

Mechanistic Insights into Elevated Temperature Photocatalytic Processes via Combined Experimental and Theoretical Approach

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*This dissertation is dedicated to my parents, Kiran Poudyal and Manju Poudyal, for their
endless support and devotion*

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Abstract

Developing new catalytic technologies that allow for the production of fuels and building-block chemicals from CO_2 and H_2O photocatalytically is one of the greatest challenges of the 21st century. H_2O and CO_2 are difficult-to-activate molecules and their successful reduction is potentially kinetically limited. The studies presented herein are aimed at providing a detailed understanding of the reaction such that photocatalysts may be rationally selected and optimized. Our efforts also aim at developing photocatalysts and reactor design that allow utilization of full solar spectrum (UV-vis and IR), which could greatly enhance the overall quantum efficiency of the system. Elevated temperature is commonly avoided in photocatalysis due to the perception that high temperature leads to rapid exciton recombination and loss of quantum efficiency. Instead, enhanced catalytic activity is encountered in our study at autogenous temperatures (350°C+) produced through IR heating by employing a concentrated solar photoreaction (CSPR) approach.

As we explore the photocatalytic synthesis of complex molecules, reaction mechanisms will involve more complex surface-bound intermediates of varying electronic character. This study highlights the interface between the classical electrochemical understanding of photocatalytic reactions where highly destabilized reaction intermediates are common and photocatalytic synthesis reactions where vibrational barriers may be contributing to active reaction pathways. Understanding the stability and electronic nature of these species on the catalyst surface may be crucial in dictating catalyst performance and selectivity. Our results have shed light onto several chemical and physical phenomena at the mechanistic level that drive elementary reaction steps on the surface. Some insights include the isolation of new H-transfer mechanisms and variation in surface chemistry under a range of experimental environments (variable temperature, variable chemical potential of reactants, kinetic isotope

effect, etc.). Results indicate that photocatalyst with a high Debye temperature, robust bulk bonding, and elevated surface chemical reactivity could directly promote new reaction intermediates produced via thermal/vibrational routes that further enhance the selectivity towards hydrogenation. Identifying and understanding the effect of the stability of atomic H and how it is energetically driven through the reaction mechanism could dramatically enhance our ability to control selectivity in photocatalytic reaction mechanisms.

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Chapter 1

Introduction

1.1 Overview

In this chapter, a brief overview of the field of heterogeneous catalysis and a short motivation of how catalysis affects the environment are provided. We then discuss the fundamentals of heterogeneous photocatalysis, which is the main focus of this dissertation. Relevant challenges pertaining to the issues of photocatalyst selection and optimization in the literature are presented and the current state-of-the-art understanding of the field with respect to H_2O splitting and CO_2 photocatalytic reduction mechanisms are briefly discussed. We then discuss some of the utilities of surface science study in heterogeneous catalysis and photocatalysis in general and the overarching goals of photocatalytic CO_2 reduction using a concentrated solar photoreaction (CSPR) approach. The chapter concludes with brief outline of the general topic, structure, and scope of the dissertation.

Overall objective of this dissertation is to utilize a combined experimental and quantum chemical modeling approach to predict the fundamental mechanistic insights associated with photocatalytic synthesis reactions on semiconductor photocatalyst surfaces. By utilizing a combined theoretical and experimental approach, we aim to 1) predict experimentally observed selectivity trends over semiconductor catalysts in photocatalytic CO_2 reduction by H_2O under variable reaction environments, 2) isolate surface chemical reactivity and electronic properties of photocatalysts that directly contribute to the catalytic activity and selectivity, 3) isolate electronic nature of reaction intermediates and surface-bound

atomic H spectroscopically and via quantum chemical calculations, and connect these to experimentally observed selectivity trends, and 4) isolate electronic properties of reaction sites on surface of catalyst that could enable tuning of catalyst selectivity.

1.2 Catalysis, Energy, and the Environment

Massive scale release of greenhouse gases from burning of fossil fuels combined with continuous growth of global energy demand has made it crucial to develop environmentally friendly chemical conversion processes from renewable resources. Catalytic technology is extremely important to achieve clean and sustainable technologies in almost all large-scale chemical processes. A vast majority of existing technologies in chemical industry are thermally driven processes, which rely heavily on fossil fuel consumption (primary contributor to the anthropogenic CO₂ in the atmosphere). Rational design of new catalytic materials through understanding of catalyst surface chemistry, surface reaction mechanisms, and how the reaction energetics are modified through catalyst composition will allow the enhancement of efficiency of existing catalytic processes by improving the efficiency in conversion of renewable resources, reducing the huge thermal energy input requirements, and creating new sustainable pathways for fuel and chemical production using alternative and renewable feedstocks (e.g. solar energy, CO₂, N₂, biomass, etc.). Utilizing solar energy is one of the most promising ways to fulfill the increasing global energy demands, since it is readily available, sustainable, and may be used to drive chemical reactions in net-zero or net-negative CO₂ producing processes. It has been predicted that more energy of sunlight strikes the earth in one hour (4.3×10^{20} J) than worldwide energy consumption in a year (4.1×10^{20} J) [109]. Successful development of sustainable processes that effectively utilize solar energy to transform waste products like CO₂ into useful fuels and chemicals will have a significant favorable impact on the environment. Adding these systems to existing chemical infrastructure where ultra-pure CO₂ is produced already may form the foundation for new CO₂ neutral chemical synthesis processes that impact the environment to a lesser degree than existing systems.

1.3 Fundamentals of Heterogeneous Catalysis

A catalyst is a substance that increases the rate of a chemical reaction without being consumed. Physical forms of catalysts can vary widely based on the applications, from biological enzymes to acid-base catalysts to solid particles of metal or ceramics. In heterogeneous catalysis, reactions take place on the surface of solid catalysts. Figure 1.1(a) illustrates the role of a catalyst in lowering the overall activation energy barrier of the reaction by changing the overall mechanism through new intermediates bound to the catalyst surface. These reactions involve three types of elementary reaction steps shown in Figure 1.1(b) – adsorption of reactants to surface, surface reactions (dissociation, diffusion, association of co-adsorbed species), and product desorption. Adsorption takes place either through a dissociative or non-dissociative process. The adsorbed species acquire significant vibrational energy resulting in breaking of old bonds and formation of new bonds. For the full catalytic cycle to complete, desorption of products from the surface need to occur by leaving the surface intact without affecting surface composition. Fundamentally, the energetics of the elementary chemical reaction steps involved in the catalytic cycle dictates the performance of a catalytic process. These reactions consist of a complex network of elementary steps that occur simultaneously. Identification of these elementary reaction steps, their energetics, and how these are connected to catalyst composition provide insights into understanding the reaction mechanism and kinetics associated with the overall reaction. Development of an efficient catalyst requires the interaction between the reactants and catalyst surface optimized in such a way that it minimizes the activation energy barriers (E_a) associated with elementary reaction steps along the reaction pathway to form the desired products.

1.4 Fundamentals of Heterogeneous Photocatalysis

Storing solar energy into chemical bonds, as in a natural photosynthesis process, is an overarching goal in photocatalysis. The first photocatalytic process of H_2O splitting on TiO_2 particles was reported by Honda and Fujishima in 1972, which marked the beginning of a new era in heterogeneous photocatalysis [55]. Following the discovery, decades’

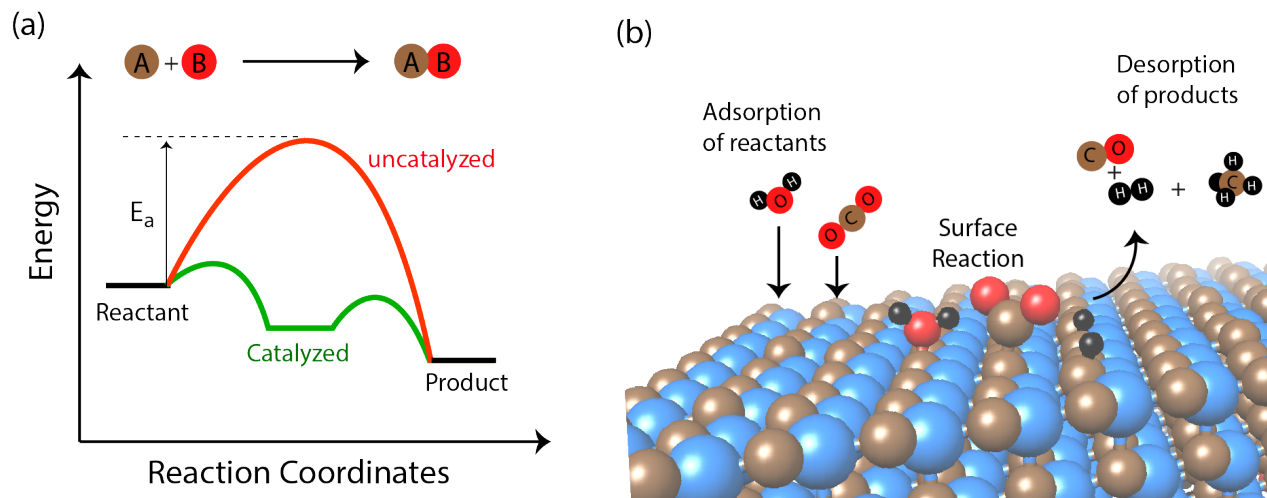


Figure 1.1: Schematics illustrating a typical heterogeneous catalytic reaction. (a) Catalyzed (green) and uncatalyzed (red) potential energy surfaces to illustrate the role of a heterogeneous catalyst to reduce the activation energy barrier (E_a). (b) Elementary processes that occur on the surface of a heterogeneous catalyst during reaction.

worth of investigations have been conducted in order to understand the fundamental processes and enhancement of catalytic efficiency [30, 31, 126, 176]. Among several applications of heterogeneous photocatalysis, photocatalytic H₂O-splitting, degradation of organic components in polluted air and wastewaters, and reduction of CO₂, N₂, NO, NO₂, and other environment pollutants to higher energy fuels and chemicals remain the most active areas of research in the field. Despite several decades of research, many fundamental aspects of the system still remain not well understood, which limits the practical use of photocatalysis for chemical synthesis. Design of efficient photocatalysts that will allow efficient harnessing of solar energy will need atomic level fundamental understanding of the elementary reaction processes.

In a heterogeneous photocatalysis process, photo-induced chemical transformations take place on the surfaces of semiconductor photocatalysts. Semiconductors are materials that consist of a filled valence band (outermost electron orbital of an atom) that is separated in energy from an empty conduction band (set of orbitals higher in energy) by a void region called band gap. Heterogeneous photocatalytic processes involve the electronic excitation of catalysts or substrates by light radiation, such as ultraviolet or visible light of suitable wavelengths. The activation occurs if the energy of excitation is ideally equal to or larger

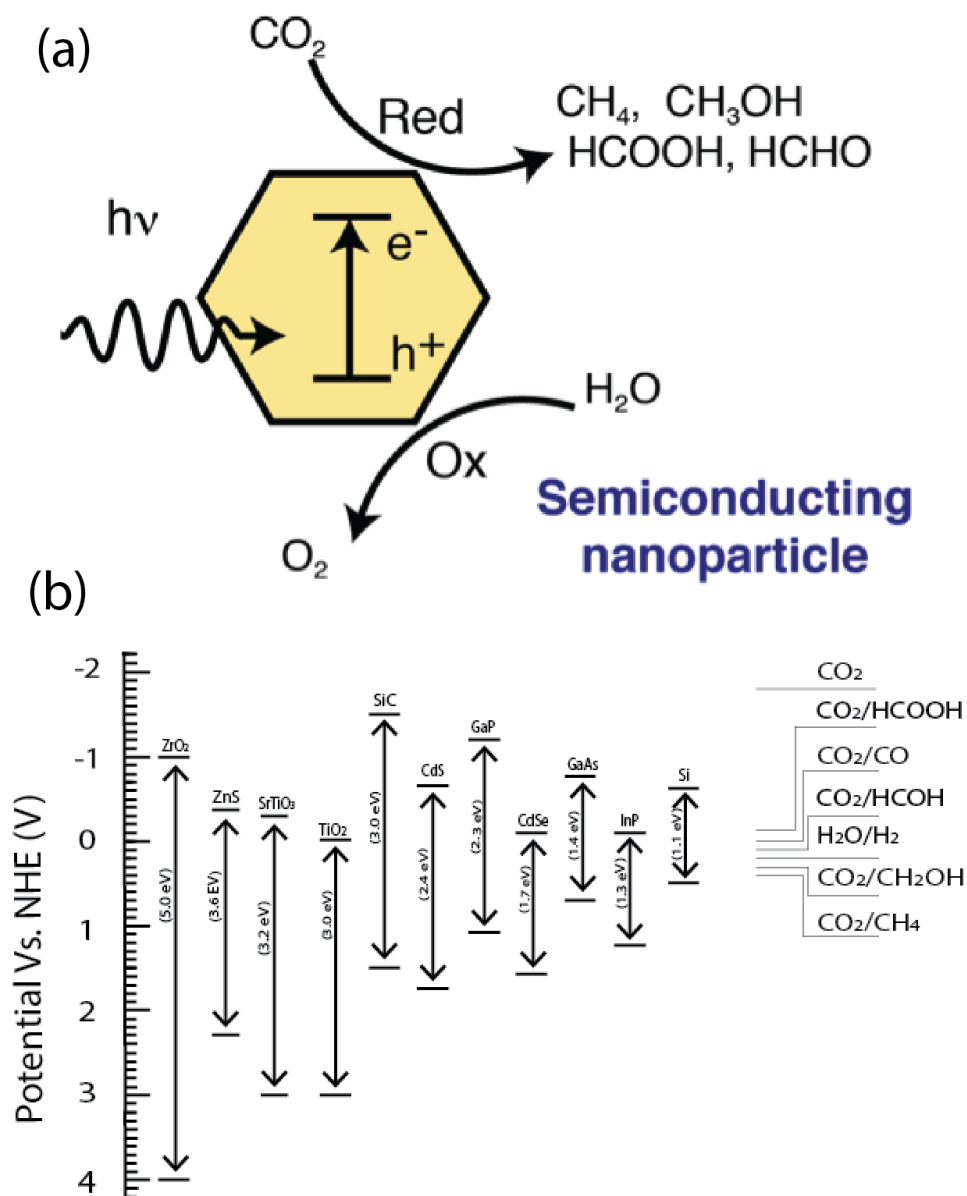


Figure 1.2: (a) Schema illustrating a typical heterogeneous photocatalytic reaction, which initiates with absorption of photon energy equal to or higher than the band gap energy, hence generating an e^-/h^+ pair. (b) Band structure of semiconductor and redox potentials of water-splitting that dictate the H_2O -splitting catalyst optimization.

than the band gap energy. Through the absorption of a photon, an excited electron/hole (e^-/h^+) pair is generated. Excited e^-/h^+ pair contain energy appropriate perform reduction or oxidation reactions at the surface of the catalyst as though they are highly reactive reagents in a chemical reaction [114]. The charge carrier generation is followed by electron-transfer processes to/from reactants performing coupled-redox reactions. Energetically, the band gap dictates the energy of the e^-/h^+ pair and the band edge alignments influence the rate of electron transfer to/from electron acceptor/donor species. Figure 1.2(a) shows the main processes involved in a heterogeneous photocatalytic reaction. For photocatalysts to operate sustainably and at the highest possible rate of reaction, both oxidation and reduction reactions must occur simultaneously [114, 107]. The desired capabilities of an efficient photocatalyst are – 1) efficiently absorb solar energy (UV, vis, and IR), 2) channel the absorbed solar energy (in forms of both light and heat energy) into new chemical bonds, and 3) selectively perform photocatalytic reactions.

1.5 Heterogeneous Photocatalyst Selection and Optimization

Classically, heterogeneous photocatalyst selection and optimization has relied upon concepts developed for electrochemical systems and charge carrier dynamics of a material. Bulk electronic properties of the solid photocatalyst are the dominant variables that drive materials selection and optimization. Main criteria for a photocatalytic reaction to take place are – 1) band gap energy of semiconductor photocatalyst with a suitable width such that the energy of the incident light is greater than or equal to the band gap energy to generate the charge carriers (e^-/h^+ pair) and 2) the alignment of conduction and valence bands of semiconductor photocatalyst with respect to the redox potentials of oxidation or reduction reactions. The alignment of the band edges with respect to reduction and oxidation potentials are what dictate the minimum band gap energy necessary for the reaction. For instance, for an efficient water-splitting photocatalyst, the alignment of conduction band has to be more negative than the redox potential of the H^+/H_2 (0 V vs. NHE) and the

alignment of valence band has to be more positive than the redox potential of $\text{O}_2/\text{H}_2\text{O}$ (1.23 V). Reactions may require higher energy depending upon the redox energetics. There needs to be a driving force for electron transfer to take place for reduction or oxidation reactions. However, no clear correlation has been put forward between both the band gap and the driving force for electron transfer from the conduction band minimum to H^+ and the measured photocatalytic activity and product distribution in case of photocatalytic synthesis of complex molecules such as CH_4 , CH_3OH , H_2CO , HCOOH , or NH_3 evolution. Figure 1.2(b) presents relationship between band structure and redox potentials of some commonly utilized water-splitting photocatalysts.

Besides the two main criteria, stability of photocatalysts under harsh photocatalytic reaction conditions is necessary. For example, although the band gap energy and band alignments of CdS are appropriate for water splitting reaction, unfavorable changes that occur at the surface of catalyst such as metal element dissolution into the liquid or surface oxidation/reduction under harsh photocatalytic reaction environment due to ineffective charge transfer processes make it inactive towards photocatalytic water splitting [104]. In competition with the transfer of charge carriers to adsorbed species on surface upon photoexcitation, recombination of charge carriers can occur. Recombination of e^-/h^+ pair is detrimental to the efficiency of a photocatalytic process [114]. Non-radiative recombination of charge carriers is dominant when reaction is run at elevated temperatures approaching the photocatalyst's Debye temperature (temperature at which the lattice vibrations of a crystal become appreciable [116]). Hence, high Debye temperature photocatalysts are desired when operating at elevated temperatures [175, 142]. High crystallinity of photocatalysts is also desired since charge separation and migration of photogenerated charge carriers could be drastically limited due to defects that operate as trapping and recombination centers between photogenerated charge carriers [114].

1.6 Heterogeneous Photocatalytic CO₂ Reduction

1.6.1 Motivation

Excessive CO₂ emissions from massive burning of fossil fuels such as coal, natural gas, and oil have resulted in serious and detrimental environmental concerns. Global temperature rise, one of the most serious threats to human society, has been directly correlated to the CO₂ concentrations in the atmosphere for the past five decades (See Figure 1.3) [191, 2]. Highly thermodynamically stable CO₂ contributes to the increase in global temperature through absorption and re-emission of IR radiation [130]. The contribution is estimated to be more than 64% of the greenhouse effect [34]. This makes it very crucial to figure out highly efficient technologies that mitigate CO₂ from the environment as well as directly utilize renewable resources as replacements for fossil fuels to meet global energy demands. Several catalytic technologies that have been applied so far towards CO₂ mitigation include electrochemical conversion [79, 86], photocatalytic reduction [142, 87, 104], thermocatalytic reduction [21, 161], photothermal conversion [93, 76], and photoelectrocatalytic conversion [176, 63] to light hydrocarbons and oxygenates.

Achieving the production of hydrocarbons, alcohols, and other chemical building blocks from thermodynamic minimum molecules (CO₂ and H₂O) and sunlight is a promising route to a truly sustainable and more environmentally friendly chemical industry. These processes would enable the use of waste or atmospheric CO₂, H₂O, and the appreciable energy present in solar radiation photons for the production of renewable chemicals. Photocatalytic reduction of CO₂ to hydrocarbons or oxygenates is promising because these value-added chemicals could be directly utilized in industrial processes, could be used as building block chemicals for the synthesis of complex molecules, and/or produce CH₄ rocket fuel in Mars [Newton]. Production of smaller molecules like CO and H₂ are highly valuable as these could be directly utilized as feed in Fischer Tropsch synthesis to produce liquid hydrocarbons [12].

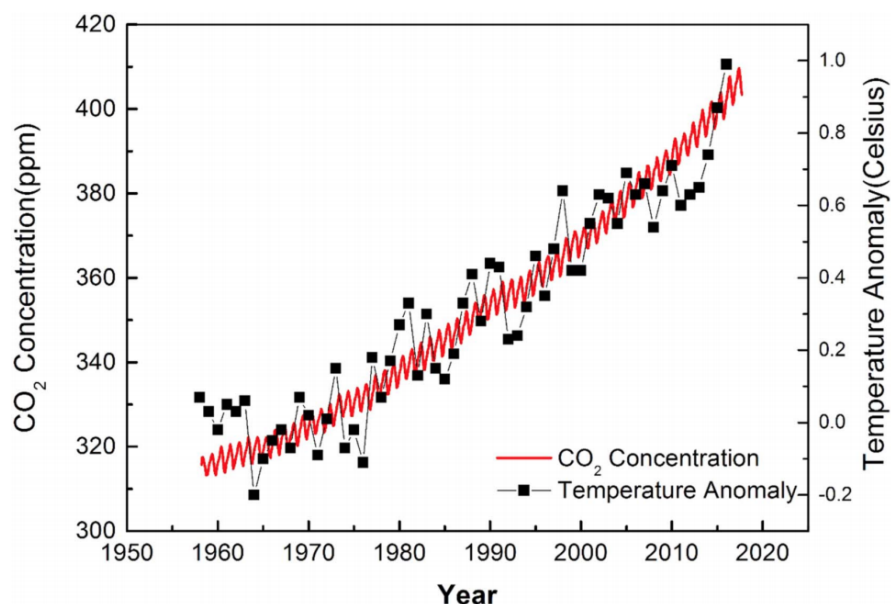


Figure 1.3: Correlation between global temperature and CO₂ concentration from 1958 to 2017. Plot reprinted from Nanotechnology 29 (2018) 052001 [191, 2]. Data is sourced from US Department of Commerce’s National Oceanic and Atmospheric Administration, NASA Goddard Institute for Space Studies.

1.6.2 State-of-the-art

The earliest reports of photocatalytic CO₂ reduction over semiconductor particles goes back to the late 1970s by Inoue et al. [85] Following the discovery, many semiconductor oxides, nitrides, phosphides, sulfides, selenides, perovskites, graphitic materials, etc. have been employed towards CO₂ reduction [176, 104, 164]. As diverse as these studies have been with respect to designing photocatalysts over several decades, unfortunately, a significant deficit of understanding with respect to both materials properties, electronic and surface chemical properties, and reaction mechanisms that drive selective production of hydrocarbons, oxygenates, alcohols, or H₂ still persist. Of specific difficulty is achieving appreciable catalytic activity when utilizing only CO₂ and H₂O as reductant. Despite many claims of appreciable activity being measured, careful studies that avoid organic contamination show rates below a few micromoles of product per gram catalyst per hour [85, 87, 193, 5, 42, 137, 111, 57]. The source of the low rates is also still mostly unknown, yet C–O or O–H cleavage is often assumed to be the rate-determining step in the reaction [27, 32, 74].

Despite the significant success of the approach to select and optimize water-splitting photocatalysts using electronic structure of catalysts and redox properties of electrochemical system, it fails to take into account the material-dependent kinetics associated with surface reactions. In a relatively simple photocatalytic H_2O -splitting mechanism, this selection criteria appears to sufficiently capture the rate determining step of the overall reaction likely because of the strong ionic nature of the reaction intermediates [114, 176, 170, 30, 48, 159]. A conceptual outline of the mechanism for photocatalytic H_2O splitting and CO_2 reduction are presented in Figure 1.4 (a-b), which includes initial steps and examples of possible surface intermediates. From decades of success of predominantly using bulk electronic structure properties to drive H_2O -splitting catalyst discovery, it is clear that at least H_2O dissociation and H_2 and O_2 evolution steps are governed by electrochemical effects due to ionic intermediates. This phenomena has been demonstrated on several oxide/nitride photocatalysts [51, 122, 124, 119, 9]. However, when encountering more complex organic intermediates like those suggested in Figure 1.4(b) in CO_2 photocatalytic reduction, it is difficult to imagine these fragments as weakly bound charged species. In fact, it is known that these types of electronically relaxed intermediates can bind strongly to the surfaces of oxides, carbides, nitrides, sulfides, and selenides and still be catalytically active [29, 37, 64, 68]. Imagining the system in this way leads us to the classic ideas of heterogeneous catalysis where the stability of surface bound intermediates directly affects the overall catalytic rate of the system if these are rate determining steps. Moreover, the stability of these intermediates may dictate the product selectivity. In case of photocatalytic synthesis of complex molecules such as CH_4 , CH_3OH , H_2CO , HCOOH , or NH_3 evolution, it is not clear how the bulk electronic properties of photocatalysts dictate the measured photocatalytic activity and product distribution. These trends suggest that mechanistic aspects of the photocatalytic CO_2 reduction reaction system may not be captured well by a purely excited-state and electrochemical-reduction/oxidation treatment of the mechanism and may necessitate a surface science approach.

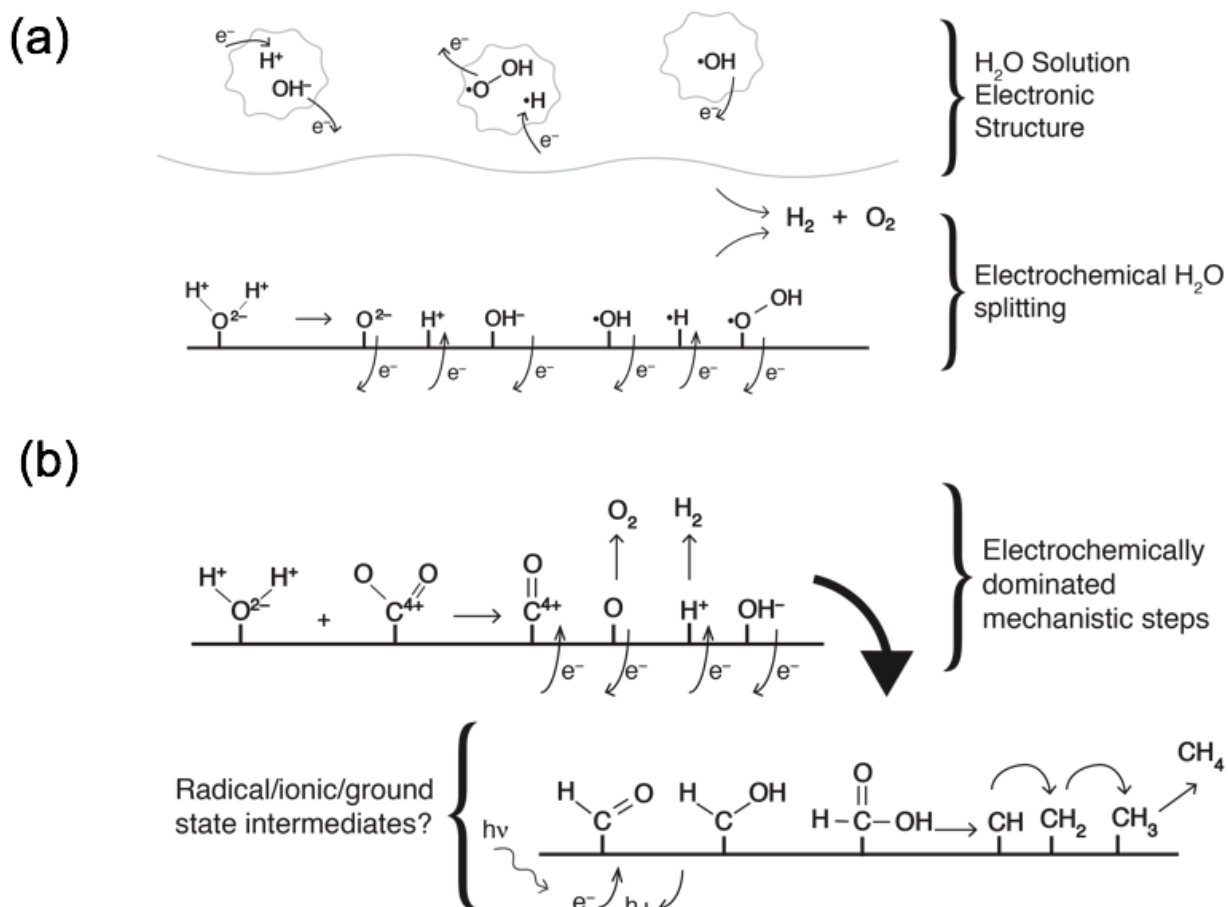


Figure 1.4: Electrochemical vs. surface science view of the overall photocatalytic reduction of CO_2 mechanism. Few and select intermediates are shown to facilitate the example. (a) conceptual outline of H_2O splitting reaction and (b) possible reaction intermediates in CO_2 photoreduction reaction with variable electronic nature

1.7 New Directions in Developing Fundamental Understanding

1.7.1 Comparisons to Established Surface Science Concepts

Heterogeneous catalysis field has relied upon well defined surface science experiments to develop mechanistic level understanding of surface reactions [46, 45, 17, 16, 15, 167, 166]. Surface science reactions are performed over single crystal of catalysts that provide homogenous distribution of active sites on the surface. These well-defined experiments are performed under the ultra high vacuum (UHV) conditions. Reactants are loaded in reaction vessels to allow reaction to occur on pristine catalyst surfaces. Several valuable fundamental insights such as electronic structure and vibrational characteristics of surface adsorbates can be probed from these experiments.

In this dissertation, understanding from already existing surface science literature (both computational and experimental studies) such as energetics of adsorption and dissociation of probe molecules, desorption of product molecules from clean surfaces, and general surface reactivity towards O, C, and H atoms were utilized in the selection of photocatalysts. These already available insights coupled with quantum chemical calculations and photocatalytic experiments from this work have allowed to identify several correlations that exist between photocatalytic experimental conditions, innate surface reactivity of photocatalysts, electronic properties of photocatalysts, H-transfer mechanisms, and experimentally observed catalytic activity and product distribution.

1.7.2 Computational Study

The advent of fast parallel computing resources and density functional theory (DFT) has allowed the accurate and fast modeling of reaction systems. Like in surface science experiments, calculations can model reactions on atomically defined surfaces. Periodic slabs efficiently mimic the real world catalytic surfaces. These calculations can capture all the elementary reaction steps involved in catalytic processes and can be easily connected to reaction conditions such as variable temperature or pressure via ab initio thermodynamics

method. Understanding the elementary reaction steps in a reaction mechanism is necessary to tune catalytic properties, however it is extremely difficult or even impossible to probe all reaction steps in a mechanism using experiments. DFT allows direct access to the fundamental phenomena that governs reactions on catalytic surface. The application of DFT in catalysis can significantly contribute to the rational design of novel catalysts by 1) providing atomic level insights into fundamental mechanisms on surface that can affect catalytic performance, 2) enable surface reactivity trends with respect to experimental performance and selectivity, 3) enable accurate description of adsorbate-surface interactions, etc.

In this work, a ground-state DFT modeling approach was applied to map out all the possible reaction pathways involved in the CO_2 photoreduction reaction with H_2O and predict the lowest energy most favorable reaction pathway that could directly contribute to the overall reaction rate and product selectivity. It is important to note that accurately capturing the dynamics of excited states with respect to driving surface reactions is very computationally expensive or impossible at this time due to the lack of accurate methods. Hence, approximations are still necessary in efforts to model photocatalytic systems at this point. The validity of this approach is determined by making direct comparisons with experimental results. The primary mechanistic question we have tried to answer in this work is that how catalyst surface reactivity and intermediate stability correlates with observed catalytic performance under variable reaction conditions. Moreover, the potential of new H-transfer mechanisms via non-electrochemical routes over non-oxide/nitride semiconductors comprised of less electronegative p-block elements is explored.

1.8 CO_2 Photoreduction via Concentrated Solar Photoreaction (CSPR) Approach

The ultimate goal in artificial photosynthesis is to develop processes that are able to sequester the large amount of energy present in entire solar spectrum that includes $\sim 49.4\%$ of solar irradiance power from the infrared (IR) region. Solar concentrators are utilized in a number

of energy applications, which allow relatively diffuse sunlight to be concentrated down to a higher intensity. See Figure 1.5 for commonly utilized CSP technologies at commercial SCP plants. Concentrated solar power (CSP) provides an unlimited source of clean, non-polluting, high temperature autogenous heat energy (upto 2000°C) and solar flux upto 2000 suns ($1 \text{ sun} = 1 \text{ kW/m}^2$) attainable with large-scale CSP systems [66]. CSPR technology has been utilized in redox approaches to drive thermal cycle or enhance the efficiency of a photo-energy-generation process [158, 96, 198]. This approach shows much promise to expand photocatalytic transformations to industrially relevant upgrading using small carbon-rich reactants such as saturated hydrocarbons (CH_4), small oxygenates (CO), or CO_2 to C_{2+} hydrocarbons and oxygenates through carbon-carbon coupling. The CSPR environment also shows promise to allow for unique photothermal catalytic transformations that would be difficult or impossible to achieve solely through photocatalytic or thermocatalytic routes.

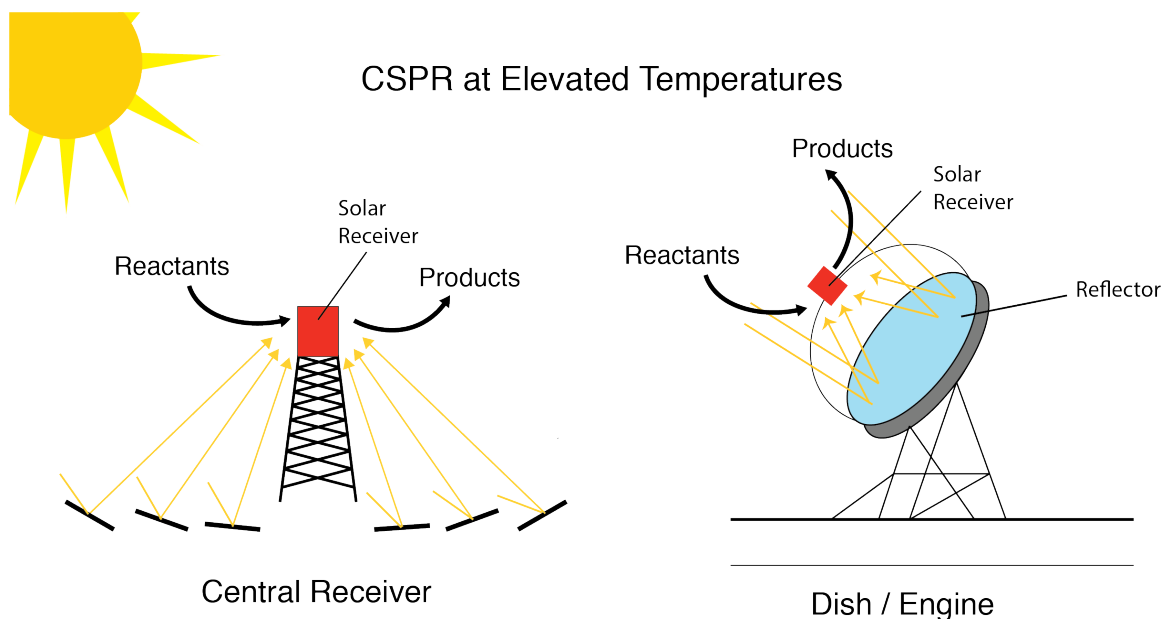


Figure 1.5: Schematics of concentrated solar power (CSP) technologies currently applied at commercial CSP plants – central receiver (left) and dish/engine systems (right).

A mostly unexplored approach in photocatalysis is combining thermal and photon energy inputs within one photocatalytic reaction mechanism. This approach may enable new reaction mechanisms that improve overall performance in CO_2 reduction and may dramatically improve the overall efficiency by sequestering the large amount of energy

present in the infrared (IR) region of the solar spectrum when catalysts with high Debye temperature and appropriate surface chemistry and bulk electronic properties are employed. The approach could be enabled if an understanding of the role of surface chemical reactivity and thermochemical reaction steps in photocatalytic synthesis reactions could be understood.

1.9 Dissertation outline

Overall objective of this dissertation is to utilize a combined experimental and quantum chemical modeling approach to predict the fundamental mechanistic insights associated with photocatalytic synthesis reactions on semiconductor photocatalyst surfaces. The studies presented herein are aimed at providing the community with a detailed understanding of the reaction such that catalyst may be rationally selected and optimized.

In Chapter 2, the theoretical framework on which all the theoretical work discussed in this dissertation are based, is presented. Brief introduction to quantum mechanics, Schrödinger’s equation, Density Functional Theory (DFT) method, *ab initio* thermodynamics, and calculation details are presented. Then, the detailed description of experimental methods such as catalyst synthesis, reactor design, characterization methods, and the underlying principles that govern the operation of each experimental technique is presented.

In Chapter 3, experimental results from this work utilizing a new approach of combining thermal and photon energy inputs within one photocatalytic reaction mechanism is presented. A suite of semiconductors, namely, SiC, Si, Pt/TiO₂, and GaN that together present a significant range of surface chemical reactivity and bulk electronic properties were tested under a new gas phase flow and batch, concentrated solar photocatalytic reaction conditions (350°C) to investigate the effect of elevated surface reactivity of photocatalyst and reaction conditions on catalytic performance towards C–O cleavage and selectivity towards hydrogenation versus H₂ evolution. All four catalysts are found active towards CO₂ reduction under CSPR conditions, yet clear differences are encountered in selectivity towards hydrogenation (CH₄ production) and H₂ evolution. Catalysts that exhibit high Debye temperatures and elevated surface reactivity may enable the production of new reaction intermediates that facilitate C–O cleavage and full CO₂ reduction to CH₄. Tests at variable

temperatures (250°C and 350°C) over top-performing catalysts, SiC and Si, were performed to further understand the effect of surface-chemical and thermal-input contributions towards C–O cleavage and H₂O dissociation.

In Chapter 4, a ground-state Density-Functional Theory (DFT) modeling approach is utilized to shed light upon observed catalytic performance and selectivity towards hydrogenation versus H₂ evolution over SiC and GaN, respectively in CO₂ reduction by H₂O. Through comparisons with experimental results presented in Chapter 3, the validity of the computational approach is determined. Clear correlations between photocatalyst surface chemical reactivity, the degree of stability of surface-bound reaction intermediates and atomic H, electronic nature of atomic H, and catalytic activity and selectivity derived from experiments are presented. Positive correlations in this study suggest that photocatalyst surface reactivity may play a critical role in driving C–O cleavage and stabilizing reaction intermediates to limit reverse reactions and promote full reduction of CO₂ to CH₄. Both the stability of atomic H and carbonaceous intermediates appear to contribute to this effect. Electronic analysis also suggested protonic H⁺ from H₂O dissociation would relax to neutral H⁰ over SiC and that a new H-transfer mechanism may be responsible for elevated hydrogenation selectivity over SiC. Less stable protonic H⁺ over GaN, on the other hand, correlated with a higher selectivity towards H₂ production.

In Chapter 5, we delve into understanding the role of electronic nature of surface bound atomic H and its stability on catalyst surfaces in dictating photocatalytic activity and selectivity. We utilize throughput experimental testing (kinetic isotope effect, thermal effects in reaction) and spectroscopy (SSNMR) as well as DFT calculations to gain insights into the H-transfer mechanisms and to spectroscopically isolate the oxidation states of atomic H on SiC and GaN surfaces. Significant KIE over SiC towards hydrogenation (CH₄ production) while no KIE over GaN suggested two different H-transfer mechanisms are active over these materials, which likely result in the selectivity differences encountered in experiments. Results all collectively suggested a new H-transfer mechanism that involves the transfer of neutral atomic H and exhibit a significant vibrational barrier may be active in the hydrogenation of carbonaceous intermediates over SiC, while an electrochemical H-transfer pathway may dominate over GaN.

In Chapter 6, we expand the understanding of role of nature of atomic H on catalyst surfaces on catalyst product selectivity towards dictating hydrogenation versus H_2 evolution by first investigating whether this effect is general or catalyst specific. Upon incorporating O atoms on the pristine SiC surface (SiC core with a partially oxidized shell), a drastic selectivity change from CH_4 to H_2 evolution was observed. DFT investigation as well as SSNMR of atomic H adsorbed to an O atom of partially oxidized SiC surface revealed less stable protonic H^+ on the surface, indicating the presence of two different reaction sites (C and O) responsible for two different nature of atomic H (H^0 on C and H^+ on O). Selectivity trend observed over the same material further solidifies the effect of stability of atomic H and its oxidation state in dictating the product selectivity. This study also focused on understanding the role of electronegativity of reaction sites by utilizing other electronegative atoms to achieve tunability of photocatalytic activity and selectivity.

In Chapter 7, we broaden our approach in understanding the role of non-metal atoms and the enhancement of covalent bonding of transition metal (TM) ceramics in driving oxygen reduction reaction (ORR) in electrocatalytic systems. We employed a first principles quantum chemical modeling approach and chemical hydrogen electrode (CHE) model [135] to first understand the chemical composition of active sites of FeN_x/C and CoN_x/C electrocatalysts (single-site catalysts with TM embedded in N-doped graphene), and how the chemical activity of these existing catalysts could be replicated at high reaction site density, nearing the activity of Pt metal in ORR. Results indicated that metal-rich forms of bulk Fe and Co carbides and nitrides are highly reactive towards O^* and OH^* intermediates, while the reactivity decreased remarkably if less metal rich forms were encountered. Select combinations of transition metals (Fe and Co) and non-metals (N, P, S, and Se) were isolated in this study to show appropriate reactivity towards ORR due to the enhancement of covalent bonding of TM ceramics to the carbon support via TM-S-C, TM-P-C, or TM-Se-C bonds. Clear directions are suggested with respect to the compositional space of TM + p-block elements that may produce appropriate surface reactivity towards O^*/OH^* such that high ORR activity may be achieved.

In Chapter 8, we summarize the findings of this study by presenting a bigger picture of how various aspects of the study provide a basis for understanding the mechanism such that

new efficient photocatalysts may be selected in a more rational way. Conclusions are followed by suggestions for future work. In the future work, fundamental questions concerning how we could expand this work to design better photocatalysts that could perform oxygen evolution, isolate optimal chemical potentials of reactants and understand synthesis mechanisms that could lead to C–C coupling to produce C₂₊ hydrocarbons and oxygenates are presented.

Chapter 2

Theoretical and Experimental Approach

2.1 Overview

A detailed discussion of the theoretical technique and experimental methods (reactor design, reaction conditions, catalyst synthesis, microscopy and spectroscopy) utilized in this work are discussed in this chapter. The fundamental principles behind the operation of each experimental and characterization techniques are also discussed.

2.2 Introduction to Computational Methods

2.2.1 Density Functional Theory (DFT)

Density Functional Theory (DFT) was utilized to determine potential reaction mechanisms involved in photocatalytic synthesis reactions. Specifically, the adsorption energies, binding geometries, vibrational frequencies of adsorbates on surfaces and molecular species, stability of reaction intermediates, activation energy barriers, and transient state geometries associated with elementary steps in the reaction mechanisms were obtained from DFT calculations. These valuable insights allowed us to map out all the possible reaction pathways involved in the CO₂ reduction reaction and predict the lowest energy most favorable reaction

pathway that could directly contribute to the overall reaction rate and product selectivity. The accuracy of the energetics obtained from DFT is within a 0.1 eV of experimentally established energetics. Periodic boundary conditions enable the modeling of extended catalyst surfaces, which provide good representation of real catalyst surfaces.

The main problem in the determination of electronic structures of a material is to solve the Schrödinger's equation (2.1) for the wavefunction, Ψ , which contains all information about the system including the probability of distribution of all the particles and energy associated with the particle configuration and is a solution to the N-electron many-body problem of $3N^N$ dimensions.

$$E\Psi = H\Psi \quad (2.1)$$

The Hamiltonian for this many-body problem is given by:

$$H = \frac{-\hbar^2}{2m} \sum_i \nabla_i^2 - \sum_{i,I} \frac{Z_I e^2}{|r_i - R_I|} + \frac{1}{2} \sum_{i,j} \frac{e^2}{|r_i - r_j|} - \frac{\hbar^2}{2M} \sum_I \nabla_I^2 + \frac{1}{2} \sum_{I,J} \frac{Z_I Z_J e^2}{|R_I - R_J|} \quad (2.2)$$

The first three terms of the Hamiltonian are the kinetic energy of the electrons, the interactions of electrons with nuclei and electron-electron interactions, respectively. The fourth and the fifth terms are the kinetic energy of nuclei and the nuclei-nuclei interactions. Hence, the many-body wavefunction relies upon all the spatial coordination of the particles ($3N^N$) making the solution of the Schrödinger equation very difficult.

DFT formalism was developed by Hohenberg, Kohn, and Sham in the 1960s, however the major breakthrough of DFT applications was not realized until the 1990s when major advancements in parallel computing resources took place. Hohenberg and Kohn showed that the ground state total energy of a system of interacting electrons is a unique functional of the electron density in its ground state [78]. Hence, the N-electron many-body problem of $3N$ dimensions, $\Psi(r_1, r_2, \dots, r_N)$, reduces to just a 3-dimensional problem $\Psi(\rho(r))$, which considerably reduces the computational efforts and time to calculate the electronic properties of materials. Later in 1965, Kohn and Sham showed that a set of non-interacting electrons in an effective (fictitious) external potential that has same electron density as in a real system

could be used to exactly map the many interacting electrons in the external potential [99]. The Kohn-Sham equations derived from this method are a set of self-consistent, one-electron, Schrödinger-like equations (2.3-2.6) that can be written as:

$$E(\rho(r)) = T_s(\rho(r)) + V_{elec-nuc}(\rho(r)) + V_{elec-elec}(\rho(r)) + E_{xc}(\rho(r)) \quad (2.3)$$

$$T_s(\rho(r)) = \sum_i \int \Psi_i^*(r) \left(-\frac{1}{2} \nabla^2 \Psi_i(r) \right) dr \quad (2.4)$$

$$V_{elec-nuc}(\rho(r)) = \int \nu_{nuc}(r) \rho(r) dr \quad (2.5)$$

$$V_{elec-elec}(\rho(r)) = \frac{1}{2} \int \phi(r) \rho(r) dr \quad (2.6)$$

where, T_s is the kinetic energy of non-interacting electrons, $V_{elec-nuc}$ is the electrostatic interaction between the electron and the nucleus, $V_{elec-elec}$ is the electrostatic interaction between electrons, and E_{xc} is the exchange correlation energy. Ground state energy is calculated using eqn. (2.3) given that E_{xc} energy is provided. The exact E_{xc} functional is an unknown parameter, however there are several approximations that are quite accurate. The accuracy of DFT calculations are dependent upon the accuracy of exchange correlation functional utilized.

Generalized gradient approximation (GGA) and local density approximation (LDA) are the two main types of approximations used in DFT to approximate the exchange-correlation energy as a functional of electron density. LDA is based on the uniform electron gas model in equilibrium [99]. Although LDA results in a realistic description of atomic structure, it was found that it is not accurate to describe the energetics of chemical reactions (normally heat of reaction and activation energy barriers) resulting in the overestimation of binding energies of atoms or molecules.

$$E_{xc}^{LDA}(\rho) = \int \rho(r) \epsilon_{xc}(\rho) dr \quad (2.7)$$

GGA is based on the local density as well as the gradient of electron density in space to overcome the deficiencies encountered by using LDA. For instance, it has shown a more realistic description of energy barriers in the dissociative adsorption of hydrogen on metal and semiconductor surfaces [134, 26]. GGA was utilized in our calculations since it has been shown to exhibit a desired chemical accuracy [62]. A number of GGA functionals have been developed based on the reaction systems such as Perdew-Burke-Ernzerhof (PBE), revised PBE (RPBE), Perdew-Wang 91 (PW91), PBE-solids (PBE-sol), etc. PBE-sol was utilized in this work as it more exactly captures the electronic structure and bonding within semiconductor solids as well as accurate account of adsorption energies for atoms and molecules to surfaces [138, 41].

$$E_{xc}^{GGA}(\rho) = \int \rho(r) \epsilon_{xc}(\rho, \nabla \rho) dr \quad (2.8)$$

2.2.2 Calculation Methods

Density functional theory (DFT) calculations were performed using Vienna *Ab Initio* Simulation Package (VASP 5.3.3). The generalized gradient approximation (GGA) exchange-correlation functional PBE-sol was utilized, as it more exactly captures the electronic structure and bonding within semiconductor solids [138, 41]. The hydrogens were modeled using an ultra-soft pseudopotential. DFT+U method of Dudarev et al. was employed to impose on-site Coulomb and exchange interactions (Hubbard U correction) to calculate the highly correlated electronic structure of TiO₂ [82]. The effective Hubbard repulsion value (U_{eff}) was 2.0 eV for TiO₂ [53]. Positive and negative reaction energetics quoted throughout indicate endothermic and exothermic reaction energies, respectively. A planewave cutoff energy of 400 eV was used and its effect on reaction energetics was checked. The effect of thickness of slabs was investigated, which contributed 0.02 eV to the reaction mechanism energetics. Periodic boundary conditions were utilized to model materials as infinite slabs. Surface unit cells were commonly of the 2x2 or 3x3 surface unit cell size and contained at least 2-3 stoichiometric layers or at least six atomic layers. All periodic slabs were separated by a 15 Å vacuum gap in the z-direction. The topmost two stoichiometric layers of the slab

along with the adsorbates were allowed to relax and optimize. Rest of the slab was fixed. K-point mesh of 2x2x1 was utilized for 3x3 slab and 5x5x1 for 2x2 slab to sample the Brillouin zone. The convergence of adsorption energies with respect to k-points was investigated and did not change our conclusions. Forces within the models were relaxed to a value less than 0.1 eVÅ. The charge distribution on the adsorbed H atom was analyzed using Bader charge analysis code [11, 71].

2.2.3 *Ab Initio* Thermodynamics

To convert the DFT calculated internal electronic energies to energetics at operating conditions (T,P) of catalytic reaction, *ab initio* thermodynamics method was utilized [144, 145]. The temperature and pressure corrections were applied in this study to calculate the entropy (S(T,P)) of gas molecules, and ultimately the Gibb's free energy (G(T,P)) of adsorbed species using the following equations:

$$G(T, P) = F(V, T) + PV(T, P) \quad (2.9)$$

and,

$$G = H - TS \quad (2.10)$$

The contribution of pressure-volume term to formation energies is almost negligible, which allows direct connection between thermodynamics and DFT calculations. The change in Gibb's free energy can be calculated as:

$$\Delta G(T, P) = G_{final}(T, P) - G_{initial}(T, P) \quad (2.11)$$

$$\Delta G(T, P) = \Delta H - T\Delta S \quad (2.12)$$

$$S(T, P) = S_{trans} + S_{rot} + S_{vib} - k_B \ln\left(\frac{P}{P_0}\right) \quad (2.13)$$

ΔG is calculated taking into account the experimental temperature and pressure of the reaction system. Entropy corrections were only applied to the adsorption and desorption steps of the reactant product molecules, respectively. Entropy change in the surface reaction steps can be assumed negligible.

Surface Facet Determination

The choice of surface facet for each material was motivated by established computational studies. The most favorable surface facets of anatase $\text{TiO}_2(101)$ [72], GaN(0001) [15], 3C-SiC (111) [52], and Si(111) [83] were taken from published literature. The TiO_2 -anatase(101) surface was modeled by using a 2x2 slab containing two stoichiometric layers of TiO_2 , terminated on both sides stoichiometrically by oxygen. Anatase $\text{TiO}_2(101)$ surface facet was selected because it has been shown to be the most stable and mostly observed facet on anatase- TiO_2 [46, 59]. The GaN(0001) surface was modeled by using a 2x2 slab containing three stoichiometric layers. (0001) surface of GaN has been determined to be the lowest surface energy facet, and several research groups have reported thermodynamically favorable water-splitting on GaN(0001) surface [14, 28]. The Si(111) surface was modeled by using a 2x2 slab containing six layers of Si. (111) surface facet of Si metal has been shown to be the most stable facet via equilibrium shape analysis of Si [83] and active towards water splitting reaction. Du et al. reported that SiC (111) surface was most energetically favorable surface facet towards water splitting when contrasted with other SiC surfaces [52]. The C-terminated beta-SiC surface was modeled by using a $(\bar{1}\bar{1}\bar{1})$ surface with 3x3 slab containing three stoichiometric layers of SiC. Due to asymmetry in the crystal in the z-direction, the bottom of the slab was carbon free and required OH termination to remove the effect of surface states.

Surface Termination Determination

To determine the surface termination of catalysts, an ab initio thermodynamics approach was utilized [144, 145]. We calculated Gibbs free energies of different surface compositions to isolate the surface termination under reaction conditions (reaction at 350°C, 90 mol% H_2O at 1 atm pressure). Stoichiometric non-metal rich surfaces were modeled to reflect the surfaces

from freshly cut bulk or surfaces closest to when they are first introduced to the reaction environment. Non-metal atom lean surfaces were produced by removing non-metal atoms one by one from the catalyst surface by reacting with H atom from H_2O to produce balance products (carbide surface to produce CH_4 and O_2 or nitride surface to produce NH_3 and O_2) until the surfaces were completely metal rich. Surfaces were also loaded with additional non-metal atoms to manually produce a non-metal rich surface. The stability of surface was determined at a point where the thermodynamics of removing an atom from the surface sequentially changed from endothermic to exothermic. Assuming a flow reactor regime where products formed would be continuously swept away from the catalyst surface, the chemical potentials of the products were assumed to be negligible. This resulted in the calculations only dependent on the chemical potential of H_2O and formation energies of the products. Ab initio calculation results over SiC and GaN are presented below in Figure 2.1. Results indicate that both stoichiometric SiC and GaN are in fact lowest energy surfaces.

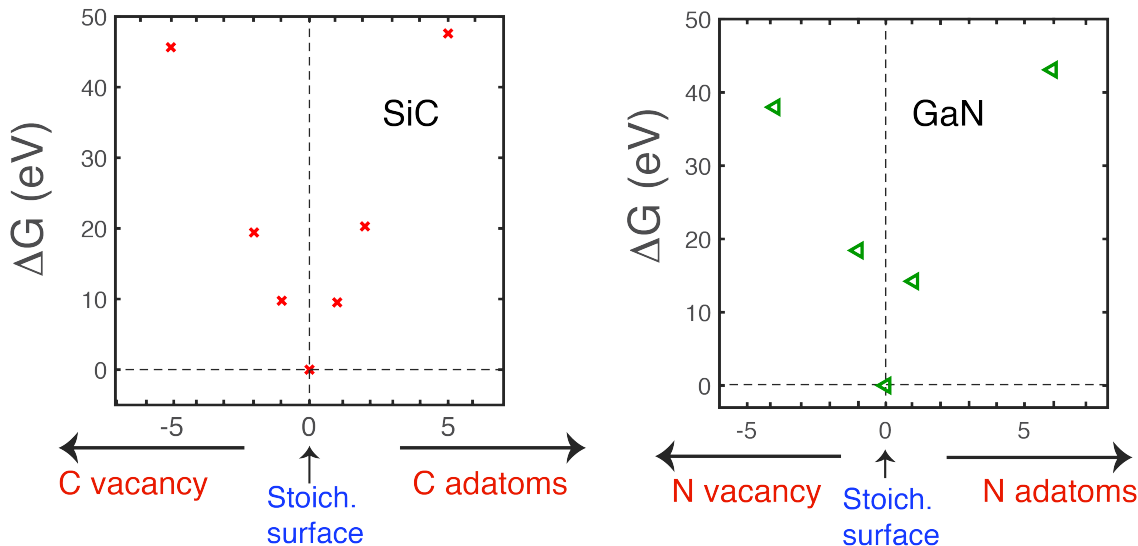


Figure 2.1: Ab initio thermodynamic energetics were utilized to isolate the surface termination of (left) SiC and (right) GaN. Gibbs free energies were calculated by taking hydrogenated C (CH_4) and N (NH_3) as references for atoms added or removed from the surfaces of SiC and GaN, respectively. Results suggested that stoichiometric surfaces are most stable in both cases.

2.2.4 Transition state and activation barrier calculations

The transition states and activation barriers for each elementary surface reaction was determined by Nudged Elastic Band (NEB), climbing NEB (cNEB), and DIMER method. In NEB method, the minimum energy pathway is mapped between initial state and final state in an elementary reaction step by first constructing a chain of images of the system via linear interpolation between the initial and final states. Each image correspond to the specific geometry of atoms along the pathway (a snapshot of the reaction path). The images are held together by a spring interaction that ensures the continuity of the reaction pathway, which causes the chain to act like an elastic band. The optimization of band is performed by minimizing the energy of each image which combine to form the minimum energy path and the saddle point is determined. In case when NEB method does not exactly land at the saddle point, cNEB is a feature added to NEB to identify the highest image on the band. In this method, the highest energy image converges to the saddle point by climbing the image up and down the potential energy surface until the saddle point is determined. The thermodynamically favorable initial and final states of elementary reaction step are determined prior to running the NEB. Unlike NEB method, DIMER allows to search for the transition state on a potential energy surface by starting from any initial configuration. It works by searching in any direction for the nearby saddle point. This method is even useful to look for transition states corresponding to unknown reaction mechanisms.

2.3 Experimental Methods

2.3.1 Catalyst synthesis

Organic-free synthesis of all materials was required to ensure products observed were not originating from organic contaminants. P25-TiO₂ (25-30 nm) was purchased from Acros Organics and was calcined at 600°C under ultra-high purity air. To limit the effect of re-adsorption of organics from ambient after cleaning, it was further cleaned *in situ* under illumination under ultra-high purity air flow for an hour before reaction. Pt/TiO₂ was synthesized by depositing 1.0 wt% Pt on TiO₂ via incipient-wetness using a PtCl₄ precursor.

After the deposition, the catalyst was dried under Ar flow for eight hours at 120°C and then reduced under 1.0% H₂/Ar flow at 350°C for two hours. Pt/TiO₂ was further cleaned *in situ* under illumination under ultra-high purity Ar flow for an hour before reaction. Beta-SiC (<1μm) and Si nanopowder (50-70 nm) were purchased from US Research Nanomaterials. The surface oxide naturally present on the SiC and Si particles was removed by HF etching. This approach has been established as a standard procedure in the electronics community to produce oxide-free SiC and Si surfaces [197, 148]. After etching, the catalysts were dried under Ar flow at 120°C for eight hours and then annealed at 400°C under 1.0% H₂/Ar flow for 4 hours. This approach prompted the recrystallization of the surfaces of SiC and Si, as demonstrated by improved catalytic activity and stability. GaN was produced via the nitriding of ammonium-carbonato-dihydroxo-gallate (NH₄[Ga(OH)₂CO₃]) flowing 5% NH₃ at 700°C for 10 hours following the work of Yan et al. [184].

2.3.2 Reactor Design and Photocatalytic reaction

Photocatalytic reduction of CO₂ with H₂O over the selected photocatalysts was performed in a custom built, all metal, gas phase flow reactor at temperatures ranging between 250 < T < 350°C. The reactor system was specifically designed to be free of plastic and rubber of any kind and any other organic contaminants that would otherwise produce questionable results. The reactor outer shell was constructed from ultra-high vacuum conflat flange components, sealed with copper gaskets, and baked under flowing Ar at 400°C for 16 hours before assembly. The reactor bed assembly was machined from nickel-free grade 420 stainless steel to circumvent the formation of Ni carbonyls that would otherwise affect the quantification of CO production. An optically pure quartz viewport above the catalyst bed allowed illumination (See Figure 2.2). The central flow-through catalyst bed is temperature controlled to allow for variable temperature testing conditions. However, was unnecessary once the catalyst bed autogenously heated past 120°C. Variable catalyst bed depth (0.5 to 5 mm) allowed flow optimization to limit channeling through the planer (25.4 mm diameter) catalyst bed. Ultrapure SFC grade CO₂ and doubly distilled Milli-Q water were used as reactants to produce a hydrocarbon-free reactant flow. The H₂O to CO₂ concentration ratio was roughly 10:1. High temperature runs utilized an unfiltered solar simulator 1000 W

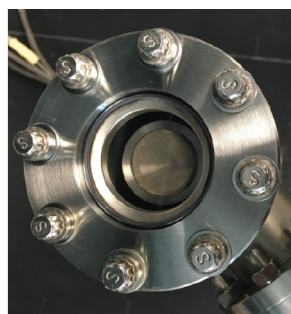
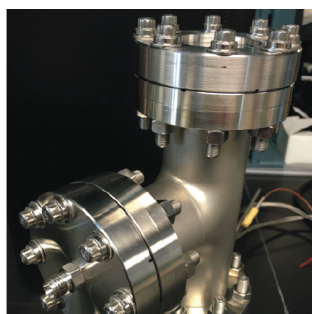
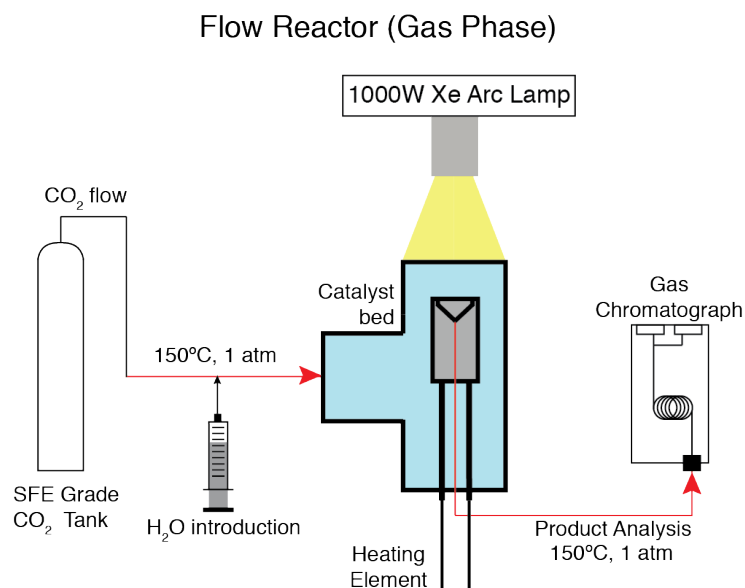


Figure 2.2: Gas phase and batch phase reactor of all metal-construction for elevated temperature photocatalysis experiments. Flow reactor was designed to allow the tuning of temperature and irradiation easily

Xe lamp ($\lambda > 240\text{nm}$). To allow for concentrated irradiation at lower temperatures, a water filter was employed. The incident illumination at the surface of the disk-shaped catalyst bed (approx. 5.1 cm^2) was approximately 100 Watts or 200 suns. Products were analyzed online with an SRI gas chromatograph using flame ionization and thermal conductivity detectors. Photoreaction tests were performed multiple times to ensure a high degree of reproducibility. Error bars in plots are the standard deviation of the data sets. Throughout all experiments, only CH_4 , CO , and H_2 were detected. Heavy water (D_2O) was employed in CO_2 photocatalytic reduction studies in place of H_2O as a reactant to gain insights into kinetically rate-limiting steps as well as the underlying mechanism of H-transfer (electrochemical versus vibrational in nature).

2.3.3 Apparent quantum yields (AQY)

AQY of all products (CO , H_2 , and CH_4) were calculated assuming that all the incident light higher in energy than the band gap energy leads to excitation. The flux of incident photons were estimated using the spectral irradiance curve provided by Newport for the 1000W lamp. Actual irradiance was calculated for each material taking into account the conversion factor for the lens material and multiplication factor for the rear reflective mirror present inside the lamp housing.

Apparent quantum yield (AQY) over all four materials was calculated by:

$$AQY(\%) = \frac{\text{Number of moles of product formed (H}_2, \text{CO, or CH}_4\text{)}}{\text{Number of incident photons}} * 100\% \quad (2.14)$$

Number of moles of product formed (H_2 , CO , or CH_4) was obtained directly from experiments. To calculate the number of incident photons, following parameters were utilized:

$$Ep = \frac{h * c}{\lambda} \quad (2.15)$$

(E_p is energy of photon with Planck's constant (h)= 6.63×10^{-34} Js; speed of light (c)= 3×10^8 m/s; wavelength (λ in m))

$$Et = P * t * S \quad (2.16)$$

(E_t is the total irradiance, P is the power density in W/m², S is the area of irradiation in m², and t is the irradiation time in s)

$$N_p = \frac{Et}{E_p} = \frac{P * S * t * \lambda}{h * c} \quad (2.17)$$

where, N_p is number of incident photons.

Table 2.1: Parameters utilized in AQY% calculations:

Parameter	Values
Area (S in m ²)	0.0005
Time of irradiation (t in s)	3600
λ -SiC (nm)	469.5
λ -GaN (nm)	345.0
λ -Si (nm)	617.7.0
λ -Pt/TiO ₂ (nm)	391.0
Absorption edge cut-off (in nm)	240
Conversion factor based on lens material	0.13
Multiplication factor for rear reflective mirror	1.6

For each material, the wavelength range was calculated above the band gap cutoff energy. A spectral irradiance curve was obtained for the 1000 W lamp from Newport. Actual irradiance was calculated for each material taking into account the conversion factor for the lens material and multiplication factor for the rear reflective mirror present inside the lamp housing. Once actual power is calculated, power density (P) is obtained by dividing actual power (in W) by spot size area (in m²).

$$\begin{aligned} \text{Actual Power (in W)} &= \text{Spectral Irradiance} * \lambda\text{-range} * \text{Conversion factor of lens} \\ &* \text{Multiplication factor for rear reflector} \end{aligned} \quad (2.18)$$

$$\text{Power Density} = \frac{\text{Actual power (W)}}{\text{Area, S (m}^2\text{)}} \quad (2.19)$$

2.3.4 Reaction Enthalpy Change

Enthalpy change of reaction was estimated by using following equation:

$$\Delta H_{rxn} = \Delta H_0 + R \int_{T_0}^T \frac{\Delta C_p^0}{R} dT \quad (2.20)$$

(ΔH_0 is the standard enthalpy change at 25°C, R is the gas constant, ΔC_p^0 is the heat capacity change of reaction, and T is the reaction temperature (350°C)).

$$\text{Enthalpy gain (\%)} = \frac{\Delta H_{rxn} \text{ at } 350^\circ\text{C (kJ)}}{\text{Enthalpy Input(kJ)}} * 100 \quad (2.21)$$

2.3.5 Kinetic Isotope Effect

Kinetic isotope effect (KIE) is a mechanistic phenomena in which one of the isotopically substituted molecule reacts at a different rate. Key assumptions in this phenomena are that isotopic substitution does not affect the potential energy surface of the reaction or energy of the electronic states and only the mass dependent properties (vibrational frequencies) are affected. KIE is an important tool utilized in catalysis to aid in the understanding of mechanisms, the nature of rate-determining steps, transition states, and many more.

In theory, the energy of the vibration levels of vibration of a bond (for example, C–H) in a molecule is given by:

$$E_n = (n + \frac{1}{2})h\nu \quad (2.22)$$

where, n = 0, 1, 2, ..., etc.

The lowest energy level or ground state energy is given by:

$$E_0 = \frac{1}{2}h\nu_0 \quad (2.23)$$

The frequency of vibration is determined by using the harmonic oscillator approximation:

$$\nu = \frac{1}{2\pi} \sqrt{\left(\frac{k}{m}\right)} \quad (2.24)$$

where, k is the force constant and m is the mass of the object. The greater the mass, the lower the E_0 (ground state energy of isotope).

The Arrhenius equation is utilized to determine the reaction rates and activation energy.

$$k = Ae^{\frac{-E_a}{k_B T}} \quad (2.25)$$

where, k is the reaction rate, E_a is the activation energy, k_B is the Boltzmann constant, A is the pre-exponential factor, and T is the temperature.

Substituting D for H in a chemical reaction, the rate equation can be written as:

$$k_H = A_H e^{\frac{-E_a^H}{k_B T}} \quad (2.26)$$

$$k_D = A_D e^{\frac{-E_a^D}{k_B T}} \quad (2.27)$$

The rates are obtained from experimental testing. The ratio of k_H/k_D gives the kinetic isotope effect of the reaction. The mass of substituted isotope is directly proportional to the vibrational barrier (See Figure 2.3). Hence, it is more difficult to break the bond. The increase in energy to dissociate a bond results in slower rate of reaction and gives rise to the kinetic isotope effect.

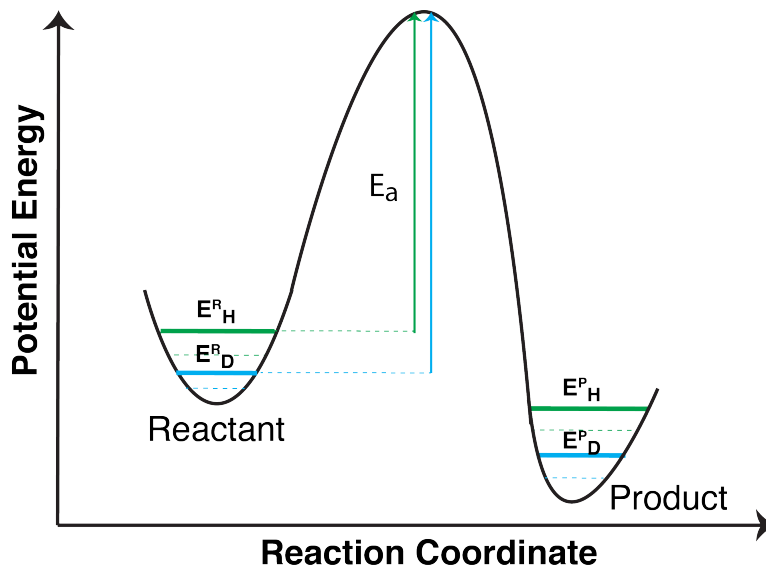


Figure 2.3: Schematic illustrating kinetic isotope effect phenomena when D is substituted for H

2.3.6 Characterization Methods

The photocatalysts in this study were characterized using several microscopy and spectroscopy techniques. Diffuse Reflectance UV-vis spectroscopy (DRUVS) was utilized to characterize all the photocatalysts in the study to capture the band gap energy and the absorption spectra in a diffuse reflectance mode. X-ray diffraction (XRD) was utilized to measure the bulk chemical composition of all materials. Transmission electron microscopy operated in the scanning TEM (STEM) mode was utilized to investigate the surface structure and to quantify the size of the catalyst particles. TEM equipped with Energy Dispersive X-ray Spectroscopy (TEM-EDS) was utilized to survey the elemental composition of catalysts. Electron energy loss spectroscopy (EELS) analysis was utilized to measure the chemical composition and electronic structure (above the Fermi level) of SiC (pristine after etching, after under reaction conditions, and after partial oxidation) and SiO₂ for comparison. Chemical composition of the catalysts, specifically the degree of oxidation before and after under reaction conditions, was quantified by X-ray photoelectron spectroscopy (XPS). XPS was used to measure the oxidation state of Si in SiC and Si nanoparticles, as well as to check the presence of fluorine coming from the etching procedure that utilizes hydrofluoric acid.

Solid-state NMR (SSNMR) was utilized to capture the oxidation state of atomic H adsorbed to catalyst surfaces.

Diffuse Reflectance UV-vis spectroscopy

UV-visible absorbance spectroscopy is used to probe electronic transitions in materials [103] by analyzing the interaction of photon energy with a material. This is achieved by using a broadband visible source that passes the photons through, or reflect from a sample and by analyzing the energy/intensity of the resulting photons. In this dissertation, diffuse reflectance UV-vis spectroscopy was utilized to analyze the interactions of photons with solid semiconductor nanoparticles. Kubelka-Munk (K-M) theory is utilized in diffuse reflectance spectroscopy to determine the band gap of semiconductors. The Kubelka-Munk function ($F(R)$) is given by equation (2.28), where R is the diffuse reflectance of the sample. The band gaps of photocatalysts can be estimated by plotting $(F(R)h\nu)^n$ versus $h\nu$, as the intercept of the extrapolated linear part of the plot at $(F(R)h\nu)^n = 0$ where $n = 1/2$ for an indirect semiconductor and $n = 2$ for a direct semiconductor.

$$F(R) = \frac{(1 - R)^2}{2R} \quad (2.28)$$

In this work, Cary 5000 UV-Vis-NIR spectrophotometer was utilized to collect absorption spectra for the materials in the wavelength range of 200-800 nm. Catalyst powder of 0.5g was loaded dry in a quartz glass cuvette for spectral analysis. The diffuse reflectance of each sample was measured in the experiments and the K-M function $F(R)$ was calculated. The band gap energy of SiC, Si, TiO_2 , and Pt/TiO_2 were estimated by plotting $(F(R)h\nu)^{0.5}$ versus photon energy ($h\nu$ in eV) for the indirect band gap transition and extrapolating the straight line portion of the curves to the X-axis. The point of intersection of this line at the X-axis is taken as band gap energy. For GaN, which undergoes direct band gap transition, band gap energy was estimated by plotting $(F(R)h\nu)^2$ versus photon energy.

X-ray Diffraction (XRD)

In this work, X-ray diffraction (XRD) was utilized to determine the crystallographic structure of the catalysts. XRD is commonly utilized to identify the crystalline phases inside catalysts. XRD occurs with the interaction of X-rays emitted from a source by atoms in a periodic lattice. The diffraction patterns obtained are used to identify the crystallographic phases present in the catalyst. The elastic scatterings with long-range order allows to probe the bulk of the catalysts. XRD measurements in our experiments were obtained on a PAN Analytical X-Pert Pro powder X-ray diffractometer. The analysis of peaks were performed using Highscore Plus software.

Transmission Electron Microscopy (TEM) and Scanning TEM (STEM)

Transmission electron microscopy (TEM) is utilized to characterize surface morphology, crystalline structure, and elemental composition of catalysts. A primary electron beam of high energy (60-300 kV) is passed through the condenser to the sample. The electrons scattered off the atoms in the samples are projected onto a fluorescent screen, which gives a two-dimension projection of the sample mass, which gives rise to an atomic resolution image of the sample upon magnification. STEM mode allows a finer probing of the sample as the beam is more focused in a small probe size (typically 0.05-0.2 nm). In this work, STEM was coupled with energy dispersive x-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS) to obtain high spatial resolution. Results of TEM reported in this work were obtained using 300 kV aberration-corrected STEM/TEM (FEI Titan S) at Center for Nanophase Material Sciences (CNMS) at Oak ridge National Lab (ORNL) and 60-200 kV ZEISS LIBRA 200 at Joint Institute for Advanced Materials (JIAM) at University of Tennessee.

Energy Dispersive X-ray Spectroscopy (EDS)

EDS coupled with TEM/STEM allows to map the elemental composition of a surface of a catalyst. In this process, an electron beam is focused on the surface of the sample, which interacts with the beam causing the excitation of core electrons to vacuum or empty energy

states [1]. The resulting hole or vacant state produced after the excitation process is then filled by another electron from a higher energy level. This causes an X-ray photon with energy equal to the difference between two excited states to be emitted. This energy of the X-ray photon is unique, hence allows the separation of elements on the sample. EDS results presented in this dissertation was produced using TALOS FEI F200X operating at 200 kV at Center for Nanophase Material Sciences (CNMS) in Oak ridge National Lab (ORNL).

Electron energy loss spectroscopy (EELS)

EELS technique allows to analyze the unique electronic structure and chemical composition of catalysts like determining oxidation states and site symmetries [1, 24]. In this technique, a sample is exposed to an electron beam with known, narrow range of kinetic energies. The interactions with the electron beam causes electrons from core shells of the atoms in the sample to be ejected to higher energy levels. This leads to the excitation of the sample. The sample can undergo de-excitation by giving up energy in form of photons, X-rays, or Auger electrons. In this process, the incident electron beam interacts with the sample, changing both its energy and momentum. The electron energy loss signal is measured by an electron spectrometer. EELS analysis on SiC and SiO₂ samples were performed in a Zeiss Libra 200 TEM operated in STEM mode at 200 kV using a 0.5 μ m monochromator slit at University of Tennessee. The monochromator energy resolution in EELS was better than 0.2 eV.

X-ray Photoelectron Spectroscopy (XPS)

XPS allows to measure the chemical composition of surface and quantify the elements present. Typically, a monochromatic X-ray source is used to excite electrons from core levels of atoms into the vacuum [177]. The relative energy of the ejected electrons provides quantitative information about the oxidation state and composition of the sample. XPS is considered to be a surface sensitive technique (escape depth of the electrons is between 1-10 nm). Binding energy ($E_{binding}$) of each of the emitted core electrons in the sample allows the identification of elements present in the sample and can be approximated by using the following equation (2.29) [177, 35].

$$E_{binding} = E_{photon} - (E_{kinetic} + \phi) \quad (2.29)$$

where, $E_{binding}$ is the binding energy of the ejected electrons, E_{photon} is the energy of the incident photons, $E_{kinetic}$ is the kinetic energy of the ejected electrons, and ϕ is the work function. The shifts in binding energy of core electrons provides the change in chemical state of the element.

In this dissertation, XPS was utilized to analyze the surface compositions of SiC and Si nanoparticles (before and after under reaction conditions) and quantify the degree of oxidation of Si on surface. The surface composition and chemical bonding states of SiC and Si metal nanoparticles before and after reaction were analyzed using a Perkin Elmer 5500LS XPS with a non-monochromatized Mg K α -X-ray excitation source of energy 1486.74 eV. A Voigt profile was used to fit the XPS data by assuming the background to have a Shirley-type shape.

Solid-state Nuclear Magnetic Resonance (SS-NMR)

The principal difficulty with the application of NMR to solids is low resolution characteristic of solid samples. Hence, solid-state nuclear magnetic resonance (SS-NMR) spectroscopy technique is utilized for molecular structure determination of samples with little to no mobility (e.g., crystalline or powder state solid catalyst). Unlike liquid phase NMR, solid samples generate broad NMR linewidths that are determined by magnetic interactions between nuclear spins and chemical shift anisotropy. One technique of reducing the linewidth of solid samples is magic-angle spinning (MAS) [10]. The magic angle corresponds to 54.74° , the angle at which the sample is spun at high speed to the applied magnetic field. In this technique, the sample is spun at spinning rate greater than the anisotropic interaction to average it to zero. In case it is spun at lesser spin rate, spinning sidebands become visible. In a typical experiment, the powder sample is tightly packed in a rotor and spun at spinning rates between 1 to 35 kHz depending upon the experiments.

In this dissertation, Varian INOVA 400 MHz was utilized for solid-state ^1H -NMR and ^{13}C -NMR. The magic angle spinning (MAS) frequency was 6 kHz and 1-dimensional spectra

was obtained with 256 scans at room temperature. The spectra was externally referenced to adamantane for chemical shift.

Chapter 3

Insights into Elevated-Temperature Photocatalytic Reduction of CO₂ by H₂O

3.1 Overview

In this chapter, we focus on understanding the effect of combining thermal and photon energy inputs within one photocatalytic reaction mechanism over a suite of semiconductors, namely, SiC, Si, Pt/TiO₂, and GaN. To complement our experimental results to improve fundamental insights, some basic insights from computational surface science investigations are employed. We found that catalysts that exhibit high Debye temperatures and elevated surface reactivity may enable the production of new reaction intermediates that facilitate C–O cleavage and full CO₂ reduction to CH₄. Elevated photocatalyst surface reactivity also correlated with dramatically improved selectivity between hydrogenation (CH₄ production) and H₂ evolution. Tests at variable temperatures (250°C and 350°C) over top-performing catalysts, SiC and Si, are presented. Results suggest the effect of surface-chemical and thermal-input contributions towards C–O cleavage and H₂O dissociation.

3.2 Introduction

Achieving the production of hydrocarbons, alcohols, ammonia, and other chemical building blocks from thermodynamic minimum molecules and sunlight is a promising route to a truly sustainable and more environmentally friendly chemicals industry. These processes would enable the use of waste or atmospheric CO₂, atmospheric N₂, H₂O, and the appreciable energy present in solar radiation photons for the production of renewable chemicals. Unfortunately, a significant deficit of understanding with respect to both materials properties, electronic and surface chemical, and reaction mechanisms that drive selective production of hydrocarbons, alcohols, or NH₃ still persist even after many decades of diligent research. Of specific difficulty is achieving appreciable catalytic activity when utilizing only CO₂ or N₂ and H₂O as reductant. Despite many claims of appreciable activity being measured, careful studies that avoid organic contamination show rates below a few micromoles per gram catalyst per hour of product [85, 87, 193, 5, 42, 137, 111, 57]. The source of the low rates is also still mostly unknown, yet C–O or N–N cleavage is often assumed to be the rate-determining step in the reaction [27, 32, 74]. Another significant issue is the difficulty in controlling the fate of hydrogen with respect to hydrogenation of reaction intermediates (selective) vs. H₂ evolution (unselective). Most studies focused upon TiO₂ or newer GaN catalysts have shown selectivity that lays heavily towards H₂ production and significantly lowered quantum efficiency with respect to oxygenate, hydrocarbon, or NH₃ production [27, 102, 155, 5]. The ability to control activity towards partial or complete reduction of CO₂ or carbon-carbon coupling for the production of C₂₊ higher hydrocarbons or oxygenates has also not been demonstrated in a reproducible fashion. Beyond selectivity, energy efficiency in general is also problematic, as most materials demonstrated as active to date predominantly utilize the ultraviolet portion of the solar spectrum at low efficiency (~3% of the total solar irradiance power) [31, 176, 85]. A selection of photocatalysts that utilize a small portion of the visible spectrum (44% of total power) have been demonstrated in water-splitting, but none have been shown to reproducibly exhibit significant activity in the total reduction of CO₂ to hydrocarbons [119, 118, 3, 176].

A mostly unexplored approach in photocatalysis is that of combining thermal and photon energy inputs within one photocatalytic reaction mechanism. This approach may enable new reaction mechanisms that improve overall performance in CO₂ reduction and may dramatically improve overall efficiency by sequestering the large amount of energy present in the infrared (IR) region of the solar spectrum (49.4% of solar irradiance power). The approach could be enabled if an understanding of the role of surface chemical reactivity and thermochemical reaction steps in photocatalytic synthesis reactions could be understood. Elevated temperature conditions are commonly avoided in photocatalysis due to the classic focus on materials that exhibit relatively low Debye temperatures and dominant e^-/h^+ recombination rates at even moderately elevated temperatures [175, 178, 114, 183, 132, 81, 75]. For example, the Debye temperature of anatase TiO₂ and GaN are 247°C and 327°C, respectively [81, 116]. Shifting to employing high Debye temperature semiconductors, where e^-/h^+ recombination does not outstrip surface reaction rates, the combination of thermal and photon energy inputs may be possible. This approach may enable beneficial contributions from new reaction intermediates only accessible via thermochemical reaction steps over photocatalysts with elevated surface reactivity, and lead to dramatic improvement of the overall activity and efficiency in photocatalytic CO₂ reduction. The design of high-temperature-active photocatalysts requires an understanding of the catalyst surface reactivity necessary for optimal reaction rates and product selectivity, which may be markedly different than classical thermocatalysts due to the relatively large energy of the excited states and reaction steps they drive. Currently, most of the understanding needed to develop these catalysts is absent in the community. Our studies aim to develop insights into how these catalytic systems operate and their viability in comparison to classical near-ambient photocatalytic systems.

Our approach was to investigate a small selection of photocatalysts (SiC, Si, Pt/TiO₂, and GaN) that together present a significant range of surface chemical reactivities towards carbon and oxygen, sufficient band gap energies, and appropriate conduction band minimum alignments with the H⁺ reduction potential under a new gas phase flow and batch, concentrated solar photocatalytic reaction condition that results in autogenous catalyst temperatures of 350°C. A subset of the catalysts whose activity towards CH₄ and CO

production was appreciable (SiC and Si) were investigated at lower temperature (250°C) to probe thermal effects in activity and product distribution. These results contrasted with published studies of near-ambient temperature tests performed in condensed aqueous phase over the same catalysts enable the effects of temperature, gas phase environment, and product distribution as a function of surface chemistry of catalyst to be understood. Photocatalysts for the study were chosen such that ample comparisons with already established studies could be made and the effect of an appreciable range of catalyst surface chemical reactivity could be investigated. These materials, through experimental and computational surface science understanding, provide a degree of surface reactivity that ranges from moderately low, as in GaN and TiO₂, the latter being less reactive, to fairly aggressive, as in SiC and Si. The latter two materials were also chosen such that non-oxide/nitride semiconductors that present more aggressive surface chemical reactivity and inherently different electronic properties could be investigated. Specifically, both SiC and Si exhibit appreciable surface reactivity towards oxygen and unique reactivity towards atomic hydrogen. No sacrificial agents or reactants beyond CO₂ and H₂O were employed in any of our studies. Reactors were built from ultra-high vacuum all-metal construction to further limit any contributions from organic contamination from rubber o-rings or polymer/rubber seals. To complement our experimental results to improve fundamental insights, some basic insights from computational surface science investigations are employed.

3.3 Results

3.3.1 Catalyst Characterization

Catalysts were characterized to determine their electronic and structural properties before and after reaction. Transmission electron microscopy (TEM) analysis was utilized to understand the particle morphology and crystal surface facet definition (See Figure 3.1(a-b)). Pt particles were observed to be roughly spherical with an average particle size of 3-4 nm and defined surface facets. TiO₂ particles appeared crystalline with well-defined facets and uniform size (avg. 25 nm). SiC exhibited a wide variability in particle size distribution of 50

nm to 1 μ m in diameter with an average size of 200 nm. Particles appeared crystalline with a mix of spherical and well-faceted morphologies. Si nanoparticles were mainly spherical with average particle size of 50-60 nm. GaN, like SiC, appeared to have a wide distribution of particle size (20-100 nm) and an average size of 60 nm.

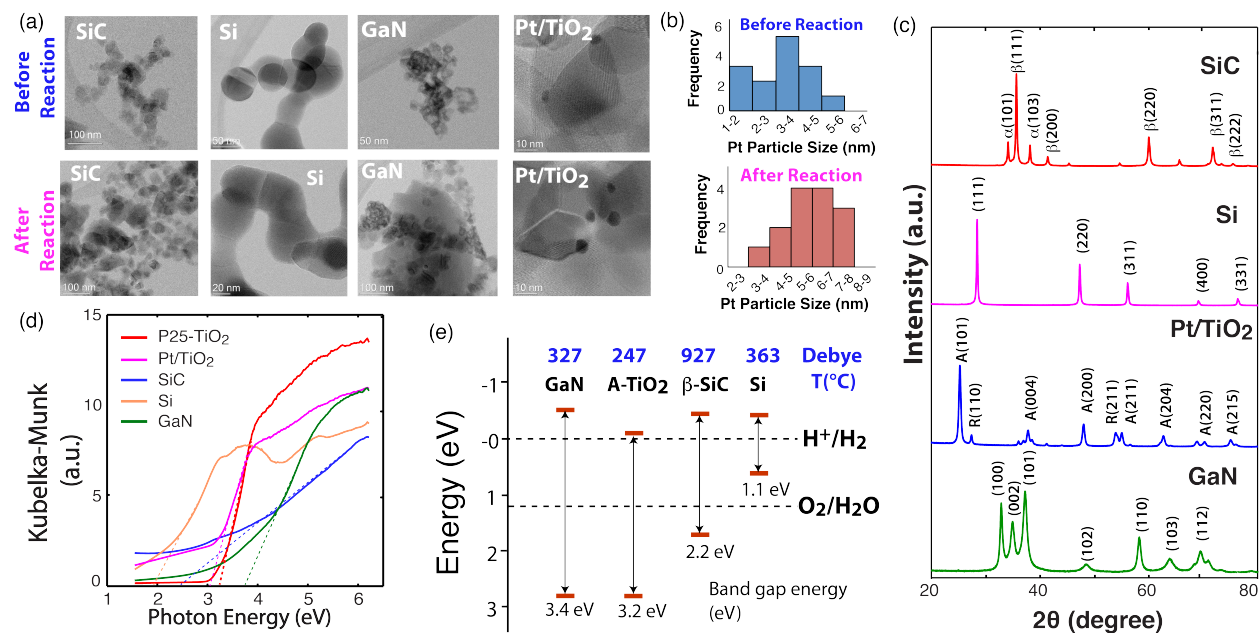


Figure 3.1: (a) TEM images of catalysts before (top) and after (bottom) reaction for approx. 12 hours (b) Pt particles sizes on TiO₂ support before (top) and after (bottom) under reaction conditions (c) XRD diffraction patterns for as-synthesized SiC, Si, Pt/TiO₂, and GaN (d) Tauc plot from diffuse reflectance UV-vis analysis and (e) Band gap energies and band edges (CB bottom and VB top) of the selected semiconductor photocatalysts vs. NHE at pH = 7. Data from refs. [182, 111].

Powder X-ray diffraction (XRD) patterns of as-synthesized and pretreated catalysts before testing in the photoreaction are presented in Figure 3.1(c). Results over Si and GaN suggested phase-pure crystalline structure, while mixed beta and alpha phase crystalline structures (roughly 85% beta and 15% alpha) were observed over SiC. Mixed anatase and rutile crystalline phases (72% anatase, 28% rutile) were encountered over Pt/P25-TiO₂, as expected. XRD reflections for Pt were not detected, likely because Pt particle size (avg. 3-4 nm) was below the detection limit. Diffuse reflectance UV-vis spectroscopy (DRUVS) analysis of as prepared catalysts was performed using Kubelka-munk analysis method to determine band gap energies (see Figure 3.1(d)). The measured band gap energy of all four

photocatalysts shown in Table 3.1 below are equal or close to the reported values in the literature [111, 172]. Si and SiC both showed broadband absorption (measured band gap energies of 1.9 and 2.5 eV, respectively), suggesting the potential of these materials to utilize infrared (IR) absorption ($\lambda > 800\text{nm}$, $\sim 49\%$ of solar spectrum) heating under autogenous elevated temperature reaction conditions. On the contrary, TiO_2 and GaN (measured band gap energies of 3.2 and 3.7 eV, respectively) showed absorption mainly in the UV region. Addition of Pt to TiO_2 caused the redshift of adsorption onset, exhibiting some absorption in the visible region. Alignment of the valence band maximum (VBM) and conduction band minimum (CBM) of GaN, SiC, and Si are such that a moderate driving force for H^+ reduction is present (see Figure 3.1(e)). On the other hand, CBM of TiO_2 presents minimal H^+ reduction driving force, thus the need for Pt addition. The valence band maximum of all photocatalysts besides Si are well suited for O_2 evolution. The individual surface areas of each catalysts before reaction were measured as 9.4, 50, 23, and $14 \text{ m}^2/\text{g}$ for SiC, Si, Pt/ TiO_2 , and GaN, respectively. These results are presented in Table 3.2.

Table 3.1: List of measured band gap energies for selected photocatalysts via diffuse UV vis analysis and reported band gap energies[182, 111]

Catalyst	Measured band gap (eV)	Reported band gap (eV)
3C-SiC	2.5	2.3
Si	1.9	1.1
TiO_2	3.2	3.2
Pt/ TiO_2	3.0	3.0
GaN	3.7	3.4

Table 3.2: Surface area of photocatalysts (m^2/g) and total surface area of 40 mg of catalysts

Catalyst	Surface Area (m^2/g)	Total Surface Area (m^2)
SiC	9.4	0.4
Si	50	2.0
Pt/TiO ₂	23.0	0.9
GaN	14	0.5

3.3.2 Control Experiments

Control runs in both gas phase flow and batch reactors were a primary focus to ensure that the carbonaceous products are originating from the supplied CO_2 reactant. Because CO_2 and H_2O are thermodynamic minimum products, if any other organics are present, they will be preferentially consumed yielding fictitious results. Therefore, the cleanliness of the reactor and catalysts must be directly verified. In general, this is a significant problem in the field at this time. A small selection of studies have begun to draw a focus directly on this problem [185, 42, 190]. In an attempt to avoid this issue, several control reaction tests were performed to ensure that the products observed were indeed produced from CO_2 and H_2O (See Figure 3.2(a)). The purity of the SFE grade CO_2 and doubly distilled Milli-Q H_2O were both checked directly using GC with FID. No organics were detected. Control experiments were performed in both batch and flow reactors of similar all-metal construction. The cleanliness of the reactors was checked by performing reactions with CO_2 , H_2O , and illumination without catalyst present in the reactor. The reactor was initially heated to 150°C for these tests. No products were observed in these test cases. Optical grade crushed and sieved quartz SiO_2 powder was calcined for cleaning and utilized as a solid diluent for the catalyst bed, thus it was also tested alone with CO_2 and H_2O under irradiation. No products were observed in this case either. Control runs with catalyst present using only CO_2 or only H_2O were also performed.

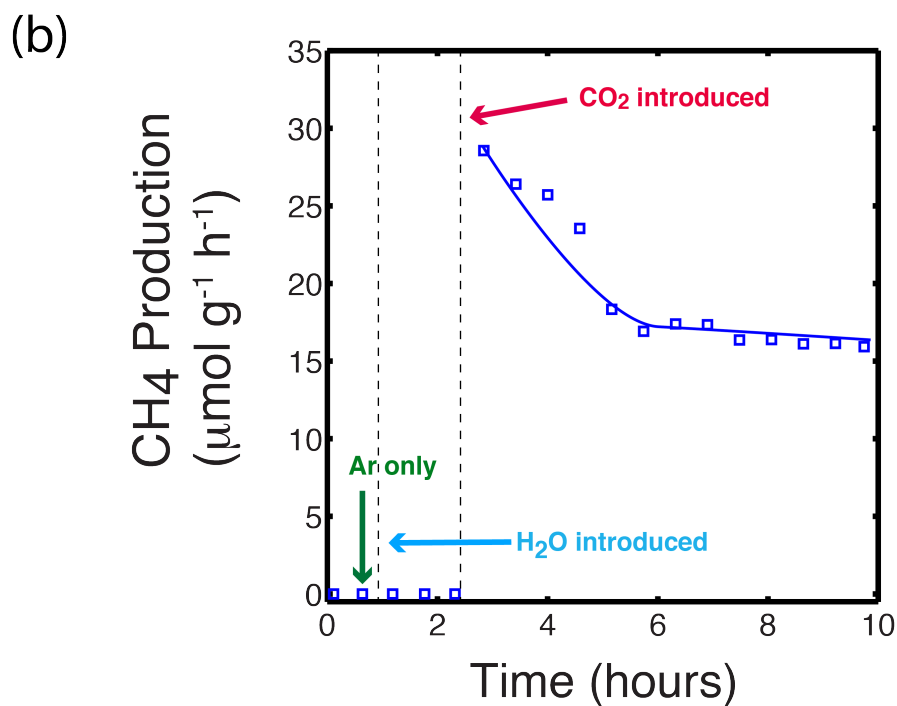
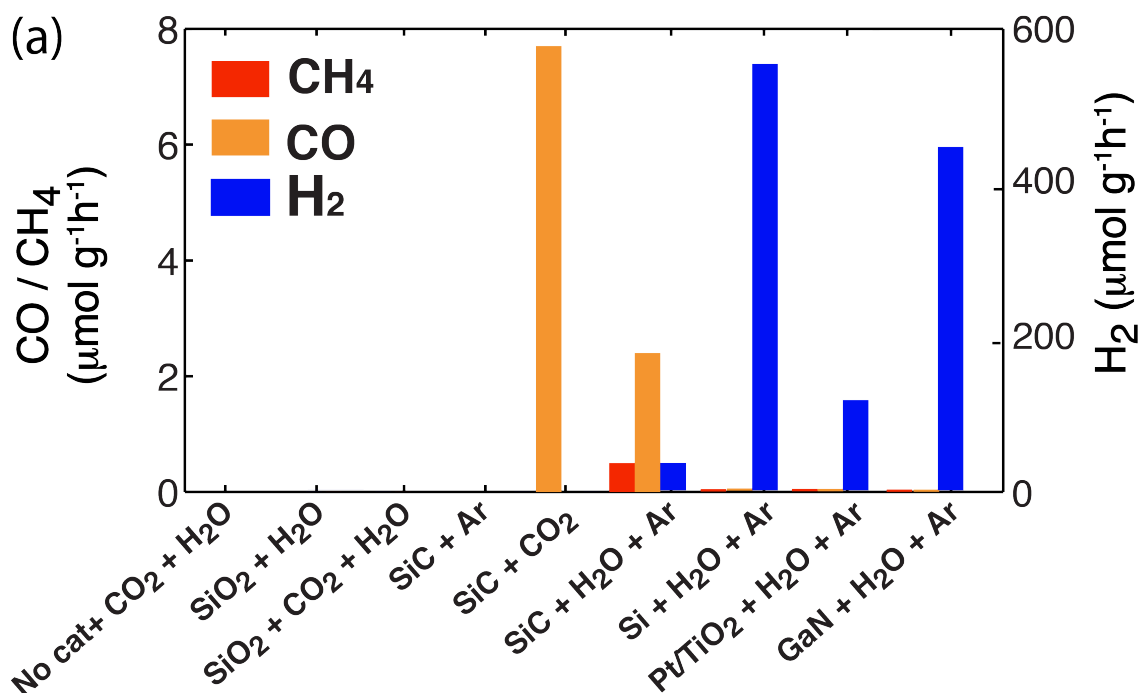


Figure 3.2: (a) Control tests over four materials investigated to ensure an organic free reaction system and (b) Photocatalytic experiment to verify the origin of C in CH₄. Catalyst was illuminated throughout the run. In the first hour, only argon was introduced. From hour 2-3, only argon and H₂O were introduced. Only after the SFC pure CO₂ was introduced at hour 3 did the evolution of CH₄ take place.

Reactions using 10 uL of H₂O and a backfill of Ar over SiC, Si, GaN, and Pt/TiO₂ under illumination for two hours showed that H₂ was the only product observed over GaN, Pt/TiO₂, and Si. Over SiC, trace amounts of CO₂, CO, and CH₄ along with the major product H₂ were observed. With only CO₂ and catalyst present in the reactor (no H₂O present), CO was observed as the only product over SiC. SiC, the top performer of the study, was further tested under three different flow reaction conditions under illumination – with Ar only, Ar and H₂O, and then CO₂ and H₂O (See Figure 3.2 (b)). Again, only a trace amount of CH₄ was observed. Only after the introduction of CO₂ with H₂O and illumination was CH₄ observed at appreciable levels. These results suggest that the CH₄ and CO encountered in our catalytic performance tests is a photocatalytic product of CO₂ and H₂O. Studies utilizing isotopically labeled CO₂ as a reactant to further confirm the origin of the carbon in products are underway currently.

3.3.3 Activity Trends

Results of autogenous temperature photocatalytic reactions at elevated temperatures (350°C) using Pt/TiO₂, GaN, SiC, and Si are considered first (see Figure 3.3). Rates have been normalized by catalyst weight and surface area. In general, results show that all four catalysts are able to perform catalytically under the concentrated solar irradiation condition at significantly elevated temperature despite the relatively low Debye temperatures of TiO₂, GaN, and Si. Indeed, dramatically improved activity in the production of all major products (CH₄, CO, and H₂) was encountered in comparison to published studies of the same catalysts tested at ambient under condensed aqueous phase reaction conditions [85, 5, 115, 160, 76, 120, 121]. It is important to note that none of the catalysts have been optimized for activity or selectivity up to this point. apparent quantum yield (AQY in %) over selected materials calculated from initial rate and calculated reaction enthalpy gain at 350°C reaction temperature are presented in Tables 3.3 and 3.4, respectively.

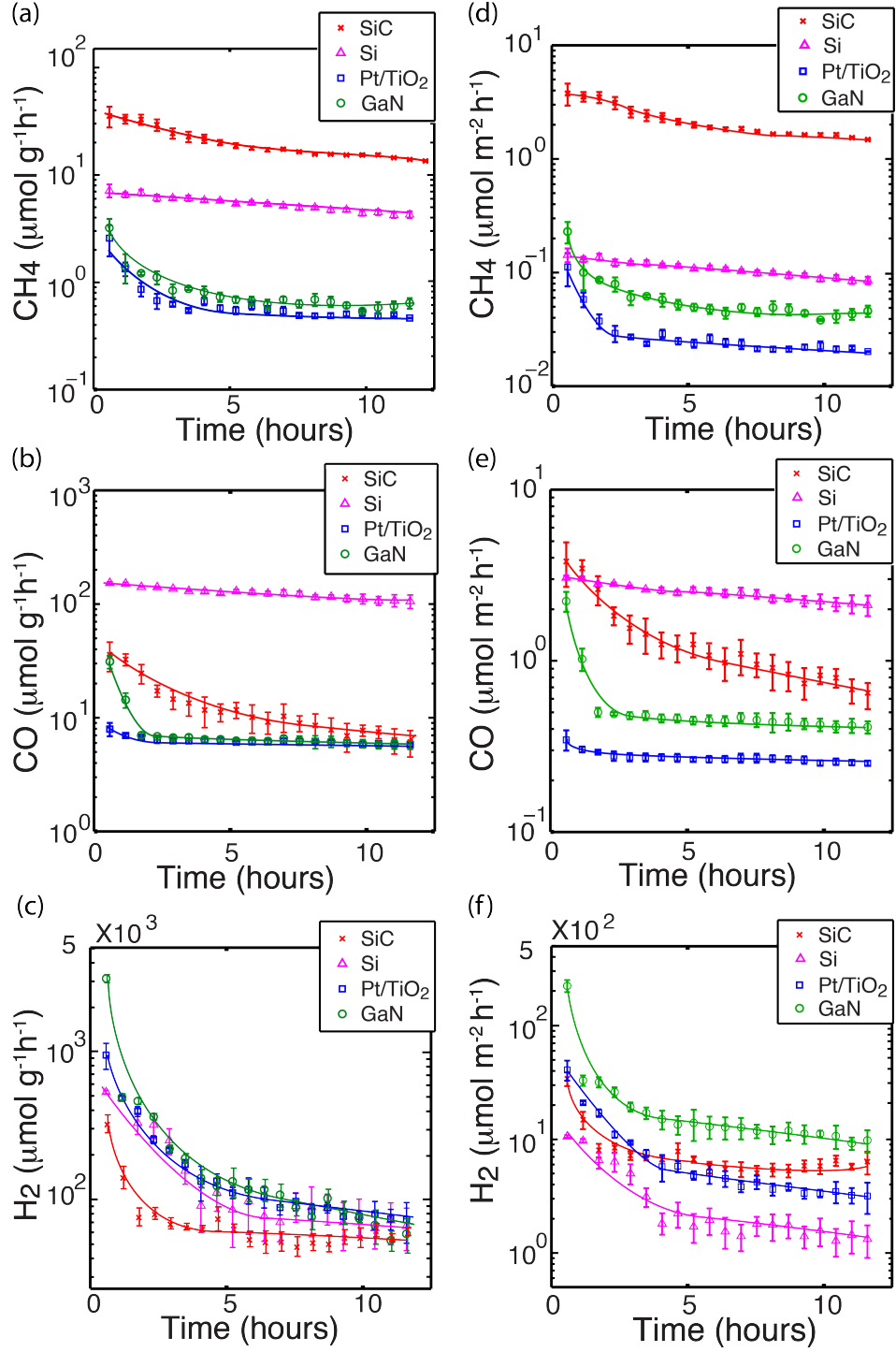


Figure 3.3: (a) CH₄ production ($\mu\text{mol g-cat}^{-1}\text{h}^{-1}$), (b) CO production ($\mu\text{mol g-cat}^{-1}\text{h}^{-1}$), (c) H₂ production ($\mu\text{mol g-cat}^{-1}\text{h}^{-1}$), (d) CH₄ production ($\mu\text{mol m}^{-2}\text{h}^{-1}$), (e) CO production ($\mu\text{mol m}^{-2}\text{h}^{-1}$), and (f) H₂ production ($\mu\text{mol m}^{-2}\text{h}^{-1}$), over selected materials.

Table 3.3: Highest apparent quantum yield (AQY in %) over selected materials calculated from initial rate. AQY at steady state are shown in parentheses.

Product	SiC	GaN	Pt/TiO ₂	Si
H ₂	0.6 (0.1)	25 (1.7)	4.4 (0.5)	0.5 (0.1)
CH ₄	0.3 (0.1)	0.1 (0.02)	0.05 (0.01)	0.03 (0.02)
CO	0.1 (0.03)	0.5 (0.03)	0.1 (0.05)	0.3 (0.2)

Table 3.4: Calculated reaction enthalpy gain at 350°C

Catalyst	ΔH_{rxn} at 350°C (kJ)	Enthalpy input (kJ)	Enthalpy gain (%)
SiC	0.1	31.6	0.4
GaN	0.8	9.2	8.5
Pt/TiO ₂	0.2	14.5	1.6
Si	0.2	53.8	0.3

Photocatalytic results towards CH₄ production followed the trend SiC > Si > GaN > Pt/TiO₂. We found that SiC exhibited the highest activity towards hydrocarbon production and a relatively low rate of deactivation. The initial activity for CH₄ production of 35.5 $\mu\text{mol g}^{-1}\text{h}^{-1}$ was followed by a steady-state activity of 13.5 $\mu\text{mol g}^{-1}\text{h}^{-1}$ after 12 hours of reaction. In the case of Si, the initial rate of CH₄ production was 7.2 $\mu\text{mol g}^{-1}\text{h}^{-1}$ and steady-state production at 4.5 $\mu\text{mol g}^{-1}\text{h}^{-1}$ after 12 hours of reaction. P25-TiO₂ exhibited no activity towards CO₂ photoreduction when it was properly cleaned before use, as expected. The use of properly cleaned P25-TiO₂ as a control experiment to check for the cleanliness of reactor and catalyst is suggested for any study of CO₂ photocatalytic reduction. Addition of 1.0wt% Pt to TiO₂ produced an initial rate of CH₄ production of 2.6 $\mu\text{mol g}^{-1}\text{h}^{-1}$ and a final steady-state rate of 0.5 $\mu\text{mol g}^{-1}\text{h}^{-1}$. The performance of GaN in the production of CH₄ was initially 3.2 $\mu\text{mol g}^{-1}\text{h}^{-1}$ and degraded to a steady-state production rate of 0.7 $\mu\text{mol g}^{-1}\text{h}^{-1}$. Focusing on the most effective catalyst for CH₄ production, SiC, at a rate of

$\sim 35.4 \mu\text{mol g}^{-1}\text{h}^{-1}$ CH_4 , is the highest encountered for proven-organic-free systems. The next highest rates reported for verifiable organic-free systems are over an order of magnitude less [85, 5]. Many others, not directly cited here for obvious reasons, suffer from significant organic contamination and fictitious results.

Trends in CO production activity showed Si metal to be the top performer followed by SiC, GaN, and then Pt/TiO₂. Si also exhibited impressive stability under reaction conditions. Si exhibited catalytic CO production of $153.1 \mu\text{mol g}^{-1}\text{h}^{-1}$ and a steady-state rate of $105.7 \mu\text{mol g}^{-1}\text{h}^{-1}$ after 12 hours. SiC showed an initial rate of CO production of $35.8 \mu\text{mol g}^{-1}\text{h}^{-1}$. However, deactivation lead to a reduction of CO production to $6.7 \mu\text{mol g}^{-1}\text{h}^{-1}$ after 12 hours of reaction. CO production over GaN was $31.2 \mu\text{mol g}^{-1}\text{h}^{-1}$ initially, but suffered rapid deactivation in the first two hours to a steady-state production rate of $6.0 \mu\text{mol g}^{-1}\text{h}^{-1}$. CO production over Pt/TiO₂ at the beginning of the runs was $7.9 \mu\text{mol g}^{-1}\text{h}^{-1}$ and reduced marginally to $5.8 \mu\text{mol g}^{-1}\text{h}^{-1}$ over the 12 hour run. The rate of CO production over Si nanoparticles ($153.2 \mu\text{mol g}^{-1}\text{h}^{-1}$ CO) is also amongst the highest rate reported for CO production in CO₂ photocatalytic reduction by H₂O when compared to organic-free systems. Our rates are surpassed by only one study using similar nanoparticle Si at a rate of $250 \mu\text{mol g}^{-1}\text{h}^{-1}$ CO under 15 suns, but H₂ was employed as a reactant which may improve rates by limiting surface poisoning by oxygen species [160]. Other clean studies that utilized In₂O_{3-y}(OH)_y on Si nanowires ($\sim 22 \mu\text{mol g}^{-1}\text{h}^{-1}$ CO) and GaN nanowires ($\sim 47 \mu\text{mol g}^{-1}\text{h}^{-1}$ CO) show activity nearing that of our system [76, 5].

Photocatalytic activity towards H₂ production followed the trend GaN > Pt/TiO₂ > Si > SiC. Pt-free TiO₂ was inert towards H₂ production, as expected. GaN showed the highest initial rate of H₂ production of all materials at $3142 \mu\text{mol g}^{-1}\text{h}^{-1}$, yet it also suffered from rapid performance loss down to a rate of $30.5 \mu\text{mol g}^{-1}\text{h}^{-1}$ after 12 hours under the CSPR conditions. Over Pt/TiO₂, we encountered appreciable H₂ production at an initial rate of $942.4 \mu\text{mol g}^{-1}\text{h}^{-1}$. The catalytic performance of Pt/TiO₂ also degraded rapidly over the first five hours resulting in a steady-state rate of $116.0 \mu\text{mol g}^{-1}\text{h}^{-1}$. H₂ production over Si metal was moderate at a rate of $529.6 \mu\text{mol g}^{-1}\text{h}^{-1}$ initially, and degraded rapidly to a rate of $111.0 \mu\text{mol g}^{-1}\text{h}^{-1}$ after seven hours and to $63.5 \mu\text{mol g}^{-1}\text{h}^{-1}$ near the end of the 12 hour run. SiC showed the lowest rate of H₂ production out of all four materials. A rate

of $320.5 \mu\text{mol g}^{-1}\text{h}^{-1}$ was found initially. H_2 production rate reduced to $51.5 \mu\text{mol g}^{-1}\text{h}^{-1}$ after seven hours. All four catalysts exhibited rapid catalyst deactivation within the first five hours of the runs. Si, GaN, and Pt/TiO₂ exhibited continued deactivation near the end of the 12 hour run. SiC appeared to reach a steady-state after approximately 4 hours. In the production of H_2 , an enhancement of rate is also seen under the CSPR conditions. GaN, in our study, produced rates of $3000+ \mu\text{mol g}^{-1}\text{h}^{-1}$ H_2 . Whereas, GaN at lower temperature, in highly optimized RuO₂/GaN:ZnO and Rh_{2-y}Cr_yO₃/GaN:ZnO systems, exhibited rates of $\sim 3200 \mu\text{mol g}^{-1}\text{h}^{-1}$ under UV-vis and $\sim 900 \mu\text{mol g}^{-1}\text{h}^{-1}$ under visible only radiation [120, 121].

Oxygen evolution is expected over all catalysts except Si where the VBM is situated above the oxygen oxidation potential. However, measuring O₂ evolution using our gas phase flow reactor setup was not possible while tracking H_2 evolution. This was due to the preferential use of argon carrier gas to enhance the TCD detector sensitivity towards H_2 and the lower detection limit of approximately $\sim 500 \mu\text{mol g}^{-1}\text{h}^{-1}$ for O₂ in this condition. Despite this lack of information, it is still useful to discuss the theoretical ability of the catalysts to evolve O₂. Pt/TiO₂ and GaN are both expected to evolve O₂ due to their lower surface reactivity towards oxygen and their appropriately aligned VBM. Despite the VBM alignment of GaN, EDS analysis showed significant oxidation of the solid to nearly 50:50 N:O after reaction. This may have been driven by the elevated temperatures or preferential filling of holes due to elevated temperature. SiC, with its greatly enhanced surface reactivity towards oxygen, may suffer from surface oxidation even though its VBM is aligned such that oxygen may be oxidized. Si, very likely cannot complete the photocatalytic reaction unless a z-schema is utilized through the addition of an oxygen-evolution co-catalyst. XPS analysis of SiC and Si after reaction show that surface oxidation does occur, yet is limited to roughly 10-11% after 8 hours under reaction conditions (See Figure 3.4). More detailed discussion of the XPS data follows in the deactivation section.

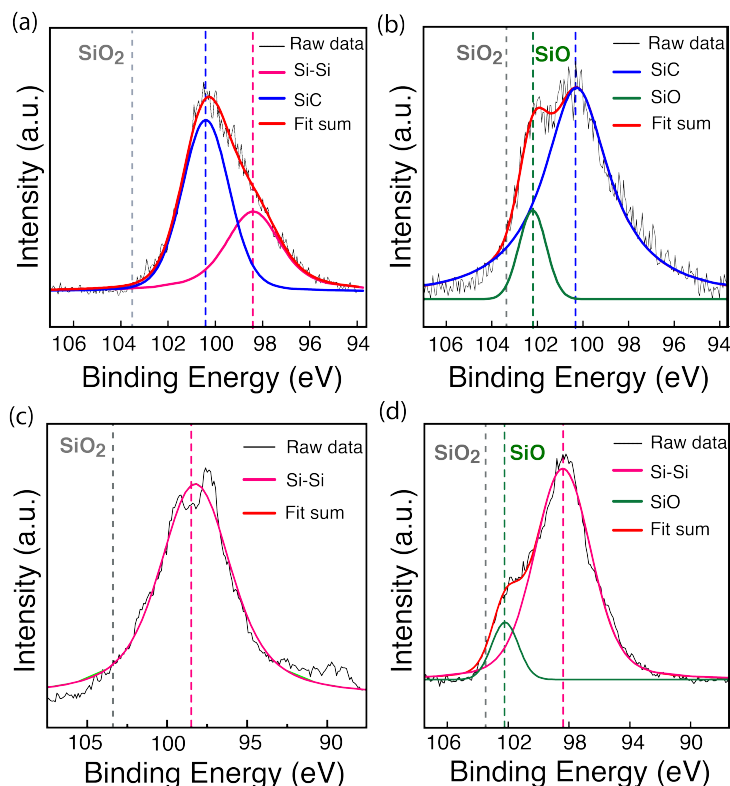


Figure 3.4: Si 2p XPS spectra of (a) SiC pre-reaction, (b) SiC post-reaction, (c) Si metal pre-reaction, and (d) Si metal post-reaction. Oxidation of $\sim 10\text{-}11\%$ was observed after catalysts subjected to reaction conditions for 8+ hours. Si of either SiC or Si does not fully oxidize to SiO_2 under reaction conditions, but instead a suboxide of SiO observed. Pure SiO_2 and SiO peak positions are indicated using grey dashed line at 103.5 eV and green dashed line at 102.3 eV, respectively.

3.3.4 Investigation of Catalyst Deactivation

An understanding of the surface-bound reaction intermediates that contribute to catalyst deactivation is still lacking due to unknown reaction mechanisms, thus we focus on correlating structural and compositional changes and surface chemistry with catalyst deactivation. In general, surface oxidation of GaN, SiC, and Si and loss of Pt-TiO₂ interface sites through Pt particle growth are likely sources for catalyst activity loss. As both Pt and TiO₂ sites are likely needed to successfully hydrogenate and activate CO₂, it is reasonable to suggest that the Pt-TiO₂ interface is the catalytically active site. The growth of Pt particles from a mean diameter of 3-4 nm to 5-7 nm over 12 hours of reaction corresponds well with the loss of catalytic activity. Carbonate formation on the TiO₂ surface may also contribute to

deactivation [190, 49], but these species were not sought via spectroscopy in our studies. CO poisoning of Pt sites may also be possible [4]. GaN, on the other hand, suffered oxidation under reaction conditions to a final composition of $\text{GaN}_{0.65}\text{O}_{0.52}$ indicating significant oxygen incorporation. Due to the elevated surface reactivity of GaN in comparison to TiO_2 , elevated temperature conditions, and a significant thermodynamic driving force for Ga oxidation, it is not surprising that oxidation occurs. Surface oxidation is also accompanied by a reduction in general surface reactivity, which may affect the ability of the catalyst to produce critical intermediates that facilitate C–O cleavage and CO and CH_4 production.

Deactivation over SiC and Si followed less aggressive trends in the production of CH_4 and CO, yet were equally rapid in H_2 production in comparison to other catalysts. Elemental analysis of the surfaces of SiC and Si by XPS indicated a relatively limited degree of oxidation occurred under reaction conditions ($\sim 10\%$) after 8 hours reaction time. Si core level shifts show that only partial oxidation occurs over both materials to produce the sub-oxide of SiO. No signal associated with the full oxide of SiO_2 was detected. This indicates the reaction environment may inhibit full oxidation due to photon absorption effects driving surface reduction. Electron escape depth effects in XPS inhibit determining whether the oxide layer is homogeneously distributed throughout the sampling depth or a more oxygen-rich shell. Despite the presence of sub-oxide layer, both SiC and Si still retained photocatalytic activity towards CO_2 reduction over 12+ hours under reaction conditions. Longer reaction tests of ~ 20 hours for SiC were performed to further investigate deactivation and no significant change in the deactivation order was encountered for CH_4 (see Figure 3.5). The significant deactivation of the catalysts towards H_2 evolution indicates the oxidation affects this portion of the reaction most significantly potentially suggesting specific reaction sites for hydrogenation vs. H–H coupling. Structural changes in SiC were mostly undetectable. Minor agglomeration of the Si nanoparticles was evident after reaction (see Figure 3.1 (a) and EDS mapping in Figure 3.6). Decoration of the surfaces of SiC and Si with strongly bound reaction intermediates or spectator species may also be responsible for the observed deactivation, but the presence of these species was not investigated.

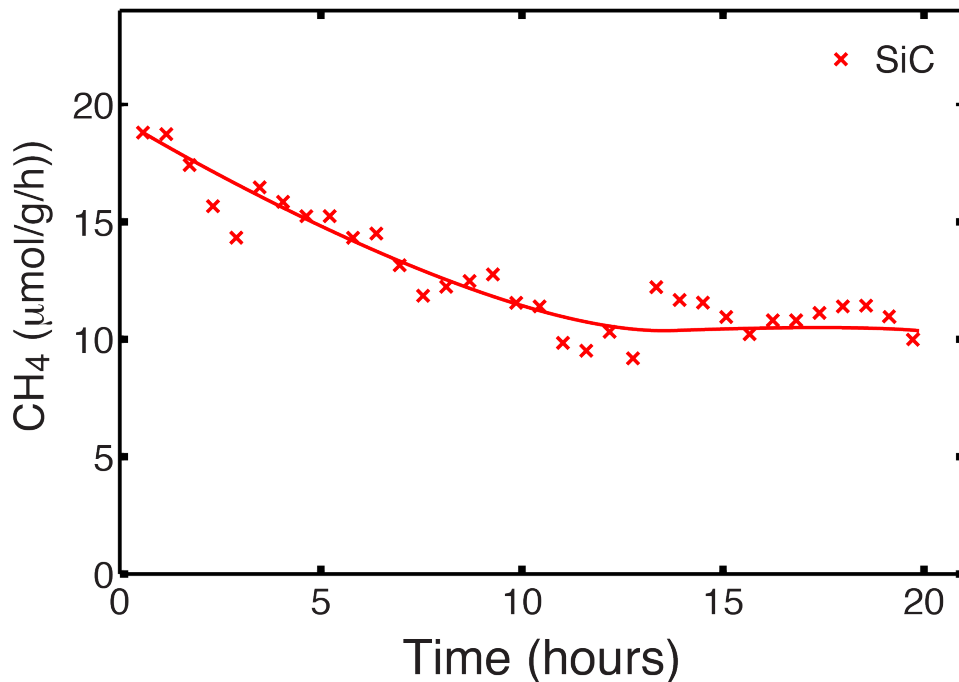


Figure 3.5: Photocatalytic CO₂ reduction over SiC run for 20 hours time. Catalyst still stable under reaction conditions at the end of 20 hours.

In an attempt to isolate correlations between CH₄ and CO production, the selectivity between CH₄ production and H₂ evolution (1:8, 1:70, 1:400, and 1:1000+, for SiC, Si, Pt/TiO₂, and GaN, respectively), and the electronic properties of the photocatalysts, no clear trends existed. Considering that all four catalysts have roughly similar CBM alignment with the reduction potential of H⁺, it can be concluded that a purely photochemical view of H⁺ reduction for hydrogenation or H₂ evolution cannot explain the observed activity or selectivity of the suite of catalysts. This lack of correlation has been highlighted for a much larger collection of published photocatalytic CO₂ reduction and water-splitting studies as well further suggesting that factors beyond bulk electronic properties and electron transfer dynamics significantly affect elementary steps in the photocatalytic reaction mechanism [170, 111, 186]. It is suggested that the effect of surface chemistry and the stability of reaction intermediates can partially explain the trends in photocatalytic activity and selectivity. It is also possible that new H-transfer mechanisms may become active over non-oxide/non-nitride semiconductor photocatalysts due to an electronic relaxation of the proton from H₂O

dissociation to either neutral or anionic atomic H — a phenomenon yet to be understood fully [83, 8, 23, 153].

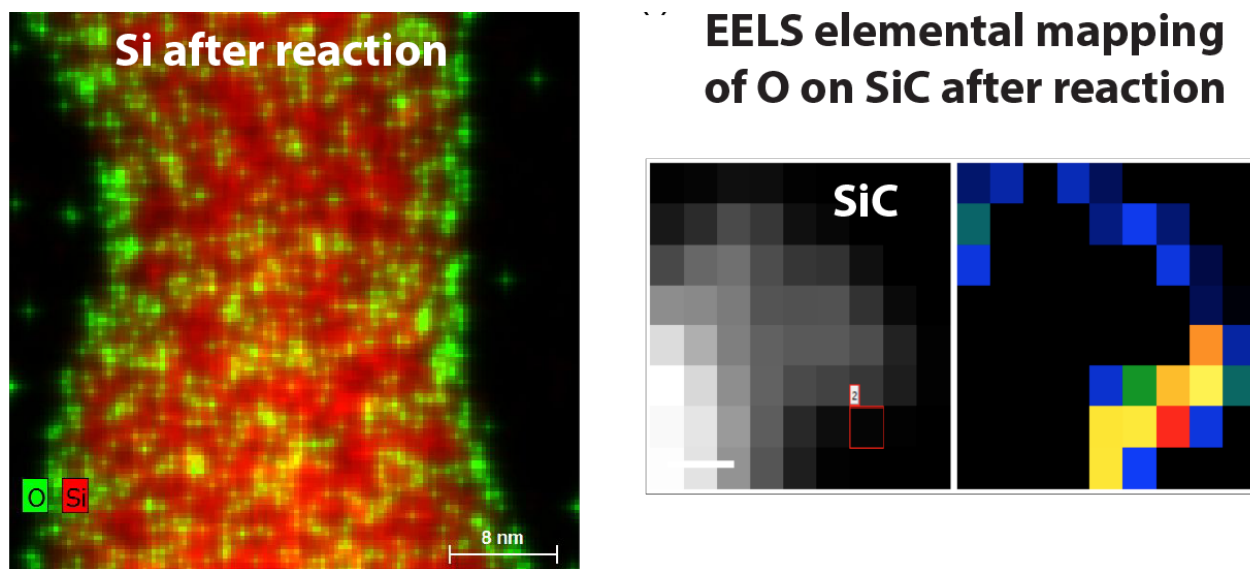


Figure 3.6: (left) EDS mapping of Si particle after reaction conditions for 12+ hours for Si (red) and O (green) distribution, and (right) Oxygen elemental mapping of SiC particle after under reaction condition for 12+ hours via EELS

3.3.5 Substudy at Lower Temperature

To facilitate an understanding of the effect of temperature on activity and selectivity of the two top performer catalysts, SiC and Si, further performance tests were conducted with the IR radiation removed from the light source with a chilled water filter filled with distilled water (see Figure 3.7). This allowed for control of the catalyst bed temperature through ancillary resistive heating. The catalyst bed temperatures began at 120°C, but heated over time to 250°C due to broadband absorption of both SiC and Si. The modified incident radiation at shorter wavelengths (from 240nm to 280nm) likely does not contribute significantly to the observed photocatalysis since both SiC and Si have band gaps excitable at significantly lower energy, 2.3 eV and 1.1 eV, respectively. Results show interesting trends in both promotion and inhibition of hydrogenation and H₂ evolution depending on the catalyst, reaction product, and temperature. Results also suggest that e⁻/h⁺ recombination effects on hydrogenation are clearly evident over Si at 350°C, yet SiC retains its photocatalytic activity.

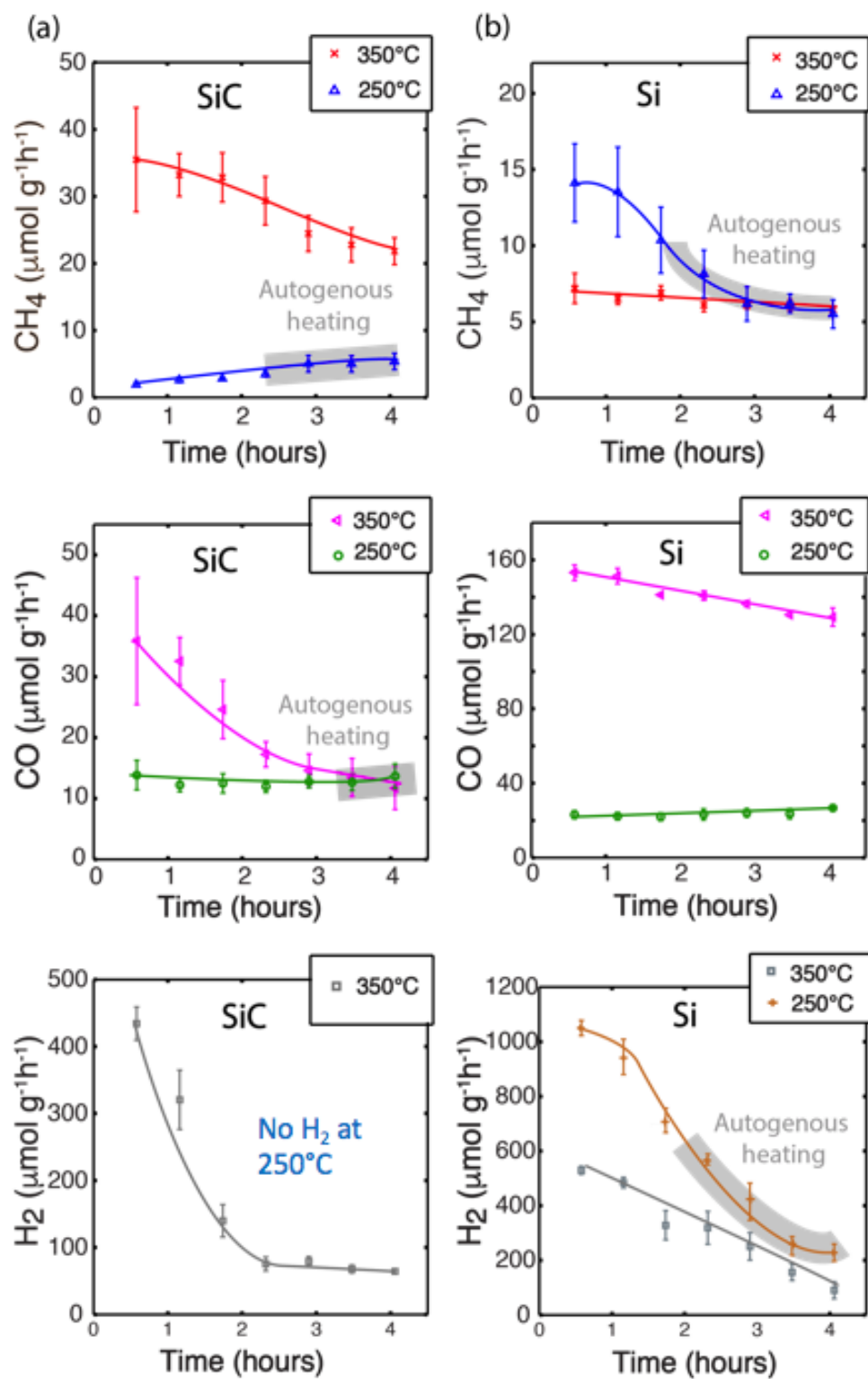


Figure 3.7: a) Photocatalytic CO₂ reduction activity over SiC at 350°C and 250°C reaction temperature. No H₂ production was detected for SiC at 250°C. (b) Photocatalytic CO₂ reduction activity over Si metal nanoparticles at 350°C and 250°C reaction temperature.

Focusing on SiC, a comparison of the activity at low and high temperatures showed a general enhancement of rates for all products. High Debye temperature of SiC may be responsible for enabling this enhancement. Initial CH₄ production at lower temperature (250°C) was an order of magnitude less than at 350°C, which may indicate that C–O cleavage or hydrogenation steps are thermally affected. CH₄ production at lower temperature increased over time as the broadband absorption of the catalyst lead to autogenous heating regardless of the removal of IR radiation from the incident light (see Figure 3.7). A similar effect of temperature on the rate of CO production was also encountered, with rates at 350°C more than double those at 250°C at the beginning of the run. However, deactivation at 350°C led to similar activity as at 250°C after 4 hours reaction time. CO production at the lower temperature was steady throughout the run. Improved CO production at elevated temperatures similarly suggested thermal inputs may be able to drive the cleavage of the 1st C–O bond in CO₂. The production of the CO intermediate may also contribute to the production of CH₄ as well. H₂ production showed the most pronounced changes as a function of temperature. At 250°C, H₂ production was below the detection limit of the TCD using Ar carrier gas (approximately $\sim 40 \mu\text{mol g}^{-1}\text{h}^{-1}$). However, at the elevated temperature, H₂ formation is clearly promoted to appreciable levels despite significant deactivation over time. H₂O dissociation promoted thermally or a simple thermally promoted cleaning of the catalyst surface may partially explain these results. Considering the reactivity to SiC towards H₂O and its dissociation, a surface-cleaning effect is suggested as more likely. All together, these results suggest that thermally promoted steps can directly participate in photocatalytic reactions potentially by producing intermediates whose production are photochemically inhibited.

Results from testing Si at lower reaction temperatures more clearly highlighted the detrimental effect of a low Debye temperature (Si, 363°C) on specific reaction steps at elevated temperature conditions. See Table 3.5 for Debye temperatures of catalysts utilized in this study. Si showed beneficial effects only for CO production and wholly detrimental effects in CH₄ and H₂ production at elevated temperatures. This was evidenced by CH₄ production at 350°C that was nearly 2-3 fold lower than at 250°C at the beginning of the run before autogenous heating occurred. As Si heated autogenously, the rate of hydrogenation

and CH₄ production were concomitantly reduced to a similar steady-state rate as that measured at 350°C. In the production of CO, a large thermal effect led to almost an order of magnitude higher rate at 350°C vs. 250°C. Contrasting this increase with the decrease in CH₄ production suggests that hydrogenation is dominantly photochemical in nature and first C–O cleavage may be thermally promoted by the innate surface chemistry of Si. Therefore, in this case, CH₄ would be promoted at lower temperature reaction conditions that allow for hydrogenation activity to be sustained while still thermally promoting 1st C–O cleavage. H₂ production showed similar effects as CH₄ production in that hydrogen coupling was limited at elevated temperatures likely due to rapid e[−]/h⁺ recombination. The rate of H₂ production at 350°C was approximately half of that at 250°C. At either temperature, the catalyst deactivation towards H₂ production was similar. The effects of Debye temperature and e[−]/h⁺ recombination vs. thermally promoted reaction steps are difficult to decipher with respect to organic intermediates, yet the effect on hydrogenation and H₂ evolution is clear.

Table 3.5: List of Debye temperatures for selected photocatalysts. Nonradiative, multiphonon recombination of photogenerated charge carriers are significant when the reaction temperature reaches the Debye temperature [116]

Catalyst	Debye Temperature (Θ , °C)
3C-SiC	927
Si	363
TiO ₂	247(A), 327 (R)
GaN	327

3.3.6 Thermocatalytic CO₂ Reduction by H₂O or H₂

Thermocatalytic reactions using CO₂ and H₂O or CO₂ and H₂ were performed to determine the contribution of purely thermal reaction mechanisms to the observed photocatalytic results (see Figure 3.8). Reactions were performed from 120°C up to 600°C. Reactions

with just CO_2 and H_2O suggest that a minority of CH_4 can be produced thermally at temperatures above 300°C , yet rates are not comparable to those of the photocatalytic system. Thermal production of CO and H_2 over Si was significant and expected due to the reactivity of Si towards oxygen. In a purely thermal reaction environment, the production of SiO_2 is expected. This contrasts with the sub-oxide SiO species detected after photocatalytic reaction conditions via XPS suggesting photo-induced inhibition of the total oxidation of Si to SiO_2 . Regardless, the concept of the production of CO intermediates and the driving of C-O cleavage thermally is also supported by these results. Thermally produced CO and H_2 over SiC was also encountered, yet rates indicate the photon energy inputs greatly enhance these rates by over an order of magnitude. Again, SiO_2 is expected to form over SiC under purely thermal conditions, yet via XPS, only a sub-stoichiometric SiO that remained catalytically active was encountered. Reactions with CO_2 and H_2 show similar effects in CO production over Si and SiC indicating a clear need for photon-driven hydrogenation steps. Over Pt/TiO_2 with H_2 present, CO_2 hydrogenation to CH_4 was possible even under thermocatalytic conditions (see Figure 3.8(e)).

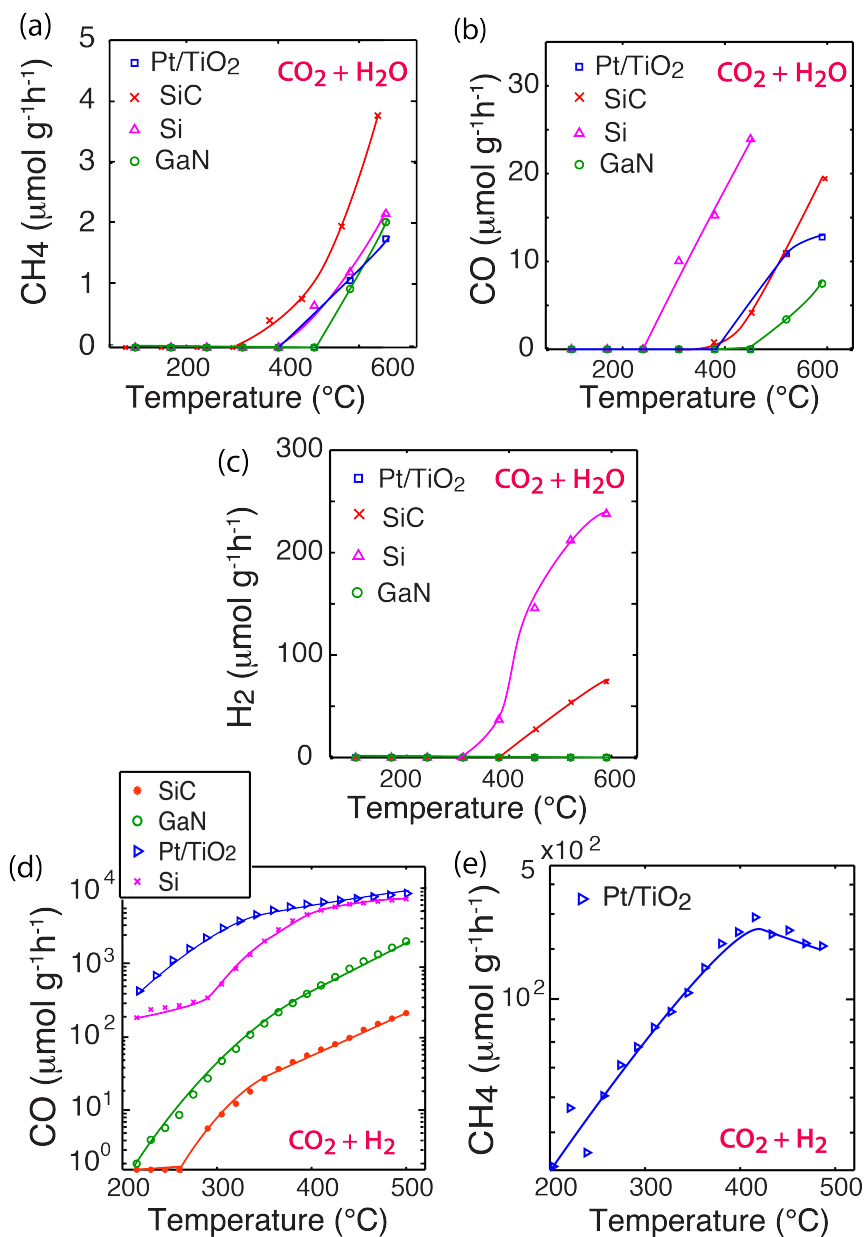


Figure 3.8: (a-c) Thermocatalytic CO₂ reduction over selected materials for a temperature range of 100-600°C using H₂O (CO₂ to H₂O ratio of 1:10). Minor levels of CH₄ were encountered under thermocatalytic conditions above 300°C, yet the rates are significantly lower compared to photocatalytic conditions. (d-e) Thermocatalytic CO₂ hydrogenation with H₂ over a temperature range of 200-500°C. Note that CH₄ production was only observed over Pt/TiO₂ in this case. Equal volume mixture of CO₂ and H₂ was diluted to 10 vol% using balance Argon.

3.3.7 Computational Study

A selection of results from a complete computational surface chemistry study over the four catalysts will be used to supplement the experimentally-derived understanding of the surface reactivity of the catalysts (see Figure 3.9). The full reaction mechanism analysis will be presented in a companion publication at a later date. Calculations utilized a classic periodic slab approach using appropriate exchange-correlation functions and approaches to capture the surface chemistry of the semiconductors (see description in Supplemental Information). Dissociative adsorption of H_2 , O_2 , and H_2O along with CO molecular adsorption suggest a clear trend in the surface reactivity of the catalysts that tracks as $\text{SiC} > \text{Si} > \text{GaN} > \text{TiO}_2$. Similarly, the relative stability of reaction intermediates on the path to CH_4 formation were investigated. The stability of the intermediates followed an identical trend as that found in the probe adsorbate investigations. These results combined with observed photocatalytic activity suggest that thermally driven steps over the more reactive catalysts, SiC and Si, are possible. Likewise, the effect of enhanced stability of reaction intermediates in a high energy reaction environment may play a role in facilitating complete reduction of CO_2 to CH_4 . This will be discussed in detail later.

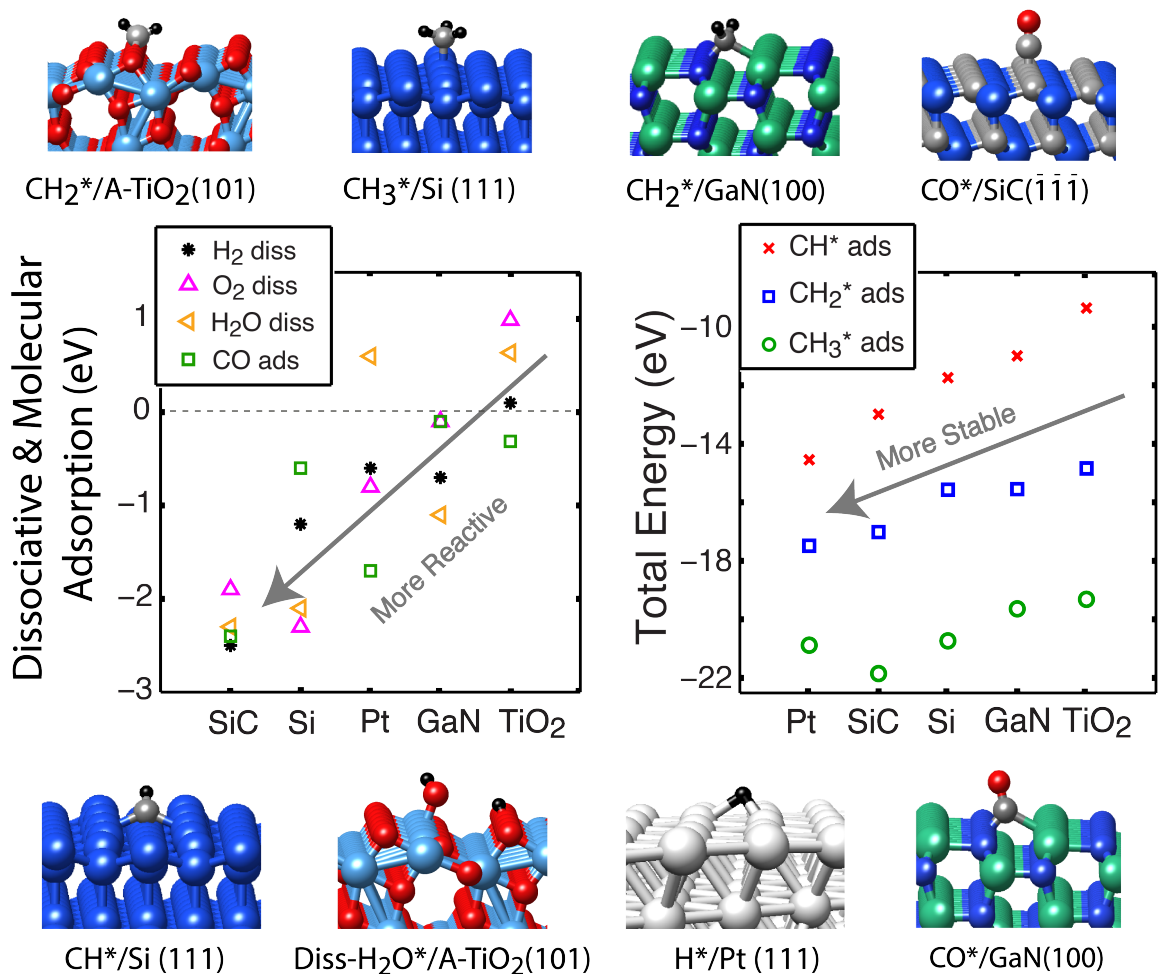


Figure 3.9: (left) Dissociative and molecular adsorption energies of probe molecules over selected materials and (right) Raw thermodynamic stability of key reaction intermediates that are potentially encountered in the reaction pathway towards CH₄ formation. A clear trend in surface reactivity is observed that tracks as SiC > Si > GaN > TiO₂.

3.4 Discussion

To aid in distilling some mechanistic insights, we will review the currently proposed reaction mechanisms for CO₂ reduction in detail in the next chapter to suggest the effect of catalyst selection, gas phase conditions, and elevated temperatures. In summary, three reaction pathways that initiate CO₂ reduction have been proposed and coined the carboxylic, formic, and redox reaction pathways [49, 188, 173, 27] (See Figure 3.10 for mechanism schema). The redox reaction pathway is often considered energetically unfavorable via a purely photochemical route due to the energy needed to transfer an electron to CO₂, yet may be active over non-oxide catalysts that exhibit elevated surface reactivity [154, 13]. The formic (HCOO) and carboxylic (COOH) reaction mechanisms involve a hydrogenation either at the carbon or oxygen of CO₂ to facilitate C–O cleavage [49, 188, 173, 27]. Other mechanisms that consist of multiple hydrogenations of CO₂ before C–O cleavage have also been suggested [32]. These types of mechanisms may be favored over catalysts that perform hydrogenation effectively, yet do not present appropriately elevated surface reactivity or electronic intermediates that facilitate C–O bond cleavage until the bond has been effectively destabilized by hydrogenation. After the first C–O bond cleavage occurs, similar types of reaction pathways that lead to CH₄ are possible, e.g., direct C–O cleavage vs. cleavage that requires pre-hydrogenation of either C or O [49, 32, 195, 7, 6]. The effect of appreciable reverse reaction activity should also be noted, as it may contribute significantly to the products encountered if C–O cleavage occurs and the intermediate produced is consumed leading to CO and H₂ production [87, 129, 50].

The general activity and degree of limited C–O cleavage when performing photocatalytic CO₂ reduction at or near ambient temperatures is best highlighted by reviewing products and rates achieved in other studies that utilize the same catalysts studied herein. Focusing on studies that could be verified to be free of organic contamination through the procedures put forth in publications, a demonstrated inability to cleave the second C–O bond is present [85, 57, 157, 160, 110, 84]. A strong selectivity preference for H₂ evolution rather than hydrogenation is also evident [176, 111]. Published results also indicate that the relative

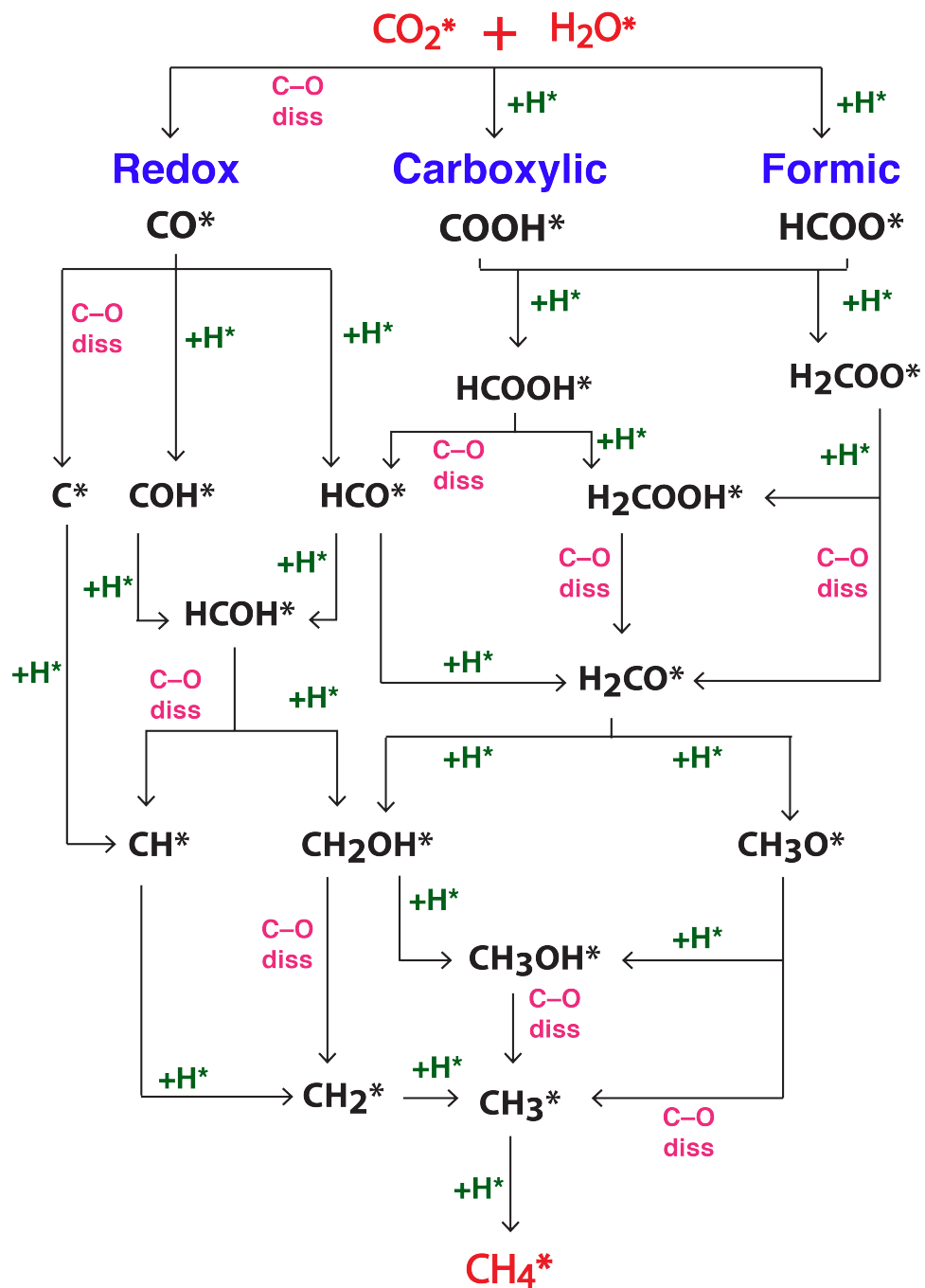


Figure 3.10: Surface reaction pathways that are likely possible in CO_2 photocatalytic reduction with H_2O to produce CH_4 . The reduction mechanism initiates via three main pathways: (i) redox, (ii) carboxylic, and (iii) formic routes.

rate of hydrogenation outstrips 2nd C–O bond cleavage in most cases [85, 57, 110, 157]. For example, partially reduced and well-hydrogenated products such as H₂CO and H₃COH have been reported over SiC (14.3 $\mu\text{mol g}^{-1}\text{h}^{-1}$ H₂CO, 76.4 $\mu\text{mol g}^{-1}\text{h}^{-1}$ CH₃OH). [85, 57] GaN and Si both exhibit activity at low-T that shows preferential 1st C–O cleavage with an inability to perform hydrogenation, as evidenced by CO being the major product in several studies (GaN: $\sim 47 \mu\text{mol g}^{-1}\text{h}^{-1}$, Si: $250 \mu\text{mol g}^{-1}\text{h}^{-1}$, and $\sim 22 \mu\text{mol g}^{-1}\text{h}^{-1}$). [5, 160, 76] In regards to hydrogen fate, GaN greatly favors H₂ evolution at a significant rate, e.g., GaN: $\sim 570 \mu\text{mol g}^{-1}\text{h}^{-1}$. [5] CO₂ reduction studies that report H₂ evolution over SiC and Si are quite limited, but Si nanowires have been shown to be an effective water-splitting catalyst with rates of $\sim 2812 \mu\text{mol g}^{-1}\text{h}^{-1}$. [115] Rates of CH₄ production in published studies are relatively low, e.g., GaN: $\sim 1.3 \mu\text{mol g}^{-1}\text{h}^{-1}$ [5], SiC: trace amounts [85], and Pt/TiO₂ $\sim 0.13\text{--}0.57 \mu\text{mol g}^{-1}\text{h}^{-1}$ [193]. Contrasting these results with our studies next yields many mechanistic insights on the changes that are brought about by the elevated temperature reaction conditions of CSPR CO₂ reduction.

Trends in activity at elevated temperatures for the four materials suggests they fall within two groups: those that are marginally affected and those that significantly benefit from the CSPR environment. Pt/TiO₂ and GaN both showed significant increases in products associated with C–O cleavage and even substantial improvements in H₂ production, yet overall CH₄ production that is still quite low [5, 193, 122, 199]. On the other hand, SiC and Si show disparate changes in CH₄ and H₂ production due to significantly different Debye temperatures yet consistent increase in CO production [76, 160, 85]. In the production of CH₄ and CO, Pt/TiO₂ and GaN clearly present similar mechanisms due to their product distribution and response to elevated temperatures. Likewise, both show an inability to produce carbon-containing intermediates, which further suggests an inability to promote C–O cleavage through hydrogenation via the formic or carboxylic reaction mechanism or insufficient surface reactivity to stabilize reaction intermediates leading to rapid reverse reaction rates (See schema presented in Figure 4.1). The absence of hydrogenated small oxygenates at elevated temperatures further suggests that these catalysts suffer from rapid reverse reactions that are promoted by thermal inputs. In regards to their inability to produce hydrogenated products, both are substantial H₂ evolution catalysts at elevated

temperature, thus production of hydrogenation-active atomic H is demonstrably possible. However, the lack of carbon-containing intermediates may explain the marginal production of CH₄ even in the presence of successful hydrogenation of CO₂ or other intermediates. It is useful to note that the H-transfer mechanisms over both Pt/TiO₂ and GaN appear to be similar and potentially connected to the state of atomic H (protonic) and the stability of atomic H after activation (reduction).

Over SiC and Si, a very different mechanistic picture has evolved. In the competition between C–O cleavage and hydrogenation, SiC is able to thermally promote one or both of these reaction steps to achieve dramatically improved CH₄ production at elevated temperatures in comparison to near-ambient tests where much lower rates were encountered [85, 57, 157]. In contrast, thermal excitation of Si up to 350°C leads to enhanced first C–O bond cleavage, but inhibited hydrogenation and H₂ evolution likely due to low Debye temperature (T = 363°C) and e[−]/h⁺ recombination rates becoming appreciable. Published near-ambient tests of Si as a photocatalyst for CO₂ reduction by H₂O are not available, but results at elevated temperatures using just CO₂ with and without H₂ as a co-reactant agree with our studies [160, 76]. Comparing our results to the rates of these studies is less informative due to mismatch of physical phenomena and the use of H₂ as the reducing agent. However, selectivity towards CH₄ and CO products still dominate, as in our studies. Selectivity towards carbon-carbon coupling for the formation of C₂₊ products has not been demonstrated. Oxygenate products were not encountered in our studies suggesting that either intermediates are readily consumed if they do not progress to CH₄ formation or that 2nd C–O cleavage is kinetically limited compared to hydrogenation promoting CO and CH₄ as the main products. H₂ production as a function of temperature over SiC suggests that H₂O dissociation, second O–H cleavage, or simply a cleaning of the surface are favorably affected leading to enhanced hydrogenation and H₂ evolution.

To better understand the microscopic mechanism effects observed in our study, we review the general surface chemistry of the four photocatalysts considered. The relative reactivity of Pt, TiO₂, GaN, and Si towards oxygen and other simple molecules have been studied extensively in the field of surface science and electronics [46, 73, 70, 141, 28, 83, 25]. The surface chemistry of SiC, on the other hand, is less known to the heterogeneous catalysis

community due to its perceived inertness that stems from a passivating oxide layer [54, 166, 197]. The oxide layer may be readily removed by etching and is slow to reform thus allowing the catalytic chemistry of SiC to be employed. Both experimental and computational studies lead to a relative surface reactivity trend as $\text{SiC} > \text{Si} > \text{GaN} > \text{TiO}_2$ for most adsorbates and elements potentially encountered in the CO_2 reduction reaction (see above refs., Figure 3.3 and 3.8). This trend along with the ability of the catalyst to produce hydrogenation-active atomic H track well with the ability of the catalysts to cleave C–O to produce both CO and CH_4 .

In an attempt to bring the reaction mechanism into focus, we summarize what we believe to be reasonable explanations for the changes in catalytic activity and selectivity brought about by both catalyst and reaction environment temperature. In general, our concept of the reaction environment has developed such that there are two general cases that require different catalyst surface chemistry and reaction environment to produce appreciable observed activity. First, any vibrational barrier component within photocatalytic reaction mechanisms that are active near ambient temperatures must be quite low and appreciably surmountable at temperatures below 100°C . This view further suggests that the reaction intermediates, in general, must be relatively unstable directly after photochemical activation to produce such low vibrational barriers for forward reaction steps. This scenario would also likely result in unstable reaction intermediates that exhibit large exothermic driving forces for their consumption in reverse reaction steps favoring CO_2 and H_2O or CO and H_2 production. Because stabilizing intermediates would build in larger vibrational barriers for forward reactions, it is anticipated that photocatalysts that exhibit fairly low surface reactivity would be most active in this regime. This framework appears to be most suited for breakdown and small molecule formation (water-splitting or CO_2 -splitting), not a many-step, complex synthesis reaction where several surface-intermediate coupling events must occur (artificial photosynthesis or ammonia synthesis).

The second case revolves around catalysts that present elevated surface chemical reactivity such that reaction intermediates are stabilized and larger vibrational barriers for forward reactions are present. The idea being that this stabilization would promote coupling reactions like hydrogenation and carbon-carbon bond formation for higher hydrocarbon

production in the inherently high energy environment of photocatalysis. Stabilization of intermediates may aid in avoiding entropic driving forces that favor H_2 or CO formation over coupling reactions. The ability to produce new reaction intermediates whose production is kinetically limited by difficult photochemical steps or inherently low surface reactivity may also be possible in this case. The detrimental effect of reverse reactions may also be limited by stabilizing reaction intermediates along an overall endothermic reaction pathway. It is also envisioned that new reaction conditions, e.g., elevated temperature and less aggressive chemical potential of H_2O , would be necessary when employing elevated surface reactivity in photocatalysis. For example, H_2O may readily become a surface poison due to its high chemical potential in condensed phase at ambient temperatures. Lastly, it is critical to note that the degree of surface reactivity necessary to enable thermal effects and enhanced stabilization of reaction intermediates in a high energy photocatalytic environment has yet to be established. With these cases in mind, we believe that Pt/TiO_2 and GaN are best understood in the framework of the first case and SiC and Si , in the second. We also believe that the reactivity of SiC and Si are of the degree needed to enable the second case to be observed in practice. Detailed understanding of the reaction mechanism is currently not possible, but we highlight some perceived changes next as they correlate with the established surface chemistry of the selected photocatalysts.

Focusing on H_2O dissociation, established surface chemistry of the catalyst suggests that the driving force for H_2O dissociation via purely thermochemical mechanisms tracks as $\text{TiO}_2 < \text{GaN} < \text{Si} = \text{SiC}$. All are reported to potentially dissociate H_2O at room temperature, yet the latter three present significant driving forces for H_2O dissociation [28, 151, 83, 125, 52, 69]. This dynamic may enhance the supply of atomic H on the catalyst surfaces or present issues with respect to poisoning of the catalyst surfaces by OH^* intermediates. The greatly improved rates of H_2 production over Pt/TiO_2 and GaN at elevated temperatures suggests some aspect of H_2O dissociation is limiting over these catalysts at near-ambient conditions. On the other hand, considering the high reactivity of SiC towards oxygen and water, H_2 production over SiC being undetectable at low temperatures yet appreciable at elevated temperatures suggests a blocking of the surface or an inhibition of second O-H dissociation and a need to clean the catalyst surface. Over Si , the elevated surface reactivity that drives

H₂O dissociation appears to not inhibit the photochemical nature of H₂ evolution at 250°C, yet is inhibited via e⁻/h⁺ recombination at 350°C where the reaction temperature approaches the catalyst Debye temperature (363°C). The availability of hydrogenation-active atomic H approximately tracks with catalyst surface reactivity as SiC > Si > GaN > Pt/TiO₂. This is likely an effect of the stability of atomic H after its activation thermally or photochemically. In general, results indicate that elevated surface reactivity may play a role in promoting H₂O dissociation, the ability of the catalyst to evolve H₂, stabilization of atomic H after its activation, and catalyst inactivity through poisoning.

Enhanced catalyst surface chemistry driving the production of new carbonaceous reaction intermediates not possible or kinetically limited through purely photochemical-only pathways may directly enhance complete CO₂ reduction. Our results suggest that C–O cleavage, both 1st and 2nd for CO and CH₄ production can be promoted significantly over SiC and Si yet only marginally over Pt/TiO₂ and GaN. This phenomenon may indicate that SiC and Si thermally promote 1st and 2nd C–O cleavage producing new reaction intermediates, CO or C, that can then be effectively hydrogenated photochemically to produce CH₄. This effect combined with improved 1st C–O cleavage at 350°C leads to enhanced CH₄ production over SiC, yet only improved CO production over Si due to e⁻/h⁺ recombination effects in hydrogenation. Because both Pt/TiO₂ and GaN do not present appreciable surface reactivity to drive C–O cleavage thermally, their response to elevated temperatures is less. Considering the near-ambient results that show appreciable hydrogenation rates are possible over many catalysts, the effect of driving C–O cleavage steps may be a major contributing factor to the improved CH₄ and CO production at elevated temperatures.

The stabilization of reaction intermediates in the high energy reaction environment of photocatalysis may also aid in promoting hydrogenation and carbon-carbon coupling of organic intermediates and simultaneously lessen unselective H₂ evolution through entropic effects. The relative range of surface reactivity presented by the four catalysts studied suggests that SiC and Si both can stabilize carbon-containing intermediates significantly more than TiO₂ of Pt/TiO₂ and GaN, which correlates well with their ability to produce CH₄. Considering that the reaction being catalyzed is significantly endothermic, it is reasonable to suggest that reaction intermediate stability will be a strong function of

catalyst surface reactivity. Further, the relative endothermicity of the forward reaction steps and exothermicity of the reverse reaction steps would be directly manipulated by catalyst reactivity. Because of the significant energy involved in each reaction step and the environment in general, entropic effects may also be significant and must be limited if more complex products are the aim. Within this conceptual framework, our studies suggest that significant stabilization of reaction intermediates may be necessary to promote CH_4 production and potentially higher HCs by anchoring intermediates and limiting reverse reaction rates. In comparison to thermocatalytic surface reactions, we predict the stabilization needed in photocatalytic synthesis to be far greater due to differences in the magnitude of energy inputs. The selectivity of the catalysts towards CH_4 vs. H_2 partially shows this effect (1:8, 1:71, 1:400, and 1:1000+ for SiC, Si, Pt/ TiO_2 , and GaN, respectively) and tracks well with the relative ability of the catalysts to stabilize intermediates (see Figure 3.9).

Control of the exothermicity and rate of the reverse reaction steps is another aspect of the reaction system that is directly affected by the stability of surface-bound reaction intermediates and catalyst surface reactivity. Our investigations and comparisons with published ambient temperature reaction results suggest that catalysts with elevated surface reactivity may inhibit reverse reactions that consume intermediates that lead to CH_4 production. This is most pronounced in the comparison of the performance results over Pt/ TiO_2 or GaN and SiC or Si. Pt/ TiO_2 and GaN both present moderately low surface reactivity and what appears to be a lack of hydrogenation ability. However, the low CH_4 production may also be caused by unstable reaction intermediates being consumed to form CO and H_2 or CO_2 and H_2O . On the other hand, SiC and Si significantly stabilize intermediates (see Figure 3.9 and Figure 3.11), which limits reverse reaction driving force and slows their unselective consumption. A full DFT surface reaction mechanism analysis for the four catalysts partially confirms this effect and will be discussed in Chapter 4 of this dissertation. As reverse reaction rates have already been a focus of the community [87, 113, 133, 128], it appears that elevated surface reactivity may lend the tunable parameter necessary to limit their activity and effect in photocatalytic synthesis reactions.

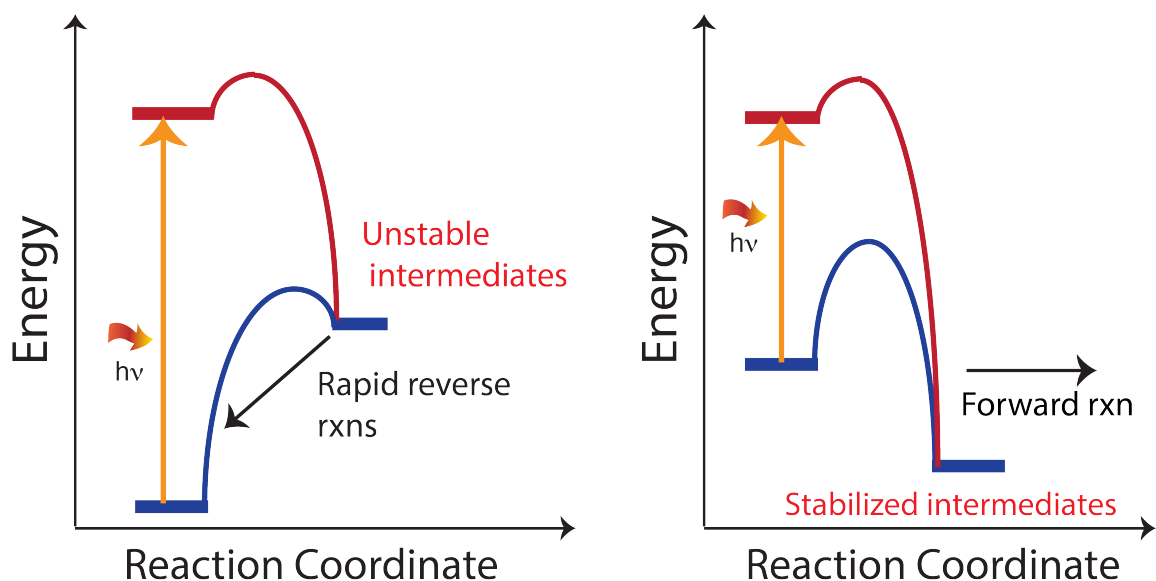


Figure 3.11: Schema to illustrate possible reaction pathways along with potential reaction intermediates towards production of CH_4 from CO_2 and H_2O . Three different reaction pathways initiate CO_2 reduction are presented, namely the carboxylic, formic, and redox reaction pathways. After the first C–O dissociation occurs, similar types of reaction pathways are possible, e.g., direct C–O cleavage vs. cleavage that requires pre-hydrogenation of either C or O towards the formation of final product CH_4 .

The rate and selectivity of hydrogenation of organic intermediates vs. H_2 evolution is another critical aspect of the reaction mechanism that controls quantum efficiency and product distributions. No clear atomic-level fundamental understanding has yet been put forth to explain the trends encountered in this regard. However, we believe it is within reason to suggest that the oxidation state of the atomic hydrogen, how it is oxidized or reduced to neutral hydrogen, the order of reduction vs. transfer, the stability of both the neutral hydrogen and organic intermediates, and the relative abundance of organic intermediates and atomic H on the catalyst surface all are candidate phenomena that may contribute to some degree to the selectivity of the reaction. Our studies indicate that choice of catalyst strongly affects hydrogenation ability and selectivity. Specifically, selectivity as a ratio of $\text{CH}_4:\text{H}_2$ production was found to be approximately 1:8, 1:71, 1:400, and 1:1000+ for SiC, Si, Pt/ TiO_2 , and GaN, respectively. Clearly, this trend does not track with CBM alignment with the H^+ reduction potential or band gap energy. Our follow-up studies focused on this phenomenon have indicated that the oxidation state of atomic H after H_2O dissociation, new H-transfer

mechanisms, and the stability of atomic H after "activation" determine hydrogenation vs. H₂ evolution selectivity. These results will be published in a future report.

3.5 Chapter Conclusions

In summary, these studies lay the foundation for much work to come focused upon understanding the reaction mechanism of photocatalytic CO₂ reduction by H₂O to hydrocarbons and oxygenates at elevated temperatures. Results shown herein hopefully have provided a basis for understanding the photocatalytic CO₂ reduction mechanism such that new catalysts may be selected in a more rational fashion. The greater results of this study indicate that special and inordinately high surface chemical reactivity may be necessary to stabilize reaction intermediates along an ever-increasing endothermic pathway to achieve hydrocarbon production from CO₂ and H₂O; that new reaction intermediates may be accessible through the combination of thermal inputs and enhanced surface reactivity; and that thermal energy inputs can be combined with photon energy within the same reaction mechanisms affecting the overall catalytic rate and product distributions in photocatalytic synthesis. Beyond the production of H₂, CO, and CH₄ shown in this study, these results can be translated to C₂₊ hydrocarbon and oxygenate production as well as photocatalytic NH₃ synthesis. Significant additional work to understand the new H-transfer mechanisms, the role of intermediate stability, carbon-carbon coupling, and nitrogen source for NH₃ production are necessary to move the field of photocatalysis into the realm of practical use at larger scale.

Chapter 4

Photocatalytic CO₂ Reduction by H₂O: Insights from Modeling Electronically Relaxed Mechanisms using DFT

4.1 Overview

This chapter will focus on understanding the reaction mechanisms and energetics determined through a classical ground-state computational surface science approach that will lend insights into the experimentally derived catalytic performance and selectivity differences between SiC and GaN towards hydrogenation and H₂ evolution, respectively. Calculations are compared to experimental results in a condensed aqueous phase near ambient temperature and in elevated temperature gas phase concentrated solar photoreaction environments to draw correlations between surface reaction energetics and experimental performance. Positive correlations found in this study suggest that photocatalyst surface reactivity may play a critical role in driving C–O cleavage and stabilizing reaction intermediates to limit reverse reactions and promote full reduction of CO₂ to CH₄.

4.2 Introduction

Deciphering and controlling heterogeneous photocatalytic synthesis reaction mechanisms is a critical step to enabling the production of fuels and chemicals from sunlight and thermochemically stable molecules like CO_2 , H_2 , and N_2 . Moreover, expanding the understanding of all possible energy sequestration pathways available in photocatalytic environments beyond classical electrochemical reduction and oxidation by excited states may dramatically improve overall efficiency and access to specific products. With respect to efficiency, photocatalysts that utilize lower energy IR radiation or couple with external thermal inputs may dramatically change the landscape of photocatalytic synthesis.

A recent study published by our group focused on understanding the effect of catalyst surface chemistry and autogenously produced elevated temperatures in concentrated solar photocatalytic CO_2 reduction has suggested that both photoelectrochemical and vibrationally-driven reaction steps may be used to sequester a larger portion of the total spectrum of sunlight and promote the full reduction of CO_2 to hydrocarbons [142]. This effect, albeit sparsely demonstrated, has been encountered in photocatalytic oxidation of ethylene over TiO_2 and in CO_2 reduction to CO over Si [175, 160]. Despite CH_4 being the dominant hydrocarbon encountered in clean reaction systems, once the mechanism is understood, catalysts may be designed to promote carbon-carbon coupling for C_{2+} hydrocarbon production.

Efforts focused upon heterogeneous photocatalyst discovery and optimization have dominantly relied upon the bulk electronic properties of materials, properties of the condensed aqueous phase-catalyst interface, and overall thermodynamics of the reactions being performed to predict electron and hydrogen transfer dynamics and catalyst performance in water-splitting and CO_2 or N_2 reduction [114, 176, 170, 30, 48, 159]. This approach has allowed for a good degree of success in the discovery and design of catalysts for water-splitting, but has been significantly less effective directing the design of CO_2 and N_2 reduction catalysts. These trends suggest that mechanistic aspects of the photocatalytic CO_2 and N_2 reduction reaction systems may not be captured well by a purely excited-state and electrochemical-reduction/oxidation treatment of the mechanism. This issue is further

highlighted by recent reports of significantly improved catalyst performance when utilizing concentrated illumination or elevated temperatures that indicate significant catalyst surface reactivity and vibrationally-driven reaction step effects [142, 160, 136, 175]. Prior studies of kinetic isotope effects in hydrogen transfer using D₂O further suggest vibrational barriers are present that would not normally be observed in a reaction mechanism that theoretically involve barriers readily surmountable at room temperature due to excited state chemistry [43, 44, 75]. We now limit our focus to photocatalytic CO₂ reduction.

Recent efforts by others in modelling photocatalytic surface reactions over TiO₂ have employed either an induced Fermi level shift by loading the model slab with additional atomic H or with electrochemical approaches developed in the field of electrocatalysis [92, 91, 48]. Within the context of CO₂ reduction by H₂O over stoichiometric TiO₂, Ji and co-workers utilized atomic-H-laden TiO₂ slabs as model surfaces for the hydrogenation of CO₂ to CH₄ [92, 91]. This approach utilizes the inherent effective electronegativity of TiO₂ to pull electrons from adsorbed atomic H artificially populating states that would otherwise be empty. Significant adsorbate-adsorbate repulsion and a highly reduced TiO₂ electronic structure produced reaction mechanism energetics that suggested TiO₂ would be able to reduce CO₂ to CH₄ without the need for a co-catalyst. In comparing with organic-contamination-free studies of the activity of TiO₂, this approach appears to be unrealistic, i.e., properly designed and cleaned reactors with clean TiO₂ show no activity in the photocatalytic reduction of CO₂ by H₂O only [142, 42, 185].

Another approach using the computational hydrogen electrode framework for studying the photocatalytic reduction of N₂ over Fe-doped, oxygen-vacancy rich, and stoichiometric Rutile TiO₂ (110) model surfaces predicted that only the more reactive oxygen-vacancy rich TiO₂ surface exhibited surface reaction and redox energetics that would suggest a potential for activity in the reaction [39]. Cleavage of the N–N bond was found to still be kinetically limiting and likely not possible near ambient temperature. Several assumptions in this approach may affect the applicability of the use of the computational hydrogen electrode. Specifically, that the reactions are performed in the gas phase in the absence of an electrolyte. This draws into question the energetics associated with the source of H⁺. Most notably the effect of the surface reactivity of the catalyst where H⁺ is bound. As few reliable experimental

studies exist for this reaction system [192, 159], it is still unclear whether this modeling approach is valid or not.

A follow-up study by the same group has suggested that the view of the mechanism has changed, and that carbon contaminants present on the catalyst surface serve as critical co-catalyst radical species that promote activation of N_2 [38]. This suggestion is more in line with the understanding that organic-contamination-free TiO_2 is completely inactive in photocatalytic reactions that require H-transfer for hydrogenation or H_2 evolution when a metal co-catalyst is absent [42, 190, 185, 142].

It is important to note that approximations are still very much necessary in efforts to model photocatalytic systems at this point since capturing the dynamics of excited states with respect to driving surface reactions is very computationally expensive or impossible at this time. A very limited selection of studies have begun to treat these systems more exactly, but have been limited to TiO_2 and were focused only on the hydrogenation of CO_2 without considering C–O bond cleavage pathways due to computational cost [100].

Our approach was to utilize a ground-state Density-Functional Theory (DFT) modeling approach to shed light upon observed catalytic performance of SiC and GaN photocatalysts in CO_2 reduction by H_2O . Through comparisons with experimental results, the validity of the approach could be determined. SiC and GaN were chosen because they present appropriate band gaps, band edge alignments, and a range of bulk material and surface chemical properties. Appropriate band edge alignments avoided the complication of including co-catalysts in the analysis. The primary mechanistic question was how catalyst surface reactivity and intermediate stability correlated with observed catalytic performance, but the investigation ultimately also suggested the potential for a new H-transfer mechanism over semiconductors comprised of less electronegative p-block elements, e.g., carbon vs nitrogen. Because we are modeling a ground-state reaction mechanism, it is expected that appropriately endothermic overall and stepwise reaction thermodynamics will be encountered. No extra charge or excited states were included in the calculations. The model systems or computational approaches were not modified to artificially produce exothermic reaction energetics, as in previous modeling efforts by others [92, 91]. Capturing these

energetics will help to shed light upon the nature and magnitude of energy inputs needed to drive the reaction forward.

The validity of the insights gained in the study was determined by comparing with our recently published experimental results that show photocatalytic CO₂ reduction is dramatically enhanced over specific catalysts at elevated autogenous temperatures (up to 350°C) under concentrated solar photoreaction (CSPR) conditions and with the published results of others at and above ambient temperature conditions. Comparisons were made only with studies that could be verified to the best of our ability to be organic-contamination free. As organic contamination is rife in the field, extreme scrutiny of all published work was necessary in this regard. If the study did not employ appropriate control tests, isotope tracking, or showed activity for pure TiO₂ in the reaction, it was deemed unreliable and not used for comparison.

As experimental results are available across a wide range of temperatures (25°C to 350°C), vibrational kinetic barriers were calculated throughout the mechanisms. The presence of this data does not suggest that these barriers will control the kinetics of the reaction when driven photoelectrochemically, but can shed light upon any effects that are associated with reaction steps that present vibrational barriers low enough to be kinetically accessible at the temperatures considered.

The possibility of vibrational excitation through applied thermal energy or non-radiative relaxation of hot electrons are also considered as potential energy sources since concentrated solar photocatalytic activity data at a temperature of 350°C is now available for comparison [142]. The latter phenomenon has the potential to drive non-redox reaction steps that would otherwise be insurmountable through direct heating and has been evoked in plasmon-assisted photocatalytic reactions recently [80]. In electron-mediated desorption studies of atomic H over Ru(111), a femtosecond laser excitation (800 nm, 60 J/m² fluence) was utilized to produce electronic temperatures of nearly 3000K that promoted H₂ evolution and exhibited a kinetic isotope effect using D₂ [43]. Electron-mediated associative desorption over metals and oxides has also been demonstrated [117, 47, 60, 22, 18]. As atomic H on SiC relaxes to neutral charge, this mechanism may be active in driving reactions on the SiC surface.

4.3 Results

4.3.1 Reaction Mechanism Determination

The most energetically favorable reaction pathways over SiC and GaN were determined via an exhaustive search. All possible reaction sites and reaction network pathways that were chemically reasonable were investigated. Thermodynamics and vibrational kinetic barriers were calculated for all pathways. The least energetically demanding pathways were selected as "most promising", but because the energy available for the reaction system is not well understood, other pathways close in energy may also be active. The reaction network in Figure 4.1 illustrates all possible reaction pathways that were investigated in our study. It is noted that reaction pathways where C–O bonds are broken and reformed multiple times were not considered as reasonable in our search. We assume that once a C–O bond has broken, it does not reform favorably along the path to the selective product CH₄.

The initiation of CO₂ reduction is possible via three pathways: i) redox (direct cleavage of first C–O bond to form CO*), ii) formic (hydrogenation to form HCOO*), or iii) carboxylic (hydrogenation to form COOH*). The redox pathway via electrochemically-promoted direct dissociation of CO₂ has been suggested as energetically unfavorable [154, 13]; however, may be possible via thermochemical routes over catalysts that exhibit higher surface reactivity towards carbon and oxygen. Over surfaces that present lower surface reactivity, hydrogenation to destabilize C–O bonds before cleavage may be necessary. The formic (HCOO*) and carboxylic (COOH*) routes initiate this destabilization of CO₂ through hydrogenation and differ solely with respect to where the initial hydrogenation takes place. Beyond the first hydrogenation, further hydrogenation may be necessary to destabilize C–O bonds enough to be cleaved. Therefore, all possible intermediates of the form H_xCO_yH_z were investigated. After the first C–O cleavage, similar reaction pathway turning points are present as well as varying degrees of C and O hydrogenation needed before 2nd C–O cleavage is accessible.

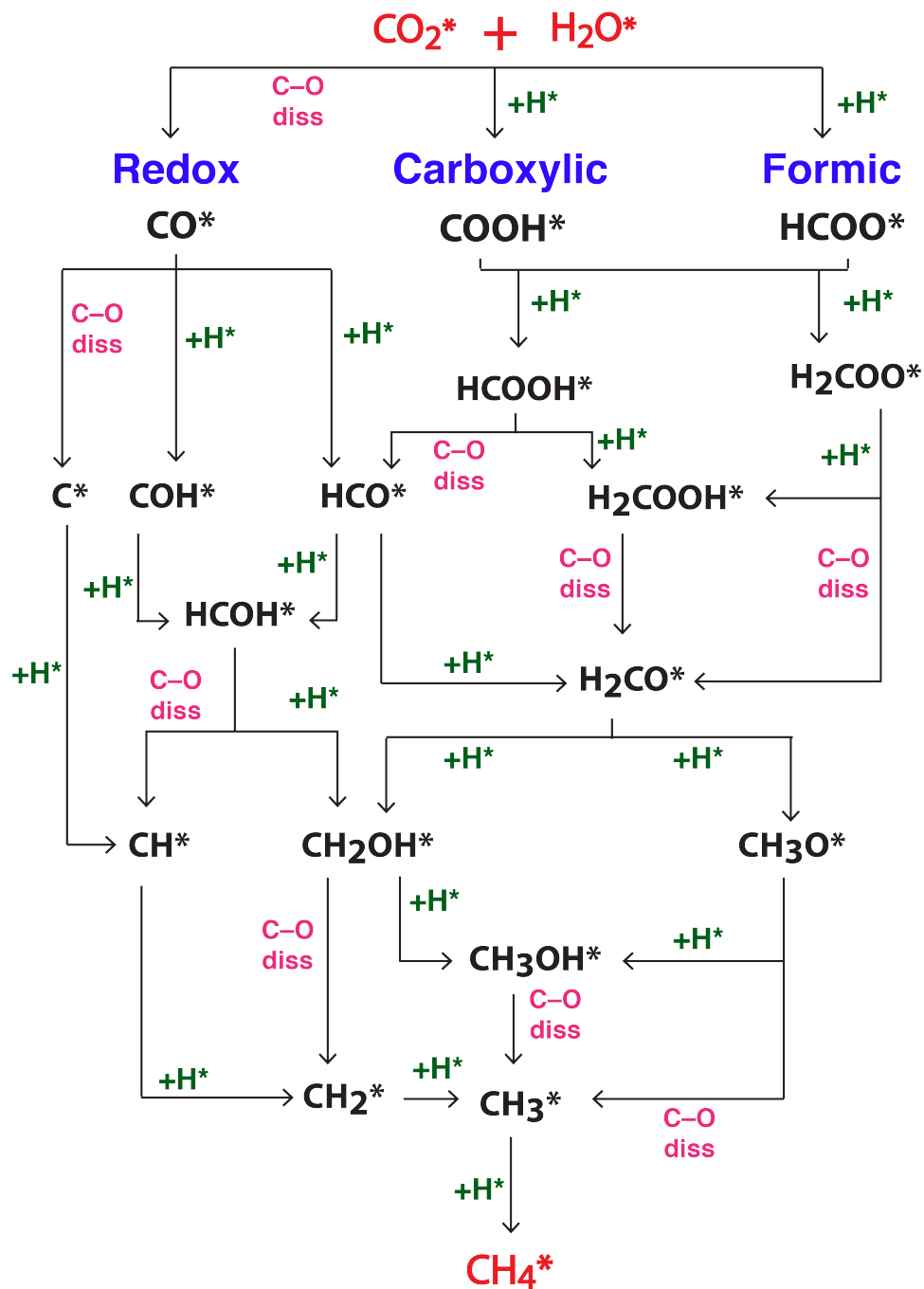


Figure 4.1: Surface reaction pathways considered in CO₂ photocatalytic reduction with H₂O to produce CH₄. The reduction mechanism initiates via three main pathways: (i) redox, (ii) carboxylic, and (iii) formic routes. All possible reaction pathways via multiple hydrogenation of CO₂ were calculated to isolate the most favorable reaction mechanism towards CH₄ production.

Water dissociation was studied first since the reaction cannot proceed without the hydrogen it supplies. Because of the stability of H_2O , its dissociation is often suggested as a kinetically limiting step in photocatalytic water splitting and CO_2 reduction over oxide and nitride-based catalysts [40]. Our results indicate that both SiC and GaN are able to dissociate H_2O with significant thermodynamic driving forces (-2.26 eV and -1.08 eV, respectively) and with nearly zero kinetic barriers ($+0.05$ and $+0.02$ eV, respectively). See Figure 4.2 for H_2O dissociation and $1/2 \text{ O}_2$ molecule evolution energetics. These results agree well with existing surface science experimental and computational studies focused on the surface chemistry of GaN and SiC [194, 15, 16, 28, 151, 83, 125, 52]. Facile H_2O dissociation encountered over both SiC and GaN suggests that this step is not kinetically limiting even at ambient conditions. Likewise, this surface chemical feature suggests that high surface coverages of H^* and OH^* may be present under reaction conditions and that the fragments may act as catalytic poisons if they are not removed through hydrogenation or H_2 and O_2 evolution steps. With high H^* and OH^* coverage, the concentration of carbonaceous species on the catalyst surface, including CO_2 , may be significantly limited leading to a reduction in overall activity or shifts in product selectivity that favor H_2 production. This phenomena could be detrimental at low temperatures in condensed aqueous phase reaction conditions where the chemical potentials of CO_2 and H_2O are at a great imbalance. Conversely, may be absent when utilizing elevated temperatures and gas phase reaction environments where CO_2 and H_2O chemical potential can be readily tuned.

In determining the dominant mechanisms across a wide range of reaction conditions, e.g., ambient vs. 350°C , condensed liquid vs. gas phase, AM1.5 vs. 100's of suns, it is assured that several reaction pathways may be active and condition dependent. Potentially unrealized H-transfer mechanisms over non-oxide/nitride catalysts may also enable significantly elevated electronic temperatures that allow higher energy pathways to be catalytically important. The lowest energy pathways presented in Figure 4.3 will be discussed as well as mechanisms that are more energetically demanding.

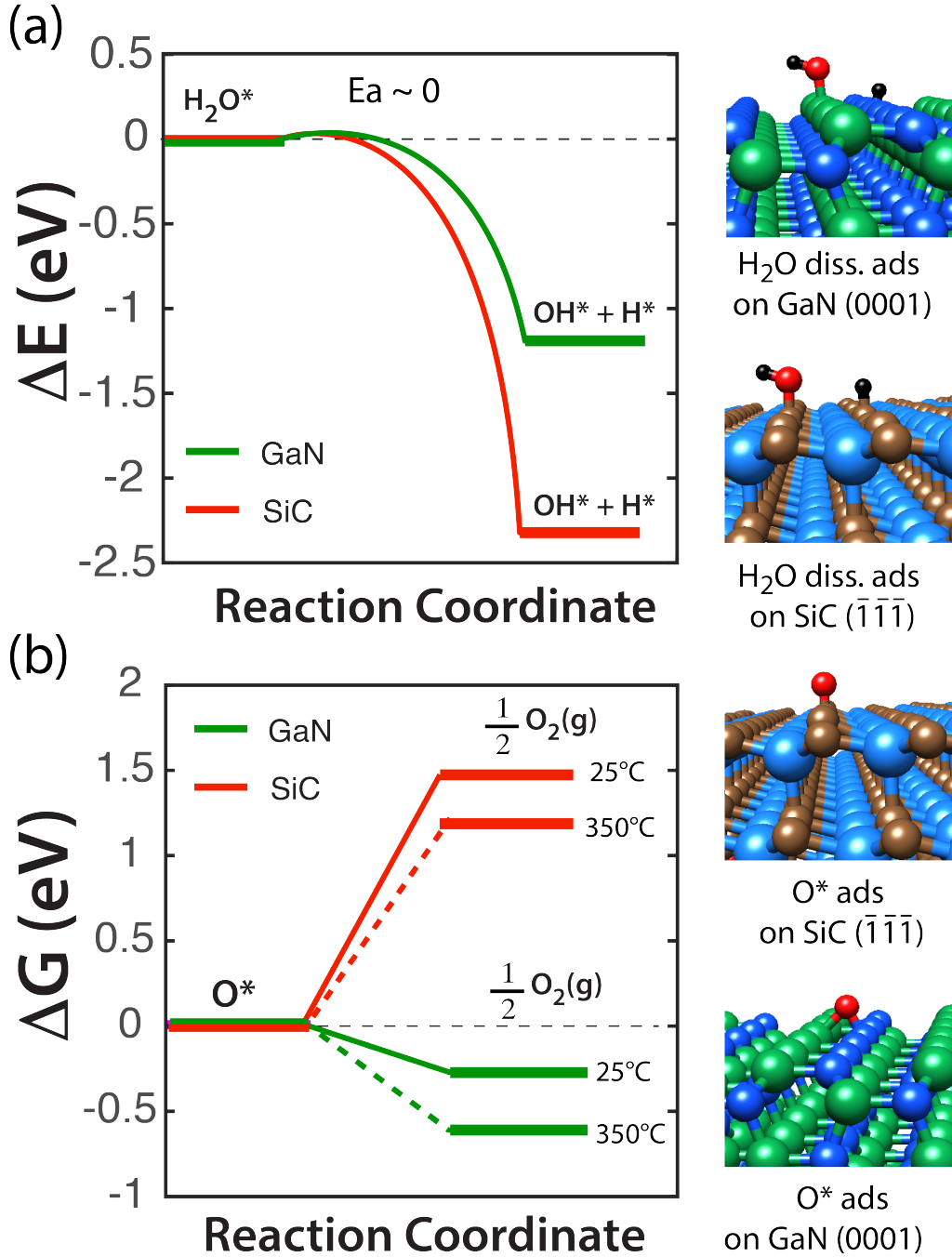


Figure 4.2: (a) H_2O dissociation energetics over SiC and GaN. Significant thermodynamic driving forces towards H_2O dissociation with low kinetic barriers ($E_a \sim 0$ eV) were encountered over both materials and (b) Gibbs free energy of $1/2 O_2$ molecule evolution over SiC and GaN at 25°C and 350°C. Energetics suggest that O_2 evolution may be readily promoted over GaN, while it might be difficult over SiC due to high oxophilicity.

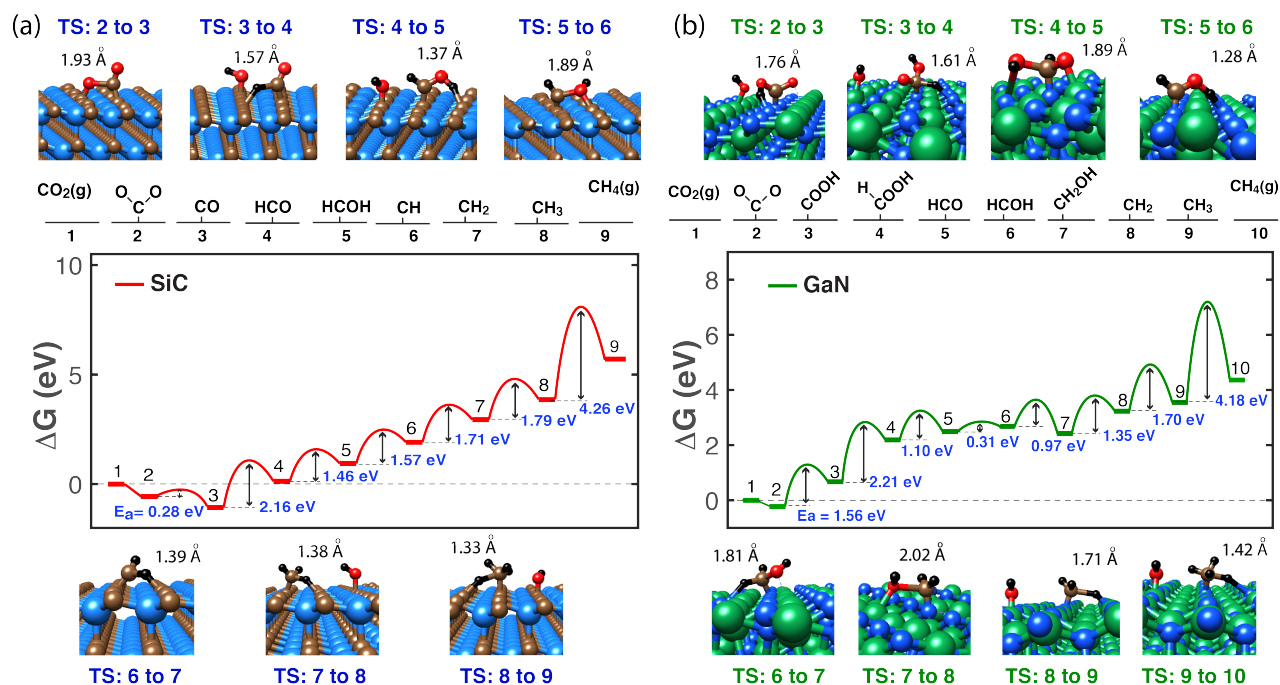


Figure 4.3: Most favorable surface reaction mechanisms isolated for CO₂ reduction over (a) SiC and (b) GaN towards CH₄ production via ab initio thermodynamics approach (T = 350 °C and ambient pressure). Redox and carboxylic routes were isolated as most favorable pathways for the initiation of CO₂ reduction over SiC and GaN, respectively. The model figures in this figure illustrate the transition states isolated in between each reaction step. Bond lengths of the transition states are indicated above the model figures.

Considering the pathways up to the first C–O bond cleavage step, the redox and carboxylic pathways were found to be most favorable over SiC and GaN, respectively. The lowest energy pathways are presented in Figure 4.3. The higher surface reactivity of SiC readily drove the direct dissociation of CO₂ to CO* and O* ($\Delta E = -0.50$ eV, $E_a = 0.28$ eV). Comparatively, hydrogenations of CO₂ over SiC in the carboxylic and formic routes were significantly more energetically demanding ($\Delta E = +1.80$ and $+1.65$ eV, and $E_a = 2.68$ and 2.88 eV, respectively). Over GaN, two hydrogenation events to produce COOH* and HCOOH* were necessary to enable cleavage of the 1st C–O bond due to the lower surface reactivity of material. Moderately endothermic 1st C–O cleavage via dissociation of HCOOH* intermediate was encountered ($\Delta E = +0.30$ eV and $E_a = 1.10$ eV). On the contrary, direct CO₂ dissociation over GaN was found to be highly energetically unfavorable ($\Delta E = +3.78$ eV, E_a not calculated). By comparison, hydrogenation steps that lead to 1st C–O cleavage over GaN were significantly more energetically demanding ($\Delta E = +0.89$ eV and $+1.52$ eV, $E_a = 1.56$ and 2.21 eV, respectively) than over SiC. Results suggest that CO* may be produced over SiC readily and is not a rate-determining step. While over GaN, hydrogenation must be achieved twice before the 1st C–O cleavage is accessible. These energetics may directly affect the CO production over the two catalysts and their general ability to utilize CO₂.

In the pathways that promote 2nd C–O cleavage, hydrogenation of intermediates was necessary over both SiC and GaN, albeit, to a lesser degree over the more reactive SiC. The formic-like route via a HCO* intermediate was found dominant over SiC ($\Delta E = +1.19$ eV and $E_a = 2.16$ eV). By comparison, the redox route via the C* intermediate ($\Delta E = +2.01$ eV and $E_a = 3.1$ eV) and the carboxylic route via the COH* intermediate ($\Delta E = +3.10$ eV and $E_a = 4.67$ eV) were found to be significantly less favorable. A second hydrogenation of HCO* to HCOH* (endothermic by $\Delta E = +0.81$ eV and $E_a = 1.46$ eV) was necessary to further destabilize the C–O bond before its dissociation over SiC. The C–O cleavage of HCOH* was found to be moderately endothermic (endothermic by $+0.97$ eV and $E_a = 1.57$ eV). Figure 4.4 presents the model figures and TS geometries of most thermodynamically favorable reaction pathways over both SiC and GaN.

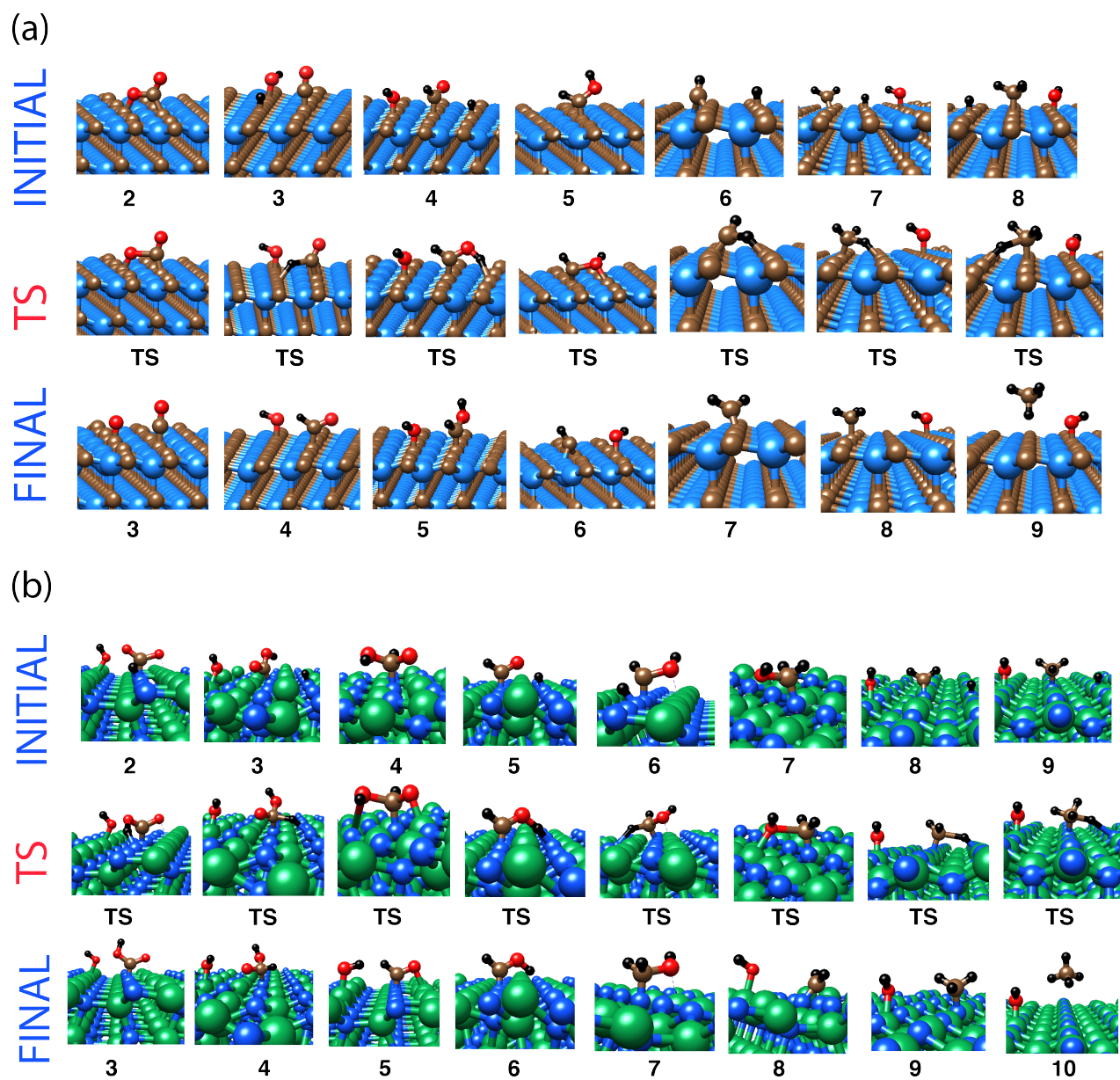


Figure 4.4: Model figures of most thermodynamically favorable reaction pathways over (a) SiC and (b) GaN: (top) initial step, (center) transition state, and (bottom) final step

Over the less reactive GaN, two hydrogenation steps prior to second C–O cleavage were found to be necessary. Hydrogenation of HCO^* to HCOH^* (endothermic by $\Delta E = +0.18$ eV, $E_a = 0.31$ eV) and then to CH_2OH^* (exothermic by $\Delta E = -0.26$ eV, $E_a = 0.97$ eV) were required to destabilize the remaining C–O bond sufficiently. Following hydrogenation, moderate endothermicity towards second C–O cleavage (endothermic by $\Delta E = +0.81$ eV, $E_a = 1.35$ eV) was encountered. The alternate pathway of C–O dissociation in the HCO^* intermediate was significantly less favorable ($\Delta E = +3.53$ eV, E_a not calculated).

Hydrogenation of the CH_x fragments to CH_3 over either catalyst was moderately endothermic (SiC: $\Delta E = +0.93$ to $+1.03$ eV and $E_a = 1.71$ to 1.79 eV; GaN: $\Delta E = +0.81$ eV and $E_a = 1.70$ eV). The final hydrogenation of CH_3^* to CH_4 was found to be most energetically demanding over both catalysts and was a likely candidate for the rate-determining step (GaN: $\Delta E = +1.99$ eV and $E_a = 4.18$ eV, SiC: $\Delta E = +2.77$ and $E_a = 4.26$ eV). Despite the energetics of this step, experimental observations by our group and others indicate that the reaction proceeds to CH_4 production [142, 5]. However, there are significant differences in overall catalytic activity and CH_4 vs. H_2 selectivity between SiC and GaN [142]. These results also agree well with results from in situ experimental investigations that tracked intermediates via DRIFTS and EPR spectroscopies [48, 7, 183]. Most notably, CH_3^* radicals were the only species identified besides H^* radicals, which is expected if the removal of the species is significantly kinetically limited [7, 48]. The stability and rigid tetrahedral geometry of this species are likely causes for its difficult removal.

The positive effects of elevated surface reactivity of the photocatalyst in driving C–O cleavage steps may also have a detrimental effect on CH_4 or O_2 evolution. In the context of O_2 evolution, general surface oxophilicity must be directly investigated. The oxophilicity of the semiconductor is a strong function of the electronegativity of the the non-metal element. The Gibb’s free energy of O_2 evolution (per oxygen atom) was calculated as -0.61 eV/O and -0.27 eV/O over GaN (calculated at 350°C and 25° under ambient pressure), respectively and ambient pressure reaction conditions). Over SiC, O_2 evolution (per oxygen atom) was less favorable ($+1.17$ eV/O and $+1.50$ eV/O, at 350°C , same conditions). Results suggest that O_2 evolution would be readily promoted over GaN considering its valence band alignment and low reactivity towards atomic oxygen [120, 112]. Despite an appropriate

valence band alignment for O_2 evolution in the case of SiC, O_2 evolution may be difficult due to the high oxophilicity of SiC. Due to the electronegativity of O, O_2 evolution may not be as easily promoted through vibrational excitation. These results agree well with the understanding that passivating oxide layers form readily on pristine SiC surface even under ambient conditions [54, 127, 142]; however, full oxidation to SiO_2 even under highly energetic photocatalytic reaction conditions at 350°C [142]. Oxides/nitrides are known to be relatively good oxygen evolution catalysts [165, 123]. The effect of catalyst surface chemistry in O_2 evolution over SiC and GaN clearly demonstrates how the classical approach of using bulk electronic properties fails to fully predict catalytic activity.

Beyond the lowest energy reaction pathways discussed already, other reaction pathways close in energy may also be active under the range of reaction conditions considered herein (1.5 AM to concentrated illumination and ambient to elevated temperatures). All reaction pathways calculated to isolate the most energetically favorable reaction mechanism have been included in Figures 4.5 and 4.6 over SiC and GaN, respectively. Kinetic barriers for reaction steps with thermodynamic energetics greater than 3.2 eV were not calculated since the barrier energetics can be assumed to be much higher than thermodynamic energetics and these pathways will likely not contribute to the overall activity and product distribution. Over GaN, 1st C–O cleavage via the formic route (CO_2^* to form HCO_2^* , $\Delta E = +1.71$ eV and $E_a = 2.88$ eV) was found closest in energy yet less favorable than the isolated most favorable carboxylic pathway via COOH^* intermediate (endothermic by $\Delta E = +0.89$ eV and $E_a = 1.56$ eV). Similarly, after first C–O cleavage over GaN, hydrogenation of HCO^* via formic-like route to form H_2CO^* ($\Delta E = +1.12$ eV and $E_a = 2.01$ eV) was found closest in energy but less favorable than hydrogenation of HCO^* intermediate via carboxylic route to HCOH^* ($\Delta E = +0.18$ eV, $E_a = 0.30$ eV). Over SiC, reaction pathways closest to the minimum energy redox pathway isolated were less thermodynamically favorable by at least 2 eV and exhibited significantly larger kinetic barriers. Hydrogenation of CO_2^* via carboxylic route (COOH^*) and formic route (HCO_2^*) were both less energetically favorable ($\Delta E = +1.80$ eV and $E_a = 2.66$ eV, and $\Delta E = +1.65$ eV and $E_a = 2.80$ eV, respectively). After the formation of CO^* , direct dissociation via redox route to form C^* was close in energy ($\Delta E = +2.03$ eV and $E_a = 3.10$ eV), yet less favorable than hydrogenation of CO^* via formic route ($\Delta E =$

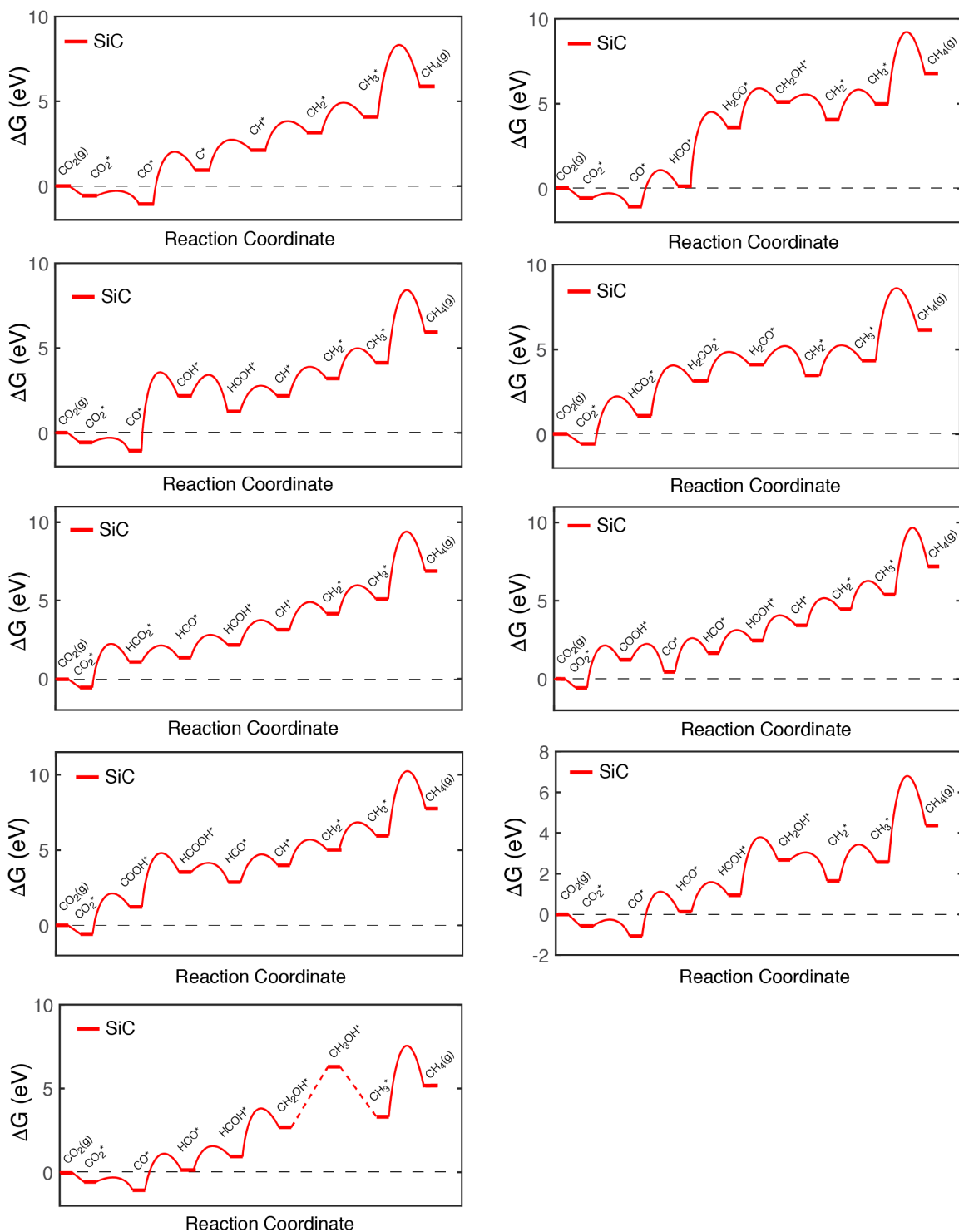


Figure 4.5: Less favorable surface reaction pathways calculated for CO_2 reduction over SiC towards CH_4 production via ab initio thermodynamics approach ($T = 350^\circ\text{C}$ and ambient pressure). Redox and carboxylic routes, isolated as most favorable pathways for the initiation of CO_2 reduction over SiC and GaN, respectively, are shown in Figure 4.1

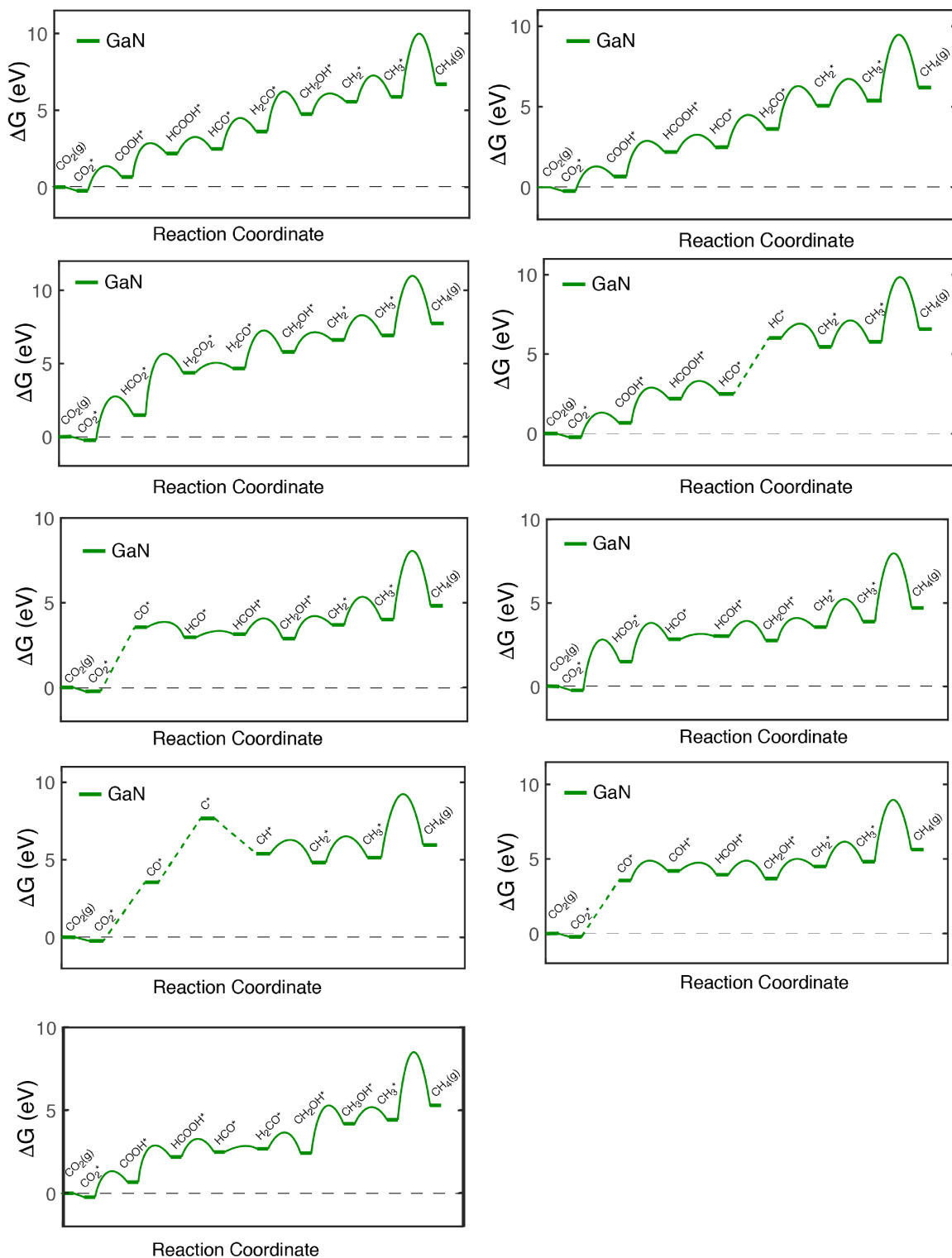


Figure 4.6: Less favorable surface reaction pathways calculated for CO_2 reduction over GaN towards CH_4 production via ab initio thermodynamics approach ($T = 350^\circ\text{C}$ and ambient pressure). Redox and carboxylic routes, isolated as most favorable pathways for the initiation of CO_2 reduction over SiC and GaN, respectively, are shown in Figure 4.1.

+1.19 eV and $E_a = 2.16$ eV). Despite the elevated energy requirements for these pathways, they may contribute to the observed catalytic activity and product distributions depending upon how the energy of the absorbed photon is partitioned between electrochemical redox reaction steps and vibrational excitation of surface-bound reaction intermediates through non-radiative excited electron energy dissipation.

4.3.2 Oxidation State of Surface-bound Atomic H

The oxidation state of hydrogen may also be an interesting tunable parameter if non-oxide/nitrides are used as photocatalysts. The hydrogen from H_2O is often assumed to be protonic and significantly affected by the gas-liquid interface, yet as the field moves to using semiconductors comprised of p-block elements that are less electronegative than O and N, atomic H^+ may electronically relax to neutral H^0 . This effect is already evident when H_2O dissociates over less electronegative transition metals [146, 8, 153, 83]. It is also likely present in any photocatalyst where H^+ is reduced at a metal co-catalyst surface [146, 153]. Anionic H may also be accessed over Si, as known from hydrogen sensor work [83, 61]. The presence of photocatalytically active neutral atomic H may indicate new vibrational H-transfer mechanisms are possible. This phenomenon may play a role in determining the hydrogenation vs. H_2 evolution selectivity. Our elevated temperature photocatalytic CO_2 reduction results already suggest that these mechanisms exist and are not wholly thermally driven, i.e., photon absorption still drives the reaction [142]. Charge analysis of atomic H adsorbed at the C and N of SiC and GaN indicated that H^+ does indeed relax to H^0 over SiC and not over GaN (see Table 4.1). These results are consistent with the electronegativity of Si, C, Ga, and N and agree with established experimental surface science understanding [180, 8, 146, 46]. How this feature of the reaction system affects catalyst activity or selectivity has not yet been directly studied, but comparisons with literature indicate it significantly affects selectivity.

Table 4.1: Calculated Bader charge analysis of atomic H adsorbed on SiC and GaN surfaces. Two distinct types of surface bound atomic H were encountered – protonic over GaN and neutral over SiC. The charges are reasonable considering the electronegativity of the constituent atoms and the electronegativity of H atom (2.2).

Catalyst	$\Delta E_{H*}(\text{eV})$	Charge on H (e^-)	Electronegativity
SiC	-2.50	+0.04	Si (1.9), C (2.5)
GaN	-0.66	+1.0	Ga (1.8), N (3.0)

4.3.3 Stability of Reaction Intermediates and Probe Adsorbates

The factors of the photocatalytic system that affect selectivity in CO_2 reduction by H_2O are still not well-established, but considering the high energy environment, it is reasonable to suggest that more stabilized intermediates may improve hydrocarbon production by limiting the energetic driving force for reverse reactions and entropic driving forces that favor small molecule production (CO and H_2). Therefore, we investigated the general reactivity of SiC and GaN towards both relevant probe molecules via molecular and dissociative adsorption (H_2 , O_2 , CO_2 , H_2O , and CO) and the raw stability of key molecular fragments that may be catalytically important (CH^* , CH_2^* , CH_3^* , HCO^* , C^* , and COOH^*). The greater reactivity of SiC is again readily apparent in comparison to GaN with both probe adsorbate and intermediates binding more strongly by at least 0.9 eV (see Figure 4.7).

Following the prediction of how intermediate stability may affect selectivity, it is predicted that SiC may lead to elevated production of CH_4 with diminished H_2 and CO evolution and visa versa over GaN. This prediction is in direct agreement with all observed catalytic activity of these two materials in contamination-free systems and appears to extend to other oxides and nitrides as well [142, 5, 119, 121]. It is also important to note that the "appropriate" surface reactivity for photocatalytic synthesis reactions has yet to be determined and may be dramatically different from the surface reactivity necessary in less energetic thermocatalytic reaction systems. However, comparisons with observed experimental performance suggests that elevated surface reactivity may be beneficial in these reactions. A similar suggestion

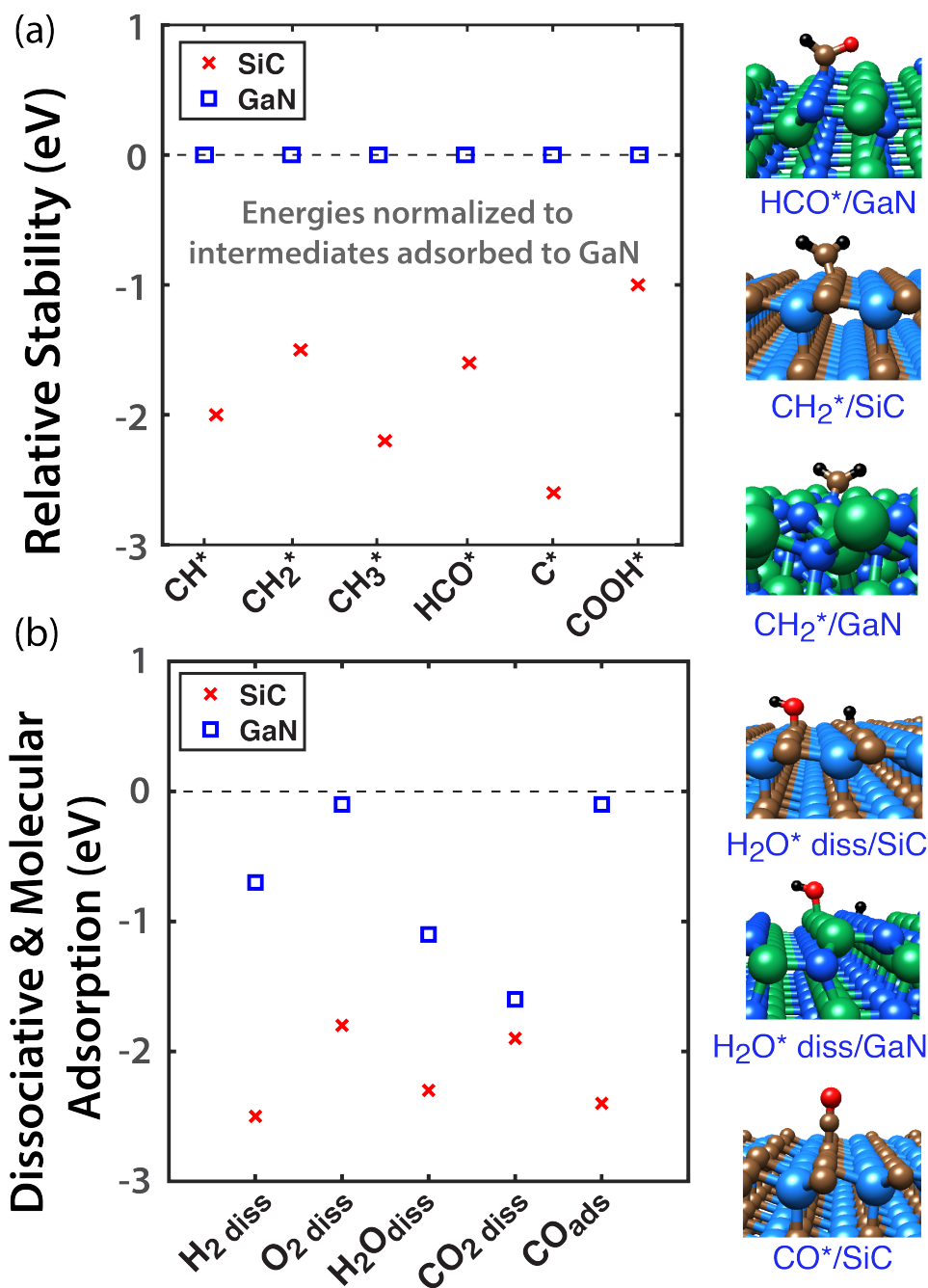


Figure 4.7: (a) Relative stability of key reaction intermediates encountered in the CO_2 reduction pathway towards CH_4 formation over SiC and GaN. Energetics suggest that SiC exhibits a reactive surface that binds all key reaction intermediates more strongly in comparison to GaN by at least 0.9 eV. (b) Dissociative and molecular adsorption energy (eV) of probe molecules. Similar differences is observed over the two materials in this case.

was put forth in the work of Medford et al. in the computational study of photocatalytic NH_3 synthesis where oxygen vacancy rich TiO_2 provided the most energetically favorable N–N cleavage energetics [39].

4.4 Discussion

Results thus far suggest that the surface chemistry of photocatalysts may play a significant role in determining surface reaction mechanisms, catalytic activity, and product distributions in a similar fashion as electrocatalysis. Additionally, charge analysis of atomic H on SiC and GaN suggests that non-electrochemical H-transfer mechanisms may be active over SiC where atomic H is of neutral charge. We now compare to other computational and experimental surface science and catalytic performance studies to ascertain whether these studies can shed light upon the behavior of real photocatalytic systems. Again, we compare only to catalytic performance studies that could be verified to be free of organic contamination through thorough control or isotope tracking studies. Because contamination effects in published literature are abundant, a fairly limited selection of studies could serve as a comparison.

4.4.1 Correlation of Computationally-Derived Mechanisms and Established Surface Science Understanding

Focusing first on the surface chemistry of GaN, H_2O dissociation over single crystal GaN(0001) has been shown to be appreciable and kinetically accessible even at low temperatures via UPS and AP-XPS surface science studies [194, 16] as well as in other computational studies [28, 151], which agree well with our results. Atomic H adsorption has been reported as moderate with thermal H_2 evolution possible at temperatures above $\sim 250^\circ\text{C}$ in UHV HREELS and TPD studies over single crystal GaN(0001) [187]. The elevated reactivity of GaN towards oxygen has been demonstrated by its oxidation under O_2 at ambient conditions. The element mobility in GaN also allowed for a moderately thick native (full) oxide overlayer to form (0.5-2nm thick) [56]. The propensity for surface oxidation is also demonstrated by the need for its removal in electronics applications through acid or base

etching of GaN [156, 197]. However, even after these treatments, a significant amount of oxygen still persists ($\sim 30\%$ of O per N detected in 1-5 nm of surface of GaN via Auger electron spectroscopy) [156]. GaN has also been shown to be more reactive than TiO_2 in the study of ethanol dissociation [169]. This elevated reactivity and ease of oxidation may be detrimental under all reaction conditions, yet post-reaction characterization of photocatalysts is sparsely performed. Our study of GaN under CSPR conditions indicated half the material was converted to Ga oxide after 12 hrs under reaction conditions [142]. The photon absorption environment appears to not limit this effect significantly.

The surface chemistry of SiC has not been a focus of the catalysis community, yet has been quantified its use in the electronics industry. The study of the oxidation of SiC by various oxygen containing molecules, e.g., O_2 , H_2O , CO_2 , and CO indicated high surface reactivity, thick oxide layer formation, and a rapid passivation of the surface that limits further oxidation [166, 88, 95, 142, 152, 167]. For instance, the oxidation of ~ 25 nm SiC particles at room temperature by ambient O_2 has been shown in a study by Vaben et al. [166]. The oxide thickness was reported as effectively one atomic layer (0.16 nm), however. The passivation layer is uniquely thin over SiC since its element mobility is one of the lowest of all materials [166]. Indeed, high temperature (800°C) was required to facilitate oxidation by H_2O , CO, and CO_2 in other studies [88, 95]. Unfortunately, the thickness of the oxide was not reported in these studies. Our studies of SiC under CSPR conditions for 12 hrs at an autogenous catalyst temperature of 350°C indicated that the oxidation of SiC stops at SiO and is limited to just the surface of the particles [142]. Others have reported similar results [152, 167]. These results agree well with our calculations and observations that the catalyst does not oxidize to SiO_2 and retains catalytic activity [142]. It is also noted that the thin oxide layer can be readily removed by HF etching [197]. Experimental surface science studies of reactivity towards carbonaceous species is quite limited, yet computational studies of others indicate strong binding of CO ($E_{ads} = -2.3$ eV with XC functional PBE) similar to our results ($E_{ads} = -2.4$ eV with XC functional PBE-sol) [174]. Adsorption of CO and NO over SiC nanotubes showed lower binding energies, yet still a moderately reactive surface [90].

4.4.2 Correlation of Computationally-Derived Mechanisms and Observed Experimental Catalyst Performance

Comparing to reliable experimental results, we first summarize our findings in concentrated solar photocatalytic reaction conditions. Reactors used were constructed from UHV conflat flange parts cleaned with a solvent sequence, baked at 400°C under flowing UHP Ar, and sealed with Cu gaskets. Doubly distilled water and SFE grade CO₂ were the only species present under reaction conditions. Many control runs were performed to verify the cleanliness of the system. In this reaction system, both SiC and GaN exhibited excellent photocatalytic activity towards H₂, CO, and CH₄ but dramatically different product distributions (SiC: $\sim 35 \mu\text{mol g}^{-1}\text{h}^{-1}$ CH₄, $\sim 36 \mu\text{mol g}^{-1}\text{h}^{-1}$ CO, and $\sim 44 \mu\text{mol g}^{-1}\text{h}^{-1}$ H₂ and GaN: $\sim 3.2 \mu\text{mol g}^{-1}\text{h}^{-1}$ CH₄, $\sim 31 \mu\text{mol g}^{-1}\text{h}^{-1}$ CO, and $\sim 3100 \mu\text{mol g}^{-1}\text{h}^{-1}$ H₂). The contribution of lattice C to the CH₄ production rate was checked using water-splitting conditions at temperature up to 350°C. CH₄ production rate in this case was $\sim 2\%$ of that of runs performed with CO₂ present. SiC exhibited one of the highest hydrocarbon production rates among verifiably organic-free systems ($\sim 35 \mu\text{mol g}^{-1}\text{h}^{-1}$). GaN also exhibited one of the highest activities towards H₂ evolution under elevated temperature CSPR conditions ($\sim 3100 \mu\text{mol g}^{-1}\text{h}^{-1}$), even comparable to highly optimized RuO₂/GaN:ZnO (H₂ evolution of $\sim 3200 \mu\text{mol g}^{-1}\text{h}^{-1}$) under UV-vis and Rh_{2-y}Cr_yO₃/GaN:ZnO catalysts (H₂ evolution of $\sim 900 \mu\text{mol g}^{-1}\text{h}^{-1}$) under visible irradiation [119, 163, 121]. At elevated reaction temperatures, e⁻/h⁺ pair recombination rate becomes a question. The temperature where this becomes appreciable is the Debye temperature. SiC exhibits much higher Debye temperature (927°C) in comparison to GaN (327°C). Despite operating slightly above the Debye temperature of GaN, a similarly improved activity to SiC was still achieved. Product selectivity for the fate of H (CH₄ vs. H₂) was 1:8 and 1:1000+ for SiC and GaN, respectively illustrating they exhibit distinctly different mechanistic features.

Considering the effect of reaction conditions in addition to the innate activity differences at ambient temperature conditions in condensed aqueous phase further underscores that the two catalysts exhibit surface chemical or electronic differences that dramatically affect their performance. Most notable are the changes in 2nd C–O bond cleavage ability and its effect on

product distribution. A preferred selectivity towards partially hydrogenated products such as H_2CO ($14.3 \mu\text{mol g}^{-1}\text{h}^{-1}$) and CH_3OH ($76.4 \mu\text{mol g}^{-1}\text{h}^{-1}$) has been reported over SiC under aqueous phase ambient photocatalytic reaction conditions [85]. These results were then reproduced with 100% selectivity towards CH_3OH production ($27.7 \mu\text{mol g}^{-1}\text{h}^{-1}$) by Gondal et al. under similar conditions [57]. When reported, CH_4 production was noted only at trace levels [85]. Production of H_2 was not quantified in these studies, unfortunately. The activity of GaN at ambient temperature in condensed aqueous phase has been reported to lean heavily towards products that are not hydrogenated and H_2 evolution. For example, CO and H_2 were the only products quantified ($\sim 47 \mu\text{mol g}^{-1}\text{h}^{-1}$ CO and $\sim 570 \mu\text{mol g}^{-1}\text{h}^{-1}$ H_2) in three different studies of GaN in CO_2 reduction [5, 119, 163]). Again, greatly diminished CH_4 production was encountered ($\sim 1.3 \mu\text{mol g}^{-1}\text{h}^{-1}$ CH_4) over unpromoted GaN nanowires under aqueous phase ambient temperature conditions [5].

4.4.3 Effect of General Surface Reactivity and the Nature of Atomic H

Revisiting our results in the light of the observed activity differences of the catalysts under two distinctly different reaction conditions, we found that the effect of general surface reactivity and the nature of atomic H are likely catalyst features that dictate activity and product selectivity in the reaction. Reaction condition also may play a significant role in dictating product selectivity. Elevated surface reactivity may aid in H_2O dissociation, promote C–O bond cleavage, and change and anchor reaction intermediates to manipulate product distributions. The nature of atomic H adsorbed to the catalyst surface and its stability also correlate well with catalyst selectivity towards hydrogenation vs. H_2 evolution in both ambient and CSPR environments.

With respect to driving H_2O dissociation, catalyst surface reactivity may manipulate the surface coverage of H^* , OH^* , and carbonaceous intermediates and influence the general ability of the catalyst to adsorb and utilize CO_2 . Experimental performance of catalysts with lower surface reactivity, TiO_2 and GaN, varies considerably as a function of reaction condition. At lower temperature in condensed H_2O , small oxygenate production is promoted

yet product distributions lean heavily towards H_2 production. Under CSPR conditions, these catalysts produce little to no small oxygenates and greatly improved H_2 evolution is encountered. On the other hand, the elevated reactivity of SiC shifts product distribution from small oxygenates at low temperature to CH_4 at elevated temperatures significantly. These correlations partially suggest the relative reactivity necessary towards H_2O and carbonaceous species needed to promote full CO_2 reduction and how their chemical potential in reaction conditions may need to be tuned. The presence of a high chemical potential of H_2O in condensed phase reaction conditions may further exacerbate these effects and significantly limit the activity of catalysts with higher surface reactivity. This is most evident when comparing the performance of SiC at low and elevated temperatures, but appears to also be an issue with less reactive catalysts that still are able to effectively dissociate H_2O at low temperatures.

Elevated surface reactivity may also allow for new reaction intermediates to be present that would otherwise be absent over materials like TiO_2 and GaN . This is most evident in the degree of hydrogenation necessary to promote C–O cleavage over catalysts of varying reactivity. Over GaN , significant hydrogenation is necessary before each C–O cleavage, yet over SiC, 1st C–O cleavage of CO_2 is possible with no need for hydrogenation and 2nd C–O cleavage requires only two hydrogenations in the most favorable reaction pathway. Observed product distributions in different reaction conditions also support this view with small oxygenates dominant at low temperature in condensed H_2O and CO , H_2 , and CH_4 dominant under gas phase CSPR conditions.

The stabilization of reaction intermediates also appears to be a critical aspect of photocatalysts that achieve the full reduction of CO_2 to CH_4 . Due to the high energy reaction environment and highly endothermic reaction energetics throughout the mechanism, it is reasonable that significantly stabilized intermediates would balance and counteract the issues inherent in producing much higher energy products while combating the reverse reactions, e.g., CH_4 formation from CO_2 and H_2O is endothermic by $\sim +9.14$ eV [168]. Additionally, the degree of stabilization needed may be markedly different from that appropriate for lower energy thermocatalytic reactions. Selective CH_4 production over SiC tracks well with more stabilized reaction intermediates, most notably in CSPR conditions where thermal energy or

non-radiative vibrational excitation may be promoted. Conversely, the relatively low surface reactivity of GaN and less stabilized reaction intermediates promotes the production of H_2 and CO since the energetics of reverse reactions are still strongly exothermic. Despite both SiC and GaN exhibiting similar surface reaction energetics later in the mechanism, there is a key stopping point in the reverse reaction pathway at CO over SiC. This feature may serve to limit reoxidation of CO to CO_2 . Entropic effects that greatly favor the release of energy through the production of small molecules may also play a significant role in the reaction. See Figure 4.8. If key intermediates are converted back to CO and atomic H, the high energy environment may favor desorption of CO and H_2 over hydrogenation. Again, more stabilized intermediates over SiC appear to limit this effect. Whereas, less stabilized intermediates over GaN correlate with significantly higher selectivity towards CO and H_2 production.

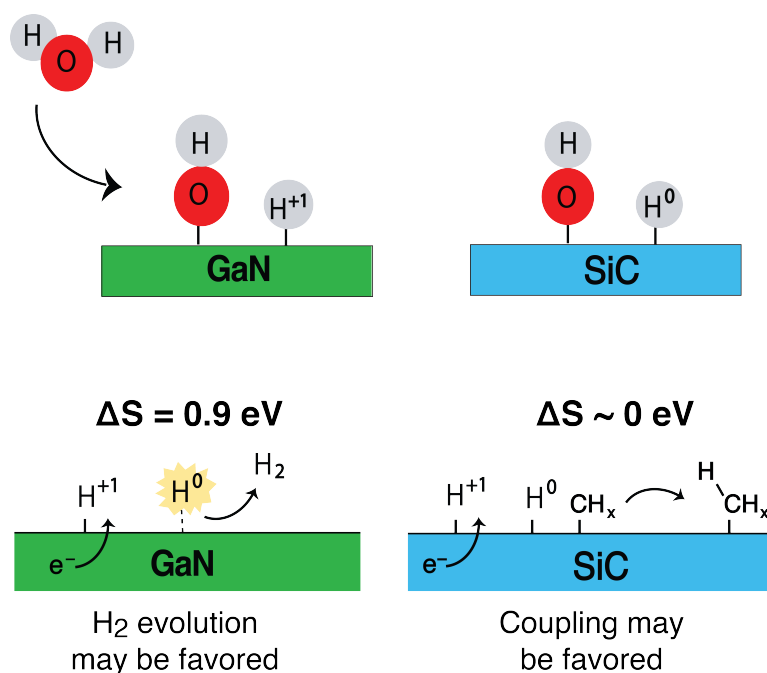


Figure 4.8: Schema to illustrate the effect of different types of surface-bound atomic H – protonic and neutral – encountered over GaN and SiC, respectively in our study. Entropy calculations for H_2 evolution step over GaN and a CH_x fragment hydrogenation step over SiC are shown. Entropy calculation results directly correlate to experimentally observed selectivity towards H_2 evolution in case of GaN and CH_4 production in case of SiC, indicating that entropy effects may favor the production of small molecules like H_2 if less stable intermediates are encountered. Positive entropy change values indicate a more disordered system.

The final feature of the reaction system suggested to control selectivity is the nature of surface-bound atomic H. The conduction band minimum edge alignments of SiC and GaN indicate both materials should present the similar H-transfer abilities, yet this does not correlate with observed selectivity between hydrogenation and H₂ production. Again, calculations suggest that the effective electronegativity of the photocatalyst may allow protonic H from H₂O to electronically relax over solids comprised of less electronegative p-block elements than O and N. The presence of less strongly bound H of protonic nature over GaN correlated well with the fate of H (CH₄:H₂ of 1:1000+ under CSPR conditions) [142]. Neutral atomic H over SiC correlated with more difficult hydrogenation at ambient conditions but greatly elevated selectivity towards hydrogenation for CH₄ production under CSPR conditions (CH₄:H₂ of 1:7).

The activity of a neutral atomic H in a photocatalytic mechanism may be unorthodox, but an understanding of the excitation of these species with energy appropriate to perform reactions has already been shown in studies of energetic electron-mediated or laser-mediated associative desorption of atomic H over metals [43, 44]. A vibrational excitation driven by non-radiative hot electron energy dissipation was suggested. The transfer of neutral hydrogen, being vibration in nature, may be affected by thermal inputs and detectable through kinetic isotope studies. Our tests of SiC at 250°C vs. 350°C have shown that elevated temperature promotes hydrogenation when surface chemistry is appropriate to stabilize carbonaceous intermediates [142]. Hydrogenation using protonic H reduced by excited electrons is possible and potentially as kinetically accessible as hydrogenation by atomic H, as indicated by rates of 10's of $\mu\text{mol g}^{-1}\text{h}^{-1}$ in the production of small oxygenates over GaN at ambient conditions and CH₄ over SiC under CSPR conditions [142, 5]. Therefore, different H-transfer mechanisms may be present over the two catalysts. Kinetic isotope effects have already been performed in our lab and have confirmed the vibrational nature of H-transfer over SiC. Solid state NMR studies have further confirmed these claims. These results will be presented in a follow-up publication.

4.5 Conclusions

In conclusion, efforts to model the photocatalytic reduction of CO_2 by H_2O using ground-state computational surface science techniques reveal clear connections between catalyst surface reactivity, nature of atomic H, and experimentally observed catalytic activity and selectivity. There are still significant questions surrounding the mechanisms determined and whether higher energy pathways contribute significantly or dominantly to the observed activity. However, correlations suggest that regardless of this ambiguity, accounting for general surface reactivity in catalyst selection may aid greatly in designing catalysts for H_2/CO or hydrocarbon production. This new understanding may also enable the production of C_{2+} hydrocarbons, which may be accessible from CO_2 and H_2O once appropriate surface reactivity is identified. Of course, a balance of surface reactivity is still a requirement for high performance catalysts. Elevated surface reactivity appears to be beneficial in the total reduction of CO_2 , yet also limits O_2 evolution. Therefore, an oxygen-evolution co-catalyst is likely necessary when using carbides. The overall degree of surface reactivity that may lead to high activity and sustained selectivity towards oxygen-free products is still not clear, yet the benefit of using materials more reactive than commonly used oxide and nitride photocatalysts has been established. The presence of neutral atomic H over SiC also correlates well with improved hydrogenation and elevated CH_4 production. Electron-mediated reaction steps that are not purely photoelectrochemical are well-known over metals in the surface science community and now appear to play a potentially critical role in light harvesting in photocatalysis.

Chapter 5

The Nature of Surface-bound Atomic H and its Role in Dictating Selectivity toward Hydrogenation vs. H₂ Evolution

5.1 Overview

In this chapter, the focus will be on gaining insights into the kinetically important steps and the role of electronic nature of surface-bound atomic H in dictating the rate and degree of hydrogenation. In the last chapter, it was suggested that a new H-transfer mechanism may be directly connected to the fate of atomic H in the photocatalytic reduction of CO₂ by H₂O. Herein, we utilize well-defined experimental testing (kinetic isotope effect, thermal effects in reaction) and spectroscopy (SSNMR) along with DFT calculations to gain insights into the H-transfer mechanisms (vibrational versus electrochemical) and to spectroscopically isolate the oxidation states of atomic H on SiC and GaN surfaces. Significant KIE was observed over SiC towards hydrogenation (CH₄ production) while no KIE was encountered over GaN. Results suggested two different H-transfer mechanisms are active over these materials, which likely result in the selectivity differences encountered in experiments. Results suggested a

new mechanism of neutral atomic H transfer with a significant vibrational barrier may be active in the hydrogenation of carbonaceous intermediates over SiC, while an electrochemical H-transfer pathway may dominate over GaN.

5.2 Introduction

Progress in the photocatalytic synthesis of increasingly complex molecules from CO₂ or N₂ and H₂O has been limited due to a lack of mechanistic understanding, design rules for catalyst discovery and optimization, and reliable experimental results not affected by organic contamination. Focusing on the photocatalytic reduction of CO₂ by H₂O and light only, design of catalysts using bulk electronic properties of the catalyst and electrochemically derived CO₂ reduction potentials for various products has otherwise failed to yield improved catalytic materials and any control with respect to product selectivity. Of specific interest is the control of the fate of atomic H in hydrogenation vs. H₂ evolution reactions and the kinetically important steps that dictate the rate and degree of CO₂ reduction and product distribution. Herein, we present the discovery of a new H-transfer mechanism that could be directly connected to the fate of atomic H in the photocatalytic reduction of CO₂ by H₂O and light.

In last two chapters and our recent publications [142, 143], we focused upon understanding the effect of catalyst surface chemistry and autogenously produced elevated temperature utilizing a concentrated solar photoreaction (CSPR) approach, which suggested that catalyst performance and the rate of oxygen removal towards full reduction of CO₂ would be greatly improved over catalysts with elevated surface reactivity and high Debye temperature. SiC exhibited one of the highest hydrocarbon production rates among verifiably organic-free systems. Verification of the CO₂ reduction activity was ultimately possible by employing several control runs that indicated lattice C do not play a significant role towards catalytic activity. GaN, on the other hand, exhibited high selectivity towards H₂ evolution, with rates nearing highly optimized RuO₂/GaN:ZnO photocatalyst [121, 118]. Selectivity differences encountered in both materials depicted a clear lack of correlation between catalytic performance towards hydrogenation or O removal from CO₂

and electronic properties commonly employed for photocatalyst selection and optimization, namely band gap energy and band edge alignments with respect to redox potentials. Elevated surface reactivity, high Debye temperature, and robust bulk bonding of SiC were found beneficial under highly reactive photocatalytic environment towards directly promoting new reaction intermediates produced via thermal/vibrational routes that further enhance selectivity towards hydrogenation. This approach revealed that stabilization of carbonaceous intermediates and surface-bound atomic H may directly contribute towards controlling catalytic activity and selectivity and suggested the possibility of new intermediates and H-transfer mechanisms that are not purely electrochemical in nature depending upon the electronic properties of non-oxide/nitride semiconductor.

Herein, we will utilize well-defined experimental testing, spectroscopy, and quantum chemical modeling approach to further elucidate the kinetically important steps in the CO₂ reduction mechanism that dictate the rate and degree of hydrogenation. We present a new H-transfer mechanism that is directly connected to the fate of atomic H in the photocatalytic reduction of CO₂ by H₂O and light, and may as well contribute to the understanding of underlying mechanisms in photocatalytic synthesis of complex hydrocarbons and oxygenates.

5.3 Results

5.3.1 Kinetic Isotope Effect (KIE)

Kinetic isotope effect (KIE) allows us to easily access the vibrational aspect of a reaction system, specifically to understand the rate determining step in the reaction mechanism that exhibits a vibrational barrier. To shed light on the nature of the hydrogen transfer over SiC and GaN, we employed D₂O as a reactant in CO₂ photocatalytic reduction under CSPR conditions. See Figure 5.1 for the results of KIE study. No KIE effect was observed over GaN towards CH₄, CO, and H₂ production, suggesting that H-transfer steps are electrochemical in nature, i.e., vibrational barriers do not play a role since atomic H are highly destabilized upon photoexcitation. On the contrary, a clear suppression in hydrogenation activity was encountered over SiC towards CH₄ production. Presence of KIE (~ 1.7 at steady state)

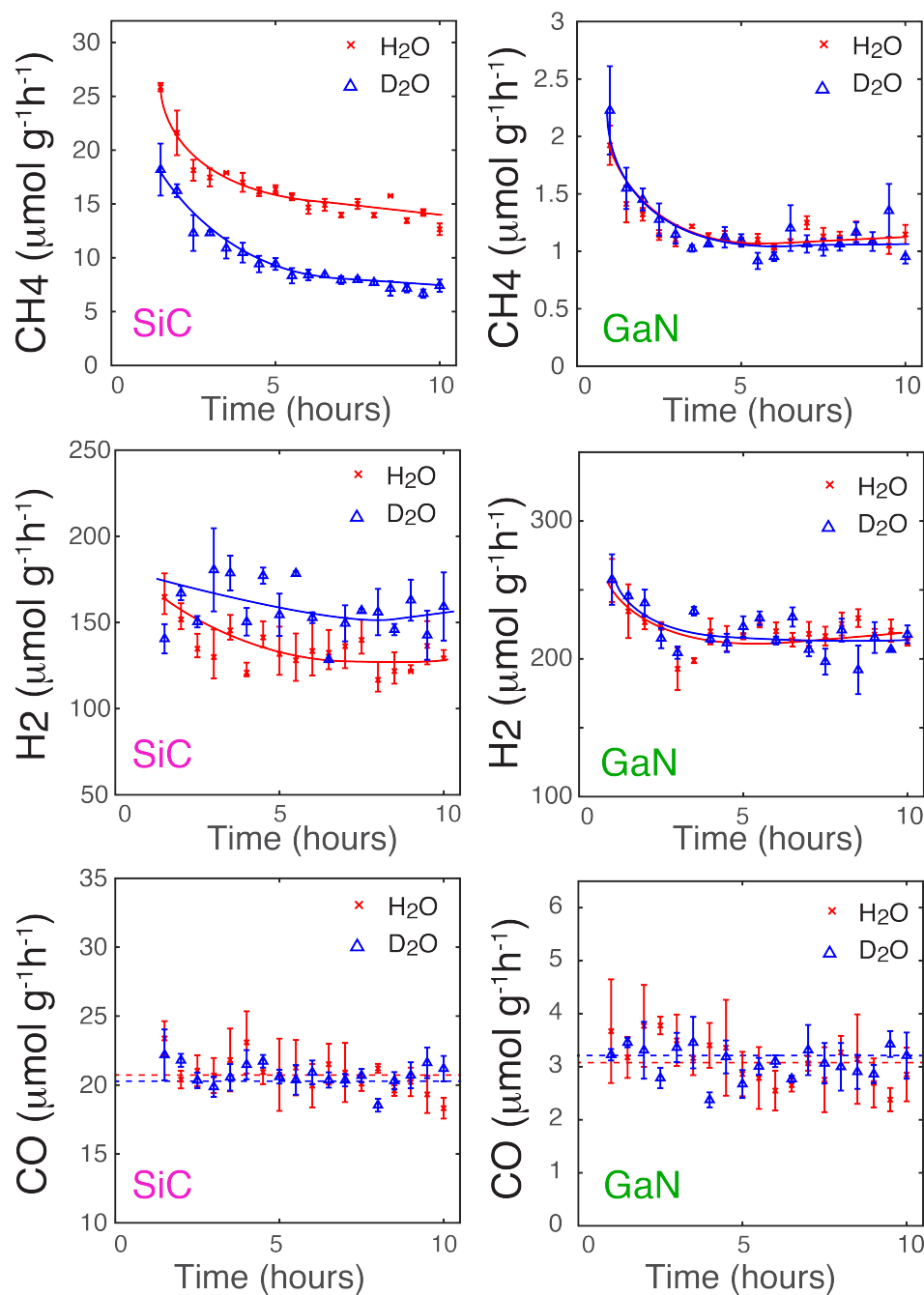


Figure 5.1: Vibrational nature of H transfer over SiC (left) and electrochemical H transfer over GaN (right) isolated via kinetic isotope effect. SiC exhibited KIE (~ 1.7 towards hydrogenation at steady state). No KIE was observed in case of CO production. D₂ evolution was slightly higher compared to H₂ evolution over SiC. GaN did not exhibit KIE towards any products.

towards hydrogenation (CH_4 production) suggested a non-electrochemical H-transfer mechanism active that results in significant vibrational barrier, and hydrogenation step is likely the rate determining step in the reaction mechanism. CO production showed no KIE suggesting a direct CO_2 dissociation (redox mechanism) involving no H-transfer steps may be active towards first C–O cleavage. D_2 evolution, on the other hand, showed slight enhancement compared to H_2 production. The enhancement may be reasonable when taking into account the decrease in rate of hydrogenation. However, it could also result from a combined effect of electrochemical as well as non-electrochemical H-transfer mechanisms active over SiC because SiC also exhibits appropriate electronic structure towards electrochemical H-transfer. Hydrogenation products such as CH_3OH and HCOOH have been encountered over SiC in low temperature aqueous phase CO_2 photoreduction studies, which suggest readily surmountable vibrational barriers present at near ambient conditions. Furthermore, order of magnitude lower activity towards all products was encountered in pure thermocatalytic tests over both SiC and GaN. These results may suggest that two different H-transfer mechanisms are active over SiC and GaN that likely result in the selectivity differences encountered in experiments.

5.3.2 Solid-state-NMR (SSNMR) and DFT results

The differences encountered in kinetic isotope effect and selectivity towards hydrogenation versus H_2 evolution over SiC and GaN may suggest two distinct nature of atomic H on surface of each catalyst. To probe the electronic nature of surface-bound atomic H, solid state H-NMR was utilized. An adsorbate-free SiC surface was achieved by heating the catalysts (upto 400°C) under active turbo pump vacuum ($1\text{E-}6$ Torr) for 30 minutes (See Figure 5.2). Residual H^0 and H^+ (from OH) were observed on pristine SiC surface (black spectra). In case of GaN, clean surface was difficult to achieve because of the synthesis method employed that utilized a high chemical potential of NH_3 under high temperature (700°C) leading to an already hydrogenated GaN surface with a low signal of protonic H^+ (shift ~ 3.6 ppm). Similar effect has been reported over GaN produced by ammonolysis before [150]. Due to high surface reactivity of SiC towards H_2O dissociation, two major species of hydrogens are

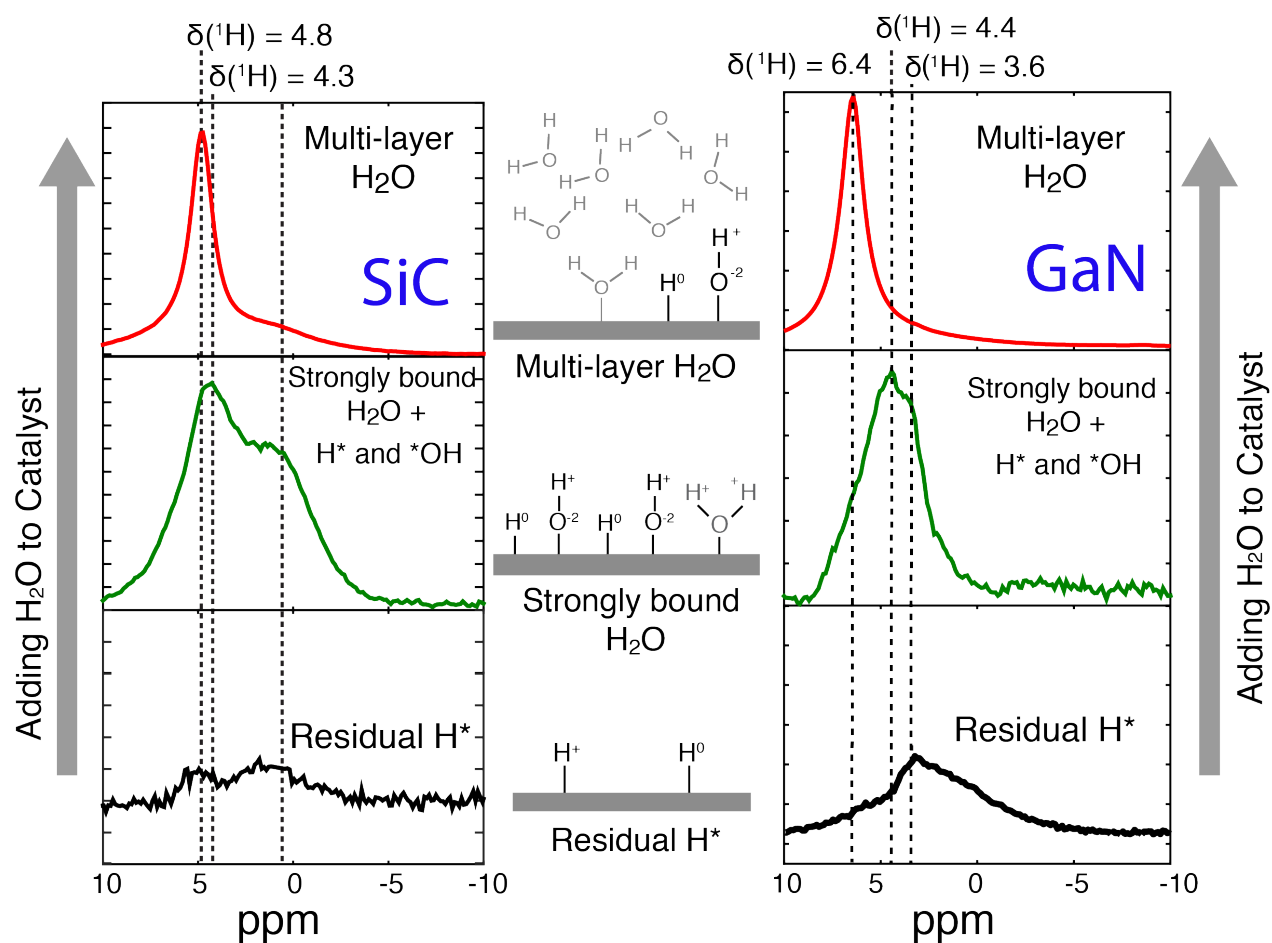


Figure 5.2: Proton SS-NMR analysis of SiC (left) and GaN (right) with increasing concentration of water. Two distinct atomic H oxidation states are isolated from the results – H⁺ shift at ~3.6 ppm on GaN and H⁰ shift at ~0 ppm on SiC.

detected upon the introduction of $\sim 1\text{ML}$ of H_2O – a neutral H^0 (shift at ~ 0 ppm) and a protonic H^+ with a shift similar to that of H^+ in H_2O (shift at ~ 4.3 ppm). Ready dissociation of H_2O was also encountered over GaN with a protonic N-H^+ (shift ~ 3.7 ppm) and another protonic H^+ from OH (shift at ~ 4.4 ppm) close to that of H^+ in H_2O (green spectra). Higher loading of H_2O ($\sim 2\text{ML}$) was utilized to further track the different H oxidation states produced via dissociative and molecular H_2O adsorption. Addition of more H_2O resulted in a deshielding effect, hence a solution-like sharp peak signal dominated in both cases (red spectra).

^1H -NMR results revealed a connection of the oxidation state of atomic H encountered on the catalyst surface and the stability of H on surface with the propensity of surface to perform hydrogenation versus H_2 evolution. ^1H -NMR results directly agree with oxidation state of surface-bound atomic H and binding sites encountered in DFT calculations (neutral H^0 adsorption atop C site of SiC and protonic H^+ adsorption atop N site of GaN). Results are in direct agreement with electronegativity of constituent atoms of both SiC and GaN. DFT energetics further suggest highly stabilized surface-bound atomic H over SiC ($\Delta E = -2.51$ eV), while comparatively less stable atomic H over GaN ($\Delta E = -0.66$ eV). Results collectively suggest that the transfer of surface-bound H to co-adsorbed carbonaceous intermediates towards hydrocarbon synthesis may be directly connected to the production and stability of neutrally charged atomic H (See Figure 5.3). Understanding this strange new H-transfer mechanism that involves the production and transfer of neutrally charged H may be necessary in photocatalytic synthesis processes to allow successful tuning of selectivity towards C_{2+} hydrocarbons and oxygenates.

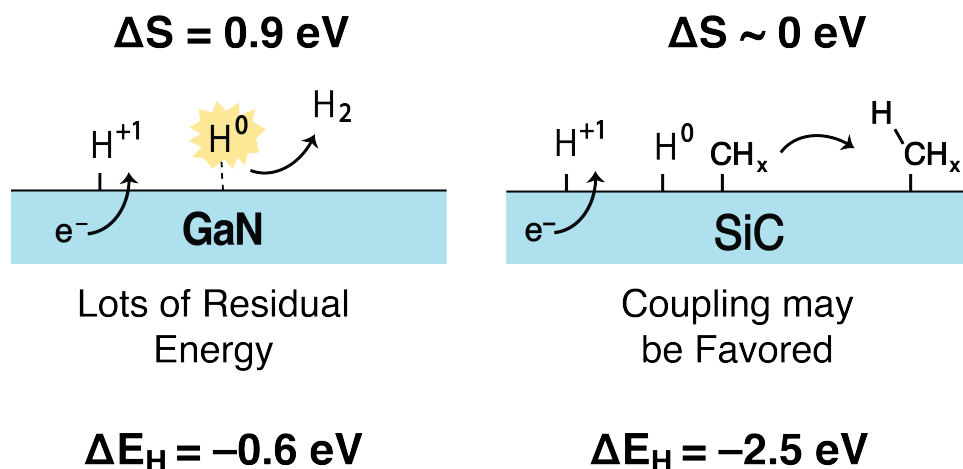


Figure 5.3: Schema to illustrate the entropy effect due to the stability of atomic H on the catalyst surface and how this dictates hydrogenation vs. H_2 evolution

5.3.3 Surface site manipulation

To investigate whether the effect of oxidation state of atomic H on catalyst product selectivity towards hydrogenation versus H_2 evolution is general or catalyst specific, we attempted to modify pristine SiC surface by incorporating O atoms on the surface (SiC core with a partially oxidized shell). CO_2 photocatalytic reduction experiments under CSPR conditions in fact showed a drastic selectivity change from CH_4 to H_2 evolution upon oxidation of pristine SiC (oxidized at 400°C under air for 4 hours). See Figure 5.4 for performance results. DFT investigation of atomic H adsorbed to an O atom of partially oxidized SiC surface (1/3rd ML O coverage) revealed less stable protonic H^+ ($\Delta E = +0.65 \text{ eV}$). Results revealed an interesting phenomena presence of two different reaction sites (C and O) resulted in two different nature of atomic H (H^0 on C and H^+ on O). Again, more stable neutral H^0 over pristine SiC correlated to selectivity towards hydrogenation and less stable H^+ over partially oxidized SiC correlated to selectivity towards H_2 evolution. Selectivity trend observed over the same material further solidifies the effect of stability of atomic H and its oxidation state in dictating the product selectivity.

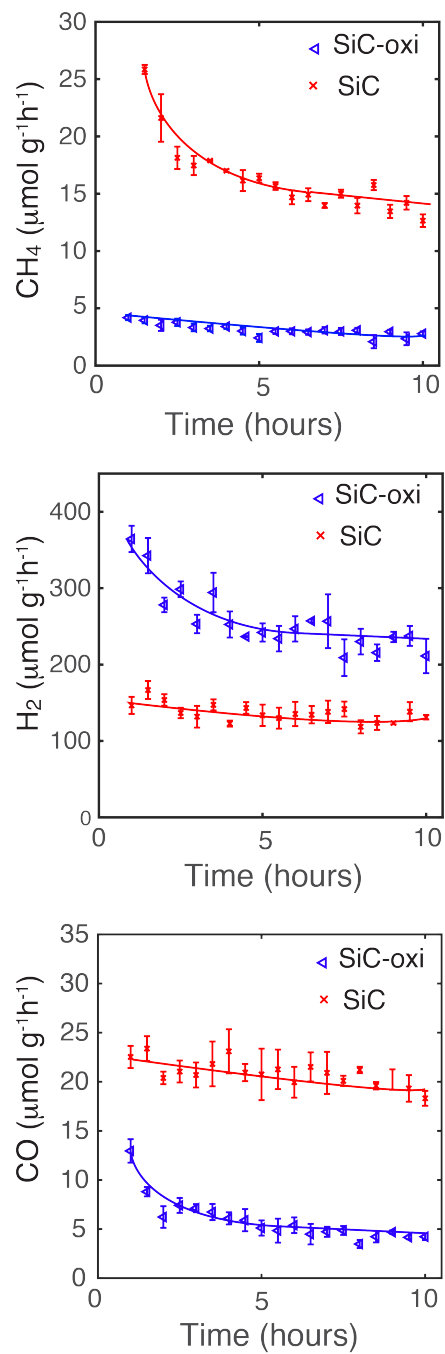


Figure 5.4: Drastic switch in selectivity from hydrogenation (CH_4 production) to H_2 evolution encountered after pristine SiC surface is incorporated with more electronegative O atoms (oxidation under air at 400°C for 4 hours)

5.3.4 Analysis of Surface Composition

Surface composition of catalysts after under reaction conditions for 12+ hours and after purposeful oxidation were probed by Talos EDS, EELS, and XPS analysis. See Figures 5.5 for TEM analysis results and Figure 5.6(a-e) for EDS, EELS, and XPS results. After purposeful oxidation of pristine SiC, Talos EDS revealed $\sim 5\%$ surface oxidation. EELS analysis suggested a partial oxidation in the form of SiC_xO_y and not a fully formed SiO_2 , even after aggressive oxidation at 400°C under air for 4 hours. Results are in agreement with the extremely low element mobility of SiC, which prevents full oxidation to SiO_2 . XPS analysis of pristine SiC after under reaction conditions of 12+ hours revealed $\sim 10\%$ surface oxidation. No full oxidation to SiO_2 was observed in all cases. On the other hand, EDS analysis revealed significant oxidation of GaN after under reaction conditions for 12+ hours (1:1 ratio of N to O). Results suggest that despite some compositional changes in catalyst surface, catalytic activity and selectivity differences encountered in experiments are likely unaffected. Catalysts were analyzed via transmission electron microscopy (TEM) before and after reaction conditions for 12+ hours to investigate the particle morphology and crystal surface facet definition as well as surface structural changes after reaction. No structural changes were observed after under reaction conditions for 12+ hours. However TEM-EDS revealed significant oxidation of GaN (almost 1:1 N to O atomic ratio). Again, XPS revealed $\sim 10\%$ surface oxidation in case of SiC after under reaction conditions for 12+ hours.

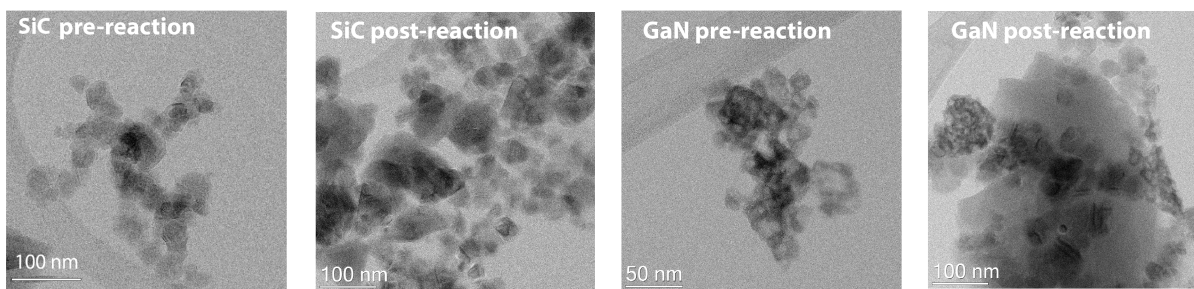


Figure 5.5: TEM investigation of both SiC and GaN before and after under CSPR conditions for 12+ hours. Results indicate no change in particle morphology and crystal surface facet.

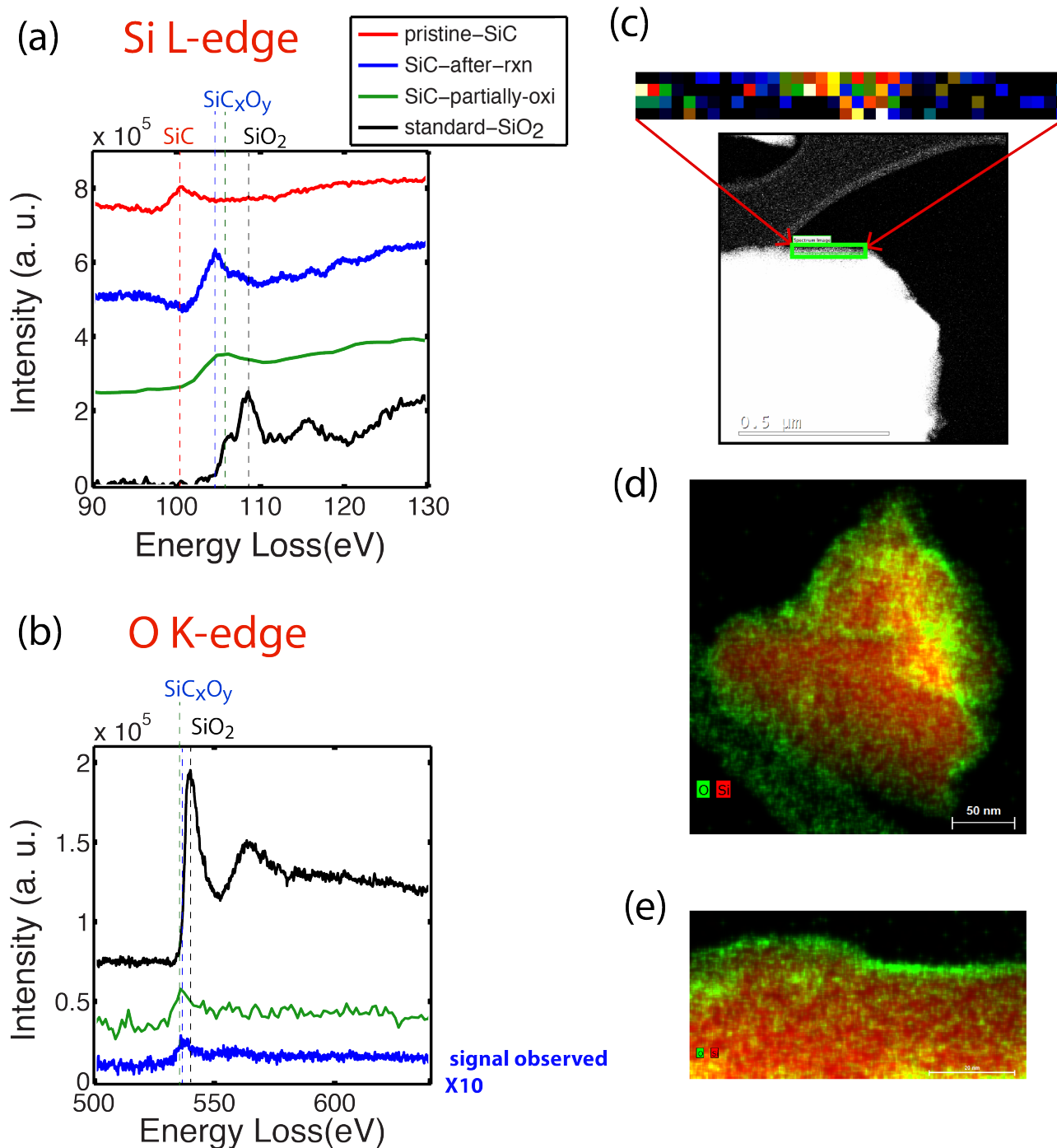


Figure 5.6: Elemental characterization of SiC via (a-b) Electron energy loss spectroscopy. EELS analysis of Si L-edge and O K-edge indicated that even after under reaction conditions for 12+ hours or under aggressive oxidation conditions (oxidation under air at 400°C for 4 hours), SiC does not fully oxidize to SiO₂ but forms a partially oxidized SiC_xO_y state. SiO₂ was analyzed for reference purpose. (c) EELS elemental mapping of surface of partially oxidized SiC particle. (d-e) TALOS-EDS of partially oxidized SiC particle. Quantification of O on surface via this technique revealed $\sim 5\%$ oxidation.

5.3.5 Discussion

The presence of neutrally charged atomic H over SiC surface suggests a new non-electrochemical H-transfer mechanism in the hydrogenation of carbonaceous intermediates towards hydrocarbon production. We postulate that an electron-mediated H-transfer via vibrational excitation of H^0 may be occurring over SiC surface. Similar mechanism has been previously reported over metal surfaces described as hot substrate electron-mediated mechanism, which have been demonstrated to dramatically enhance desorption rates, change selectivity of reaction, and exhibit large kinetic isotope effect in comparison to pure thermocatalytic processes [43, 22, 43, 105, 97]. In this process, hot electrons generated upon excitation transiently populate an unoccupied adsorbate state that transfers the adsorbate-catalyst complex to an electronically excited potential energy state, causing the system to acquire significant vibrational energy. The vibrational energy can dissipate via coupling of co-adsorbed species on the surface [44, 105, 22] or associative desorption of molecular fragments once sufficiently destabilized [97]. Although widely studied over metal surfaces, similar mechanism have been demonstrated in electron/photon stimulated desorption of ionic/molecular species over semiconductor oxide and nitride surfaces [196, 139, 140, 101, 47, 189, 147]. Our results over SiC all collectively suggest a similar vibrational excitation mechanism may be present for the neutral H^0 transfer. The proposed vibrational excitation H-transfer mechanism over SiC and proposed photoelectrochemical H-transfer over GaN are illustrated in Figure 5.7(a and b, respectively). Table 5.7(c) presents the differences encountered in stability of atomic H and oxidation states of atomic H adsorbed over SiC and GaN.

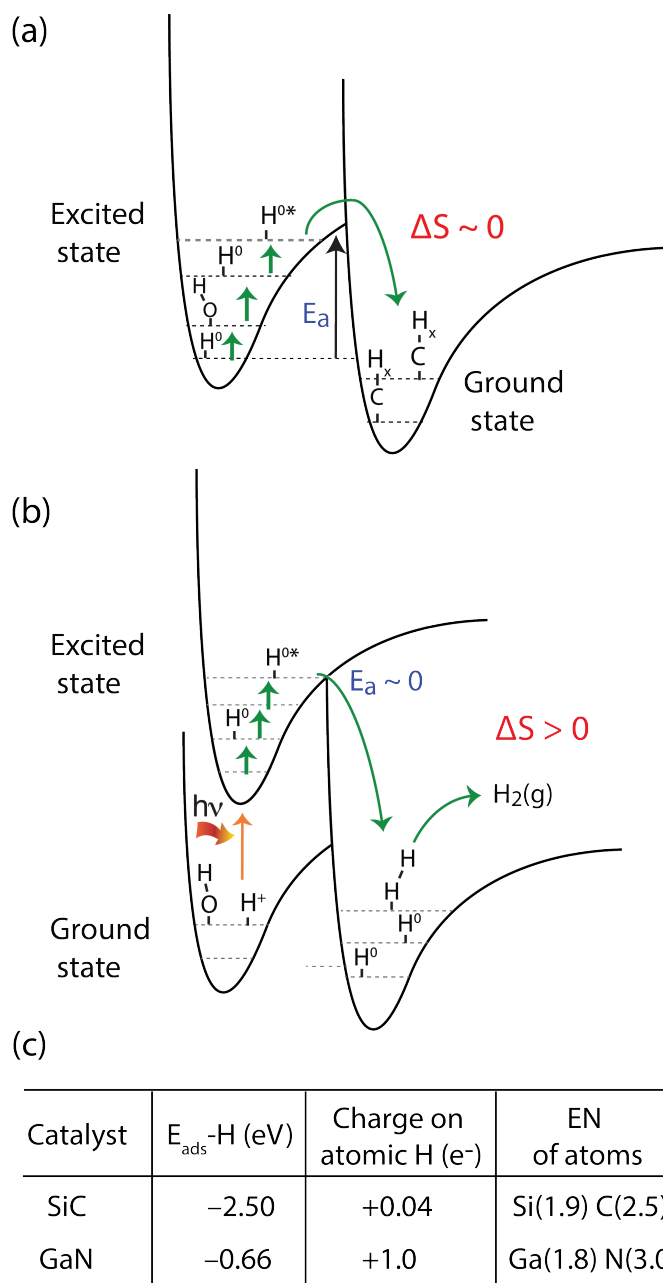


Figure 5.7: (a) Proposed vibrational excitation H-transfer mechanism over SiC that leads towards H-transfer to carbonaceous species on surface to perform hydrogenation. (b) Huge entropy driving force to evolve H_2 molecules as a result of destabilized atomic H on the surface of GaN. (c) Table showing stability of atomic H on catalyst surface and bader charge of surface-bound atomic H, which are in agreement with the electronegativity of the constituent elements of SiC and GaN.

5.4 Conclusions

A new reaction pathway and correlations that may directly contribute towards controlling selectivity in photocatalytic synthesis reactions were presented. The electronic nature of surface-bound atomic H and its stability on a semiconductor surface is likely connected to how the dissipation of energy takes place upon photoexcitation. We have isolated two different types of surface-bound atomic H via H-NMR and DFT – highly stable H^0 over SiC and less stable H^+ over GaN. KIE along with thermal effects in photocatalytic reactions further suggest the presence of vibrational barriers in photocatalytic reactions and a new H-transfer phenomena via vibrational excitation. Results over SiC indicate that destabilization of intermediates upon excitation may be enough to surmount any vibrational barriers present. Stabilized H^0 and carbonaceous intermediates over SiC correlate with enhanced activity and selectivity towards hydrogenation (CH_4 production). On the contrary, KIE study and H-NMR suggested an electrochemical pathway over GaN. Relatively less stable H^+ and carbonaceous intermediates correlate with selective H_2 and CO evolution, suggesting dissipation of energy through production of small molecules due to entropic effects that could be rampant at elevated temperature conditions. All results collectively point to different nature of H and H-transfer mechanisms present that could be directly contributing towards selectivity differences observed in experiments, i.e, hydrogenation vs. H_2 evolution.

Chapter 6

Identification of Surface Reaction Sites in Photocatalytic Synthesis that Dictate Hydrogenation versus H₂ Evolution

6.1 Overview

In this chapter, we expand the understanding of role of nature of atomic H on catalyst surfaces on catalyst product selectivity towards dictating hydrogenation versus H₂ evolution by first investigating whether this effect is general or catalyst specific. Upon incorporating O atoms on the pristine SiC surface (SiC core with a partially oxidized shell), a drastic selectivity change from CH₄ to H₂ evolution was observed. DFT investigation as well as SSNMR of atomic H adsorbed to an O atom of partially oxidized SiC surface revealed less stable protonic H⁺ on the surface, indicating the presence of two different reaction sites (C and O) responsible for two different nature of atomic H (H₀ on C and H⁺ on O). Selectivity trend observed over the same material further solidifies the effect of stability of atomic H and its oxidation state in dictating the product selectivity. This study also focused on

understanding the role of electronegativity of reaction sites by utilizing other electronegative atoms to achieve tunability of photocatalytic activity and selectivity.

6.2 Introduction

Despite several decades' worth of work, progress in the photocatalytic synthesis of increasingly complex molecules from CO_2 and H_2O has been limited due to a significant lack of mechanistic understanding, specifically understanding of surface compositions and active reaction sites, and the design rules for catalyst discovery and optimization. Focusing on the photocatalytic reduction of CO_2 by H_2O , selection, design, or optimization of catalysts using bulk electronic properties of the catalyst and electrochemically derived CO_2 reduction potentials for various products have otherwise failed to yield improved catalytic materials and any control with respect to product selectivity. Understanding the catalyst surface composition changes and the nature of surface reaction sites that could control the fate of atomic H and surface bound reaction intermediates, and ultimately the overall product selectivity is highly desired. Herein, we present the identification of two different surface reaction sites on the surface of a photocatalyst (SiC) that are directly connected to the fate of atomic H in the photocatalytic reduction of CO_2 by H_2O and light. The ultimate aim of this work is to develop a surface-activity relationship in photocatalysis that would allow direct tuning of selectivity towards C_{2+} products.

A few studies have focused on isolating the reaction sites and understanding the surface compositions of catalysts that are responsible for photocatalytic surface reactions. Most of the focus in the photocatalytic field has been on TiO_2 catalyst where O vacancies on the surface are proposed as reaction sites as a result of excitation environment [149, 46]. The Ti^{3+} sites are also proposed to be active reaction sites as a result of excited electrons in the system [162, 20, 46]. It is commonly assumed that surface chemistry mainly occurs on metal sites [162, 20, 65], however this assumption does not explain the surface chemistry effect of oxides that show stoichiometric surfaces perform reactions [181, 106, 58, 39]. Investigation of non-oxide/nitride catalysts have further indicated that p-element vacancies may be highly energetically unfavorable and may not be the active reaction sites under appreciable chemical

potential of H_2O and CO_2 [74, 39]. The vacancies may not exist on the catalyst surfaces at all, however, could still be present in the bulk [149, 67]. The transfer of excited electrons to the O species present on the surface (e^- transfer between OH^- and reactants) in photooxidation studies by Hoffmann et al. suggested that O sites are reaction sites [77]. The mechanism may be similar to population of the lattice O states [77]. Similarly, O_2 acting as electron trap in photooxidation studies to decrease e^-/h^+ recombination rates suggest that electronegativity of O may contribute to the location of excited electrons [183]. All these studies collectively suggest that non-metal sites on the surface may play a role in controlling selectivity of a photoreaction, highlighting the importance to develop a surface composition and activity relationship in photocatalytic reactions.

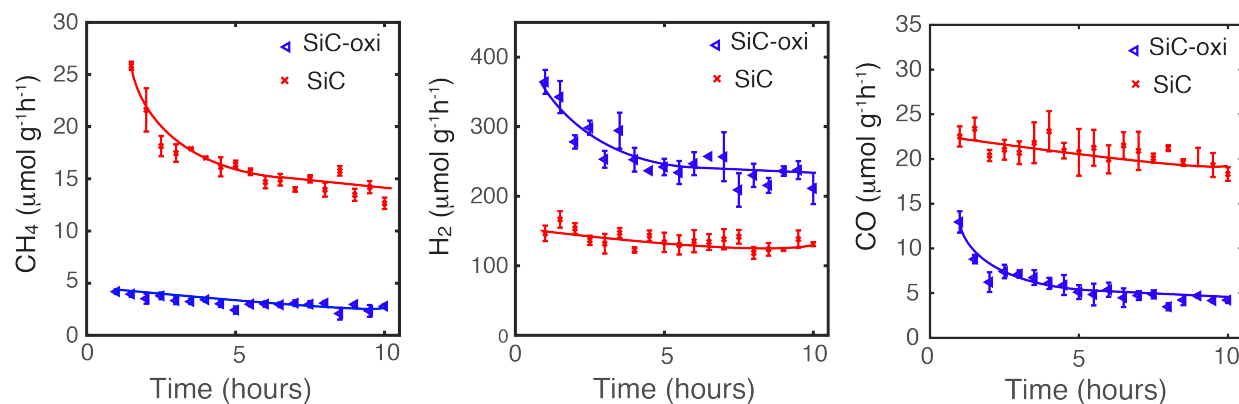
Previous chapter was focused on understanding the role of electronic nature of adsorbed atomic H and the stability of surface bound atomic H as well as stability of carbonaceous intermediates to gain tunability in photocatalytic activity and product distribution. Despite employing two prominent photocatalysts that exhibit similar conduction band edge alignment with respect to the H^+/H_2 redox potential and appropriate band gaps towards hydrogenation/ H_2 evolution, we found a drastic contrast in their performance (SiC selective towards CH_4 and GaN towards H_2 evolution). SSNMR and DFT results indicated presence of two oxidation states of surface bound atomic H may be responsible for the selectivity difference encountered. Neutral and highly stabilized H^0 was found connected with CH_4 evolution likely via a vibrational excitation H-transfer mechanism, while a less stable protonic H^+ was found connected with H_2 evolution via an electrochemical pathway. It is possible that these distinct H-transfer mechanisms on two surfaces may be dictated by the distinct catalyst compositions at the surface. Surface chemical reactivity of these photocatalysts were found to significantly affect the selectivity towards hydrogenation and H_2 evolution (Chapter 3). Herein, we will focus on identifying the surface reaction sites and the structure-activity relationship that may provide a high resolution control of catalytic activity and product selectivity.

6.3 Results and Discussion

To investigate whether the effect of oxidation state of atomic H on catalyst product selectivity towards hydrogenation versus H_2 evolution is general or catalyst specific, we modified the pristine SiC surface by incorporating O atoms on the surface (SiC core with a partially oxidized shell). CO_2 photocatalytic reduction experiments under CSPR conditions showed a drastic selectivity change from CH_4 to H_2 evolution upon oxidation of pristine SiC (oxidized at 400°C under air for 4 hours). The H_2 evolution almost doubled, while CH_4 and CO evolution diminished by almost an order of magnitude. Results suggest that incorporation of more electronegative O sites on surface reduced the number of C sites, hence diminishing CO and CH_4 production. This would also suggest that C sites are the active reaction sites for CO and CH_4 evolution. It should be noted that the lattice C atoms on pristine SiC surface do not contribute significantly to the observed activity towards CH_4 and CO production (See Figure 3.2 in Chapter 3). It is also reasonable to suggest that higher electronegativity of O sites on the surface could lead to less electron density of atomic H bound to surface O sites, and the excited electrons in the system may prefer to move to more electronegative sites on the surface. H^+ adsorbed to O sites may undergo electrochemical H_2 evolution. Results over SiC and partially oxidized SiC corroborated with the drastically different selectivity encountered over pristine SiC and GaN surfaces towards hydrogenation and H_2 evolution, respectively.

DFT calculations were utilized to gain further insights into the nature of reaction sites and surface-bound atomic H over partially oxidized SiC surface (1/3rd ML O coverage). Investigation revealed less stable protonic H^+ ($\Delta E = +0.65$ eV) on O site of partially oxidized SiC surface compared to highly stabilized H^0 on C site of SiC surface ($\Delta E = -2.5$ eV). Results suggested an interesting phenomena – presence of two different reaction sites (C and O) resulted in two different nature of atomic H (H^0 on C and H^+ on O). Again, more stable neutral H^0 over pristine SiC correlated to selectivity towards hydrogenation (CH_4 production) and less stable H^+ over partially oxidized SiC correlated to selectivity towards H_2 evolution. Selectivity trend observed over the same material further solidifies the effect of stability of atomic H and its oxidation state in dictating the product selectivity.

(a)



(b)

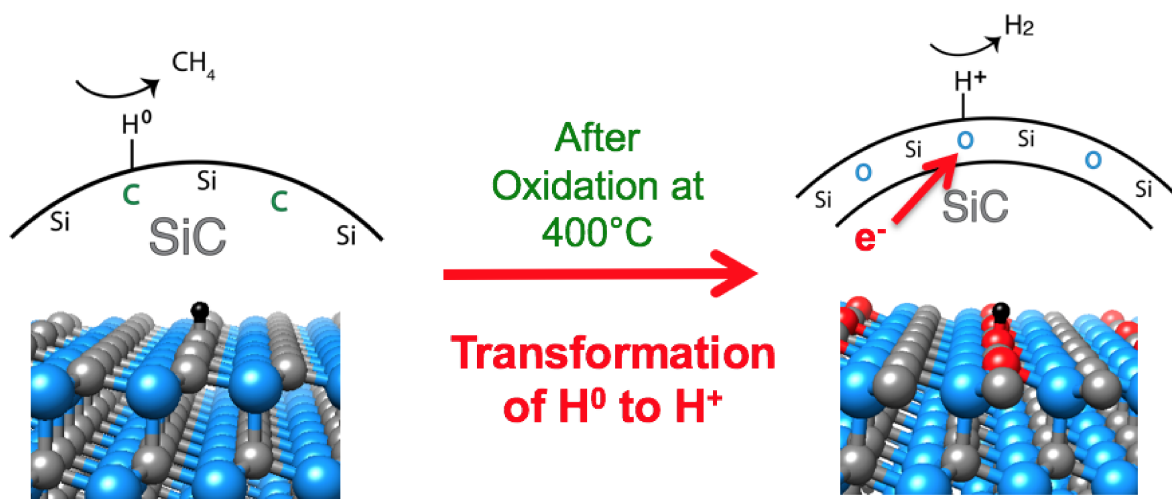


Figure 6.1: (a) Switch in selectivity from CH_4 to H_2 evolution after incorporation of O sites on surface. (b) DFT calculations suggest a stable H^0 at C site transforms to a less stable H^+ at O site, highlighting the role of reaction sites that result in different oxidation states and stability of surface-bound atomic H.

Surface composition of catalysts and verification of incorporation of O atoms after purposeful oxidation were probed by Talos EDS and EELS analysis (See Figure 5.6 in Chapter 5). After purposeful oxidation of pristine SiC, Talos EDS revealed $\sim 5\%$ surface oxidation. EELS analysis suggested a partial oxidation in the form of SiC_xO_y and not a fully formed SiO_2 , even after aggressive oxidation at 400°C under air for 4 hours. Results are in agreement with the extremely low element mobility of SiC, which prevents full oxidation to SiO_2 . XPS analysis of pristine SiC after under reaction conditions of 12+ hours revealed $\sim 10\%$ surface oxidation. No full oxidation to SiO_2 was observed in all cases. Results suggest that despite some compositional changes in catalyst surface, catalytic activity and selectivity differences encountered in experiments are likely unaffected.

H-NMR results further revealed a connection of the oxidation state of atomic H encountered on the catalyst surface and the propensity of the surface to perform hydrogenation (in case of pristine SiC) versus H_2 evolution (in case of oxidized SiC). SSNMR results are presented in Figure 6.2. Residual H^0 signal was observed on a clean partially oxidized surface at ~ 0.6 ppm. Reduction of catalyst under 2% H_2 at 700°C for an hour resulted in two H signals – H^0 at ~ 0.6 ppm at C site and H^+ at ~ 2.5 ppm at O site. Results directly agree with oxidation state of surface-bound atomic H and binding sites encountered in DFT calculations (neutral H^0 adsorption atop C site of SiC and protonic H^+ adsorption atop O site of partially oxidized SiC surface) and with electronegativity of constituent atoms of SiC and SiC_xO_y . DFT and ^1H -SSNMR results collectively suggest that the transfer of surface-bound H^0 to co-adsorbed carbonaceous intermediates may be directly connected to the production and stability of neutrally charged atomic H on the C site of SiC. Similarly, the recombination and desorption of H_2 from O site of SiC_xO_y may be directly connected to the production and stability of protonic H^+ on the O site. Understanding the nature of surface reaction sites that are responsible for the transfer of H^0 or H^+ towards hydrogenation or H_2 evolution steps may allow successful tuning of selectivity towards C_{2+} hydrocarbons and oxygenates.

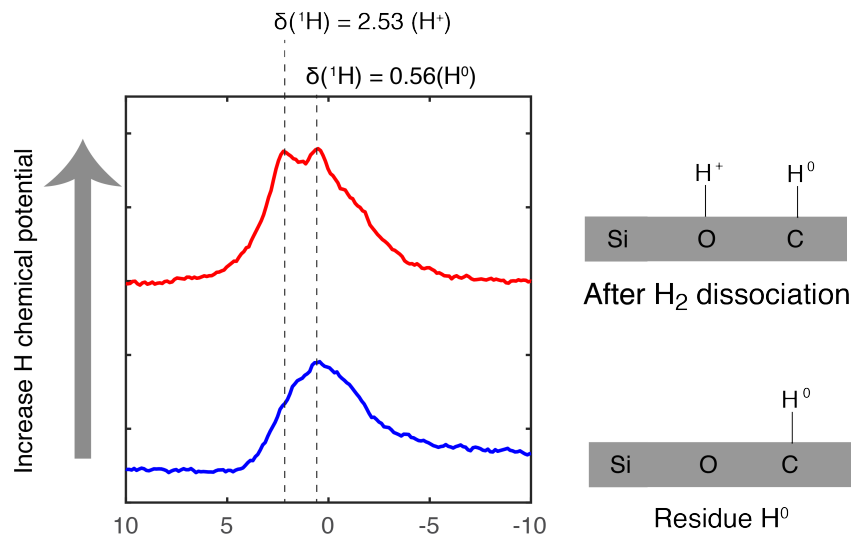


Figure 6.2: Vibrational nature of H transfer over SiC (left) and electrochemical H transfer over GaN (right) isolated via kinetic isotope effect. SiC exhibited KIE (~ 1.7 towards hydrogenation at steady state). No KIE was observed in case of CO production. D₂ evolution was slightly higher compared to H₂ evolution over SiC. GaN did not exhibit KIE towards any products.

The effect of change of electronic structure of reaction sites due to the presence of more electronegative reaction sites on photocatalytic synthesis reactions was further probed by adding other electronegative atoms (I and Cl) to pristine SiC surface in separate experiments. Results are presented in Figure 6.3. The aim of this study was to understand whether the preferential transfer of excited electrons is dictated by the presence of more electronegative atoms like O, which could directly affect the catalyst selectivity. Addition of just 3 mol% of Cl atoms to the catalyst surface resulted in dramatically diminished CH₄ and H₂ evolution activity. Similar effect was observed when 0.6 mol% and 3 mol% I was incorporated on the surface of pristine SiC, however the effect was less pronounced compared to Cl. The electronegativity of Cl and I atoms are higher than C atom by 0.6 and 0.1 on a Pauling scale. Although the overall photocatalytic activity diminished in these studies, a clear trend between electronegativity of surface reaction sites and activity could not be established because O still promotes H₂ evolution despite being highly electronegative (3.44 on Pauling scale). However, results suggest that more electronegative atoms may act as electronic sink to excited electrons in the system.

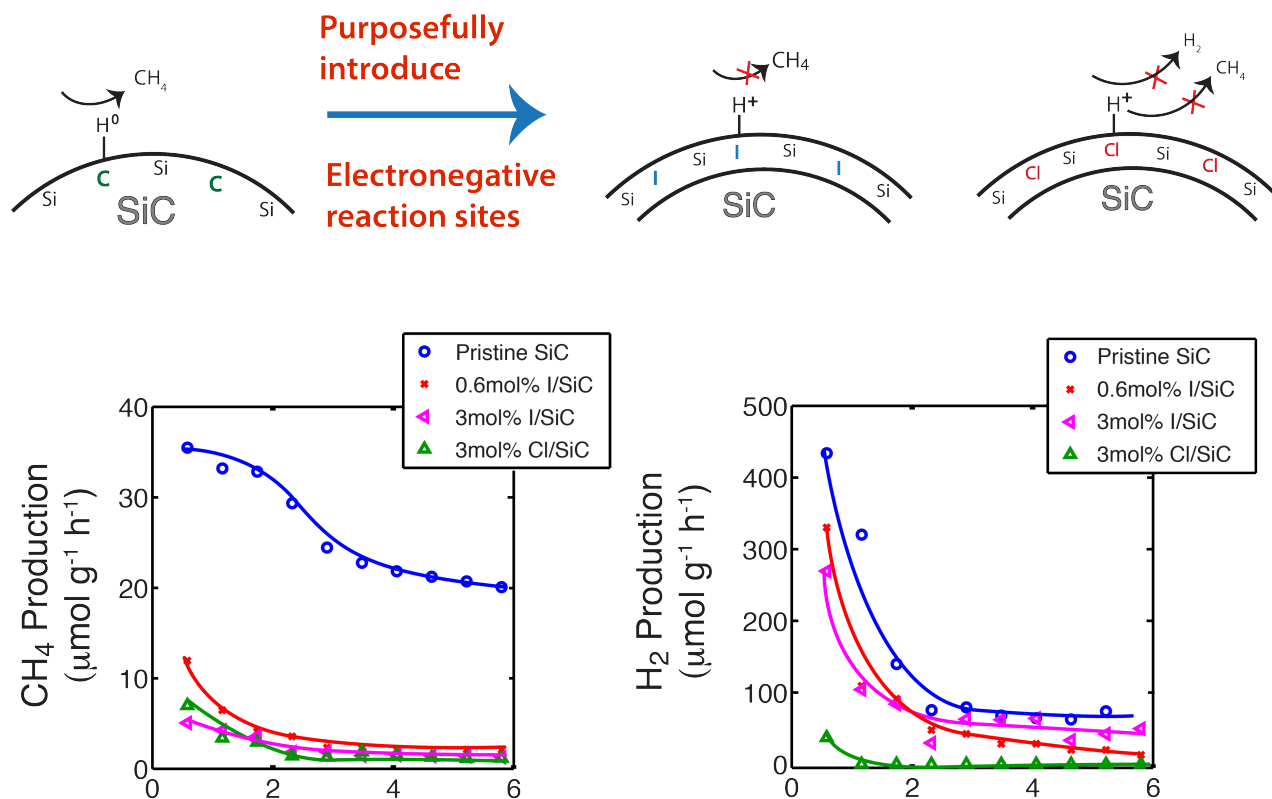


Figure 6.3: Vibrational nature of H transfer over SiC (left) and electrochemical H transfer over GaN (right) isolated via kinetic isotope effect. SiC exhibited KIE (~ 1.7 towards hydrogenation at steady state). No KIE was observed in case of CO production. D_2 evolution was slightly higher compared to H_2 evolution over SiC. GaN did not exhibit KIE towards any products.

6.4 Conclusions

Through this study, we demonstrated that identifying the surface reaction sites and the structure-activity relationship may provide a high resolution control of catalytic activity and product selectivity in photocatalytic synthesis processes. Results suggested that two different surface reaction sites, C and O, are responsible for hydrogenation and H₂ evolution, respectively. These reaction sites directly correlated to the electronic nature of surface-bound atomic H (H⁰ on C and H⁺ on O, respectively), which resulted in different selectivity towards hydrogenation and H₂ evolution, respectively. ¹H-SSNMR results coupled with DFT calculations indicated the transformation of neutral atomic H⁰ on C site of pristine SiC to protonic H⁺ on O site of partially oxidized SiC surface. These findings directly suggested the transfer of excited electrons to more electronegative sites on surface. Although clear trend between degree of electronegativity of surface reaction sites and catalytic performance is not solidified at this point, our results already suggest that understanding the surface reaction sites and structure-activity relationship may allow more tunability of photocatalytic activity and selectivity.

Chapter 7

Insights into Improving Reaction site Density in Single-site ORR Electrocatalysts

7.1 Overview

In this chapter, we utilize computational surface science approach to direct the development of non-noble metal oxygen reduction reaction (ORR) catalysts consisting of TM ceramic nanoparticles covalently connected to doped carbon supports. Developing an electronic structure and surface chemical understanding of inexpensive electrocatalysts is crucial to enable rapid and rationally directed development of new and improved fuel cell devices. By first understanding the composition and reactivity of the active sites of the single-site FeN_x/C catalyst, clear directions forward may be developed with respect to the TM ceramic composition space that is promising to investigate experimentally for ORR catalysts. In this study, we have developed a reactivity map that correlates the composition of TM ceramics with their oxygen affinity and ORR activity. Out of these screening studies, TM sulfides and selenides show the greatest promise and the largest degree of tunability with respect to activity.

7.2 Introduction

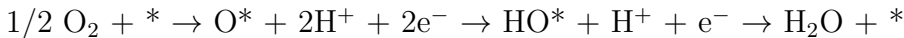
Non-noble metal ORR catalysts based on first row transition metals embedded in nitrogen-rich carbon supports exhibit overpotentials comparable to platinum in acidic media [108, 89]. These materials are promising replacements in low temperature fuel cells, but they still suffer from low current density due to the low density of active surface reaction sites and stability issues at higher voltage excursions [171, 19]. These catalysts consist of single atoms of TM metals like Fe, Co, Ni, or Cu chemically bonded to nitrogen in nitrogen-rich carbon supports [19]. The reaction sites have been characterized as (TM) N_x /C sites with covalent TM-N-C bonds linking the nitrogen and carbon to the TM [98, 94]. Efforts to boost this site density by simply increasing the loading of the non-noble metal has shown that the current density increases to a limit, plateaus, and then decreases again [171]. Unfortunately, even at their maximum performances, these catalysts are not sufficiently active to reasonably compete with Pt in size constrained fuel cell units. ORR catalysts based on non-noble metals also suffer from over oxidation and leaching of the TM elements under reaction conditions due to unselective hydrogen peroxide formation and weak TM-support bonds [19, 33]. Hence, by understanding the covalent bonding of the TM ceramics and their connections to the doped carbon support, the stability and durability of the ORR catalysts can be improved.

We utilize a fundamental surface science approach to understand if activity towards oxygen reduction reaction (ORR) could be improved by densifying the active reaction sites of single-site catalysts of Fe, which could favorably impact the performance of fuel cells. Because the single-site Fe catalysts have been reported to exhibit overpotentials similar to Pt experimentally [36, 19], their computationally derived surface reaction energetics can also be expected to be similar to that of Pt. However, rational catalyst design of these single-site catalysts with high reaction site density is still a challenge, besides some very recent work on improving the site density [179]. By first understanding the composition and reactivity of the active sites of the single-site FeN_x/C catalyst, directions forward can be developed with respect to the TM ceramic composition space that is promising for ORR catalysts. Investigating the bulk ceramic materials will help us understand if there exist any similarity of these compositions with the single-site catalysts. This will also allow us

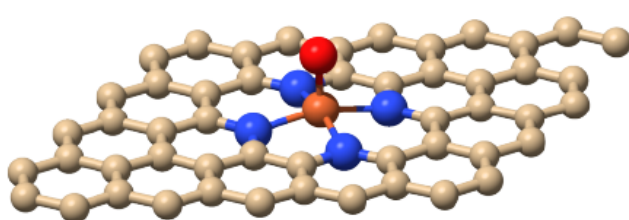
to understand the strength of bonding between TM and non-metals as well as reactivity of variable stoichiometry of non-metals. Furthermore, focus on TM ceramics as ORR catalysts may alleviate the concerns of S, CO, and other poisons present in reformat gases. The fundamental understanding and new materials developed in these studies may also be applicable for the development of electrocatalysts for the use of small oxygenate fuels such as methanol, ethanol, formic acid, etc.

7.3 Computational Method

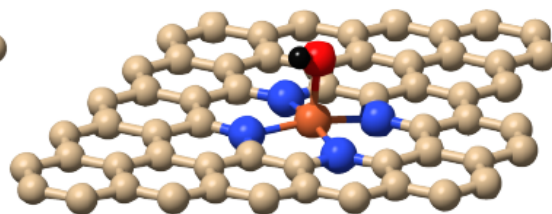
The study of ORR is carried out using DFT calculations to provide molecular-scale insight into the thermodynamics of adsorbed intermediate states. DFT calculations were performed using Vienna ab initio simulation package (VASP 5.3.3). The generalized gradient approximation (GGA) with PBE-sol was utilized to describe the exchange correlation functional because PBE-sol has been proven to capture the electronic structure of ceramic solids fairly well [138, 41]. Adsorbate coverage of 0.25-0.33 ML was utilized in each calculation depending on the unit cell size of the ceramic solids. Chemical hydrogen electrode (CHE) method developed by Norskov et al. [135] was utilized to model the elementary reactions involved in ORR. In this method, the free energy of the proton-electron pair is assumed to be equal to that of hydrogen gas at standard conditions [135]. Only dissociated ORR mechanism pathways were investigated in this study. The dissociative mechanism undergoes the following elementary reaction steps:



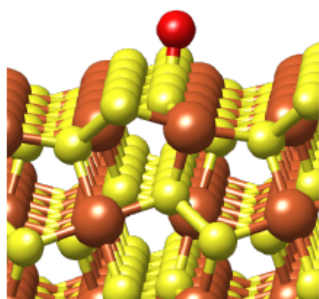
Extensive suite of model systems comprised of single Fe atoms and zero to four N atoms bound to the lattice carbons of graphene sheets were investigated (See Figure 7.1). These configurations of TM embedded in graphene or doped graphene systems have been extensively suggested via spectroscopy and quantum chemical calculations [98, 108, 89, 19]. Utilizing the established chemical hydrogen electrode model to screen reaction site compositions and geometries [135], stability of O^* and OH^* intermediates have been calculated in this work over different stoichiometries of stable forms of carbides, nitrides, phosphides, sulfides, and selenides of Fe metal. The most favorable adsorption sites of two



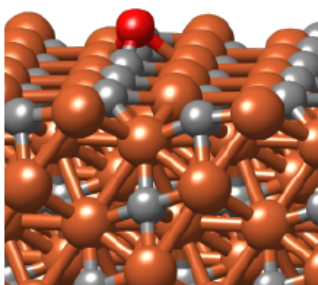
O* ads on FeN₄/G



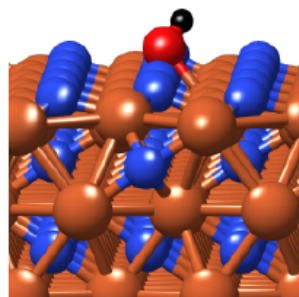
OH* ads on FeN₄/G



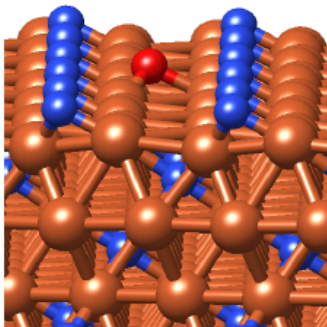
O* ads on FeS₂



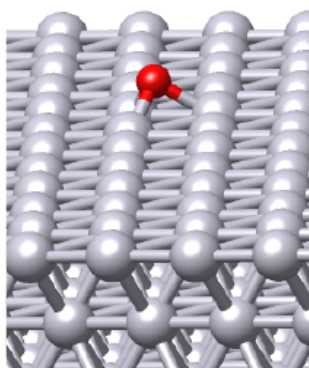
O* ads on Fe₂C



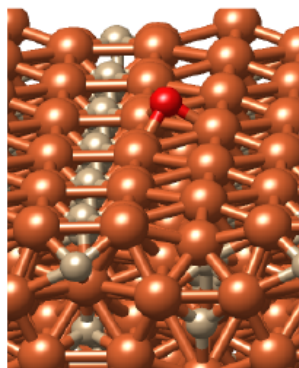
OH* ads on Fe₂N



O* ads on Fe₄N



O* ads on Pt



O* ads on Fe₃C

Figure 7.1: Model figures showing single-site catalysts and Fe ceramic surfaces with O* and OH* adsorbates.

ORR intermediate species – O^* and OH^* – were calculated over all catalysts by checking all possible adsorption sites on the surface.

7.4 Results and Discussion

Investigation of bulk ceramic forms of the single-site Fe catalysts suggested that bulk Fe carbide and nitride nanoparticles at the most energetically favorable bulk stoichiometry (Fe_3C and Fe_4N) are too chemically reactive towards O^* and OH^* intermediates and would be poor ORR catalysts (See Figure 7.2). This trend can be understood by considering that the metal-rich nature of the Fe carbide and nitride results in reactivity towards oxygen that is closer to that of bulk metal. To circumvent this problem, we investigated the surface reactivity of the available metal lean forms of the same materials of Fe (Fe_2C and Fe_3N). It was found that increasing non-metal content systematically decreased the reactivity towards O^* and OH^* , but the reactivity was still not enough to be appropriate ORR catalysts. Including the single-site FeN_4/C in this trend, clearly indicates that metal-to-nonmetal ratio can be used as a general tunable parameter to modify ORR activity. Results indicate that the metal-rich nature of nitrides and carbides make these materials highly reactive towards O^* and OH^* intermediates, hence diminishing the ORR activity.

We further expanded the study of TM ceramics to naturally nonmetal-rich ceramics of Fe and Co sulfide, phosphide, and selenide to understand the effect of electron-filling and orbital-orbital overlap as we change the non-metal atoms. A strong electronic effect is found to be present over these materials, yet the trend previously encountered still holds. Non-metal rich FeS_2 was found to exhibit reactivity towards O_2 and ORR intermediates similar to that of Pt and $FeSe_2$ was less reactive but showed promise towards ORR. However, Fe_2P was too reactive. We also extended this investigation to single site catalysts of Co/N/C and Cu/N/C. Like in case of Fe ceramics, both CoS_2 , and $CoSe_2$ showed activity close to Pt towards ORR. Co_2P , like Fe_2P , was found too reactive towards binding O^* and OH^* intermediates. Out of these screening studies, TM sulfides, and selenides showed great promise and the largest degree of tunability with respect to ORR activity. Results suggest that improved bonding

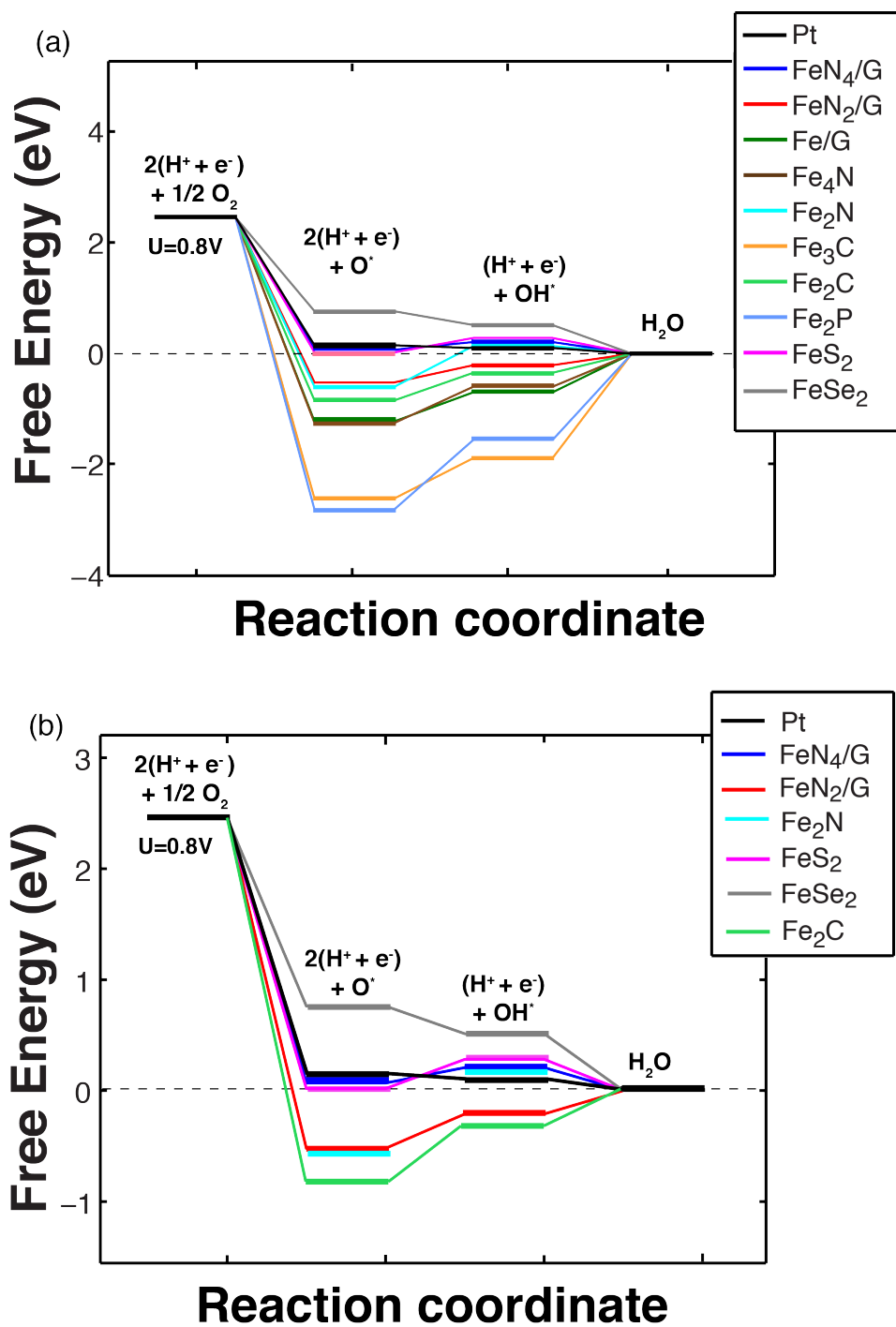


Figure 7.2: Free energy pathway for ORR over Fe single-site catalysts and Fe ceramic solids calculated at (a) 0.8V and (b) zoomed in plot of (a) showing materials that exhibit activity closer to Pt.

7.5 Conclusions

In summary, results indicated that significant decrease in overpotential and a concomitant increase in fuel cell durability may be achieved by using strong TM-non-metal-graphene bonds and metallic-like TM ceramics. The reasoning being that the ceramic can be directly covalently linked to the carbon support through strong TM-S-C, TM-P-C, or TM-Se-C bonds. The connection between S, P, and Se bonds to TMs are robust and provide an intermediate connection to the carbon, which may lead to greatly improved stability. We found that densifying the active reaction sites of single site catalysts of Fe and Co by utilizing bulk metal-rich nitrides and carbides of Fe and Co is not possible since these bulk forms are too reactive towards O^* and OH^* intermediates. More appropriate surface chemistry towards ORR was encountered over ceramics with larger p-block non-metal elements (iron and cobalt sulfides and selenides), nearing the activity of Pt in ORR, as the bonding within the constituent elements in the ceramic materials is improved by increasing the orbital-orbital overlap between the metal and non-metal atoms. Results suggest that understanding the strength and chemical nature of bonding between the constituent elements in ceramic materials is crucial in designing ORR catalysts to replace highly expensive Pt group metals.

Chapter 8

Conclusions and Future Directions

8.1 Overview

In this dissertation, we have investigated several chemical and physical phenomena at the mechanistic level that drive the photocatalytic synthesis of hydrocarbons and oxygenates from CO_2 with H_2O at elevated temperatures. Results hopefully provide a basis for understanding the mechanism such that new efficient photocatalysts may be selected in a more rational way. Using a combined ground-state computational surface science modeling and experimental approach under CSPR conditions, some clear connections between catalyst surface reactivity, thermodynamics stability of surface-bound atomic H and carbonaceous intermediates, and experimentally observed catalytic activity and selectivity have been isolated. Results provide insights into the role of surface chemistry and the development of new H-transfer mechanisms in photocatalysis that have not been explored previously, which have enabled the tunability in the selectivity between hydrogenation to produce hydrocarbons and oxygenates versus H_2 evolution – a critical efficiency aspect of the system.

8.2 Chapter 3. Insights into Elevated Temperature Photocatalytic Reduction of CO₂ with H₂O

By employing a concentrated solar photoreaction (CSPR) approach (350°C reaction conditions) over four prominent semiconductor photocatalysts, we demonstrated that inordinately high surface chemical reactivity may be necessary to stabilize reaction intermediates along highly endothermic pathway (e.g., CH₄ formation energy ~ 9 eV) to achieve hydrocarbon production from thermodynamic sink molecules such as CO₂, H₂O, and potentially even N₂ reduction to NH₃, and that new reaction intermediates may be accessible through the combination of photo and thermal energy inputs from the solar energy and the enhanced surface reactivity of the catalysts. This study and comparisons with published ambient temperature reaction results suggested that catalysts with elevated surface reactivity may inhibit reverse reactions that consume intermediates that lead to CH₄ production. Most pronounced effect is observed in the comparison of the performance results over Pt/TiO₂ or GaN and SiC or Si. Pt/TiO₂ and GaN both present moderately low surface reactivity and what appears to be a lack of hydrogenation ability, most likely due to unstable reaction intermediates being consumed to form CO and H₂ or CO₂ and H₂O. On the other hand, SiC and Si were found to significantly stabilize intermediates, which limits reverse reaction driving force and slows their unselective consumption. Sub-study of most active catalysts towards hydrogenation – SiC and Si – at a lower temperature (250°C) revealed that elevated temperature conditions can be detrimental to photocatalysts with inherently low Debye temperatures. Inhibited hydrogenation and H₂ evolution was observed over Si likely due to low Debye temperature ($T = 363^\circ\text{C}$) and e^-/h^+ recombination rates becoming appreciable. In contrast, SiC is able to thermally promote one or both of C–O cleavage and hydrogenation steps to achieve dramatically improved CH₄ production at elevated temperatures in comparison to near-ambient tests where much lower rates were encountered [85, 57, 157]. Elevated surface reactivity appears to be beneficial in the total reduction of CO₂ yet limits O₂ evolution, hence an oxygen-evolution co-catalyst is likely necessary when using more reactive surfaces such as carbides to balance the reactivity.

8.3 Chapter 4. Mechanistic understanding into controlling selectivity towards hydrogenation versus H_2 evolution

By employing a ground-state Density-Functional Theory (DFT) modeling approach, we tried to answer the primary mechanistic question of how catalyst surface reactivity and intermediate stability correlated with observed catalytic performance over SiC and GaN photocatalysts in CO_2 reduction by H_2O . This study and comparisons with our elevated temperature experimental results as well as published ambient temperature reaction results revealed clear connections between catalyst surface reactivity, stability of surface bound atomic H and carbonaceous intermediates, and experimentally observed catalytic activity and selectivity. Selective CH_4 production over SiC was found to track well with more stabilized reaction intermediates. Conversely, the relatively low surface reactivity of GaN and less stabilized reaction intermediates showed promotion of H_2 and CO production since the energetics of reverse reactions are still strongly exothermic. Entropic effects that greatly favor the release of energy through the production of small molecules may also play a significant role in the reaction. Furthermore, energetics suggested final hydrogen transfer to form CH_4 on the surface as rate limiting step. Elevated surface reactivity appeared to be beneficial in the total reduction of CO_2 , yet O_2 evolution was found to be limited. Therefore, a oxygen-evolution co-catalyst is likely necessary when using highly reactive photocatalysts. Results also suggested a different H-transfer mechanism may be present on SiC surface associated with a neutrally charged stable atomic H and improved hydrogenation. Although the transfer of neutrally charged atomic H is not clear, an electron-mediated vibrational H-transfer that is not photoelectrochemical and is well-known over metals in the surface science community was postulated.

8.4 Chapter 5. The Nature of Surface-bound Atomic H and its Role in H-transfer Mechanisms and Catalyst Selectivity toward Hydrogenation vs. H₂ Evolution

By employing throughput experimental testing, spectroscopy, and quantum chemical modeling approach, we isolated two different types of surface-bound atomic H via H-NMR and DFT – highly stable H⁰ over SiC and less stable H⁺ over GaN. KIE along with thermal effects in photocatalytic reactions suggest the presence of vibrational barriers in photocatalytic reactions and H-transfer via vibrational excitation. Results over SiC indicated presence of vibrational barriers that could be surmounted upon excitation due to the destabilization of intermediates. Stabilized H⁰ and carbonaceous intermediates over SiC correlated with enhanced activity and selectivity towards hydrogenation (CH₄ production). On the contrary, KIE study and H-NMR suggested an electrochemical pathway over GaN. Relatively less stable H⁺ and carbonaceous intermediates were encountered, which correlated with selective H₂ and CO evolution. This suggested dissipation of energy through production of small molecules due to entropic effects at elevated temperature conditions. All results collectively pointed to different nature of H and H-transfer mechanisms present that could be directly contributing towards selectivity differences observed in experiments, i.e, hydrogenation vs. H₂ evolution.

8.5 Chapter 6. Identification of surface reaction sites in the photocatalytic synthesis of hydrocarbon and H₂ evolution

We demonstrated that the effect of oxidation state of atomic H on catalyst product selectivity is not catalyst specific but a general phenomena. Hence, identifying the surface reaction sites and the structure-activity relationship may provide a high resolution control of catalytic

activity and product selectivity. In this study, we demonstrated a drastic change in selectivity from CH_4 to H_2 evolution upon partial oxidation of SiC to purposefully incorporate highly electronegative O atoms onto the surface. Results revealed that two different reaction sites (C and O) are connected to the two different nature of atomic H (H^0 on C and H^+ on O, respectively), which result in the selectivity difference observed in experiments. SSNMR results coupled with DFT calculations further suggested the transformation of neutral atomic H^0 on C site of pristine SiC to protonic H^+ on O site of partially oxidized SiC surface. These findings directly suggested the transfer of excited electrons to more electronegative sites on surface. Results suggested that understanding the role of electronegativity of reaction sites may allow more tunability of photocatalytic activity and selectivity.

8.6 Chapter 7. Understanding the bonding within non-noble metal ceramic oxygen reduction reaction (ORR) catalysts

To understand if activity towards oxygen reduction reaction (ORR) could be improved by densifying the active reaction sites of single site catalysts of Fe and Co, we investigated the performance of bulk metal-rich nitrides and carbides of Fe and Co towards ORR. Bulk carbides and nitrides (Fe_3C , Fe_4N , CoN , and Co_2C) were found too reactive towards O^* and OH^* intermediates due to their high inherent surface reactivity. Moving to higher non-metal stoichiometry (Fe_2C , Fe_2N), these ceramics were found still too reactive towards ORR, however showed improved activity compared to their higher metal-rich forms. More appropriate surface chemistry towards ORR was encountered over ceramics with larger p-block non-metal elements (iron and cobalt sulfides and selenides), nearing the activity of Pt in ORR, as the bonding within the constituent elements in the ceramic materials is improved by increasing the orbital-orbital overlap between the metal and non-metal atoms. Results indicated that understanding the strength and chemical nature of bonding between the constituent elements in ceramic materials is crucial in designing ORR catalysts to replace highly expensive Pt group metals.

8.7 Outlook on Future Work

As we explore the photocatalytic synthesis of complex molecules, reaction mechanisms will involve more complex surface-bound intermediates of varying electronic character. Understanding the stability and electronic nature of these species on the catalyst surface may be crucial in dictating catalyst performance and selectivity. However, a significant lack of understanding with respect to catalyst electronic properties, surface chemistry, and surface reaction mechanisms that drive CO₂ reduction towards selective production of hydrocarbons or oxygenates still persists. Hence, many questions remain to be answered in the field of photocatalytic synthesis reactions in general.

8.7.1 Investigation of High Debye Temperature Photocatalysts

SiC was employed in this study since it exhibits several outstanding properties like high Debye temperature (927°C), low element mobility, appropriate band gap (2.4 eV), and appropriate surface chemistry towards C, H, and O. Testing other high Debye temperature photocatalysts under CSPR conditions will allow to expand the understanding of elevated temperature photocatalysis beyond the materials we investigated. Some materials with variable Debye temperatures that could be potentially utilized are NbC (467°C), WC (348°C), CrC (727°C), TiC (677°C), etc. The screening of other materials will not only allow us to test whether the elevated surface reactivity effect observed over SiC is general, but also to investigate the nature of atomic H and how that affects reaction selectivity.

8.7.2 Designing Better Photocatalysts with Balanced Surface Reactivity towards OER

In Chapters 3 and 4, our results suggested that catalysts with elevated surface reactivity may inhibit reverse reactions that consume intermediates that lead to C–O cleavage and hydrocarbon production. However, utilizing photocatalysts with elevated reactivity also results in high surface oxygen affinity and the limited O₂ evolution. Employing O₂ evolution reaction (OER) co-catalysts that exhibit high Debye temperatures may alleviate surface

oxidation by balancing out the high surface reactivity exhibited by selected carbide catalysts. A Z-scheme approach may be employed to enhance O_2 production using an added co-catalyst. Investigation of the electronic coupling of catalyst that exhibits elevated surface reactivity with a small selection of high Debye temperature oxides and nitrides that are predicted to be effective in O_2 evolution at elevated temperatures, namely NbN (357°C), ZnO (427°C), AlN (717°C), and Si_3N_4 (697°C) will allow to shed light on how the balance of reduction and oxidation reactions affect the overall performance of SiC and similar materials in hydrocarbon production from CO_2 and H_2O . Specifically, enhancement of reduced product evolution in the presence of an effective OER catalyst will indicate that a general balancing of e^+/h^+ is critical. On the other hand, if select reduced products are enhanced, namely CH_4 or H_2 and CO, the presence of both electrochemical and vibrational reaction steps will be further clarified. Performing these reactions over a range of temperatures may further allow us to understand the effect of the presence of charge balancing in the reaction and how e^+/h^+ recombination may affect the O_2 evolution catalyst detrimentally.

8.7.3 Understanding the Reactant Surface Coverage Effects

Reactant surface coverage effects need to be investigated by employing different chemical potential of CO_2 and H_2O to understand the effect in selectivity towards hydrogenation, C-C coupling, and H_2 evolution. In this study, we encountered that catalysts with elevated surface chemical reactivity are ideal for photocatalytic synthesis. Hence, it is not surprising that the reaction conditions employed can significantly affect the overall activity and selectivity of the reaction due to surface coverage effects. By employing some preliminary batch phase reaction tests, we have found that the SiC catalyst activity is quite sensitive to the amount of water present in the system indicating a poisoning effect at high H_2O loadings that must be avoided. This can be rationalized by noting the high surface reactivity of SiC towards H_2O , as understood by experimental and computational results ($E_{\text{ads}} = -1.2 \text{ eV}$), may lead to a completely H_2O covered surface with less access to CO_2 adsorption for its reduction. This preliminary study has suggested that catalyst-dependent optimal reaction conditions need to be determined depending upon the catalyst surface chemical reactivity to understand the selectivity changes as a function of CO_2 and H_2O chemical potential as well as the

temperature of the catalysts. Elevated pressure tests to find the optimal chemical potential of CO₂ and H₂O on the surface of the catalyst may allow significant tunability in catalyst selectivity towards C-C coupling products. These well-defined experiments are expected to shed significant light on several unknown aspects of the system that will lead to successful hydrogenation and limited H₂ evolution.

8.7.4 Understanding what drives the C–C coupling reaction by utilizing other reaction intermediates

Understanding how carbon-carbon coupling may be promoted and balanced with hydrogenation to achieve C₂₊ hydrocarbons and oxygenates from CO₂ and H₂O would dramatically enhance the efficiency of the process. Probe reactants such as methanol, ethanol, formaldehyde, acetaldehyde, etc. could be utilized to produce one and two carbon reaction intermediates via oxygen removal in the presence of H₂O to force photocatalytic C–C coupling and investigate hydrogenation selectivity. Our preliminary reactions utilizing methanol and ethanol with H₂O have already suggested that photocatalytic C–C coupling is definitely possible and that catalyst selection directly affects selectivity between saturated and unsaturated HC production.

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