 °C), pressure = 1 atm , velocity = 49.1 cm/s, catalyst length = 1.0 cm, and catalyst area per unit reactor volume $A_c/V_R = 200 \text{ cm}^{-1}$.

4.1 Identification and Refinement of Important Parameters

Sensitivity analysis was carried out with respect to the pre-exponential factors to identify the most influential reactions. The normalized sensitivity coefficient is defined as $\frac{d \ln R}{d \ln P}$, where $d \ln P$ is the change in parameter (pre-exponential factor) and $d \ln R$ is the change in model response (conversion or selectivity). As the pre-exponentials are already optimized to ensure entropic consistency, a pairwise sensitivity analysis was conducted [87] to maintain that consistency, i.e., pre-exponential factors of both the forward and backward reaction pair were perturbed by the same factor so that the equilibrium constant

is not perturbed. A sample set of the highest sensitivity coefficients are shown in Figure 4.2. While choosing the magnitude of parameter adjustment for a particular model response, the simultaneous impact on the other model responses is considered as well, i.e., we attempt to change only those parameters, which have the highest sensitivity coefficient for a particular model response *and* a low sensitivity coefficient, and hence low impact, for the other model responses.

Figure 4.2: Sensitivity analysis for all model responses (ethanol conversion at 985 °C and selectivities of H₂, CO, CH₄, H₂O, and C₂H₄ at 1135 °C) with respect to the pre-exponential factors in the initial thermodynamically consistent surface reaction mechanism with a perturbation factor of 2. Operating conditions are the same as those in Figure 4.1.

Based on this sensitivity analysis, only pre-exponential factors for seven surface reaction pairs were adjusted to improve the agreement with the experimental data. No bond indices or binding energies were adjusted. Although adjustment of the bond indices from the empirical value of 0.5 has recently been shown to improve the agreement between UBIQEP and DFT calculations [70], there is not enough information from DFT calculations to determine a more appropriate bond index value for each reaction in our surface reaction mechanism. As the initial estimates for pre-exponential factors may have an uncertainty off a factor of 10-100, we have chosen to optimize only the important pre-exponential factors.

The optimized parameters used in the final surface reaction mechanism are also listed in parentheses in Table 1. Reaction pair 9-10 (H_2 adsorption/desorption to/from 2H^*) was adjusted to improve water selectivity predictions by keeping hydrogen on the surface and available to react with OH^* . Reaction pair 25-26 (CH_4 adsorption/desorption to/from $\text{CH}_3^* + \text{H}^*$) was tuned to decrease methane selectivity at low temperatures and increase it at higher temperatures. Reaction pair 41-42 (CO_2^* scission/formation to/from $\text{CO}^* + \text{O}^*$) controls CO selectivity, particularly at higher temperatures as the contribution of this reaction to CO_2^* consumption increases with increasing temperature. Tuning of reaction pair 45-46 (OH^* scission/formation to/from $\text{H}^* + \text{O}^*$) helped to improve water selectivity predictions. Reaction pair 61-62 (CH_3^* decomposition/formation to/from $\text{CH}_2^* + \text{H}^*$) is important in controlling methane selectivity, as the alternate route for CH_3^* consumption is to form methane. Finally, tuning of reaction pair 83-84 (ethanol dehydration/formation to/from $\text{C}_2\text{H}_4^* + \text{H}_2\text{O}^*$) and reaction pair 85-86 (ethanol dehydration/formation to/from $\text{CHCH}_3^* + \text{H}_2\text{O}^*$) helped to control ethylene selectivity.

4.2 Mechanism Predictions against Experimental Data

Figure 4.1B shows the predictions of the optimized surface reaction mechanism. The overall agreement with the experimental data is significantly improved, as compared to Figure 4.1A, especially for the CO, CH₄, and C₂H₄ selectivities. We note that there is a large discrepancy for the H₂ selectivity predictions, especially at the lowest temperature of 922°C. We believe that the H₂ selectivity experimental data point at 922°C is a possible outlier for four reasons: (i) Salge *et al.* state that at low C:O ratios the mixture was unstable [22]. (ii) Product selectivities for methane and ethylene are not reported at this temperature [22], which further indicates the uncertainty in the measurements. (iii) The model predictions in Figure 4.1B are in good agreement with all the other reported selectivity values. (iv) Based on the model predicted trend for the H₂ selectivity, it should be a low value at 922 °C, which should be more difficult to measure. Nonetheless, it is important to note that the microkinetic model shows good agreement with the overall experimental data with the adjustment of a few kinetic parameters. To understand the fundamental chemistry on Pt under the operating conditions, next the findings from detailed mechanistic and reaction path analysis are discussed.

CHAPTER 5: Mechanistic Analysis and Reaction Zones

Reaction Path Analysis (RPA) as well as analysis of coverage profiles, mole fraction profiles, and rate ratios, were used to investigate the dominant species and reactions as a function of the catalyst length. In RPA, the relative contribution of competing pathways in producing/consuming a selected species is computed. Repeating this for all species yields the network of the most dominant reactions. Reaction pathways were determined for both the gas and surface phases. Combination of RPA with coverage profiles, mole fraction profiles, and reaction rate ratios provides information about how the dominant chemistry varies over the catalyst length – potentially valuable information in reactor design/optimization. Axial profiles of gas species mole fractions at three temperatures (922 °C, 1035 °C and 1135 °C) are shown in Figures 5.1A-C. It is observed that at lower temperature, oxygen is available for reaction almost throughout the catalyst length. On the other hand, at high temperature, oxygen is consumed close to the catalyst entrance, forming H₂O and CO₂. The CO₂ profile shows a maximum, thus indicating subsequent consumption in other reactions. Computation of the overall rates for production/consumption of species and their relative rate ratios revealed four reaction zones over the catalyst length, which will be further elucidated in Sections 5.1-5.4. RPA schematics for those zones are shown in Figures 5.2-5.8.

Figure 5.1 : Simulated mole fraction profiles for ethanol partial oxidation at 922 °C (A), 1035 °C (B), and 1135 °C (C). Operating conditions are the same as those in Figure 4.1.

5.1 Zone 1: Ethanol Dehydration and Oxidation

The first zone at the beginning of the catalyst is dehydration and oxidation of ethanol, leading to high levels of H_2O , CH_4 , CO , CO_2 , and H_2 , as well as some C_2H_4 . A schematic of the dominant reactions using RPA is shown in Figure 5.2. Ethanol goes through two dehydration reactions creating water and either C_2H_4^* (~6%), which desorbs into the gas phase, or CHCH_3^* (~94%) on the surface. CHCH_3^* undergoes a carbon-carbon scission, to form CH^* and CH_3^* species. Most CH_3^* (~80%) combines with hydrogen to form CH_4 ; this is evident from the mole fraction profiles (Figures 6A-C). At the inlet, there is a large amount of oxygen available, which adsorbs dissociatively and participates in dehydrogenation of CH_x^* species. The remaining CH_3^* can undergo oxidation with O^* and OH^* species, or thermal dehydrogenation to form CH_2^* . CH_2^* undergoes thermal dehydrogenation to form CH^* , contributing to about 15% of CH^* on the surface; the rest originates from CHCH_3^* scission. About half of CH^* is oxidized by O^* to form CO^* and the other half undergoes further thermal dehydrogenation to C^* . The C^* species is oxidized via either O^* or OH^* to form CO^* . Most CO^* (~70%) desorbs into the gas phase and the remaining undergoes further oxidation to CO_2^* , all of which desorbs into the gas phase. The decrease in ethanol and spike in CO_2 is clearly seen in the mole fraction profiles at high temperatures, while the spike is less pronounced at low temperatures. This chemistry is valid until oxygen is completely consumed. A small percentage of ethanol is consumed in the gas phase to produce CH_3CHO , which participates in the subsequent zones. The RPA of the gas is shown in Figure 5.3. Based on the rate ratios for the dominant species, the *approximate* stoichiometry of the overall reaction in this zone at 1035 °C is as follows (some reactions do not balance exactly due to rounding and the stoichiometry may be different at other temperatures):

Surface chemistry (90.3%):

Gas chemistry (9.7%):

0.1 H_2O_2

Figure 5.2: Schematic of the primary surface reaction pathways in the first zone (ethanol dehydration and oxidation). Green boxes designate gas phase reactants and final products, whereas blue boxes designate surface species.

Figure 5.3: Schematic of the primary gas phase reaction pathways in the first zone (ethanol dehydration and oxidation). Green boxes designate reactants and final products, whereas white boxes designate intermediate species.

5.2 Zone 2: Transition: Ethanol Oxidation and Dry Reforming

After the first zone of ethanol dehydration and oxidation, gas phase CO₂ (formed from oxidation) adsorbs back on the surface (Figures 5.1A-C). A schematic of the dominant surface reactions using RPA is shown in Figure 5.4, however it should be noted that gas phase chemistry is important in this zone, and the gas phase RPA is shown in Figure 5.5. Surface chemistry in this transition zone is similar to the previous zone, including dehydration of ethanol, except CO₂ provides re-adsorbed CO₂^{*} for reaction with C^{*} (originating from CHCH₃^{*}) to form CO^{*} through the reverse Boudouard reaction (C^{*} + CO₂^{*} → 2CO^{*}), followed by CO^{*} desorption. The consumption of CO₂ and spike in CO is seen in the mole fraction profiles as well. In this transition zone, the rate of O₂ consumption decreases as it becomes depleted, whereas the rate of CO₂ consumption increases. The boundaries of this zone are defined as when CO₂ begins to adsorb on the surface until the rate of O₂ consumption is less than 1% compared to that of CO₂. Based on the rate ratios for the dominant species, the *approximate* stoichiometry of the reaction when O₂ and CO₂ have similar rates in this zone at 1035 °C is as follows:

Surface chemistry (26.9%):

Gas chemistry (73.1%):

Figure 5.4: Schematic of the primary surface reaction pathways in the second zone (transition between ethanol oxidation and dry reforming). Green boxes designate gas phase reactants and final products, whereas blue boxes designate surface species.

Figure 5.5: Schematic of the primary gas phase reaction pathways in the second zone (transition between ethanol oxidation and dry reforming). Green boxes designate reactants and final products, whereas white boxes designate intermediate species.

5.3 Zone 3: Dry Reforming of Ethanol

In this zone, ethanol undergoes the same dehydration reactions as in the first oxidation zone, but after the C-C scission of CHCH_3^* on the surface, the CH^* and CH_3^* species now undergo only thermal dehydrogenations, due to lack of O^* . A schematic of the dominant reactions using RPA is shown in Figure 5.6. As described before, C^* reacts with the adsorbed CO_2^* , and forms CO^* through the reverse Boudouard reaction. In this region, most of the CH_3^* formed on the surface from CHCH_3^* reacts with hydrogen to form CH_4 , and the majority of the CO formed originates from CH^* (via C^*). There is a small contribution of acetaldehyde formed from ethanol in the gas phase of the first and second zone. CH_3CHO decomposes to CH_3CO^* , which subsequently decomposes to provide CH_3^* and CO^* . Though the gas phase contribution is small, a schematic of the gas phase RPA is shown in Figure 5.7. Based on the rate ratios for the dominant species, the approximate stoichiometry of the overall reaction in this zone at 1035 °C is as follows:

Surface chemistry (93.8%):

Gas chemistry (6.2%):

Figure 5.6: Schematic of the primary surface reaction pathways in the third zone (dry reforming of ethanol). Green boxes designate gas phase reactants and final products, whereas blue boxes designate surface species.

Figure 5.7: Schematic of the primary gas phase reaction pathways in the third zone (dry reforming of ethanol). Green boxes designate reactants and final products, whereas white boxes designate intermediate species.

For the lowest temperatures simulated, viz., 922 °C and 985 °C, this zone and the following zone are not observed as oxygen and ethanol are never completely converted or consumed at these temperatures. This is observed from the mole fraction profiles as well (Figure 5.1A).

5.4 Zone 4: Dry and Steam Reforming of Methane

At higher temperatures, ethanol begins to become depleted, and methane formed during the first three zones adsorbs back to the surface (Figures 5.1B-C). This transition is almost immediate and there is not a significantly long “transition zone” as in zone 2. The beginning of the zone is defined as when ethanol consumption is less than 1% in comparison to that of methane. A schematic of the dominant reactions using RPA is shown in Figure 5.8. CH₄ re-adsorption provides CH₃* species on the surface. The CH_x* species undergo thermal dehydrogenations until C* is formed, most of which then reacts with adsorbed CO₂* to form CO*, followed by desorption to CO. In this zone, water formed in the first three zones also re-adsorbs on the surface and contributes (via OH*) to about 10% of C* consumption. This is also evident from the slight decrease in the H₂O mole fraction profiles at high temperatures (Figures 5.1B-C). CH₃CHO formed in the first and second zone continues to adsorb on the surface and decompose to CH₃CO*, which further decomposes to provide about 20% of CH₃* and 10% of CO* on the surface. Based on the rate ratios for the dominant species, the *approximate* stoichiometry of the overall reaction when ethanol and methane has similar rates in this zone at 1035 °C is as follows:

Surface chemistry (100%):

Figure 5.8: Schematic of the primary surface reaction pathways in the fourth zone (dry and steam reforming of methane). Green boxes designate gas phase reactants and final products, whereas blue boxes designate surface species.

For the lowest temperatures simulated, viz., 922 °C and 985 °C, where oxygen and ethanol are never depleted, CH_4 does not re-adsorb from the gas phase back to the surface and its mole fraction continues to increase. This is observed from the mole fraction profiles as well (Figure 5.1A).

5.5 Summary of Reaction Zones

The reaction zones are well demonstrated by the axial profiles of surface species coverages as well, which are shown at 922 °C, 1035 °C and 1135 °C in Figure 5.9A-C. At lower temperatures, CH^* is the most abundant reaction intermediate (MARI) on the surface. At higher temperatures, CH^* initially covers the surface, then decreases as it is consumed by reaction with O^* in the initial oxidation zone. CH^* continues to have low coverage at higher temperatures where the forward reaction rate for CH^* dehydrogenation is higher than the backward reaction.

Figure 5.9: Simulated coverage profiles for ethanol partial oxidation at 922 °C, 1035 °C, and 1135 °C.

Figure 5.10 shows the locations of the reaction zones. Simulations at high temperatures displayed four reaction zones (including one transition zone from oxidation to dry reforming). However, we observed only two reaction zones at low temperatures (922 °C and 985 °C) in which oxygen and ethanol are not completely consumed. Typically, two reaction zones have been observed in earlier literature studies for partial oxidation of CH_4 – an oxidation zone followed by reforming [16,72]. For higher C-containing species such as ethanol, the presence of up to four zones indicates the complexity of the overall chemistry.

Despite the role of CH_3CHO and H_2O in zone 4, it should be noted their stoichiometric coefficients are low. Therefore, neglecting these smaller contributions, zone 4 could also be approximated as a zone of only dry reforming of CH_4 .

Figure 5.10: Distribution of the four reaction zones at various reaction temperatures

5.6 Reaction Order Analysis

Pairwise sensitivity analysis showed that oxygen adsorption/desorption is the rate determining step (RDS) for ethanol conversion in the initial oxidation zone of the reactor. In the initial oxidation zone, the reaction orders with respect to oxygen and ethanol are 3.1 and -2.8, respectively. Such analysis could be conducted for various responses (product selectivities) in all the reaction zones. However, due to the presence of multiple reaction zones and the changes in operating conditions, the RDS and reaction orders also vary. Rigorous validation of the predicted RDS and reaction orders is desirable, but it requires additional experimental data and analysis.

CHAPTER 6: Mechanism Validation against Dry Reforming Experiments

The mechanistic analysis presented in the previous section reveals that dry reforming is a major component in three of the four reaction zones (Figure 5.10). Therefore, it is critical to ensure that the mechanism is rigorously validated against additional dry reforming experiments. The CH₄ dry reforming conversion data reported in typical literature studies is close to being equilibrium limited (e.g., [88,89]). Therefore, we carried out CH₄ dry reforming experiments on Pt in our fixed bed setup. In this section, we report the experimental details followed by the mechanism predictions without adjusting any kinetic parameters. Brief analysis of the dry reforming reaction pathways is also presented.

6.1 BenchCAT Fixed Bed Reactor Experiments

Methane dry reforming experiments were carried out in the temperature range of 600-1000 °C with an Altamira BenchCAT fixed bed reactor system, shown in Figure 6.1. 5% Pt/Al₂O₃ powder catalyst was synthesized using incipient wetness impregnation from Pt salt (PtCl₄, Sigma Aldrich). The reaction was carried out on 115 mg of catalyst loaded in a 0.34 cm i.d. quartz tube reactor inside a temperature controlled furnace. CH₄ (100%, Airgas) was supplied with 10% CO₂ in Argon using mass flow controllers. In the first set of experiments, gases were supplied at a CH₄:CO₂ molar ratio of 1:1, whereas the molar ratio was changed to 2:1 in the second set of experiments to provide additional data for mechanism validation. Products (CO, CO₂, H₂) and unreacted reactant (CH₄) analysis was carried out with an Agilent 3000A microGC equipped with a thermal conductivity detector. A condenser was used to remove any water formed before the product analysis; however no water formation was observed.

Figure 6.1: Schematic of the experimental setup used for methane dry reforming experiments.

6.2 Mechanism Validation for Dry Reforming of Methane

The surface reaction mechanism reported in Table 1 is also used to predict the CH_4 dry reforming experimental data. Figure 6.2 shows the comparison of model predictions vs. experimental data of the conversions of CH_4 and CO_2 for the 1:1 molar ratio case. Equilibrium conversion (same for CH_4 and CO_2 in this case), calculated using Gaseq software [90], is also shown.

Figure 6.2: Mechanism validation against the methane dry reforming experimental data collected using the setup of Figure 6.1. The operating conditions are as follows: 55 sccm of 9.1% CO₂, 9.1% CH₄, and 81.8% AR, pressure = 1 atm, weight of the 5% Pt/Al₂O₃ catalyst = 115 mg, velocity = 2.54 cm/sec, catalyst length = 7.8 mm, and $A_c/V_R = 600 \text{ cm}^{-1}$. The 100-step optimized reaction mechanism is used in the simulations.

The experimental data is not equilibrium limited. Measured and predicted species mole fractions are shown in Figure 6.3A. For the 2:1 CH₄:CO₂ molar ratio, similar results are shown in Figure 6.3B. Overall, the microkinetic model predicts experimental data over

the entire temperature range, for both the inlet composition conditions, without any further adjustment of kinetic parameters.

Figure 6.3: Comparison of model predicted and experimental mole fractions for methane dry reforming for inlet $\text{CH}_4:\text{CO}_2$ molar ratios of 1:1 (panel A) and 2:1 (panel B). Operating conditions for panel A are the same as those in Figure 6.2. Operating conditions for panel B are as follows: 60 sccm of 8.3% CO_2 , 16.7% CH_4 , and 75% AR, pressure = 1 atm, weight of the 5% Pt/ Al_2O_3 catalyst = 115 mg, velocity = 2.75 cm/sec, catalyst length = 7.8 mm, and $A_c/V_R = 600 \text{ cm}^{-1}$.

6.3 Mechanistic Analysis and Dominant Reaction Pathways

RPA of CH₄ dry reforming is shown in Figure 6.4, where various pathways are emphasized depending on temperature. It is observed that the reaction proceeds via thermal dehydrogenations of CH_x^{*} species until C^{*} is formed. C^{*} then reacts with the adsorbed CO₂^{*} through the reverse Boudouard reaction to form CO^{*}, which desorbs. H^{*} atoms removed from the CH_x^{*} species combine to form gas phase H₂. An alternative pathway for consumption of CO₂ and production of CO, is the reaction of CO₂^{*} with H^{*} to form CO^{*} and OH^{*} (reverse Water-Gas Shift (RWGS)). This pathway accounts for ~10% of CO₂ consumption at 700 °C and decreases as the temperature increases until it does not occur at all at 1000 °C. In this RPA, we find the dehydrogenation of CH₃^{*} to CH₂^{*} as the rate determining step, whereas all other reactions are in partial equilibrium. This aligns well with the reaction scheme proposed by Wei and Iglesia for dry reforming of methane on Pt [91], where they report that only the activation of the C-H bond is kinetically relevant and all other reactions are quasi-equilibrated. Our predicted reaction pathway corroborates this and specifically identifies the dehydrogenation of CH₃^{*} as the dominant reaction for C-H bond activation in methane dry reforming.

Figure 6.4: Schematic of the primary reaction pathways for the methane dry reforming. Green boxes designate gas phase reactants and final products, whereas blue boxes designate surface species.

CONCLUSIONS

In this work, we present the first microkinetic model for ethanol partial oxidation and reforming on Pt, which is developed and validated against data from literature [22] and our experiments. Using a microkinetic modeling approach, a 100-step (50 reversible) thermodynamically consistent surface reaction mechanism is proposed. Starting from the initial kinetic parameter estimates, sensitivity analysis is carried out to identify the most important parameters that control the ethanol conversion and products selectivities. A total of seven kinetic parameters (pre-exponential factors) are adjusted during mechanism development. The model predicts ethanol conversion as well as multiple products (C_2H_4 , CO , H_2O , and CH_4) selectivities fairly well in most cases. A detailed mechanistic analysis of the reaction pathways reveals that there are four distinct reaction zones (ethanol dehydration and oxidation, transition from ethanol oxidation to dry reforming, dry reforming of ethanol, and dry and steam reforming of methane) over the catalyst length. As dry reforming dominates most of the catalytic chemistry, the surface reaction mechanism is further validated against our experimental data for dry reforming of CH_4 on Pt. Without any further adjustment of kinetic parameters, the microkinetic model predicts the dry reforming experimental data well. Despite the assumptions and limitations of the overall microkinetic modeling approach, this mechanism provides a starting point to gain a fundamental understanding of oxygenates reforming kinetics, with which detailed reactor and rational catalyst design could be carried out.

FUTURE WORK

In general, the model would greatly benefit from further optimization and validation for a larger range of operating conditions than those discussed in this work. There also several ways in which the model can be improved to address the assumptions and limitations discussed earlier in this work. Minimizing the uncertainty arising from the assumptions used in this work would lead to a more rigorous model in which more confidence could be held in the output. This is important in applying the model to reactor design.

Removing model uncertainty would be greatly aided by more detailed information from both an experimental and computational aspect. Experimentally, a temperature profile would certainly be an asset to the model and remove uncertainty related to isothermal assumptions. Accounting of minor products, like acetaldehyde, would allow for further mechanism refinement and validation. Computationally, determination of binding energies via DFT would be beneficial. Many binding energies are already taken from DFT, but from many different sources. To generate binding energies from the same method would be more astute for the model. DFT could also be utilized to generate more appropriate bond indices, or even fully determine activation energies, for important reactions.

The model can be further developed to consider more important catalyst aspects that are addressed with various assumptions in the current model. Currently, the model does not account for metal loading, which surely has a large effect on reaction performance. This might be addressed with a linear scaling of active catalyst area with metal loading. The mechanism does not consider the metal support, which might be

incorporated by added reactions with support as well as considering support in the determination of reactant binding energies. The mechanism also does not account for deactivation or coking, which, though not an issue for Pt, can be very problematic on other catalysts like Ni. Accounting for loss of active sites as they deactivate and adding coking reactions to the mechanism could make the model more realistic.

A mean-field approximation is used in this model but a kinetic Monte Carlo approach to modeling the metal surface as individual sites and is updated in real time would make the model more realistic [92]. This approach would allow for the proximity of adsorbates to be considered as well as different facets of the metal and their corresponding differences in binding energies.

The model could also be extended and validated for other catalysts. As the mechanism is dependent on binding energies of the metal catalyst, a well validated, robust mechanism could quickly assess materials for reforming performance. This would achieve the objective of computational studies, saving the time and cost of experimental testing.

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