Nanomaterials for Sustainability: Using Spectroscopy and Quantum Chemistry for Microkinetic Modeling of Thermo- and Photo- Catalysts

Amir Rahmani Chokanlu
University of Maine, amir.rahmani@maine.edu

Follow this and additional works at: https://digitalcommons.library.umaine.edu/etd

Part of the Chemistry Commons

Recommended Citation
https://digitalcommons.library.umaine.edu/etd/3569

This Open-Access Dissertation is brought to you for free and open access by DigitalCommons@UMaine. It has been accepted for inclusion in Electronic Theses and Dissertations by an authorized administrator of DigitalCommons@UMaine. For more information, please contact um.library.technical.services@maine.edu.
NANOMATERIALS FOR SUSTAINABILITY: USING SPECTROSCOPY AND QUANTUM CHEMISTRY FOR MICROKINETIC MODELING OF THERMO- AND PHOTO- CATALYSTS.

By
Amir Rahmani Chokanlu
M.Sc. University of Tehran 2012
B.Sc. Sharif University of Technology, 2010

A DISSERTATION
Submitted in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy (Chemistry)

The Graduate School
The University of Maine
May 2022

Advisory Committee:
Brian G. Frederick, Associate Professor of Chemistry, Co-advisor
François G. Amar, Professor of Chemistry, Co-advisor
Robert J. Lad, Professor of Physics
Thomas J. Schwartz, Assistant Professor of Chemical and Biomedical Engineering
Carl. P. Tripp, Professor of Chemistry
Heterogeneous catalysis, including thermal- and photocatalysis, is a key technology toward developing industrial processes for a sustainable future. Therefore, the study of surface reactions and catalyst properties includes most studies in this area. There has been extensive work put into developing experimental and computational tools to understand surface and interface phenomena, describe mechanistic chemical transformations, and simulate the behavior of surface reactions to develop better catalysts and more efficient processes.

This thesis describes experimental and theoretical investigations to explain the reaction mechanism of ethanol conversion to value-added products over an MgO/SiO₂ catalyst, a kinetic model describing the surface changes during pretreatment of WO₃ as hydrogenation and hydrodeoxygenation catalyst, and a fundamental study of the electronic structure of sulfur-doped TiO₂ to explain the enhanced photocatalytic activity of this material.

The main goal of all the chapters of this thesis is to generate knowledge of these heterogeneous catalysis systems and add a small step in the bridge toward a sustainable future.
DEDICATION

To my wife, Elnaz and my parents, who always believed in me and supported me.
ACKNOWLEDGEMENTS

Throughout the writing of this dissertation, I have received a great deal of support and assistance.

First and foremost, I am incredibly grateful to my supervisor, Dr. Brian Frederick, for guiding me well throughout the research work. He is my mentor and a better advisor for my doctorate study beyond the imagination. He is the best teacher I have had, and I will always appreciate his efforts throughout my professional career as a scientist.

A special thanks to my co-advisor, Dr. François Amar, for his valuable inputs and suggestions throughout my Ph.D. program.

A sincere thanks to Dr. Thomas Schwartz for his mentorship and support. His expertise in catalysis and chemical engineering point of view enriched my vision as a chemist.

Apart from my Supervisors, I won't forget to express my appreciation to the rest of the team: Dr. Robert Lad, and Dr. Carl Tripp, for giving encouragement and sharing insightful suggestions. They all have played a significant role in polishing my research writing skills. Their endless guidance is hard to forget throughout my life. I have been lucky to sit in their classes to enrich my solid-state physics and spectroscopy knowledge.

I take this opportunity to express gratefulness to all my friends at the University of Maine Catalysis Research Group for their support and making my Ph.D. an interactive learning experience.

I would like to acknowledge the presence of my wonderful friends Shadi and Sina for being there for me. This would have been a much more difficult feat without you. Thank you all for your unwavering support and for reminding me to take breaks and have fun when I've been stressed out.

I am grateful for my parents, whose constant love and support keep me motivated and confident. My accomplishments and success are because they believed in me. Deepest thanks to my sister, who keeps me grounded, reminds me of what is important in life, and always supports my adventures.

Finally, I owe my deepest gratitude to Elnaz, who is my love. I am forever thankful for the unconditional love and support throughout the entire thesis process and every day.
TABLE OF CONTENTS

DEDICATION .................................................................................................................. iv

ACKNOWLEDGEMENTS ........................................................................................... v

LIST OF SCHEMES ..................................................................................................... x

LIST OF FIGURES ....................................................................................................... xi

LIST OF TABLES .......................................................................................................... xiv

1 INTRODUCTION ....................................................................................................... 1

1.1 Motivation ............................................................................................................. 1

1.2 Strategies to slow down, and reverse the course of climate change ................. 3

1.2.1 Batteries ........................................................................................................... 6

1.2.2 H\textsubscript{2} and NH\textsubscript{3}, Today’s high demand chemicals and fuel of tomorrow .......... 11

1.2.2.1 Carbon-neutral ammonia ............................................................................. 12

1.2.2.2 Carbon-neutral Hydrogen ............................................................................ 18

1.2.2.2.1 Production of Hydrogen fuel ................................................................. 20

1.2.2.2.2 Solid state technology of hydrogen storage ........................................ 26

1.2.2.2.3 Hydrogen fuel cell .................................................................................. 28

1.2.3 Carbon-neutral process for carbon-based chemicals and fuel .................... 30

1.2.3.1 Biomass derived value-added hydrocarbons ............................................. 31

1.2.3.2 Direct atmospheric CO\textsubscript{2} reduction to hydrocarbons .................... 38

1.2.3.2.1 Thermal catalytic routes ..................................................................... 39

1.2.3.2.2 Electrochemical CO\textsubscript{2} reduction ................................................ 41

1.2.3.2.3 Photocatalytic reduction of CO\textsubscript{2} to hydrocarbons ...................... 43

1.3 Scope of this thesis ............................................................................................. 46

vi
KINETIC ANALYSIS OF ETHANOL CONVERSION OVER MgO-SiO$_2$................. 49

2.1 Abstract........................................................................................................... 49

2.2 Introduction..................................................................................................... 49

2.3 Materials and methods .................................................................................. 54
  2.3.1 Catalyst synthesis....................................................................................... 54
  2.3.2 Reaction kinetics measurements............................................................... 56
  2.3.3 Catalyst characterization............................................................................ 58

2.4 Results............................................................................................................. 60
  2.4.1 Catalyst selectivity and stability ................................................................. 60
  2.4.2 Reaction kinetics measurements............................................................... 62
  2.4.3 Hydrogen/deuterium isotope effect........................................................... 63
  2.4.4 Pyridine inhibition ...................................................................................... 64
  2.4.5 Catalyst characterization............................................................................ 65
  2.4.6 Operando FTIR spectroscopy .................................................................... 70

2.5 Discussion....................................................................................................... 73

2.6 Conclusions.................................................................................................... 82

2.7 Supporting Information.................................................................................. 83
  2.7.1 Butadiene Production................................................................................. 83
  2.7.2 Catalyst Deactivation.................................................................................. 84
  2.7.3 Deactivation Correction............................................................................. 85
  2.7.4 Catalyst Characterization Data ................................................................. 86

3 MICROKINETIC MODELING OF WO$_3$ HYDROGEN BRONZE FORMATION...... 87
3.1 Introduction................................................................................................................... 87

3.2 Formulation of a microkinetic model to describe bronze formation ....................... 95
  3.2.1 Elementary reaction network and associated rate equations............................... 98
     3.2.1.1 Step 1, H₂ Dissociation ................................................................. 100
     3.2.1.2 Step 2, H surface diffusion............................................................. 101
     3.2.1.3 Step 3, Dehydroxylation and H₂O desorption .................................. 102
     3.2.1.4 Step 4, oxygen vacancy diffusion on surface ...................................... 103
  3.2.2 Thermodynamic evaluation of the reaction network ........................................... 104
  3.2.3 Material balance equations and MATLAB code .............................................. 107

3.3 Results and discussion ............................................................................................... 109

3.4 Conclusion .................................................................................................................. 120

4 SULFUR-INDUCED DEEP ELECTRON AND HOLE TRAPS IN TITANIA ............. 122

4.1 Abstract ...................................................................................................................... 122

4.2 Introduction ............................................................................................................... 123

4.3 Results and discussion ............................................................................................. 127

4.4 Supporting information and Experimental and Theoretical Methods .................... 146
  4.4.1 Materials and methods ...................................................................................... 146
  4.4.2 In situ DRIFT and UV-vis DRS ........................................................................ 147
  4.4.3 Computational methods .......................................................... 149
  4.4.4 Additional experimental results ................................................................. 149
     4.4.4.1 Material Characterization .................................................................. 149
        4.4.4.1.1 X-ray diffraction ....................................................................... 149
LIST OF SCHEMES

**Scheme 2-1.** The generally accepted route for conversion of ethanol into butadiene................. 51

**Scheme 2-2.** Proposed mechanism of acetaldehyde and ethylene formation.............................. 53

**Scheme 2-3.** Proposed mechanism for acetaldehyde and ethylene production........................... 78
LIST OF FIGURES

Figure 2-1. Selectivity to acetaldehyde and ethylene with respect to time-on-stream. .. 61
Figure 2-2. Site time yield with respect to inverse weight hourly space velocity .......... 61
Figure 2-3. Influence of ethanol partial pressure on the normalized rates .................. 63
Figure 2-4. Formation rates measured in the presence of 0.48 kPa of pyridine .......... 65
Figure 2-5. DRIFT spectra of CO2 adsorbed MgO/SBA-15 .................................. 67
Figure 2-6. DRIFT spectra of SBA-15 ................................................................. 68
Figure 2-7. DRIFT spectra showing the stepwise desorption of ethanol ................. 71
Figure 2-8. Operando DRIFT spectra of continuous feed of Ar/ethanol ................. 72
Figure 2-9. Acetaldehyde and ethylene selectivity .............................................. 80
Figure 2-10. Parity plots of the experimental and predicted rates ............................. 81
Figure 2-11. Butadiene production over 0.08% MgO/SBA-15 ................................ 83
Figure 2-12. Catalyst deactivation during acetaldehyde and ethylene production ..... 84
Figure 2-13. Catalyst deactivation during acetaldehyde and ethylene production .... 84
Figure 2-14. Correction of the deactivation for acetaldehyde and ethylene production rates. .... 85
Figure 2-15. Pore size distributions catalysts ......................................................... 86
Figure 2-16. X-ray diffractogram for MgO/SBA-15 .............................................. 86
Figure 3-1. Proposed catalytic cycle for the reduction of acrolein ............................ 91
Figure 3-2. Illustration of the TGA and MS data during bronze formation ............. 94
Figure 3-3. Surface moieties defined for a 2-D WO3 bronze formation kinetic model ... 99
Figure 3-4. PES of the proposed reaction network for 2D model ............................ 106
Figure 3-5. Influence of the temperature on the simulated TGA experiment .......... 109
Figure 3-6. The effect of concentration of terminal oxygen vacancies. ........................................... 112

Figure 3-7. Changes in concentration of surface moieties.............................................................. 113

Figure 3-8. Changes in the Partial Pressure of water................................................................. 113

Figure 3-9. Changes in the equilibrium constant of step 2-4......................................................... 115

Figure 3-10. Changes in concentration of oxygen vacancies..................................................... 116

Figure 3-11. The effect of variation of equilibrium constant....................................................... 117

Figure 3-12. The effect of variation of the Ea2 on the rate of the mass loss. ............................. 119

Figure 4-1. Absorbance difference spectra in the UV-vis, and IR regions................................. 129

Figure 4-2. DRIFT spectra of sulfated anatase (AA) sample referenced to KBr............................ 135

Figure 4-3. Total density of states (DOS) and partial density of states (PDOS) ...................... 137

Figure 4-4. Difference spectra calculated based on Harb et al.356 ........................................... 139

Figure 4-5. Schematic mechanism of sulfur induced partially occupied states......................... 142

Figure 4-6. X-ray diffractograms of P90, P25, rutile, SA, USR, and Nanografi......................... 150

Figure 4-7. XPS analysis of the as-received TiO2 samples......................................................... 150

Figure 4-8. DRIFTS spectra of anatase SA recorded during the step-wise calcination.......... 152

Figure 4-9. DRIFTS spectra of anatase SA recorded during the step-wise calcination.......... 153

Figure 4-10. DRIFTS spectra of anatase BC recorded during the step-wise calcination......... 153

Figure 4-11. Spectral analysis of the BEA features................................................................. 154

Figure 4-12. Difference DRIFTS spectra recorded during the reaction of the rutile sample. ... 156

Figure 4-13. Absorbance spectra in the UV-vis, and IR regions.................................................. 158

Figure 4-14 Difference DRIFTS spectra of NG during H2 dissociation experiment............. 159

Figure 4-15. Difference DRIFTS spectra recorded during the reaction of P90......................... 162

Figure 4-16. UV-vis spectra of calcined BC and AA under O2 flow at 300°C......................... 163
Figure 4-17. Difference spectra of SA and NG samples.......................................................... 164

Figure 4-18. DRS spectra of AA sample in IR and UV-vis regions during H₂ reaction. ........ 165

Figure 4-19. Surface condition of the AA anatase sample. ...................................................... 166

Figure 4-20. Surface condition of the AA anatase before and after washing. ...................... 167

Figure 4-21. DRIFT spectra of AA materials investigated by ICP-OES.................................. 170

Figure 4-22. Plot of the intensity of the BEA as a function of time for the AA. ...................... 173

Figure 4-23. Rietveld refinement plots for AA and BC samples............................................ 177

Figure 4-24. Correlation between the Ti vacancy concentration........................................... 178
LIST OF TABLES

Table 2-1. Hydrogen/deuterium isotope effects for acetaldehyde and ethylene production........ 64

Table 2-2. Nitrogen physisorption measurements............................................................................ 66

Table 2-3. Thermodynamic and kinetic parameters used in the microkinetic model. ............... 81

Table 3-1. Calculated composition of tungsten oxide bronzes by TGA................................. 95

Table 3-2. Sequence of reactions describing WO$_3$ bronze formation and rate equations........ 100

Table 3-3. Differential equation describing changes in concentration........................................ 108

Table 3-4. Simulated stoichiometric coefficient and chemical formula of WO$_3$ bronze.......... 120

Table 4-1. Elemental and BET analysis of the as-received TiO$_2$ samples............................... 151

Table 4-2. Sulfur concentration in AA measured by ICP-OES ..................................................... 171

Table 4-3. Ti site occupancy, Ti vacancy concentration............................................................... 175
INTRODUCTION

1.1 Motivation

Do we live in a sustainable world? To find an answer to this question, we need to evaluate if we are compromising the ability of future generations to meet their needs while providing our current needs. Since 1970, each year, the annual worldwide consumption of natural resources exceeds the ability of the biosphere to meet humanity's demand. Earth Overshoot Day marks the exact day we cross Earth's biocapacity each year. For example, the Earth Overshoot Day for 2021 was the 29th of July! Currently we are using natural resources 1.7 time faster than ecosystem can regenerate. The metrics for our ecological footprint are measured based on how much productive land/volume (for example, land of a country or the planet earth) it takes to produce what a population (an individual, population of a city, or the world) consumes and is needed to absorb its waste, such as CO$_2$ or swage. Globally, we have been in overshoot and running deficits since the mid-1970s, which means we are in an accumulated ecological debt state. Examples of the effects of accumulating an ecological debt are depleted fisheries, deforestation, and the build-up of CO$_2$ in the atmosphere. The answer to the beginning question is, No. We are not in a healthy relationship with our planet, and unlimited economic growth is impossible on a finite planet. Therefore, we need to change our growth models to a balanced condition swiftly. Otherwise, the scarcity of resources and the oncoming effects of climate change will slow down economic growth and possibly destroy our past progress, with consequences such as frequent and intense drought, storms, heatwaves, rising sea levels, and wars on resources.

In order to mitigate these adverse consequences, several nations are embarking on new efforts by changing their energy guidelines and working towards the production of cleaner, sustainable energy instead of using oil and coal and enhancing the performance of recycling
processes aiming for a cleaner and green future. The concept of a circular economy is the outcome of these ongoing efforts and the search for more sustainable industry sectors and society in general. This idea has attained popularity in recent years among the younger generation of developed countries. Moreover, it has been an active part of the agendas of many governments and major private organizations. According to Geissdoerfer et al., a circular economy is a regenerative system in which resource input and waste, emission, and energy leakage are minimized by slowing, closing, and narrowing material and energy loops. This sustainable model can be achieved through long-lasting design, maintenance, repair, reuse, remanufacturing, refurbishing, and recycling.

Despite the last two decades of movements and massive funding for research on reversing climate change's effects, the scale of the changes induced by human activity is significantly large, and regional policy changes and restrictions are not helpful and would not guarantee a sustainable future. Nevertheless, in 2015, nearly all countries ratified an agreement (known as the Paris Climate Agreement), and each committed to submit a target to reduce greenhouse gas (GHG) emissions, in the case of the rich countries, or slow their levels of increase in the case of developing countries. The agreement acknowledged the need for decisive action to limit the average global warming to below 2°C (compared with pre-industrial levels) and to try to limit warming to just 1.5°C. Furthermore, within this agreement, countries were given the freedom to design and develop their ways of achieving their respective "Nationally Determined Contribution" to stay committed to the agreement's essence. Worldwide, the emissions due to fossil fuels increased a shattering 60% from 1990 to 2013 and CO₂ emissions from the power sector alone have increased by more than 45% between 2000 and 2016. In 2018 global CO₂ emissions from all sources hit record levels. In 2020, because of the reduction of transportation and shutdown of industrial activities due to the COVID-19 global pandemic, the overall greenhouse gas (GHG) emission in
2020 was ∼4% (8.5% reported by Sweeney\textsuperscript{6}) less than the previous year. While this temporary outcome seems positive environmentally, the 4% reduction in GHG emission will only contribute to about two-thirds of what is required to meet the annual limits to meet the 1.5°C increase target.\textsuperscript{8} An unfortunate outcome of analyzing these statistics demonstrate that even with the level of the limitation enforced to the human activities and industrial restrictions with its economic impacts, we are not yet meeting the requirements for slowing down the global warming, let alone reversing its effects. By no means it is possible to reduce daily human movements and economical transactions far more than what we had experienced during the pandemic and to solve the climate change problem, more pragmatic technological approach within our energy production and material conversion process is needed.

### 1.2 Strategies to slow down, and reverse the course of climate change

While working out the circular economy and sustainable development principles, handling some of society's energy problems is sophisticated. For example, despite the substantial implemented measures to reduce the effects of GHG using renewable electrical energy sources for transportation, still, the operation of many commercial vehicles (e.g. ships, aircraft, and trucks) based on the state-of-the-art battery technology is not a practicable approach due to the significantly smaller energy densities of batteries compared to the high energy-density hydrocarbon fuels.\textsuperscript{9} In the years that lie ahead, the challenging target of nations is developing sustainable energy or energies that solely or collectively replace the relatively cheap, high energy density fossil fuels. These challenges include developing a cost-effective renewable fuel, enabling high-performance solar power generation and wind energy, delivering sustainable electricity, and safe and efficient long-term energy storage.\textsuperscript{8}
It is important to notice that the increase in emission of GHG and the adverse effects on the environment are not solely due to oil and coal. The accelerating increase in the need for chemicals to produce fertilizer, lubricants, polymers, and other essential materials for economic growth, plays a significantly destructive role along with fossil fuels. In this manner, the concept of a biorefinery has been suggested to be a promising plan to reduce the environmental impact and meet the needs of the chemicals industries. In the biorefinery process, renewable biomass materials are converted to value-added, marketable compounds in high demand for modern human needs. These products are the analogy of the conventional oil refinery. Moreover, since biorefinery processes are consuming CO\textsubscript{2} through photosynthesis, they could contribute to a circular economy strategy as a carbon-neutral or carbon-negative process, depending on their uses with limited waste and pollution.

In a carbon-neutral process, there is a balance between the amount of emitted and adsorbed CO\textsubscript{2}, or no CO\textsubscript{2} release at all. In case of energy, there are several different carbon-neutral energy sources. Nuclear energy is a carbon-free approach to produce energy in form of heat and electricity. Nuclear energy is the most concentrated form of energy based on energy density measures. This can be demonstrated easily by comparing a liter of uranium, which could release $1.54 \times 10^8$ MJ energy, with the equivalent volume of gasoline, which only can release 34.2 MJ. However, the primary environmental concern related to nuclear power is the production of radioactive wastes. These materials can stay radioactive and dangerous to human health for thousands of years. Also, nuclear incidents such as Chernobyl and Fukushima raise the concern of unknown crippling costs in case of a nuclear disaster.\textsuperscript{10} Other low-risk renewable energy approaches such as wind, geothermal, solar thermal, and hydro energies generate electricity with no direct CO\textsubscript{2} and associated air pollution emissions.
Although these approaches are promising and, without a doubt, would be one of the main players in the future energy logistics of the world, they share a big limitation; their availability is regional and depends on expensive infrastructures, which reduces their cost-effectiveness and out of reach of underdeveloped or developing countries. Also, from a practical point of view, these energy vectors need to be converted to electricity to transport from the production location to the destination through power grids, making their availability very limited.

These limitations are especially magnified in the transportation and mobility sector. Transportation activities demand 1/4 of the total annual global energy consumption.\(^{11}\) Mobility demands an efficient energy storage technology in the form of fuel and the ability to carry the fuel as part of the vehicle's power train (in cars, trains, planes, or ships). Classically liquid hydrocarbon fuels fulfilled all of these requirements, and our societies are largely based on the use of liquid hydrocarbons derived from refining oil.

In addition to the demand for energy storage techniques, to eliminate the addition of CO\(_2\) and other GHGs to the environment through crude oil, and the consequential environmental and national security problems arising from the economical dependency on crude oil, production of essential chemicals such as hydrogen, unsaturated hydrocarbons, and ammonia through renewable energy sources and chemical resources such as lignocellulosic biomass or triglycerides is of great interest.

Historically, surface chemists and heterogeneous catalysis scientists have been at the front line of addressing the diverse challenges to provide platforms for manufacturing human needs on a large scale. The recyclability of heterogeneous catalysts allows the development of platforms for green and sustainable manufacturing processes eliminating the need to separate the products and catalysts (unlike homogeneous catalysis) and reducing the production of chemical waste.
Currently, heterogeneous catalysts play an essential function in producing more than 80% of all chemical products in the world.\textsuperscript{8}

As anticipated, the heterogeneous catalysis and surface chemistry principles have been used to fight climate change and create a sustainable future\textsuperscript{11}. Heterogeneous catalysis is one of the pillars of the chemicals and energy industries and will be a central science in driving the transition from fossil fuel based industrial processes toward carbon-neutral and carbon-negative operations.\textsuperscript{11} In addition, the most energy-intensive industrial manufacturing processes, such as Haber-Bosch and Fischer-Tropsch, rely on heterogeneous catalysis. Hence, there is a major opportunity to decrease energy consumption and reduce environmental impact by developing new catalytic systems or increasing the efficiency of current catalytic processes using surface chemistry.

In this respect, some of the research potentials and current challenges of heterogeneous catalysis and surface chemistry in the popular approaches toward developing carbon-neutral and carbon-negative processes will be discussed.

1.2.1 **Batteries**

Electricity can be stored in Li-ion batteries and used in electric vehicles. In these electrochemical energy storage systems, a high energy density is key to efficiently utilizing the renewable energy generated from carbon-neutral sources, such as solar and wind, in the transportation sector. Unfortunately, although significant progress has been made during the last two decades in various battery systems, no current battery system, even Li-ion batteries, can
compete with gasoline's flexibility and energy density in lightweight vehicles.\textsuperscript{12} The problem is even more severe in heavy vehicles (trucks, buses, etc.) or airplanes.

The performance of batteries strongly depends on the properties of their electrode and electrolyte materials.\textsuperscript{13} Accelerating the development of batteries that could compete with gasoline energy density requires revolutionary breakthroughs in electrochemically active materials that enable a high voltage and multi-electrons per redox center for high energy density, improved charge transport, and electrode kinetics, and satisfactory structural and interfacial stability while being cost-effective.\textsuperscript{13-15} Many advances in the engineering of nanostructures and reactivity of catalyst surfaces are often at the basis of the latest developments of Li-ion batteries.\textsuperscript{11}

Batteries (including Li-ion batteries) are composed of three main components: a cathode, an anode, and an electrolyte. Cations move from the cathode to the anode through the electrolyte, or vice versa, during electrochemical reactions. In this ion transportation process, there are three steps: cation diffusion within solid-state electrode materials, a charge transfer reaction at the interface between the electrode and electrolyte, and cation movement in the electrolyte. These reactions are highly reversible, and therefore, a battery is rechargeable. However, some irreversible reactions could occur instead of the reversible reaction on the interface. For example, in Li-ion batteries, one of the irreversible reactions is the decomposition of electrolytes on the surface of the electrode materials, which results in forming a solid electrolyte interphase.\textsuperscript{16-17} Based on kinetic studies, the mobility of Li ions in this solid interface is considered the rate-determining step. Therefore, an increase in the solid layer would hinder the battery's performance.\textsuperscript{18} On the other hand, a thinner and more ionic conductive solid electrolyte interphase shows better kinetics. However, the low energy density of batteries is not the only limitation for application of these systems. The solid layer plays an important role in the safety and cyclability of electrode materials.
Without the formation of the stable oxide layer, the irreversible reactions on the surface of the electrodes will not be stopped. This could result in a short circuit and uncontrolled release of the potential energy and eventually explosion.\textsuperscript{16, 19} Recently to balance this tradeoff, surface chemistry and the principle of heterogeneous catalysis have been used to investigate this phenomenon and provide possible solutions with coating the surface of electrodes to enhance the charge transfer and redox kinetics\textsuperscript{12, 16, 18} or application of solid-state electrolytes\textsuperscript{20-22}.

Jeong et al. discovered that the heterogeneous catalysis to promote the fragmentation of LiPS based on the ultrastrong adsorption on TiN can markedly improve the discharge capacity and rate capability of lithium-sulfur batteries. Based on their combined computational and experimental analysis, the unique catalytic property of TiN on their electrode surfaces is due to its strong chemical bonding with sulfur.\textsuperscript{12} As a result of this cathode modification their electrodes exhibit a 5.5 times improvement in discharge capacity compared to that of the conventional cathode. This effort confirms that heterogeneous catalysis on metal compound surfaces having strong bond formation with elemental sulfur could eventually develop Li-ion batteries with significantly increased cyclability and better charge/discharge rates.

Zn-S batteries could bridge the energy gap between lead-acid batteries and Li-ion batteries in the market share and lower energy storage costs for general applications, such as energy storage in passenger cars, house or emergency power units.\textsuperscript{23-24} The typical metal-sulfur chemistry, mainly the Li-S and Na-S batteries, are troubled by the uncontrollable dissolution and precipitation and sluggish redox kinetics.\textsuperscript{25} Zhang et al. demonstrate that utilizing a redox catalytic process can promote the activation of sulfur redox reaction, which can be used for developing high performance, energy-dense solid-state Zn-S batteries. They have built batteries using a high-capacity cathode, fabricated by in situ interfacial polymerization of Fe(CN)\textsubscript{6}\textsuperscript{4--}--doped polyaniline
within the sulfur nanoparticle in a yolk-shell structure. The functional polymer shell with Zn$_{x}$Fe$^{II/III}$(CN)$_{6}$ redox hotspots anchored on its framework served as a cation reservoir to accelerate the slow sulfur redox kinetics.$^{20}$

The utilization of liquid or polymeric electrolytes is the Achilles heel of the current battery technology in use. The use of metallic lithium in conventional Li-ion batteries leads to severe chemical and mechanical instability issues due to their high reactivity with liquid organic electrolytes and propagation of Li dendrites. In case of damage to the battery's structure or a short circuit from Li dendrites, these hydrocarbon-based electrolytes, confined in a closed system, could result in explosions.$^{26}$ For safety reasons, the number of cells per battery and the distance of the electrodes need to be adjusted, which affects the size of the cells, reducing the energy density.

An alternative approach is using solid-state electrolytes to replace organic liquid solvents that cause most safety issues.$^{26}$ In a solid-state battery, the liquid electrolyte is replaced with solid-state electrolyte materials which gives a has higher energy density to these types of batteries compared with current Li-ion batteries that use liquid electrolyte solution.$^{25}$ It does not risk explosion or fire, so there is no need to have components for safety, thus saving more space. Then we have more space to put more active materials, increasing battery capacity. Cubic garnet-type solid-state electrolytes have been found to possess high lithium-ion conductivity and are macroscopically stable against metallic Li.$^{27}$ However, at the anode interface, microscopic investigation of the interaction between a cubic garnet-type solid-state electrolyte and metallic Li revealed a phase transformation for several atomic layers due to trace concentration of impurities, which alters the ion transfer mechanism and hinders the rate of the redox event.$^{28-29}$

Kelber et al. have reported an effective strategy of combining surface chemistry and interlayer-based migration mechanisms to tailor the interface between Li and garnet-type solid
state electrolytes and increase the chemical stability of the anode/solid-state electrolyte interface. In their work, extensive surface chemistry studies were performed using in situ X-ray photoelectron spectroscopy (XPS), and the electrochemical properties of the improved interface were thoroughly investigated. This study clarifies that including an interlayer is always required to prevent the degradation of garnet-type electrolytes in ambient storage and transfers. In addition, the interlayer must be modified to prevent electron tunneling that induces lithium dendrites across the electrolyte.\textsuperscript{21}

In summary the Li metal battery is viewed as one of the most optimistic prospects for carbon-neutral, high-energy-density energy storage devices in our modern and technology-based society.\textsuperscript{16} However, uncontrollable lithium dendrite growth induces poor cycling efficiency and severe safety concerns due to the organic liquid electrolytes, eliminating lithium metal batteries for practical applications. Solid-state electrolytes are considered attractive to handle several safety issues of nonaqueous electrolytes, including leakage, poor chemical stability, and flammability. However, their lower ionic conductivity, compared to conventional electrolytes and surface instability against Li metal, and the poor interface between these electrolytes and Li metal, render them a long way from their practical application.\textsuperscript{25} Nevertheless, recently, a growing number of studies based on surface chemistry and catalysis have been conducted to determine the root cause of these limitations, improve our overall understanding and provide new approaches to bypass or solve the current challenges. Thus, it is believed we may find a breakthrough technology in surface chemistry for lithium-ion batteries, which could reposition this carbon-neutral energy storage technology as a prime choice, as was expected before.
1.2.2 H$_2$ and NH$_3$, Today’s high demand chemicals and fuel of tomorrow

The current and future need for carbon-neutral, carriageable, storable, cost-effective, energy-dense liquid or gas fuels for mid-and long-range commercial or private transportation is inevitable due to the inherent limitation of electricity storage systems. Hence, the development of zero-carbon fuel seems very attractive and crucial to decarbonizing the energy industry and transportation sectors mitigating climate change and providing the platform for a circular economy. Two of the most promising zero-carbon fuel options are hydrogen and ammonia.

These materials have no direct carbon emissions at the point of use. Hydrogen and ammonia are already widely used in industry and agriculture, and their production is massively scalable. Both of these high demand chemicals are versatile and capable of being produced and used in many ways, including production from renewable resources and applications for decarbonization challenges in agriculture, industries, and energy storage for houses and transportation. However, ironically, their current production carries a significant greenhouse gas footprint. Currently, hydrogen is mainly used in the refining industry and chemical sectors. It is produced from crude oil resources using fossil fuel energy, accounting for 6% of global natural gas use and 2% of coal consumption and responsible for 830 Mt CO$_2$ of annual CO$_2$ emissions. Conventionally, ammonia is produced from natural gas via steam methane reforming, the water-gas shift reaction, and the Haber–Bosch process. The process uses fossil natural gas, which leads to 2.6 metric tons of CO$_2$ emissions per metric ton of ammonia produced. With ammonia being the second most-produced chemical globally, its production accounts for approximately 2% of worldwide fossil energy use and generates over 420 million tons of CO$_2$ annually.

The implementation of NH$_3$ and H$_2$ as a carbon-neutral chemical energy storage for mid- and long-distance commercial transportation is key to achieving a circular economy model in
upcoming decades.\textsuperscript{33} Although currently producing these alternative fuels adds a significant amount of CO\textsubscript{2} and other GHGs to the atmosphere, the increasing global population, energy cost, and demand for H\textsubscript{2} and NH\textsubscript{3} have motivated continued research to develop more efficient catalyst technologies for these materials. Furthermore, technological advancements in surface chemistry and heterogeneous catalysis with approaches in electrocatalysis and photocatalysis will impact hydrogen and ammonia's viability as renewable energy storage mediums and vectors. In parallel, the technological advances in the production of vehicles based on ammonia and hydrogen fuel cells possibly create a huge market for these fuels, which drives further investment in the research and development of carbon-neutral approaches. In the following, the current approaches for producing NH\textsubscript{3} and H\textsubscript{2} based on heterogeneous catalysis and surface chemistry and the challenges ahead will be briefly discussed.

\textbf{1.2.2.1 Carbon-neutral ammonia}

Although ammonia has widely been used for many years for production of fertilizers, household cleaning chemicals, refrigerants, and disinfectants, it has started regaining attention from researchers, scientists, engineers, and technologists due to its carbon-free nature which can be used as a potential liquid fuel to reduce the CO\textsubscript{2} emissions.\textsuperscript{34} Historically the first time ammonia was used as fuel in vehicles was during World War II in Belgium. Due to the shortage of diesel fuel for public transportation during the war, engineers mixed ammonia and coal gas to solve the problem.\textsuperscript{35} The US Army started the research on the utilization of ammonia for internal combustion engines during the second war. Army's approach was to build mobile nuclear reactors (to generate electricity) and produce ammonia locally to fuel their vehicles; with this approach, they could overcome the need for transportation of gasoline, which was 65\% of their combat payload and
transport operations during wartime. In addition, a locally produced fuel would decrease their transport costs and increase their independence towards third parties.\textsuperscript{36} Lately, there have been multiple attempts to use ammonia in internal combustion engines and gas turbines. The California Public Utilities Commission has started a program to consider replacing the diesel generators with ammonia-driven ones starting by 2021.\textsuperscript{34} Japan has launched a serious action plan for ammonia use, especially in electricity production. It is expected that Japan's ammonia-driven internal combustion engines will meet 1% of electricity consumption. In addition, a Japanese marine company has announced starting a project on ammonia-fueled ships and their fuel supply systems.\textsuperscript{34} However, there are significant technical challenges to adopting liquid or gas ammonia as an alternative fuel for internal combustion engines. These include corrosivity, high ignition temperature, low flame velocity, and nitrogen oxides during combustion.\textsuperscript{34} Ammonia fuel cells are an alternative approach to using ammonia as fuel. The general operation of these cells is similar to H\textsubscript{2} fuel cells. An electrochemical cell converts the chemical energy from a fuel into electricity through an electrochemical reaction of fuel with oxygen or another oxidizing agent. Several studies have investigated ammonia as a fuel source for different types of fuel cells. However, this technology is not yet at a commercialization stage, and further investigation is required.\textsuperscript{37}

Nevertheless, we need to consider the elephant in the room. The current approach for ammonia is a significant GHG emitter. Therefore, there should be carbon-neutral industrial-scale alternatives for ammonia production as fuel. Using renewable electricity to produce ammonia from elemental nitrogen is an attractive piece to complete the puzzle of the carbon-neutral energy strategy approach.\textsuperscript{38} We can harvest the wind, hydro, thermal solar, and nuclear energy within this strategy and fuel the transportation sector. The first attempt for electrochemical synthesis of ammonia was in 1998.\textsuperscript{38} Marnellos et al. demonstrated ammonia synthesis from its elements at
atmospheric pressure in a solid-state proton cell. Gaseous H₂ and N₂ were introduced over the anode and the cathode, respectively. H₂ was converted into protons at the anode, which was electrochemically transferred to the cathode and reacted with N₂ to produce NH₃. Several research groups have tested this approach in the past two decades to minimize material and energy consumption and developed this method further to substitute H₂ with water to reduce the indirect GHG emission of the electrochemical approach. However, there are two main obstacles to commercializing these technologies that have been identified and need to be solved for this route to be compatible with the industrial ammonia production process. The first one is the poor proton conductivity of the cells. Regardless of the hydrogen source, nitrogen must react with H⁺, which must be supplied electrochemically. The highest proton fluxes reported until the end of 2015 were of the order of 10⁻⁷ gram of hydrogen per s⁻¹ cm⁻². The second is the slow catalytic activity of the cathodic electrode and poor selectivity. On the surface of cathode electrodes, the H₂ evolution reaction competes with the reaction of NH₃ synthesis, resulting in a significant decrease in faradaic efficiency (The efficiency with which electrons in a system facilitate an electrochemical reaction.). These values are generally lower than 10%. At temperatures <100 °C, most reported values are of the order 1%. Similar to battery development research, heterogeneous catalysis and surface chemistry have been used to identify the limitation of the electrode surface and ion transfer mechanism and provide a process to improve or eliminate these issues. Bicer et al. have described that the hydrogen evolution problem could be bypassed by conducting the reaction within molten salt media consisting of molten hydroxide as NaOH and KOH and with nano-Fe₃O₄ catalysts instead of using a solid-state electrolyte or membrane. With this approach the N³⁻ ions would react with H₂ gas on the anode surface. They have reported the maximum faradaic efficiency of 9.3% with a reaction
temperature of 210 °C. Multiple studies have shown that coating the surface of the electrodes with metal nitride would significantly enhance the rate and the Faradic Efficiency of the NH₃ synthesis via the Mars-van Krevelen mechanism. For example, Zhang et al. have shown the development of efficient earth-abundant electrocatalysts for N₂ reduction to NH₃ under atmospheric pressure at room temperature with a Faradaic efficiency of 2.25%. They have used a VN nanosheet array on Ti mesh as an active and selective electrocatalyst for the N₂ reduction reaction. Notably, such catalyst material also exhibits high selectivity (no formation of N₂H₄) and electrochemical stability. Furthermore, their theoretical studies confirmed that ammonia is synthesized via a Mars-van Krevelen mechanism.

Another carbon-neutral approach for ammonia synthesis is the direct utilization of solar energy to reduce N₂ and produce ammonia. While the efforts to set a path toward a carbon-free future were getting notice among societies during the past decade, photocatalytic production of ammonia has gained significant attention. This approach promises reduction of N₂ to NH₃ under very mild reaction conditions with solar energy. While the rates of photocatalytic ammonia synthesis are still not meeting practical requirements, some encouraging photocatalytic materials have already been identified, which stimulates more comprehensive research in this field.

The catalytic sites in nitrogenase serve as a useful guide for developing higher throughput yet sustainable catalytic systems for N₂ fixation. The first experimental evidence of photocatalytic ammonia production was reported by Dhar et al. as a result of a series of pioneering experimentation on sterilized soil samples under sunlight. Further studies showed that metal oxides (such as TiO₂, ZnO, and Fe₂O₃) existing in sterile soils were responsible for the direct transformation of N₂ fixation into NH₃. Schrauzer and Guth conducted the first methodical research on photocatalytic NH₃ synthesis in 1977. They uncovered that TiO₂ shows a significant
nitrogen fixation to ammonia activity, with the byproduct hydrazine also forming in the presence of gaseous nitrogen and humidity. Motivated by these findings, several more comprehensive studies were conducted to explore the effect of TiO$_2$ crystalline phases, surface defects, and metal or metal oxide modification on the photocatalytic conversion of N$_2$ to NH$_3$. The research on this area soon expanded to other semiconductor oxides materials such as Fe$_2$O$_3$, WO$_3$, ZnO, and Ga$_2$O$_3$. Although very comprehensive research has been done on photocatalytic ammonia production throughout the last 80 years, and we have achieved strong progress over the past few decades, the photocatalytic NH$_3$ synthesis rates still remain insufficient for industrial applications. In addition to the low ammonia yields, poor photocatalyst stability and low solar-to-chemical conversion efficiencies are the additional blockages that restrict the expansion of photocatalytic ammonia synthesis. Therefore, to enhance semiconductor-based photocatalysts' performance for ammonia synthesis, a much more comprehensive understanding of the reaction mechanism at the atomic level is needed to allow the rational design of photocatalysts and optimized photochemical reaction systems.

The current strategies for optimizing photocatalytic ammonia synthesis on semiconductor-based catalysts focus on electronic structure and surface engineering. These approaches include facet design, vacancy design, doping design, structure design, and co-catalyst design. For example, Bai et al. reported their controllable syntheses of Bi$_5$O$_7$I with different dominant facets. Based on their report, the [0 0 1] facets show a much higher activity towards N$_2$ conversion to ammonia compared to the other [1 0 0] facets. The higher conduction band position of [0 0 1] facets is attributed to the enhanced activity. Two-dimensional (2D) materials are another hot topic in facet design to promote photocatalytic ammonia synthesis. In Sun’s work, ultrathin MoS$_2$ was synthesized where Trions (two electrons combined with a hole) were generated under light
irradiation. The Trions assist the simultaneous transfer of six electrons to reach a high ammonia synthesis rate of 325 μmolh⁻¹g⁻¹ without using any sacrificial scavengers or noble metal co-catalyst. The 6-electrons’ transfer allows high selectivity to ammonia because its by-products receive fewer electron-protons, resulting in unfavorable formation.\textsuperscript{58} In another example of current advances, Li et al. reported negligible N₂ reduction by the oxygen vacancy-free BiOBr. They explained that the low activity of the catalyst is because the conduction band position of BiOBr is not high enough to reduce N₂ directly. Generation of oxygen vacancies (V₀) enabled electrons to be trapped and donated to the adsorbed N₂ molecules. The promoting function of V₀ is highly associated with the position of V₀ on the facets of BiOBr.\textsuperscript{61} Wang et al. reported that ultrathin Bi₅O₇Br nanotubes with a diameter of 5 nm were synthesized, and V₀ was induced by light excitation. In a similar report they have proposed that the trapped electrons be directly inserted into the dinitrogen molecules chemisorbed on the V₀ site, which is essential for the higher reducing ability in the nitrogen reduction. A 1.38 mmol h⁻¹g⁻¹ rate of ammonia production and 2.3% quantum efficiency was achieved using pure water to scavenge holes.\textsuperscript{56} In another approach, Feng et al. implemented co-doping of oxygen and sulfur to C₃N₄ which resulted in significant increase in photocatalytic synthesis of ammonium. The co-doping of O and S into C₃N₄ elevated the conduction band and valence band positions and resulted in the heterostructure of C₃N₄ between doped and undoped ring clusters, improving the charge separation which eventually doubled the catalyst activity.\textsuperscript{62}

Currently, electrocatalytic and photocatalytic ammonia synthesis is in its very infancy. Nevertheless, significant essential advancement has been made in recent years to suggest that these carbon-neutral NH₃ productions at modest scales will be viable in the near future. Currently, a
huge opportunity exists for new researchers in surface chemistry and heterogeneous catalysis to move into this field and make their influence.

1.2.2.2 Carbon-neutral Hydrogen

The first attempt to use H₂ for transportation was done by Count Ferdinand von Zeppelin, who invented the first balloon in 1900 that used hydrogen to maintain the buoyancy of an airframe. Airships to cross the Atlantic were put into service during the 1920s and 1930s.⁶³ NASA executed the concept of using hydrogen as fuel in 1961. Later the Soviet Union completed a flight with an aircraft using liquid hydrogen fuel in 1988.⁶³ Like other emission-free energy concepts, using hydrogen as an alternative fuel gained popularity in the last two decades due to climate change and the need for fast changes in our energy consumption habits. Hydrogen is considered clean energy and is a chemical feedstock for production of essential chemicals. However, over 95% of the current hydrogen is derived from fossil fuels, primarily through steam methane reforming.⁸ This process uses the reaction of high-temperature water vapor and methane on the surface of a metal-based catalyst to produce H₂ and carbon dioxide. Generally, this process produces low purity hydrogen and a large emissions footprint. An approach to improve this technique and reduces its huge carbon footprint is to capture CO₂ right after the steam reforming process. The produced hydrogen through this method is called blue hydrogen. Nevertheless, carbon-neutral processes such as electrocatalysis, and photocatalysis are being developed for hydrogen production.

There are some complications with the large-scale carbon-neutral process for H₂ production, storage, transportation, and consumption as a fuel. The efficiency for the whole fuel cycle (electricity to hydrogen and hydrogen to mechanical work) is low compared to its rival technology, battery-powered vehicles. Further issues exist with the transmission and distribution
of hydrogen. The molecule's chemical properties make it incredibly prone to leakage and embrittlement of metal pipes and tanks, making the storage of the elemental hydrogen as fuel very challenging. In addition, the low energy-to-volume ratio of hydrogen fuel in the gas phase, makes it expensive and impractical for commercial transportation. This material needs to be stored at high pressure and low temperature in liquid form to be considered as a viable fuel. Finally, hydrogen for the mobility industry is in its infancy stage, making it not very attractive for investors and resulting in slow research and development progress.

The current efficiency of water electrolysis can reach 86%. However, the energy required to compress hydrogen to 700 bar and deliver it to a vehicle as a liquid fuel can cost between 5% and 20% of the hydrogen energy density. Consequently, a conventional fuel cell can achieve an efficiency of approximately 60%. This yields a combined efficiency that may vary between 41% and 49%. Electric vehicles are approximately 59–62% efficient in the conversion of energy from the electric network to the mechanical work at their wheels. This value for internal engines is between 25–45%.

Reducing cost and improving performance and durability are the two most significant challenges to hydrogen fuel commercialization. Production, storage systems, and fuel cell systems must be cost-competitive. In addition, they need to perform as well or better than current electric vehicles or traditional power technologies over the system's life. In the following, the contribution of surface chemistry and heterogeneous catalysis in the current advances through adaptation of H₂ fuel and alternative approaches for mentioned challenges will be briefly discussed.
1.2.2.2.1 Production of Hydrogen fuel

One of the benefits of H\textsubscript{2} as an energy vector is that its production is very flexible, and all direct resources such as fossil fuels and carbon-neutral energy sources (solar, wind, hydro, thermal solar, and nuclear power) could be used for its production. Furthermore, H\textsubscript{2} can be produced from any chemical having hydrogen atoms on its structure, such as hydrocarbons, water, and organic matter.\textsuperscript{63} Therefore, the different technologies utilize mainly these compounds as starting materials for the final H\textsubscript{2} molecule formation. In addition, it can be readily produced from synthesized hydrogen carriers such as methanol and ammonia, which bring the possibility of storing hydrogen in the form of these chemicals for cheap long-distance transportation.\textsuperscript{63} The production of H\textsubscript{2} from biomass-derived hydrocarbons will be discussed later in the following section.

Currently, just 5 % of H\textsubscript{2} derives from the electrolysis of water.\textsuperscript{66} Electrolysis is an electrochemical method to obtain hydrogen using electricity by splitting the water molecule into H\textsubscript{2} and O\textsubscript{2}. This reaction is carried out by electron displacement between electrodes immersed in cells containing an aqueous electrolyte. In practice, water electrolyzers require effective catalysts to facilitate both reactions. Currently, Pt-group metals are the most effective catalysts for hydrogen evolution, while the benchmark catalysts for the counterpart reaction, oxygen evolution reaction, are Ir/Ru-based compounds. Regardless, these metals' high cost and scarcity restrict their general use.\textsuperscript{67} As a result, a major effort has been made to find cost-effective alternative materials to replace the rare noble metal-based electrodes. Examples of these studies demonstrating cost-effective electrocatalysts include transition metal sulfides, carbides, and phosphides for both half reactions, hydrogen evolution and oxygen evolution reactions.\textsuperscript{67-72} The main operational challenge in electrocatalysis of water is the overpotential of the electrolysis system, which hinders the performance. In order to reduce the overpotential problem, the water electrolysis is mostly
conducted in either strongly acidic or basic solutions. However, this condition poses a challenge for most non-noble metal water-splitting catalysts as a highly active catalyst in acidic conditions may be inactive or unstable in alkaline electrolytes\textsuperscript{67, 73} resulting in developing new electrochemical cells which separate the hydrogen and oxygen evolution half-reactions by operating the reactions in two different cells, adding complexity and cost to these systems.

Recent achievements in water splitting catalysts have made it possible to construct water electrolyzers using a bifunctional catalyst material that is active for catalyzing both the hydrogen and oxygen evolution reactions in the same condition. Therefore, integrating the merits of these bifunctional electrocatalysts in a cell greatly benefits improving overall water splitting activity. In addition, using a single bifunctional catalyst simplifies the overall system design and lowers the cost. For example, transition metal oxides have been widely explored as outstanding bifunctional electrocatalytic materials for full water electrolysis in wide spectra of pH\textsuperscript{74-75}. Hao et al. demonstrated a MnCo\textsubscript{2}O\textsubscript{4}-based nanowire array as an active and efficient catalyst for water splitting under near-neutral conditions\textsuperscript{76}. It is important to mention that the authors suggested that the oxygen evolution activity can be largely enhanced when the MnCo\textsubscript{2}O\textsubscript{4} nanowire arrays are electrochemically oxidized into Mn–Co-borate nanowire arrays in potassium borate solution. Hence, with Mn–Co-borate nanowire arrays and MnCo\textsubscript{2}O\textsubscript{4} as anodic and cathodic electrocatalysts, respectively creates complementary water-splitting electrocatalysts under benign conditions which conducts oxygen evolution reaction and hydrogen evolution reaction with high efficiency\textsuperscript{76}.

In another approach, transition-metal nitrides or carbides have appeared as promising choices as bifunctional catalysts in a wide pH range because of the strong corrosion resistance and super conductivity\textsuperscript{74}. Xie et al. developed a core-shell heterostructured catalyst (Ni\textsubscript{3}N@Ni–Bi NS/Ti), which is composed of metallic Ni\textsubscript{3}N nanosheet array covered by a Ni–Bi film on a Ti
mesh. Owing to such chemical composition and special structure, the prepared catalyst achieved highly efficient full water-splitting performance under a near-neutral condition.\textsuperscript{77} Recently, in another breakthrough by Liu’s group, a 3D hybrid of NiCo-based nitride nanoparticles anchored on NiCo\textsubscript{2}O\textsubscript{4} nanoflakes on the graphite fiber substrate (NiCo-nitrides/NiCo\textsubscript{2}O\textsubscript{4}/GF) was fabricated via a simple electrochemical deposition and subsequent nitridation treatment, and was used as general catalytic materials for whole water splitting over a broad pH range for the first time.\textsuperscript{78}

Regardless of these advances, numerous challenges must be addressed before cost-effective bifunctional water splitting electrocatalysts get commercialized and applied for practical uses in sustainable hydrogen production. There is a large need for theoretical and in situ spectroscopic studies in this area.\textsuperscript{67} Most of the studies in this field mainly focus on developing new materials and wishing for the best. Theoretical and kinetic studies could shine a light on the reaction pathways on the surface of these electrodes and bring more progressive and systematic research.

Photocatalytic water-splitting using metal oxides for hydrogen production offers a promising way to carbon-neutral and low-cost hydrogen production. Around 50 years ago, Fujishima and Honda published their results on utilizing a light-irradiated semiconductor material for water splitting for the first time. A TiO\textsubscript{2} photoelectrode was used for light absorption, which resulted in photoelectrochemical overall water splitting.\textsuperscript{79-80} Photocatalytic water splitting is feasible by heterogeneous photocatalysis. In heterogeneous photocatalysis, the metal oxide semiconductor materials are irradiated with light. When the energy of the incoming photon is higher than the bandgap of the irradiated semiconductor, electron-hole pair charge carriers are generated on the surface or bulk of the semiconductor material by excitation of electrons from the valence into the conduction band. The excited charge carriers in the semiconductor, electrons in
the conduction band, and holes in the valence band diffuse to the surface (or created on the surface) undergo redox reactions. Reduction of protons in water with the electron in the conduction band results in H₂ production. As the other half-reaction, oxidation of water can result in the production of oxygen through reaction with holes in the valence band. In the 1980s and 1990s, many new metal oxide photocatalysts active for water splitting were discovered and reported. Usually, these materials are classified into two classes, materials containing metal cations with d⁰ (Ti⁴⁺, Zr⁴⁺, Ta⁵⁺, Nb⁵⁺, W⁶⁺) and d¹⁰ (Ga³⁺, In³⁺, Ge⁴⁺, Sn⁴⁺, Sb⁵⁺) electron configuration. Binary, ternary, and quaternary semiconductor oxides were prepared by different synthesis techniques, mainly solid-state reactions fusing different metal oxides to more complex compounds. A very comprehensive overview of all such materials is given in review articles.

The main problem of this photocatalytic system is that photogenerated charge carriers can recombine on their pathway to the surface, reducing the quantum yield of the process. In addition, bulk defects could act as electron traps, reducing the electron's mobility and potentially being recombination center in the bulk, decreasing the chance of a surface reaction. Furthermore, the wide bandgap of common metal-oxides such as TiO₂ limits its applications under visible light. Countless efforts have been made to resolve these limitations and make photocatalytic hydrogen production a viable option for a circular economy. Results of these ongoing developments are approaches such as (but not limited to), the addition of electron donors (hole scavengers), carbonate salts, noble metal loading, metal ion doping, anion doping, dye sensitization, composite semiconductors, and metal ion implantation. These approaches could be divided into two broad classifications of chemical additives and photocatalyst modification techniques. Here some of the advances in the latter approach will be briefly discussed.
Since the first observation of the photocatalytic activity of titania for the water-splitting reaction, several metals such as Pt, Au, Ag, Ni, and Pd have been studied. Metal loading onto TiO$_2$ has become the most widely applied surface modification method for restricting the recombination of photogenerated electron-hole pairs.$^{86}$ In case of the presence of a metal nanoparticle on the surface of the titania, the photogenerated electrons will transfer from the conduction band of TiO$_2$ to the metal nanoparticles' available electronic states through the Schottky barrier right up until their Fermi levels are equal. During this transaction, holes will certainly remain on the valence band of TiO$_2$. Therefore, the spatial separation of photogenerated electron-hole pairs can be attained, and the chance of redox reaction over the surface would increase, resulting in improved overall quantum yield. Anpo and Takeuchi employed Electron Spin Resonance spectroscopy to investigate electron transfer from TiO$_2$ to Pt particles. It was found that Ti$^{3+}$ signals increased with irradiation time, and loading with Pt reduced the amount of Ti$^{3+}$ signal. This observation indicates the occurrence of electron transfer from TiO$_2$ to Pt particles.$^{87}$ Accumulated electrons on metal particles can then be transferred to protons adsorbed on the surface and further reduced to hydrogen molecules. Therefore, noble metals with suitable work functions can help electron transfer, leading to higher photocatalytic activity.$^{86}$

However, although the mechanism described improves electron-hole pair separation, it cannot explain the enhanced activity in the visible range. Recently, Rather et al. reported that Ag nanoparticles deposited on TiO$_2$ had enhanced titania's photocatalytic activity toward H$_2$ production under 450nm light. Furthermore, they have demonstrated that when the nanostructure is irradiated with the matching plasmonic oscillation wavelength (457 nm or sunlight) the Ag nanoparticles are activated, which shift their local electric field effect towards the TiO$_2$ interface.
resulting in the transfer of electrons towards the conduction band of titania due to the formation of a Schottky barrier.\textsuperscript{88}

Non-metal dopants were more efficient than most metal ions due to the bandgap narrowing effect, thus highly responsive to visible light irradiation.\textsuperscript{86} Wang et al. reported that N-doped TiO\textsubscript{2} with a 4.91\% nitrogen content leads to narrowing the optical band gap to 2.65 from 3.20 eV. As a result, the H\textsubscript{2} production rate of the N-TiO\textsubscript{2} film is about 601 \( \mu \text{mol g}^{-1}\text{h}^{-1} \), which is higher than the un-doped TiO\textsubscript{2} film.\textsuperscript{89} Xing et al. recorded the synthesis of in-situ S-doped porous anatase TiO\textsubscript{2} nanopillars and produced 163.9 \( \mu \text{mol h}^{-1}\text{g}^{-1} \) of H\textsubscript{2} evolution under optimum temperature. By employing S-doped TiO\textsubscript{2}, the bandgap of TiO\textsubscript{2} can be reduced and is favorable for visible-light adsorption towards the improvement of photon utilization, thus increasing the photocatalytic performance.\textsuperscript{90} Therefore, these research reports demonstrate that non-metal doping is another important strategy to increase the performance of the photocatalytic water splitting reaction for H\textsubscript{2} production. In addition, we have shown that due to the ability of sulfur dopants to be present in different oxidation states, they can behave as electron and hole traps, restricting the electron-hole pair recombination and possibly increasing the quantum yield of the photocatalytic reactions. This phenomenon will be comprehensively demonstrated in chapter 4 and 5.

The g-C\textsubscript{3}N\textsubscript{4}-based semiconductors can enhance photocatalytic activity by forming semiconductor heterojunctions, significantly improving spatial charge separation and maximizing reactions' redox potential and ability.\textsuperscript{91} Yin et al. concluded that the photocatalytic activity of g-C\textsubscript{3}N\textsubscript{4} for H\textsubscript{2} evolution was significantly enhanced by NiS\textsubscript{2} nanoparticles grown on the g-C\textsubscript{3}N\textsubscript{4} surface. The enhanced activity of NiS\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4} for photocatalytic H\textsubscript{2} generation is based on the transfer of the photoelectron from g-C\textsubscript{3}N\textsubscript{4} to NiS\textsubscript{2}, whereas the NiS\textsubscript{2} co-catalyst can effectively slow down the recombination of the electron-hole pairs and acts as active sites for H\textsubscript{2} production.\textsuperscript{92}
The efficiency of photocatalytic water splitting technology is still far too low to compete with other technologies for hydrogen generation. Therefore, there is a huge opportunity to apply surface chemistry research to improve the performance of this technology. One of the least studied areas for developing efficient photocatalytic hydrogen production systems is evaluating the possibility of coupling different techniques and approaches. Furthermore, no simulation model has been developed for photocatalytic hydrogen production associating photon absorption in the model.\textsuperscript{85}

### 1.2.2.2 Solid state technology of hydrogen storage

Hydrogen can be stored in gaseous (compressed hydrogen), liquid (liquefied hydrogen, liquid hydrogen carriers), and solid (solid hydrides and nanoporous materials) states. The following opportunities and challenges of the latter approach from a heterogeneous catalysis and surface chemistry point of view will be briefly studied.

Generally, solid-state hydrogen storage can be classified into two main technologies based on physisorption of $\text{H}_2$ on sorbents, or chemisorption of $\text{H}_2$ molecules through bond dissociation, with the resulting H atoms forming chemical bonds with the storage substrate.\textsuperscript{93}

In the case of storing $\text{H}_2$ as a fuel, physisorption is an attractive method for storing molecular hydrogen. High surface area materials such as carbon nanotubes, including single-walled carbon nanotubes and multi-walled carbon nanotubes, activated carbons, zeolites, covalent organic frameworks, and metal-organic frameworks, store hydrogen via physisorption.\textsuperscript{94} The relatively low enthalpy of adsorption/desorption makes hydrogen more readily available at ambient conditions than chemisorption, which generally requires high temperatures to desorb $\text{H}_2$.
from the substrates. Activated carbons have been reported to have an enthalpy of adsorption on the order of $-1.43 \text{kcal mol}^{-1}$ at 298 K, with bonding energies on the order of $-2.15 \text{kcal mol}^{-1}$. In addition, it has been suggested that bonding energies of $-4.78$ to $-9.56 \text{kcal mol}^{-1}$ are possible with small cations or anions.

The main limitation of the physisorption approach is the poor H$_2$ uptake of these materials. Properties such as specific surface area, pore-volume, and H$_2$ adsorption energy are the critical factors governing the H$_2$ uptake capacity for any physisorption adsorbent. The higher specific surface area provides more available material surfaces for H$_2$ molecule adsorption, whereas the larger H$_2$ adsorption energy provides enhanced H$_2$ adsorption interactions and limits unwanted desorption for seasonal temperature fluctuations. Application of Metal-organic frameworks and porous carbons have been widely reported. They have been at the center of attention for the last decade. Both types of structures could reach very high surface areas, but the interactions of H$_2$ molecules and the adsorbing surfaces are fairly weak and need to be further enhanced.

Despite the fact that they are much less explored, porous boron nitrides seem to be an interesting option for H$_2$ storage that deserves more attention. Several studies report very high specific surface areas for these materials. For example, Weng et al. have reported the synthesis of porous boron nitride (BN) micro belts and microsponges with a specific surface area of 1488 and 1900 m$^2$g$^{-1}$, respectively. These porous BN structures showed a reversible H$_2$ storage capacity of up to 2.6 wt% at -196 °C and low pressure of 1 MPa. In theory, BN can form stable porous structures with surface areas up to 4800 m$^2$g$^{-1}$ and an enhanced H$_2$ adsorption energy of 17.3 kJ mol$^{-1}$, suggesting its great potential to develop porous boron nitride H$_2$ storage material. In addition to the incredible potential in surface area of these materials, the interactions between BN's surface and H$_2$ molecules are readily strong. Further chemical modifications of the BN
surfaces would enhance their affinities of H$_2$.$^{106}$ For example, substituting one B atom by one C atom in BN nanotubes or one N atom with an O atom in BN nanosheets leads to higher adsorption energy the H$_2$ molecules.$^{106}$ Lei et al. experimentally found that $\approx$4 at% oxygen doping of BN nanosheets with the SSA of 536 m$^2$g$^{-1}$ had boosted the H$_2$ uptake to 5.7 wt% under 5 MPa at room temperature.$^{107}$ Although the uptake capacity of the physisorption approach for storing H$_2$ is still not practical, further efforts in this field will certainly contribute to the development and practical applications of future clean and renewable energy.

### 1.2.2.2.3 Hydrogen fuel cell

A fuel cell consists of an anode to which hydrogen fuel is commonly supplied and a cathode to which oxygen (or air) is supplied, separated by the electrolyte. The most commonly commercialized fuel cell is the proton-exchange fuel cell. Hydrogen fuel is first oxidized at the anode surface to protons and electrons in these electrocatalytic systems. Then, the protons are transferred to the cathode with the assistance of a proton exchange membrane or an external circuit. Finally, at the cathode surface, oxygen is reduced to water by protons coupled electrons, leaving water as the product of the reaction.$^{108-109}$

The major limitation in these electrochemical cells with gas/solid interfaces is rooted in the slow kinetics (especially for the oxygen reduction half-reaction) of the adsorption/desorption of reactants, intermediates, and products to/from electrode surfaces due to low number of active sites.$^{109}$ Thus, developing low-cost and high-efficiency electrocatalysts is important and economically desirable to replace Pt and Ru electrocatalysts. To achieve this goal, it is essential to investigate the electrocatalytic mechanisms of oxygen reduction and hydrogen oxidation, and particularly the surface composition's effect on the activity of electrodes toward redox reactions.
Among studied catalyst formulations, the M-N-C catalysts, roughly consisting of nitrogen and transition metal co-doped carbons (M: Fe, Co, Mn), stand out as the best performing precious metal-free oxygen reduction catalysts for hydrogen fuel cells.\textsuperscript{108, 110-111} It has been demonstrated with a comprehensive amount of experimental evidence that the most active sites for oxygen reduction reaction on M-N-C catalyst systems are metal centers coordinated by nitrogen atoms bound to the carbon matrix.\textsuperscript{108} To increase the number of active sites, two strategic factors are important. First, increasing the density of the intrinsic active sites (such as Fe-N\textsubscript{4} and Co-N\textsubscript{4}) accelerates the oxygen reduction process rate.\textsuperscript{112} The second approach is constructing catalysts with 3D interconnected hierarchically porous structures, allowing complete exposure of the intrinsic active sites and maximizing their utilization.\textsuperscript{109, 113} However, the performances of M-N-C-based catalysts still fall far below the requirements of fuel cell technologies due to degradation of the catalyst surface by OH\textsuperscript{•} species produced as a byproduct\textsuperscript{114} and much attention remains focused on the exploration of relatively low-loading precious metal catalysts to reduce the total cost of fuel cells.\textsuperscript{108} Among the recent approaches in this regard, three-dimensional ordered electrodes have been significantly highlighted due to their unique benefits in facilitating mass transfer resistance and enhancing catalyst utilization to develop fuel cells for large current density operation at low catalyst loadings.\textsuperscript{115} The latest generation of these catalysts has been demonstrated to have extremely high catalytic activities, such as the ultrafine jagged Pt nanowires demonstrated by Li et al. This breakthrough catalyst shows 52 times greater oxygen reduction activity than Pt alloy nanoparticle catalysts.\textsuperscript{116}

At the international level, legislators have included hydrogen and fuel cells on the map of future energy strategies. They have already considered that fuel cells have great potential and can successfully meet the multidisciplinary visions of sustainable development's technical, social,
economic, and environmental objectives. As a result, hydrogen and fuel cell technology have advanced considerably over the last two decades. However, although there are examples of the application of fuel cells in passenger cars and busses (e.g., Toyota and Honda), due to the relatively poor performance of the whole cycle of the H_2 fuel system, this area continues to face significant challenges at the global level. From the production of carbon-neutral hydrogen to the consumption of H_2 molecules for mobility, multiple steps involve heterogeneous catalysis and surface chemistry, which provide a wonderful space for theoretical and experimental research and development.

1.2.3 Carbon-neutral process for carbon-based chemicals and fuel

Liquid fuels derived from fossil resources show a competitive advantage in terms of easier storage and transport. We have already built our societies and infrastructures upon the benefits and feasibility of energy-dense liquid hydrocarbons fuels, and a sudden change in energy sources and technologies is not possible economically. The most realistic approach to reducing our dependence on fossil fuels is developing an alternative carbon-neutral approach for producing hydrocarbon-based fuels to keep our infrastructures and internal combustion engines at work and eliminate the need for expensive economical surgeries. This argument is also valid in case of production of carbon-based chemical feedstocks. Oil is the most important source of the majority of the carbon-containing chemical feedstocks. The quest for sustainable resources to meet the demands of a constantly rising global population is one of the main challenges for humankind in this century, regarding the dwindling crude oil and natural gas reserves, geopolitical conflicts, and fluctuating prices. In addition, these carbon-containing materials eventually would be added to the atmosphere
in the form of CO$_2$ or other GHGs, or as hydrocarbon pollutants will pollute surface water and soils.

The most attractive approach for developing renewable hydrocarbons through a carbon-neutral process is to recycle CO$_2$ from the atmosphere. Based on the accumulated knowledge of heterogeneous catalysis and surface chemistry for refining fossil fuels for decades, there are two possible routes to recycle CO$_2$: First, using biological systems such as plants and algae to convert atmospheric CO$_2$ to biomass feedstock and converting the feedstock to hydrocarbon-based fuel. Second, direct conversion of CO$_2$ to hydrocarbon-based fuel using a renewable energy source such as clean electricity and solar energy. In the following, the current advances and challenges in these two approaches will be briefly reviewed from a heterogeneous catalysis and surface chemistry perspective.

1.2.3.1 **Biomass derived value-added hydrocarbons**

We have been using biomass as fuel for heating or construction for ages. Burning wood is considered carbon-neutral because it does not increase the amount of CO$_2$ (if controlled at a rate less than the biomass production rate) and consumption as building materials remove and fix the atmospheric CO$_2$. This concept could be adopted for our current needs for transportation and chemicals with some changes. To use biomass as fuel and feedstock, we need to convert the complex biomass molecular structure into a refined, relatively simple hydrocarbon compatible with our existing infrastructure. The most widely adopted liquid form of these materials as biofuels and chemicals are ethanol and biodiesel.$^{11}$
Ethanol is the dominant biomass-derived fuel, accounting for 90% of biofuel usage. It is produced by anaerobic fermentation of corn and sugar cane-derived sugars, and only two countries (USA and Brazil) are responsible for 90% of the world's production. The major problem with biomass-derived ethanol fuel is the way we are producing them. The fermentation process produces a dilute aqueous solution of ethanol. Therefore, a costly energy-consuming distillation step is required to remove water from the mixture completely; this reduces the net energy density of bioethanol. In addition, for ethanol to be used as a fuel in current internal combustion engines, only low-concentration (5–15%) blends with gasoline are tolerated, and additional engine upgrades are required for ethanol-rich mixtures.11,30

It has been anticipated that the application of biomass derived ethanol as a platform molecule to produce value-added chemicals will be commercialized in the near future.117 In this regard, there is a growing interest in this field. The mechanism and thermodynamics of catalytic conversion of ethanol to 1,3-butadiene and ethylene have been intensely studied recently.117-120 Catalysts and catalytic processes for ethanol conversion to other chemicals such as hydrogen and small oxygenates like acetaldehyde121-122 and 1-butanol were also reported.117 Unlike the bio-ethanol fuel that is practically being limited, the application of this material as a platform chemical is promising due to an increased availability of bioethanol and the need for developing alternative routes to convert it to other marketable chemicals. In chapter 2 of this thesis, the ethanol conversion to 1,3-butadiene will be extensively discussed.

Biodiesel is a blend of long-chain alkyl esters, generally derived from vegetable oils. It is produced by chemically mixing the oil with methanol or ethanol in the presence of a basic catalyst, in a process known as transesterification. Like ethanol, biodiesel usage is limited to low-
concentration blends with conventional diesel fuel since pure biodiesel can cause rubber and other components in the engine or fuel lines to fail.\textsuperscript{123}

The fact that these biofuels are oxygen rich results in their biggest limitation, low energy density.\textsuperscript{11} An attractive alternative to overcome these limitations would be to catalytically convert biomass to liquid fuels that are chemically similar to the fossil fuel used today. The other concern about current common biofuels is the utilization of edible biomass at a large scale as feedstocks (e.g., sugars, starches, and vegetable oils). Important moral and ethical questions arise because this practice creates competition with food for land use. These issues have driven researchers worldwide to develop technologies to process non-edible biomass (lignocellulosic biomass), thereby permitting sustainable production of a new generation of deoxygenated fuels (so-called second generation of fuels) without affecting food supplies. In this respect, lignocellulosic biomass is abundant and can be grown faster and at a lower price than food crops.\textsuperscript{124}

Today's most promising methodology for biomass processing resembles that used for oil in petroleum refineries. It involves the conversion of lignocellulosic feedstocks into simpler fractions that are subsequently converted into a variety of useful products. Current technologies for the conversion of lignocellulosic biomass into simple hydrocarbon chemicals involve three major primary routes: gasification, pyrolysis, and hydrolysis.\textsuperscript{11}

Gasification technology is more than 100 years old. In the 1920s, cars in Sweden were powered by wood gasifiers due to the shortage of petroleum resources. During the Second World War, numerous studies were conducted to optimize the design of wood gasifiers and enhance their performance.\textsuperscript{125} Gasification of biomass produces CO\textsubscript{2}, CO, and H\textsubscript{2}, known as syngas, and requires the Fisher-Tropsch process to produce organic molecules. In this approach biomass is completely converted to syngas. Advances in gasification technologies and multiple uses of syngas have
permitted gasification to integrate with several industrial processes to produce chemical feedstocks and generate power.\textsuperscript{126} This approach is mainly employed for production of chemicals, including liquid fuel, and could be classified into carbon-neutral or carbon-negative process depending on the products.

The biofuel produced through this thermochemical route could be costly because of the requirement of high pressures in the Fisher-Tropsch process. One of the main limitations of Fischer–Tropsch approach is the lack of selectivity in the final alkane product, with broad distributions that can range from C\textsubscript{1} to C\textsubscript{50}. The Anderson–Schulz–Flory polymerization model, which governs the alkane chain growth probability, indicates that neither gasoline nor diesel fuels can be produced selectively without generating a large number of undesired products.\textsuperscript{127}

The pyrolysis method involves heating the biomass in the absence of oxygen to liquefy it, at temperatures ranging from 648–800 K.\textsuperscript{128} This technique delivers a complicated viscous liquid blend containing hundreds of molecules, which is corrosive and undergoes fast aging, known as bio-oil\textsuperscript{129} and requires upgrading before being used as a fuel or platform chemicals.\textsuperscript{33, 130} Similar to gasification, an essential benefit of pyrolysis is that it converts all the organic matter in lignocellulosic biomass, including the highly resistant lignin portion. Furthermore, a large fraction of biomass energy (up to 70\%) is retained in the bio-oil, allowing strategies to concentrate the energy of biomass.\textsuperscript{11, 126} The control over the final composition of the bio-oil is very challenging since it is affected by a large number of factors such as feedstock type (wood, agricultural wastes, forest wastes), reaction conditions (temperature, pressure, residence time of vapors), reactor design, alkali content of the feedstock, particle size, and storage conditions.\textsuperscript{131}

There are important barriers to the utilization of bio-oils as transportation fuels. First, as indicated above, pyrolysis oils are complex mixtures of oxygenated compounds, which confer this
liquid with low energy density (typically 50% of conventional hydrocarbon fuels), low volatility, and low stability, which are undesirable characteristics for liquid transportation fuels. Their high acidity, viscosity, and water content could cause storage and engine issues. Therefore, bio-oils must be pretreated to be used as transportation fuels.\(^{11}\)

As an alternative to the previous technique, the cellulosic biomass undergoes catalytic hydrolysis with an energy-conservative approach, using acids either in aqueous solution (commercial method, e.g., using diluted sulfuric acid) or in a heterogeneous phase using solid catalysts or ionic liquids. The product of this approach, similar to bio-oils, contains a high level of oxygen rich functional groups (e.g., \(-\text{OH}, -\text{C}=\text{O}, \text{and } -\text{COOH groups}\)). The complex mixtures of these oxygenated compounds need to be pretreated for transportation fuels.\(^{132}\)

In order to produce liquid fuel from lignocellulosic biomass conversion products, these materials need to be transformed to increase their energy density, volatility, and thermal stability. These changes can be accomplished through more extensive removal of oxygen. One of the possibilities to reduce the oxygen content in lignocellulosic feedstock involves the application of hydrogen at high pressures and moderate temperatures in a process called hydrodeoxygenation.\(^{133}\) The hydrogenation reaction is typically carried out over sulfided CoMo- and NiMo-based catalysts, which are widely used for sulfur and nitrogen removal in the petrochemical industry.\(^{133}\) Precious metals like Pt and Ru supported over metal oxide materials have also been used for this purpose.\(^{11}\)

The hydrodeoxygenation process has several challenges that limit its economic viability. First, hydrodeoxygenation requires a high pressure of hydrogen, which is typically produced from fossil fuels. However, Czernik et al. demonstrated that this limitation could be overcome by developing processes to produce hydrogen from lignocellulosic biomass. In this approach, a
fraction of the biomass would be utilized to produce renewable hydrogen through gasification routes, which would be subsequently used for bio-oil deoxygenation.\textsuperscript{134} Second, controlling the extent of hydrogenation in hydrodeoxygenation reactions is very challenging. The feed of the hydrodeoxygenation reaction is a complex composition of the bio-liquid, which includes a large number of compounds (e.g., acids, ketones, aldehydes, alcohols, aromatics) with very different reactivities toward hydrogenation. This reaction aims to selectively remove oxygen versus full hydrogenation of aromatic compounds (derived from lignin and useful as gasoline components) to avoid unnecessary hydrogen consumption. Newman et al. showed that Ru/TiO\textsubscript{2} (P25) shows remarkable selectivity and activity for deoxygenation of phenol to benzene.\textsuperscript{135} However, the excellent selectivity and activity of the catalyst depend on the treatment procedure performed following Ru deposition. When Ru/TiO\textsubscript{2} catalysts were calcined after Ru deposition and then reduced, catalysts were more selective toward hydrogenation products. When catalysts were reduced directly after Ru deposition, they were more selective toward the deoxygenation reaction. Reductive treatment of the catalyst makes small Ru particles, while oxidative treatment of the catalyst followed by reduction makes large Ru particles.\textsuperscript{136-137} As a result, hydrogenation of the ring is the preferred pathway when Ru particles are large, while deoxygenation of phenol is the preferred pathway when Ru particles are small. These observations indicate that the deoxygenation reaction must be happening at the metal-support interface. Newman et al. speculated that the possible reasons for the excellent performance of TiO\textsubscript{2} P25 as the catalyst support could be associated with the reducible nature of TiO\textsubscript{2} or strong metal-support interactions.\textsuperscript{135} However, later Omotoso et al., by studying the conversion of m-cresol over Ru/TiO\textsubscript{2}, showed a linear correlation between rates of m-cresol conversion to toluene and Ru perimeter, and no such correlation was found between the reaction rates and Ru metal surface area.\textsuperscript{138} The outcome of these studies
emphasize the necessity of the fundamental and practical study of the surface of this class of catalysis during the pretreatment steps.

Hydrodeoxygenation of acrolein to produce propene, 1-propanol, and allyl alcohol on pretreated MoO$_3$ and WO$_3$ has been reported.\textsuperscript{139-140} Thibodeau et al.,\textsuperscript{140} by using thermogravimetric analysis (TGA) and mass spectrometry, have demonstrated that both the oxygen substoichiometric and hydrogen content of the H$_y$WO$_{3-z}$ catalytic phase, that is formed during hydrogen pretreatment at temperatures from 200 to 500 $^\circ$C, are effective for hydrogenation of acrolein to allyl alcohol at 50 $^\circ$C. TGA and reaction kinetics data indicate that the active catalyst composition is between H$_{0.9}$WO$_{2.9}$ and H$_{1.3}$WO$_{2.7}$ and that the rate of hydrodeoxygenation is comparable to the oxygen vacancy creation rate. Chapter 3 of this thesis demonstrates kinetic models describing the hydrogen dissociation and WO$_3$ bronze formation as the critical pretreatment step.

Another approach for catalytically upgrading the product of lignocellulosic biomass conversion is the ketonization reaction. Bio-oils typically contain a significant quantity (up to 30 wt\%) of carboxylic acids. Using the ketonization route, the acidic fraction of bio-oils, without utilizing hydrogen, undergoes catalytic ketonic decarboxylation or ketonization.\textsuperscript{141} Through this reaction, two molecules of carboxylic acids are condensed into a larger ketone resulting in a release of CO$_2$ and water. This reaction is typically catalyzed by inorganic oxides such as CeO$_2$, TiO$_2$, Al$_2$O$_3$, and ZrO$_2$ at moderate temperatures (573–773 K) and atmospheric pressure.\textsuperscript{142} Ketonization could find application for catalytic upgrading of biomass for multiple reasons. First, carboxylic acids in the bio-oil can be selectively removed (without affecting the rest of the compounds) and transformed into a more hydrophobic, larger ketones at temperatures and pressures typically used in pyrolysis.\textsuperscript{142} Second, this transformation takes place with the simultaneous reduction of the oxygen content of the acid (in the form of water and CO$_2$) and without using hydrogen.
Consequently, pretreatment of the bio-oil over a ketonization bed could reduce acidity and oxygen content, thereby reducing hydrogen consumption and leaving bio-oil more amenable for subsequent hydrodeoxygenation processing. Third, ketonization can also be applied to other compounds typically present in bio-oils like esters, formed by a reaction between acids and alcohols.\textsuperscript{11, 142-143}

Biomass resources are abundant worldwide and can potentially substitute crude oil in liquid fuels for transportation needs. Bioethanol is already used as an additive to gasoline, reducing the carbon footprint of our transportation system. However, its application is limited as an additive due to its low energy density and high solubility in water, properties that are reducing the quality of the fuels. The production of carbon-neutral fuels, which are molecularly similar to fossil fuels, is a promising alternative to overcome the limitations of bioethanol. The transformation of oxygen-rich biomass into oxygen-free liquid fuels can be done by catalytic processes such as gasification, pyrolysis, and aqueous-phase processing, coupled with hydrodeoxygenation and ketonization. The design and construction of catalyst materials, based on the current catalysts used in the oil industries, along with theoretical and advanced surface characterization methods, could be a great opportunity to develop an emission-free future.

1.2.3.2 Direct atmospheric CO$_2$ reduction to hydrocarbons

Reducing CO$_2$ is an attractive approach to removing or recycling this gas from the atmosphere. Capturing and converting emitted CO$_2$ into valuable products such as chemicals and fuels is an effective carbon-negative and carbon-neutral process, respectively, that could slow down and reverse climate change trends. However, thermodynamically, CO$_2$ is a well-known stable molecule ($\Delta G^o_f = -396$ kJmol$^{-1}$). Hence, conversion of this molecule to a hydrocarbon
involves a high energy process, where the C-oxidation state should be reduced from +4 to lower values, for possible production of compounds such as HCOOH, H₂CO, CH₃OH, CH₄, and other longer chain hydrocarbons.¹⁴⁴ Three major routes have been investigated for the conversion of CO₂ to hydrocarbons: the thermal catalytic route, electrochemical route, and photocatalytic route. The challenges and opportunities of these options will be briefly discussed in the following sections.

### 1.2.3.2.1 Thermal catalytic routes

CO₂ conversion into hydrocarbon-based molecules can be achieved in two ways: combining the reverse water-gas shift with Fischer-Tropsch synthesis and combining high-temperature methanol synthesis with the methanol to hydrocarbon process. These are two efficient strategies for direct CO₂ reduction to C₂⁺ hydrocarbons, including liquid hydrocarbons.¹⁴⁵ Industrial methanol synthesis from CO₂-containing syngas uses Cu-ZnO-Al₂O₃ catalysts. Recently, Lurgi and Mitsui implemented this catalytic platform for CH₃OH synthesis from atmospheric CO₂ at the pilot-plant level.¹⁴⁶ However, the limitation of this method is the formation of the undesired CO through the reverse water-gas shift, which is a competitive reaction to methanol synthesis.¹⁴⁶

The methanol synthesis reaction is known to be sensitive to support effects. Therefore, utilizing an appropriate support material can enhance CH₃OH selectivity. These effects are attributed to structural, electronic, and chemical promotional effects. For example, by using ZrO₂ support, at 200–260 °C, the selectivity toward CH₃OH significantly increased to 70%.¹⁴⁷ In this manner, recently, reducible oxides have received considerable attention due to their excellent performance with high CH₃OH selectivity in a wide range of temperatures (200–320 °C). Nearly
100% selectivity can be attained over cubic In$_2$O$_3$ nanomaterial and In$_2$O$_3$ supported on monoclinic ZrO$_2$.\textsuperscript{148} The surface oxygen vacancies surrounded by indium atoms are considered the active sites for CO$_2$ activation and hydrogen splitting, and methanol formation from CO$_2$ hydrogenation follows the cycle between generation and annihilation of vacancies.\textsuperscript{149-150} Compared with Cu-based catalysts, the biggest advantage of the reducible metal oxides (In$_2$O$_3$-based oxides or ZnO-ZrO$_2$ solid solution catalysts) is that they can effectively inhibit the undesired reverse water-gas shift reaction even if the reaction temperature is as high as 320 °C.\textsuperscript{145} Nevertheless, further research is needed to elucidate the origin of this enhanced activity by identifying the active sites and understanding the reaction mechanisms for both methanol and CO formations, which will promote the rational design of more efficient CO$_2$-to-methanol oxide catalysts.

Hans Fischer and Franz Tropsch in the early 1920s proposed the Synthol process, which gave, under high pressure (>100 bar), a mixture of oxygenated aliphatic compounds via reaction of carbon monoxide with hydrogen over alkalized iron chips at 673 K. This product was transformed after heating under pressure into a mixture of hydrocarbons.\textsuperscript{151} This reaction was at the center of attention of the oil industry due to the abundance of natural gas. Since the 1980s, it has been developed significantly and currently in many parts of the world have made it attractive to commission new plants based on this technology.\textsuperscript{151} Although this technology was initially developed for coal conversion, its advancement in the industrial scale makes the combination of reverse water-gas shift with Fischer-Tropsch synthesis a viable approach for the production of hydrocarbon fuel.

Dorner and his coworkers have proposed a process for producing hydrocarbon fuel from CO$_2$. Based on their approach at the initial stage, the CO$_2$ could be converted into CO using a Fe-based catalyst, on the following step, by hydrogenation of CO to olefins and paraffins over active
sites of Fe-carbide.\textsuperscript{152} The olefins and paraffin products are then converted into various other hydrocarbons through aromatization, hydrocracking, hydro-isomerization, oligomerization, cyclization plus H-transfer usually over a bi-functional system e.g., acidic zeolite.\textsuperscript{144} Co-catalysts are the catalysts of choice in Fischer-Tropsch application using syngas (a gas mixture of CO and H\textsubscript{2}), yielding the best performance-to-cost ratio. Co-catalysts tend to have much higher chain growth probabilities; due to their lower water-gas-shift ability, they form less undesired CO\textsubscript{2} (reverse reaction) than the Fe-based Fischer-Tropsch catalysts.\textsuperscript{144} Using co-promoters such as Pt or Ru, the conversion tends to be geared towards high wax production. The wax product can be converted to hydrocarbon fuels in the naphtha and diesel range using a selective hydrocracking catalyst. Further upgrading of the predominantly alkene products over solid acids results in commercially usable fuels,\textsuperscript{153} and provides an attractive carbon-neutral fuel. The main limitation of the thermal catalysis approach is their energy consumption, which directly affects the net energy density of the product fuel. To be truly a carbon-neutral approach, we need to integrate them with clean energy sources or use cheaper, carbon-neutral biomass fuels like biodiesel or ethanol as the energy source.

\textbf{1.2.3.2.2 Electrochemical CO\textsubscript{2} reduction}

The electrochemical conversion of CO\textsubscript{2} has recently attracted attention as a future solution for CO\textsubscript{2} removal since coupling the electrochemical CO\textsubscript{2} reduction process with renewable electricity sources can potentially enable carbon-neutral fuel production.\textsuperscript{154} Most of the electrochemical CO\textsubscript{2} reduction process studies are limited to lab-scale experiments. Nevertheless, there have been numerous attempts to establish the foundations of the CO\textsubscript{2} electrolysis systems, and to an extent, the pioneers have shown some success. There are examples that demonstrated
successful application of electrochemical reduction of CO$_2$ at pilot-scale.$^{155}$ Unfortunately, these systems are very energy-intensive and require high temperatures, limiting their commercialization.$^{154}$

The more selective metallic catalysts in this field are Sb for formic acid, Ag for carbon monoxide, and Cu for methane, ethylene, or ethanol. In addition, methanol, propanol, and 1-butanol have also been produced via CO$_2$ electrochemical reduction, albeit in small quantities.$^{156}$ The electrochemical reduction of CO$_2$ to other products proceeds in a multi-step reaction and proceeds through a complex mixture of intermediates.$^{157}$ Each of these steps involves electron transformation and proton transfers, which are often accompanied by high overpotentials. Such overpotential in electrochemical processes could be detrimental because, in many cases, it requires additional electrical energy and promotes the undesirable formation of competitive reduction products (i.e. H$_2$), which lowers both faradic efficiency and selectivity of the process. Therefore, lowering the overpotential remains one of the major tasks in improving the overall performance of the electrochemical CO$_2$ reduction process.$^{154}$ Similar to previously discussed cases, the high overpotentials leads to slow kinetics of surface reactions and mass transport limitation of reactant molecules.

With the design of effective catalysts with lower overpotential, high faradic efficiency, and product selectivity and the technology and characterization of materials combined with a continuous theoretical investigation, high-performance catalysts will be developed to overcome the problems of insufficient catalyst activity, poor product selectivity, and low faradic efficiency.
1.2.3.2.3 Photocatalytic reduction of CO$_2$ to hydrocarbons

One possible solution to efficiently utilize solar energy to produce useful fuels under visible light is photocatalytic CO$_2$ reduction to hydrocarbons. Photocatalytic reaction over semiconductor photocatalysts can reduce CO$_2$ into hydrocarbons using water as an electron donor and the source of hydrogen. Numerous publications report application of metal oxides as the CO$_2$ photocatalyst, demonstrating the formation of CH$_4$ and CH$_3$OH as primary products and CO as a secondary product.$^{158-164}$ However, the application of photocatalytic systems is limited due to low quantum yield for CO$_2$ reduction, which is similar to almost all of the other photocatalytic applications of metal oxide semiconductors. Fast recombination of the photogenerated charge carriers and the wide bandgap of stable metal-oxides, such as TiO$_2$, limit their applications under visible light.

There are several approaches to enhance the photocatalytic activity of metal oxides such as using co-catalysts, utilizing doping and co-doping of non-metal elements and composite materials. For example, it has been experimentally shown that deposition of metals such as Pt, Au, Pd, Ag, and Cu on the photocatalysts positively affects the photochemical reduction of CO$_2$. The metals catalyze the reduction reactions upon receiving electrons from the photocatalyst and improving the electro-hole pair generation.$^{165}$ Non-metal dopants like N, P or S in TiO$_2$ induce a red-shift in the absorption onset with visible absorption and superior activity compared to undoped TiO$_2$, resulting in absorption of a broader energy range of the available solar light.$^{166}$

Parallel to heterogeneous catalysis, there has been an effort in the homogeneous catalysis research area to utilize photocatalysis to develop a cost-effective carbon-neutral fuel production process. However, homogeneous catalysis systems have their own shortcomings such as involvement of high cost, time consuming synthesis procedures, instability, and nonreusable, which severely impede their practical applications in photocatalysis.$^{167-168}$ Undoubtedly, some new
approaches are being developed to couple molecular photocatalytic systems with semiconductors to improve CO₂ conversion into carbon containing chemicals.

Cobalt composites have been demonstrated as one of the most promising catalysts in this manner. Cobalt containing zeolitic imidazolate framework or Co₃O₄ metal oxides have been recently reported as novel photocatalytic systems with the assistance of a ruthenium-based photosensitizer for CO₂ reduction. Recently Zhao et al. demonstrated a metallic Cobalt–Carbon composite as a recyclable and robust magnetic photocatalyst for efficient CO₂ reduction. In their work, they have coupled photosensitized porous metallic and magnetic 1200 Co-C composites (PMMCoCC-1200) with a [Ru(bpy)₃]Cl₂ photosensitizer to reduce CO₂ under visible-light irradiation selectively and efficiently, with a superior activity compared to most reported classical heterogeneous photocatalysts. Furthermore, their systematic analysis indicates that the central metal cobalt is the active site for activating the adsorbed CO₂ molecules, and the surficial graphite carbon coating on cobalt metal is crucial for transferring the electrons from the triplet metal-to-ligand charge transfer of the photosensitizer Ru(bpy)₃²⁺, which gives rise to significant enhancement for CO₂ reduction efficiency.

Another recent approach that gathered attention is the application of graphitic C₃N₄ composites. As mentioned in the photocatalytic H₂ evolution section, a visible light-responsive graphitic carbon nitride (g-C₃N₄) photocatalyst with high reduction ability recently attracted much attention since hydrogen evolution over g-C₃N₄ had reported produced from water under visible-light irradiation. The composite of Ag₃PO₄ on g-C₃N₄ enhances the photocatalytic performance. Similarly, coupling gC₃N₄ with NaNbO₃ nanowires increases the photocatalytic performance considerably. Ong et al. have shown a method to synthesize proton-functionalized/protonated g-C₃N₄ (pCN). The positively charged g-C₃N₄ can form a hybrid
nanostructure with the negatively charged graphite oxide (rGO) sheets, forming rGO/pCN catalysts that are more active than the gC$_3$N$_4$ itself. The highest CH$_4$ production occurs for the 15 wt % rGO/pCN (13.93 μmol g$^{-1}$, 5.4 times higher than C$_3$N$_4$). The higher activity achieved by the addition of rGO is due to its lower Fermi level relative to the conduction band of C$_3$N$_4$. In most cases in these composite materials, the formation of this heterojunction hinders the charge recombination rate.

Lately, metal nanoparticles such as Au, Cu, and Ag have gathered great attention because they create localized surface plasmon resonances in the visible wavelength region. Photoexcitation of these collective electron oscillations results in the creation of hot electrons that have been seen to catalyze surface chemical transformations. Plasmonic control of CO$_2$ reduction is possible, in principle, through engineering handles, such as photon energy, excitation density, metal composition, active facet, and presence of oxide support. However, utilizing these handles to optimize efficiency and product selectivity rationally is not easy without mechanistic models.

Although photocatalytic systems have been studied for more than 50 years, there are not many examples to point out regarding their commercialized application in CO$_2$ reduction to hydrocarbon fuels. This lack of application is due to the very low yield and impracticality of these processes compared to thermal or electrical rivals. Due to the wide bandgap of most traditional semiconductors and the fast recombination rate of photo-generated charge carriers, there is a growing interest in modifying the surface of metal oxides or creating new composites. There is a great research opportunity to apply solid-state physics and surface chemistry to tailor the electronic structure of these semiconductors to improve the charge separation events and shift absorbance into the visible region. In addition, there is increasing attention to localized surface plasmon resonances of metal nanoparticles and their application for chemical processes, through generation
of high energy electrons (hot electrons) and/or plasmonic heating. Since the mechanism of these systems is not fully understood, there is a great opportunity for mechanistic studies of these systems and to provide new tools to control them. Photocatalytic reductions of CO₂ to fuel comprise an enormous research challenge in its own right. Regardless, advancements in photocatalytic applications continue fast. This approach could develop cost-effective carbon-neutral technologies that rely on solar energy in a couple of decades with this pace. Since it could be developed off-grid, it can provide great opportunities for deployment and maintenance.

1.3 Scope of this thesis

This introductory chapter has discussed some of the proposed approaches toward developing a carbon-neutral process based on a heterogeneous catalysis platform to produce an alternative energy source for the transportation sector. The previous section has brought a brief description of different carbon-neutral approaches to store energy and produce chemicals, their challenges, and recent research directions. Possible research opportunities of each approach were briefly discussed with a heterogeneous catalysis and surface chemistry perspective. The following summarizes the contribution of the research studies presented in this thesis regarding the ongoing efforts for developing carbon-neutral routes for chemical and fuel production.

In chapter 2, the use of bioethanol as a feedstock for the production of renewable butadiene with a focus on the catalytic aspects is discussed. 1,3 butadiene is widely used as a bulk chemical obtained from ethanol. Butadiene finds useful applications in the polymer industry and could replace bioethanol as a more effective drop-in fuel. The Lebedev process is utilized to directly transform ethanol into butadiene, which involves first dehydrogenating ethanol to acetaldehyde, followed by aldol condensation of the acetaldehyde to give 3-hydroxybutanal that is subsequently
dehydrated to give crotonaldehyde. In this chapter, by utilizing in-situ surface characterization methods and reaction kinetic measurements, the mechanism of two key steps of the Lebedev reaction is studied. The comprehensive surface characterization of the 0.5%MgO/SBA-15 catalyst has provided a basic understanding of the essential site requirements to achieve high selectivity to butadiene.

Chapter 3 focuses on the developing a microkinetic model to describe the hydrogen WO$_3$ bronze formation. It has been reported that reducible WO$_3$ shows activity for the hydrodeoxygenation and hydrogenation reaction of pyrolysis products. According to Thibodeau,$^{180}$ WO$_3$ HDO catalysts have two types of acid sites of mechanistic importance. Oxygen vacancy sites are Lewis acids, which are sites for selective adsorption of carbonyl and alcohol moieties. The Brønsted acidity of the catalyst determines proton transfer from surface hydroxyls to the surface intermediate. Thus, adsorption and desorption energies are controlled by the Lewis acidity of oxygen vacancy sites, while the ease of proton donation is dependent on the Brønsted acidity. In the experimental investigation by Thibodeau et al.,$^{181}$ the composition of the reduced WO$_3$ bronze was determined as a function of hydrogen pretreatment temperature which plays an important role in determining the activity of the catalyst in acrolein hydrogenation to allyl alcohol and at higher temperatures, hydrodeoxygenation allyl alcohol to propene and 1,5-hexadiene. The oxygen substoichiometry and hydrogen content at the highest hydrogenation rate was H$_{1.29}$WO$_{2.77}$ after a pretreatment temperature of 350 °C. In this Chapter, we focus on the development of a microkinetic model to describe the bronze formation mechanism with the goal of exploring and understanding the factors that control the behavior of the mass loss as a function of time at different temperatures in pure hydrogen.
Chapter 4 and 5 are devoted to study the effect of presence of sulfur in titania photocatalysts. For numerous sulfated TiO$_2$ samples the absorption onset is reported at ~500 – 800 nm (2.4 – 1.5 eV, varying by synthesis method), indicating that sulfur doping narrows the band gap$^{182-186}$ improves photocatalytic activity for oxidation of contaminants in water. While band narrowing as a result of sulfating titania is essential for visible light photoactivity, A number of studies have proposed that the sulfating process induces deep electron traps that scavenge electrons and increase the hole (h$^+$) lifetime$^{187-189}$. In these chapters we demonstrate application a unique approach to probe unoccupied electronic states without creating e-/h$^+$ pairs. We compared sulfur-free and sulfated, calcined titania to obtain direct evidence for partially filled states deep in the band gap that act as electron traps. Here we are using the dissociation of hydrogen to generate electrons that fill the lowest unoccupied states. Their energy below the conduction band minimum (CBM) is measured directly from changes in diffuse reflectance spectroscopy in the infrared and UV-vis ranges. Titania materials were rigorously cleaned of carbonates, hydrocarbons and water by calcination to 400 °C. For pure pyrogenic titania, electrons only accumulate in the conduction band, while for sulfur-free anatase electrons occupy shallow traps ~0.2 eV below the CBM. For all commercial sulfur-containing anatase materials tested, we show that conversion of tridentate sulfate species into sulfur substituted on lattice sites occurs under highly oxidizing conditions above 400 °C and leads to partially empty states ~2.8 eV below the CBM.
2.1 Abstract

The Mg-catalyzed dehydrogenation of ethanol to yield acetaldehyde is an important step in the Lebedev reaction. In this work, we prepared a model MgO-SiO$_2$ catalyst by impregnation of MgO onto an SBA-15 support and used this material to study the reaction kinetics of ethanol dehydrogenation to acetaldehyde. The rates of acetaldehyde and ethylene production were measured for ethanol partial pressures ranging from 1 to 3 kPa. Both rates are fractional order at 723 K, decreasing to nearly zero-order at 648 K. Consistent with the literature for MgO-SiO$_2$ Lebedev catalysts, both basic sites and Lewis acidic sites were observed on this catalyst. The rates of both acetaldehyde and ethylene were inhibited by pyridine but not by 2,6-diterbutylpyridine, suggesting that both reactions involve not only basic but also Lewis acidic sites. To elucidate the origin of this cooperativity, a microkinetic model was constructed using a recently published mechanism for the Lebedev reaction catalyzed by MgO. The model was fit to our data using 4 fitting parameters, which suggests that well-mixed MgO-SiO$_2$ catalysts differ from MgO by decreasing the strength of Mg$^{2+}$-O$^{2-}$ site pairs, leading to lower barriers for dehydrogenation and a lower surface coverage by ethoxide and hydrogen.

2.2 Introduction

Research during the past two decades has focused on the use of alternative resources for producing high-value chemicals. This proposed reliance on renewable resources has the potential to limit the need for environmentally unfriendly fossil resources.$^{190-191}$ The current trend in the
U.S. and Europe towards the use of lighter feedstocks is also driving a push to find alternative sources of molecules with four or more carbons.\textsuperscript{192} Biomass is the only currently-available renewable source of carbon, which makes it unique in its suitability for the production of fuels and chemicals,\textsuperscript{190, 193} and its oxygen content makes it particularly attractive as a feedstock for chemicals, which generally require some degree of oxidation.\textsuperscript{126, 194} However, the selective activation of C-O bonds is difficult to achieve solely by chemical catalysis, and strategies that combine both chemical and biological catalysis allow for the production of chemicals that cannot be conveniently accessed by either discipline alone.\textsuperscript{195} In this regard, the use of ethanol as a feedstock for chemicals production is attractive due to the significant technological developments in the production of ethanol fuels,\textsuperscript{196-197} and several recent studies have reported its conversion to 1,3-butadiene (BD), ethylene, acetaldehyde, acetic acid, ethyl acetate, and diethyl ether.\textsuperscript{118} Of these, BD is the only C\textsubscript{4} species, making it an especially important product for the current market.

Ethanol can be upgraded to BD via C-C bond formation in the Lebedev process, following the reaction network shown in Scheme 2-1,\textsuperscript{118, 198} and a variety of Lebedev catalysts have been reported to date.\textsuperscript{199} In particular, magnesia-silica mixed oxides (MgO-SiO\textsubscript{2}) are some of the most widely studied catalysts for BD production, with reported BD yields ranging from 9 to 42\%.\textsuperscript{200-205} The groups of Bruijnincx and Weckhuysen,\textsuperscript{118, 204} Sels,\textsuperscript{200} and Baltrusaitis\textsuperscript{205} have studied in detail BD formation over undoped MgO-SiO\textsubscript{2} catalysts, each observing that the catalyst preparation method has a significant influence on the BD yield. As discussed more below, one important contributor to low BD yields over MgO-SiO\textsubscript{2} is the unwanted dehydration of ethanol to form ethylene, which is fast compared to the desired ethanol dehydrogenation to yield acetaldehyde (see Scheme 2-1) and is the motivation for the use of transition metal dopants, such as Cu, Ag, and Zn, that can accelerate acetaldehyde production.\textsuperscript{206} However, that there are reports of high yields of
BD obtained using undoped MgO-SiO$_2$ catalysts suggests that this selectivity challenge can be overcome even without the use of transition metals. Consequently, further study of the competition between ethanol dehydrogenation (to make acetaldehyde) and dehydration (to make ethylene) over simple (i.e., undoped) MgO-SiO$_2$ is needed, particularly for future rational design of new MgO-based catalytic materials.

**Scheme 2-1.** The generally accepted route for conversion of ethanol into butadiene and the competing path to ethylene.

The importance of the ethanol dehydrogenation reaction catalyzed by these materials is emphasized by Taifan et al.\textsuperscript{205} who used in situ temperature-programmed surface reaction-mass spectrometry (TPSR-MS) to study the kinetics of the overall reaction sequence. Importantly, they note that, in the presence of an acetaldehyde co-feed, the aldol condensation and Meerwein-Ponndorf-Verley reactions are quite facile, suggesting that low BD yields and high ethylene selectivities over MgO-SiO$_2$ may be a consequence of the acetaldehyde formation being rate-limiting, which is consistent with much of the other literature on undoped MgO-SiO$_2$ catalysts.\textsuperscript{201-202, 204, 207} Such an explanation would also be consistent with the generally higher yields of BD obtained over transition-metal-doped catalysts that facilitate dehydrogenation,\textsuperscript{208-210} which is also the conclusion obtained by Da Ros et al. and Sushkevich et al.\textsuperscript{211-212} Notably, the vast majority of studies of the reaction network catalyzed by MgO-SiO$_2$ (both with and without dopants) have
focused on the overall reaction network, and the kinetics of the individual reactions in the overall network remain to be elucidated in detail.

Outside of the context of butadiene formation, ethanol dehydrogenation and dehydration have been well-studied over a variety of catalysts that have included both acidic and basic sites, although none have yet investigated the reaction over MgO-SiO$_2$. Importantly, acidic and basic sites (both Brønsted and Lewis) have been observed on MgO-SiO$_2$ catalysts.$^{213}$ Di Cosimo and coworkers have studied acidic and basic sites on the related class of MgO-Al$_2$O$_3$ mixed oxides,$^{214}$ and they suggest that the distribution of acid vs. base sites can be controlled in part by the Al content.$^{215}$ Based on FTIR spectroscopy of adsorbed CO$_2$, they suggest that pure MgO contains strong basic sites, while they observe that increased Al content correlates with an increase in the number of low- and medium-strength basic sites. Interestingly, this group also notes that the selectivity for both dehydrogenation and dehydration of ethanol$^{214}$ and 2-propanol$^{215}$ depends on the number and strength distribution of Lewis-acid-base site pairs, which relates to the hypothesis advanced by Angelici et al.$^{213}$ that such reactions are due to cooperative acid-base effects.

Similar to the class of MgO-based materials, γ-Al$_2$O$_3$ is known to catalyze both ethanol dehydration to ethylene and dehydrogenation to acetaldehyde, although the selectivity to ethylene is much higher over γ-Al$_2$O$_3$ than over MgO-SiO$_2$. That purely Lewis acidic γ-Al$_2$O$_3$ is active for these reactions is important to consider when evaluating catalysts for the Lebedev reaction, because the literature often ascribes the formation of unwanted ethylene to Brønsted acid sites, following classical organic chemistry descriptions of dehydration.$^{216-217}$ However, Lewis acid sites, such as those predicted to exist on MgO surfaces,$^{218}$ are well known to catalyze ethylene formation,$^{219}$ an observation dating at least to the work by Knözinger’s group.$^{220}$ It is thus useful
to consider the work of Bhan and coworkers, who have evaluated both ethylene\textsuperscript{221-222} and acetaldehyde\textsuperscript{221} formation over \( \gamma \)-\( \text{Al}_2\text{O}_3 \). They show, using rigorous steady-state reaction kinetics measurements, that ethylene is produced via a concerted \( \text{E}_2 \) mechanism (which is also consistent with recent density functional theory (DFT) calculations\textsuperscript{223}) while acetaldehyde is formed by sequential removal of hydrogen atoms from ethanol, as shown in Scheme 2-2.\textsuperscript{222} Importantly, their work shows that dehydrogenation to form acetaldehyde proceeds over Lewis acid sites and that both ethylene and acetaldehyde formation rely on a common intermediate that they hypothesize is ethoxide (bottom, Scheme 2-2).

There is, thus, a substantial body of literature on ethanol dehydrogenation and dehydration, both in the context of the Lebedev reaction for BD formation and more broadly. Importantly, there is some disagreement about the mechanisms for ethanol dehydrogenation and dehydration. Weckhuysen, Bruijnincx, and coworkers\textsuperscript{118, 204, 213} find that dehydration occurs only on Lewis acid centers over Lebedev catalysts, while Di Cosimo,\textsuperscript{214-215} Iglesia,\textsuperscript{214} Davis,\textsuperscript{224-225} and Flaherty\textsuperscript{226} suggest that dehydration occurs at Lewis-acid-base site pairs. Similarly, the frequent inclusion of transition metal promoters leads to sometimes contradictory descriptions of dehydrogenation over the general class of Lebedev catalysts. These discrepancies may be due to a lack of steady-state

\[ \text{Scheme 2-2. Proposed mechanism of acetaldehyde and ethylene formation over } \gamma \text{-Al}_2\text{O}_3. \text{ Note the ethoxide intermediate that is shared by both reactions. Adapted with permission from DeWilde et al. Copyright 2013 American Chemical Society.} \]
kinetics data for ethylene and acetaldehyde formation collected using the mixed oxide catalysts used for the Lebedev reaction.

To address the limitations of the existing literature for ethanol dehydrogenation and dehydration catalyzed by MgO-SiO$_2$ Lebedev catalysts, we report here the results of steady-state reaction kinetics measurements for formation of acetaldehyde and ethylene from ethanol. To simplify our analysis, we have used MgO-impregnated SBA-15 as a well-defined model catalyst. We have coupled our reaction kinetics analysis with hydrogen/deuterium isotope effect measurements, pyridine inhibition experiments, and in situ FTIR spectroscopy, which we used to identify a reaction sequence and abundant surface intermediates that are similar to that shown in Scheme 2-2 and that involve not only basic sites but also Lewis acidic sites. Finally, we have confirmed this cooperativity using a microkinetic model constructed based on the recently published mechanism of Taifan et al.$^{227}$ and fit to our data using 4 fitting parameters.

2.3 Materials and methods

2.3.1 Catalyst synthesis

MgO supported on SBA-15 was used as a model catalyst for our reaction kinetics studies due to its unique structure consisting of mesopores and micropores and also its high surface area and thermal stability.$^{228}$ 0.08 wt% MgO/SBA-15 was prepared by incipient wetness impregnation, with the Mg loading selected to maintain high dispersion of MgO inside the SiO$_2$ pore walls. In a typical synthesis, 2 g of SBA-15 (ACS Material) were impregnated with a solution of 0.01 g Mg(NO$_3$)$_2$•6H$_2$O (Acros Organics, 99.9995%) dissolved in Milli-Q grade water (18 MΩ). After impregnation, the catalyst was dried at ambient temperature for 1 hour and then overnight at 373
K. The catalyst was then heated in flowing air to 773 K with a temperature ramp of 4.8 K min$^{-1}$ and calcined for 5 h at 773 K.

Our goal in this work is to develop fundamental insight into the mechanism by which the Lebedev reaction proceeds over MgO–SiO$_2$ catalysts, which is facilitated by the use of a catalyst with a uniform surface structure possessing a small number of distinct active sites. Such a catalyst is not necessarily the most active on a per-mass basis; accordingly, we note that it is explicitly not the goal of this work to develop a next-generation catalyst for the Lebedev reaction. We used incipient wetness impregnation of Mg(NO$_3$)$_2$ into SBA-15 to encourage high dispersion of Mg sites on the SiO$_2$ surface, leading to Mg–O–Si sites similar to those suggested to exist on catalysts synthesized by the popular wet kneading methods but without the heterogeneity inherent in that preparation method.$^{202, 204-205, 213}$ That the Mg coverage be kept low is critical for comparison to reactions performed with catalysts synthesized by wet kneading; Taifan and Baltrusaitis have previously shown that these catalysts, while prepared with bulk Mg/Si ratios near unity, actually possess surfaces low in Mg concentration,$^{205}$ similar to the catalyst used here. Moreover, it is known that catalysts prepared by incipient wetness impregnation exhibit low selectivity for the Lebedev reaction when using Mg/Si ratios near unity.$^{204}$ To favor selectivity to acetaldehyde (and along the pathway of the Lebedev reaction more generally), we chose to keep the Mg coverage on SBA-15 well below a monolayer, which should promote Mg–O–Si interactions and disfavor the formation of bulk MgO-like sites, similar to the approach taken by Wachs and co-workers for studying other bulk-oxide-catalyzed reactions.$^{229}$
2.3.2 Reaction kinetics measurements

Ethanol dehydrogenation and dehydration measurements were carried out in a packed-bed continuous flow reactor made of stainless steel (1/4-inch ID and 5.25-inch length). The gas lines were 1/8-inch diameter stainless steel tubing, and the liquid delivery line was 1/16-inch stainless steel tubing. Gas flow was controlled with a digital mass flow controller (Brooks Instrument, Model 5850E). A syringe pump (New Era Pump Systems, Model NE-1000) was used to feed ethanol to the reactor, which was vaporized by heat tracing the feed lines to 450 K. The reactor temperature was varied between 648-723 K. The reactor tube was contained within aluminum heat transfer blocks that were wrapped with heating tape and controlled by a temperature controller (Automation Direct, Solo ADC1105). Temperature was measured by a K-type thermocouple (Omega) placed in intimate contact with the reactor tube. The catalyst was packed between two plugs of quartz wool and mixed with fused SiO$_2$ to improve heat transfer. The reactor was heated to the desired reaction temperature in flowing helium. Reactions were carried out using ethanol (Acros Organics, 99.5%) or ethylene (Matheson, Research Grade) in a helium sweep gas stream (Matheson, UHP, 99.999%). Kinetic isotope effect experiments were performed using CH$_3$CH$_2$OD and CD$_3$CD$_2$OD (both from Cambridge Isotope Labs, 99%). Experiments using pure SBA-15 did not lead to any measurable ethanol conversion. The weight hourly space velocity (WHSV) was calculated as the ratio between total ethanol gas flow (g min$^{-1}$) and the catalyst weight (g). The product mixture was analyzed by a gas chromatograph (GC, SRI Instruments, Model 8610C) equipped with a flame ionization detector (FID) and an MXT-1 capillary column (Restek, 0.53mm × 60 m, 5.00 µm). The expected products and intermediates (acetaldehyde, ethylene, ethanol, and small traces of butene in the first two hours) were used as reference standards (SCOTTY® Specialty Gasses, Supelco). Carbon balances were generally closed to
within 10%. For the reaction kinetics experiments, the catalyst was first aged in flowing ethanol (3.92 kPa) for 8 hours at 723 K, after which the temperature and space velocity were adjusted to give ethanol conversions within the range from 3-10%, indicating that the reactor was operated in differential mode. Selectivity was calculated according to Equation 1, where $F_i$ corresponds to the molar flowrate of species $i$ leaving the reactor.

$$\text{Selectivity}_i = \frac{F_{\text{product},i}}{\sum_i F_{\text{product},i}} \times 100\%$$

(1)

Hydrogen/deuterium isotope effect experiments were run following the same procedure as the other kinetics measurements, using CH$_3$CH$_2$OD and CD$_3$CD$_2$OD (both from Cambridge Isotope Labs, 99%). The catalyst was first aged in CH$_3$CH$_2$OH as described above, after which the space velocity was adjusted to give ethanol conversions less than 10% and rates ($r_H$) were measured for several hours. Then, deuterated ethanol (either CH$_3$CH$_2$OD or CD$_3$CD$_2$OD) was fed at the same condition and again rates ($r_D$) were measured over the span of several hours. Finally, CH$_3$CH$_2$OH was again fed to the reactor and the rates measured. Deactivation was corrected for using the rates measured with CH$_3$CH$_2$OH, and the isotope effect ($r_H/r_D$) was calculated.

The acid sites on the catalyst were titrated using pyridine and 2, 6-Di-tert-butylpyridine (DTBP), which were delivered to the reactor using the same syringe pump used to feed ethanol for the other kinetics measurements. Ethanolic solutions of either 15 vol% pyridine or 5 vol% DTBP were prepared and fed to the reactor at typical reaction conditions, and the rates of acetaldehyde and ethylene production were measured. Deactivation due to carbon deposition was corrected for using the same deactivation rate constants employed during other kinetics measurements. Importantly, all feed lines were heat traced to 675 K, and the lines were flushed copiously with helium between experiments until no pyridine or DTBP was observed in the GC/FID.
chromatograms. The cleanliness of the reactor was validated by re-measuring the rate of acetaldehyde production (without pyridine or DTBP co-feed) following reactions performed using pyridine or DTBP.

To evaluate the influence of catalyst acidity on the rates of acetaldehyde and ethylene formation, pyridine and 2,6-di-tert-butylpyridine were delivered to the reactor using the same syringe pump used to feed ethanol for the other kinetics measurements. Ethanolic solutions of either 15 vol % pyridine or 5 vol % DTBP were prepared and fed to the reactor under typical reaction conditions, and the rates of acetaldehyde and ethylene production were measured. Deactivation due to carbon deposition was corrected for using the same deactivation rate constants employed during other kinetics measurements. Importantly, all feed lines were heat traced to 675 K, and the lines were flushed copiously with helium between experiments until no pyridine or DTBP was observed in the GC/FID chromatograms. The cleanliness of the reactor was validated by remeasuring the rate of acetaldehyde production (without pyridine or DTBP co-feed) following reactions performed using pyridine or DTBP. Pyridine and DTBP have both been observed to adsorb to acid sites at high reaction temperatures, although it is important to note that the experiment described above is merely an inhibition experiment, not a titration, and the results should be interpreted only in a qualitative sense.

2.3.3 Catalyst characterization

The surface area of the 0.08wt% MgO/SBA-15 and pure SBA-15 catalysts were determined from the Brunauer-Emmett-Teller (BET) equation using nitrogen physisorption at 77 K with a Micromeritics ASAP 2020 instrument. Following the method of Pollock et al. the samples were degassed under vacuum at 393 K for 8 h and the nitrogen adsorption isotherms were
measured at 77 K. Typically, 0.1-0.12 g of sample was used for the measurement. Pore diameters and pore volumes were obtained using the Barrett-Joyner-Halenda (BJH) equation$^{235}$ corrected as described by Kruk, Jaroniec, and Sayari (KJS)$^{236}$ using the adsorption branch of the N$_2$ isotherm. While the desorption branch is generally assumed to be in equilibrium and would thus be appropriate for use in estimating pore diameters and volumes,$^{235}$ we have applied the BJH/KJS approach using the adsorption branch of the isotherm as it has been shown to accurately describe the pore structure of large-pore MCM-41 materials$^{236}$ and SBA-15 materials$^{234}$ where the pore sizes are independently measured by small-angle X-ray scattering and small-angle neutron scattering.

DRIFT spectra were recorded on a Nicolet 6700 FTIR spectrometer (Thermo Fisher Scientific) equipped with a Praying Mantis™ accessory for DRIFT applications and a high-temperature reaction chamber (Harrick Scientific Production, IBC), in the range of 4000-500 cm$^{-1}$ (8 cm$^{-1}$ resolution, 1024 scans/spectrum). CO$_2$ adsorption on the catalyst was accomplished by heating the catalyst under Ar flow at 723 K for 20 minutes, followed by exposure to 1% CO$_2$ flow (balance He) until saturation coverages were reached at 303 K. Each spectrum was recorded _in situ_ as a difference spectrum referenced to the catalyst prior to exposure to CO$_2$, under Ar flow at 303 K, and after sequential desorption at 303 K, 373 K, 473 K, 573 K, and 673 K.

The effect of MgO deposition on the distribution of hydroxyl groups on the catalyst surface was studied using DRIFT measurements under dry conditions at elevated temperatures. About 30 mg of sample were loaded over calcined KBr powder, used as reference material, and a spectrum was obtained at 303 K. To achieve dry conditions, the gases introduced to the environmental chamber were passed through a U-shaped trap filled with 5Å molecular sieves cooled to 195 K in a dry ice- acetone bath. Prior to the analysis, the catalyst was activated for one hour at 773 K (8 K
min$^{-1}$ ramp rate) in 100 sccm of dry O$_2$. Then the catalyst was cooled in flowing dry Ar to 373 K in four 100 K steps and held for 3 hours at each step until the absorbances in the phonon region of the spectrum (2100 – 1400 cm$^{-1}$) stabilized. Several spectra were collected at each step during the cooling process (8 cm$^{-1}$ resolution, 512 scans/spectrum).

2.4 Results

2.4.1 Catalyst selectivity and stability

To validate that the MgO/SBA-15 catalyst used here is a suitable model for bulk MgO-SiO$_2$ catalysts, we evaluated ethanol conversion at low space velocity (0.017 hr$^{-1}$) and 698 K. We observed low yields of BD. The catalyst was observed to deactivate over the course of 8 hours of time-on-stream (see Figure 2-10 in Supporting Information section), with an initial yield of 1,3-butadiene approximately 7%, which is consistent with the reports of Weckhuysen,$^{204}$ Sels,$^{200}$ and Baltrusaitis.$^{205}$ Additionally, we observed acetaldehyde, ethylene, butene, acetone, diethyl ether, butanal, and crotyl alcohol, again consistent with the literature for undoped MgO-SiO$_2$ catalysts. Therefore, we suggest that MgO supported on SBA-15 is a suitable, well-defined model for the bulk MgO-SiO$_2$ catalysts generally discussed in the literature.

The selectivities to acetaldehyde and ethylene at high space velocities (3.7-21 hr$^{-1}$) and 723 K are shown in Figure 2-1. The selectivity to acetaldehyde was greater than that to ethylene. Due to the higher space velocities, only small traces of BD were observed during the first 8 hours of the reaction. Additionally, trace amounts of butene were observed for the first 20 hours of reaction, likely due to ethylene oligomerization. As shown in Figure 2-2, the selectivity was independent of space velocity over the range studied here. That the selectivities are non-zero when extrapolated
to infinite space velocity (*i.e.*, that these curves intercept the y-axis at non-zero values) indicates that ethylene and acetaldehyde are primary products from ethanol.

Upon increasing the WHSV sufficiently to drop the conversion into the differential range, rapid deactivation was observed during the first 8 hours of time-on-stream, after which the deactivation slows (see Figures 2-11 and 2-12 in section 2.7). Thus, for each of the reaction

**Figure 2-1.** Selectivity to acetaldehyde (▲) and ethylene (●) with respect to time-on-stream. Reaction conditions: 0.02 g of catalyst, 723 K, WHSV = 0.062–0.35 min⁻¹, ethanol partial pressure 3.39–8.71 kPa, and total pressure 101 kPa.

**Figure 2-2.** Site time yield of acetaldehyde (▲) and ethylene (●) with respect to inverse weight hourly space velocity. Reaction Conditions: 0.02 g of catalyst, 723 K, WHSV= 0.062–0.35 min⁻¹, ethanol partial pressure 3.39-8.71 kPa, and total pressure 101 kPa.
kinetics experiments reported here, the catalyst was aged in flowing ethanol (3.92 kPa) for 8 hours, and the residual deactivation was fit to two parallel first-order processes (see Figure 2-13 in section 2.), similar to what has been observed previously for phenol HDO on Pt/BEA zeolite. Thus, all rates reported here correspond to the state of the catalyst following 8 hours of exposure to ethanol.

2.4.2 Reaction kinetics measurements

The rates of acetaldehyde and ethylene formation were measured while varying the partial pressure of ethanol from 0.42 kPa to 2.57 kPa at temperatures ranging from 648 K to 723 K, as shown in Figure 2-3. Each data point shown is an average of several consecutive GC injections collected at steady state, and some data points were also averaged across 2-3 duplicate runs. Typical uncertainties were on the order of ±5%. The data were normalized to the acetaldehyde rate measured at 3.8 kPa. Both the dehydrogenation and dehydration rates are fractional-order with respect to the partial pressure of ethanol over the range measured, which indicates that the active sites on the MgO-SiO$_2$ catalyst are inhibited by strongly bound surface intermediates. Unsurprisingly, as the temperature is decreased from 723 K to 648 K, both reactions approach zero-order with respect to ethanol pressure. Apparent rate constants were obtained from the data shown in Figure 2-3 and used to calculate apparent activation energies for dehydrogenation and dehydration. The activation barrier measured for acetaldehyde formation (19±8 kJ mol$^{-1}$) is much lower than would be expected for a reaction that occurs at 500 - 600 K. Such low barriers can be an indication that the rate could be limited by internal mass transfer. Accordingly, we calculated the Weisz-Prater number for acetaldehyde formation. At the worst-case conditions (i.e., 723 K and 2.57 kPa ethanol pressure, and assuming Knudsen diffusion in the micropores of SBA-15, reported to have a diameter of ~0.55 nm$^{234}$), the Weisz-Prater number is 4.8×10$^{-5}$, which indicates
that these data were collected in the absence of internal mass transfer limitations. Instead, we postulate (*vide infra*) that the apparent barrier for acetaldehyde formation is lowered by the presence of a strongly-bound abundant surface intermediate, which is also consistent with the reaction occurring in a fractional-order regime. The dehydration reaction was observed to have a barrier of 67±8 kJ mol\(^{-1}\).

### 2.4.3 Hydrogen/deuterium isotope effect

![Graphs showing the influence of ethanol partial pressure on the normalized acetaldehyde (▲) and ethylene (●) formation rates. Rates were normalized to the acetaldehyde production rate at 3.8 kPa. Reaction conditions: (a) 723 K, (b) 698 K, (c) 673 K, (d) 648 K, 0.0067 g of catalyst, WHSV = 0.1-0.6 min\(^{-1}\), ethanol partial pressure 0.42-2.57 kPa, 648-723 K, and total pressure 101 kPa. No ethylene formation was observed at 648 K.](image-url)
The rates of acetaldehyde and ethylene production were both measured in the presence of ethanol-OD and ethanol-d₆. As shown in Table 2-1, a hydrogen/deuterium isotope effect was observed using perdeuterated ethanol for both acetaldehyde and ethylene formation, which we attribute to a primary kinetic isotope effect (KIE). Notably, there is also a small hydrogen/deuterium isotope effect when using ethanol-OD for acetaldehyde production, which could be an equilibrium isotope effect or, as discussed by Knözinger and Scheglila²²⁰ and Bauer,²³⁸ the value of this isotope effect represents the minimum KIE that would be expected in the limit of the high temperatures used in our reactions.

Table 2-1. Hydrogen/deuterium isotope effects for acetaldehyde and ethylene production.

<table>
<thead>
<tr>
<th>Products</th>
<th>Reactant</th>
<th>CH₃CH₂OD</th>
<th>CD₃CD₂OD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>(r_H/r_D)</td>
<td>1.58±0.03</td>
<td>2.10±0.04</td>
</tr>
<tr>
<td>Ethylene</td>
<td>(r_H/r_D)</td>
<td>1.31±0.02</td>
<td>1.81±0.02</td>
</tr>
</tbody>
</table>

a. Reaction conditions: 0.0067 g of catalyst, 698 K, 3.11 kPa of CH₃CH₂OH, CH₃CH₂OD, or CD₃CD₂OD, and total pressure 101 kPa.

2.4.4 Pyridine inhibition

The production rates of acetaldehyde and ethylene were inhibited by the presence of 0.48 kPa of pyridine at 698 K, as shown in Figure 2-4. Pyridine adsorbs indiscriminately to both Brønsted and Lewis acid sites. The observed inhibition by pyridine suggests that the dehydrogenation and dehydration mechanisms both require acid sites, which is consistent with other reports for similar catalysts that suggest the existence of acid sites on the surface of MgO-SiO₂ materials.²¹³

It has been reported that 2, 6-Di-tert-butylpyridine (DTBP) adsorbs only to Brønsted acid sites, due to steric hindrance at the heterocyclic N atom by the tert-butyl groups.²³⁹ To probe
whether these sites are Brønsted or Lewis acid sites, a similar inhibition experiment was performed using 0.18 kPa of DTBP, which did not lead to significant decreases in the ethylene or acetaldehyde rates, as shown in Figure 2-4. These results suggest that both the dehydrogenation and dehydration reactions require Lewis acid sites and that Brønsted acid sites do not participate in the formation of either acetaldehyde or ethylene.

Figure 2-4. Acetaldehyde (▲) and ethylene (●) formation rates measured in the presence of 0.48 kPa of pyridine (a) or 0.18 kPa of 2, 6-Di-tert-butylpyridine (b). Reaction conditions: 0.0067 g of catalyst, 698 K, 3.79 kPa ethanol partial pressure, and total pressure 101 kPa.

2.4.5 Catalyst characterization

Nitrogen physisorption measurements, shown in Table 2, indicate that the BET surface area increases from 596 m² g⁻¹ to 753 m² g⁻¹ following calcination at 773 K of the parent SBA-15 material, concomitant with an increase in the pore volume. Importantly the pore diameter calculated using the BJH/KJS method remains nearly constant. There is a small increase in pore volume and surface area following calcination, which suggests that some polymer was left in the micropores of the commercial SBA-15 material following synthesis and which was removed during calcination here. That the pore diameter remains nearly constant indicates there is minimal,
if any, reconstruction of the SBA-15 during this calcination. The pore size distributions are shown in Figure 2-14 in section 2-7.

Table 2-2. Nitrogen physisorption measurements.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET Surface Area (m² g⁻¹)</th>
<th>BJH/KJS Pore Volume (cm³ g⁻¹)ᵃ</th>
<th>BJH/KJS Pore Diameter (nm)ᵇ</th>
<th>Surface Mg Concentration (Mg nm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parent SBA-15ᶜ</td>
<td>600</td>
<td>0.87</td>
<td>1.00</td>
<td>N/A</td>
</tr>
<tr>
<td>Calcined SBA-15ᵈ</td>
<td>750</td>
<td>1.06</td>
<td>0.93</td>
<td>N/A</td>
</tr>
<tr>
<td>0.08 wt% MgO/SBA-15ᵈ</td>
<td>740</td>
<td>1.05</td>
<td>0.94</td>
<td>0.016</td>
</tr>
</tbody>
</table>

ᵃ. Calculated from the adsorption branch of the N₂ isotherm. ᵇ. Taken as the maximum in the primary mesopore peak of the pore size distribution. ᶜ. Used as received. ᵈ. Calcined at 773 K.

No substantial differences in surface area, pore volume, or pore diameter were measured for the sample containing MgO. Moreover, careful inspection of the pore volume distribution in the micropore region suggests that some of the micropores of SBA-15 may be occupied with MgO surface species. It is likely, based on the low surface concentration of Mg (0.016 Mg nm⁻², see Table 2-2) compared to the typical density of silanols in SBA-15 (5-6 OH nm⁻²)²⁴⁰ that the MgO is highly-dispersed on the pore walls. X-ray diffraction (XRD) of the MgO/SBA-15 catalyst supports this picture, as no MgO reflections were detected indicating that any MgO nanoparticles formed are less than ~3 nm (see supporting information-Figure 2-15).

CO₂ binds in three configurations to three unique types of basic sites on MgO surfaces: unidentate carbonate (strong O²⁻ anions), bidentate carbonate (medium-strength Mg²⁺-O²⁻ pairs) and unidentate bicarbonate (OH⁻ anions) which are classified as high-, medium-, and low-strength,
respectively.\textsuperscript{28} The presence of such basic sites was confirmed by FTIR spectroscopy of adsorbed CO\textsubscript{2}. Figure 2-5 shows DRIFT spectra obtained for the 0.08 wt\%MgO/SBA-15 sample following CO\textsubscript{2} adsorption at 303 K and desorption of bound CO\textsubscript{2} at 303 K, 373 K, 473 K, 573 K, and 673K. An absorbance band was observed between 1610 cm\textsuperscript{-1} and 1645 cm\textsuperscript{-1}, belonging to the asymmetric O-C-O stretch of bidentate carbonate, which suggests the presence of medium-strength basic sites that exist as Mg\textsuperscript{2+}-O\textsuperscript{2-} pairs. The corresponding asymmetric O-C-O stretch, which was expected in the region between 1320 cm\textsuperscript{-1} and 1340 cm\textsuperscript{-1} region, is masked by strong absorbance features due to the SiO\textsubscript{2} support. There may be a small number of low-strength basic sites based on a weak shoulder at 1650-1700 cm\textsuperscript{-1}, attributed to the asymmetric O-C-O stretch of unidentate bicarbonate, which is further confirmed by the absorbance around 1420 cm\textsuperscript{-1}. That both absorbances disappear at elevated temperature is consistent with these being low-strength basic sites that do not bind CO\textsubscript{2} strongly. The lack of absorbance features between 1510-1560 cm\textsuperscript{-1} suggests a lack of strong base sites.

Figure 2-6 shows clearly that the presence of MgO has a direct effect on the silanol groups present on the surface of SBA-15. For direct comparison of different samples, the SiO\textsubscript{2} phonon

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2-5.png}
\caption{DRIFT spectra of CO\textsubscript{2} adsorbed on 0.08 wt\% MgO/SBA-15 in the presence of gas-phase CO\textsubscript{2} (a) and collected during stepwise temperature-programmed desorption at 303 K (b), 373 K (c), 473 K (d), 573 K (e), and 673 K (f).}
\end{figure}
modes in both spectra were normalized following the procedure described by McCool et al.\textsuperscript{241} Comparing the normalized peak area of the silanol groups at 3744 cm\textsuperscript{-1} to the Si-O-Si bulk phonon modes in both the parent SBA-15 and the 0.08 wt\% MgO/SBA-15 catalyst suggests that loading of MgO resulted in a reduction in the number of silanols. The peak areas of the isolated silanol groups in the 3505-4000 cm\textsuperscript{-1} range were ratioed to the peak area under the SiO\textsubscript{2} phonon mode integrated between 1736-1955 cm\textsuperscript{-1}. The ratio of normalized peak areas decreased from 3.6 for SBA-15 to 3.1 for 0.08 wt\% MgO/SBA-15 respectively. According to the inset in Figure 2-6, the presence of MgO on the SBA-15 surface led to a decrease in the IR absorbance of a band centered near 3825 cm\textsuperscript{-1} and the broad absorbance between 3700 to 3500 cm\textsuperscript{-1}. These vibrational modes have previously been assigned to isolated silanol groups perturbed by steric hindrance as a result of interparticle contact, defect sites, or pore sites.\textsuperscript{241} This observation could suggest that the MgO has been preferentially absorbed into the micro-pores of SBA-15\textsuperscript{234} or in the interstices between

\textbf{Figure 2-6.} DRIFT spectra of SBA-15 (a) and 0.08 wt\% MgO/SBA-15 (b) collected under dry conditions at 373 K; spectra offset for clarity. Inset: silanol region after normalization of both spectra to the absorbances of the phonon modes.
grain boundary regions, and it further supports the observations from N₂ physisorption and XRD that the MgO is highly dispersed.

To distinguish adsorbed ethanol from adsorbed ethoxide species on the MgO/SBA-15 catalyst, we carried out DRIFT measurements during stepwise temperature-programmed desorption of ethanol. Prior to ethanol exposure, the catalyst was heated to 573 K under a rigorously dry Ar flow, following procedures we have described previously.²⁴² Silanol vibrational modes remain after thermal treatment, as illustrated in Figure 2-6, indicating that the majority of the SBA-15 surface contains silanol groups; however, no Mg–OH modes were detected in spectra (not shown) of the treated catalyst relative to KBr after cooling to room temperature. Rigorously dried absolute ethanol was then introduced to the environmental chamber at room temperature, which led to the observation of vibrational modes for ethanol but not water, confirming the dryness of the system. DRIFT spectra were recorded after heating to 373 K, as shown in Figure 2-7A, which reveal the characteristic ν(CH₃) and ν(CH₂) modes of ethanol interacting with the surface silanols. Strong bands were observed at 2983, 2940, and 2907 cm⁻¹, along with a shoulder at 2887 cm⁻¹, all of which have been assigned to undissociated, adsorbed ethanol.²⁰⁵,²⁴³ The weaker bands marked at 2956, 2921, and 2845 cm⁻¹ are consistent with the CH₃ and CH₂ stretching modes of adsorbed ethoxide species on MgO centers, as previously identified by Birky et al. using a similar stepwise temperature-programmed desorption experiment.²⁴³ The observed red shifts of these bands are in agreement with the predicted red shifts when ethanol adsorbs dissociatively on MgO.²⁴⁴ The intensities of the ethoxide modes are weak, consistent with the intentionally low loading of MgO on the SBA-15 support (vide supra), but importantly they persist as the temperature was raised to 523 K while the intensity decreased for vibrations associated with molecularly adsorbed ethanol. Further evidence for the dissociative adsorption can be gleaned
from careful examination of the OH stretching region shown in Figure 2-7B. At 373 K, the surface is covered with ethanol, but after heating to 523 K, there is a decrease in the amount of molecularly adsorbed ethanol, and a small absorbance feature at 3776 cm\(^{-1}\) appears, as shown in the inset, which aligns well with the Mg–OH mode reported at 3765 cm\(^{-1}\) by Taifan and Baltrusaitis.\(^\text{205}\) Unfortunately, strong absorption by SiO\(_2\) phonon modes below 1300 cm\(^{-1}\), coupled with the low loading of MgO, precluded detection of the characteristic C–C–O and C–C modes of ethanol and ethoxide, which have been widely used in the literature\(^\text{225, 227, 243}\) to demonstrate dissociative adsorption of ethanol on MgO. Further preliminary measurements using operando FTIR spectroscopy (see the section 2.7) corroborate the presence of ethanol covering the SBA-15 surface under ethanol flow conditions and production of acetaldehyde, presumably on MgO–SiO\(_2\) sites, consistent with the production of acetaldehyde in our flow reactor on the MgO/SBA-15 catalyst but not bare SBA-15.

### 2.4.6 Operando FTIR spectroscopy

To identify the surface species during ethanol conversion under reaction conditions, we performed the reaction at elevated temperatures by feeding Ar/ethanol to the Harrick Praying Mantis environmental chamber and collecting spectra referenced to the clean surface of MgO/SBA-15. Prior to the reaction, the catalyst surface was pretreated at 673 K, 623 K and 573 K under dry Ar flow for 2 hours at each temperature. Several single beam spectra were collected at each temperature. During the reaction 50 SCCM flow of Ar/ethanol stream was generated by pass Ar through a gas washing bottle filled with absolute ethanol at 296 K, and this stream was fed to the environmental chamber. The temperature was then heated stepwise to 573 K, 623 K and 673
K and held for several hours until a steady state condition was confirmed by comparison of two spectra recorded at least one hour apart.

Figure 2-8 shows a summary of the DRIFTS spectra collected at steady state during reaction of the MgO/SBA-15 with a continuous flow of Ar/ethanol at the indicated temperatures. The spectra, referenced to the clean surface at each temperature, show interaction of ethanol with the silanol groups of SBA-15, resulting in a strong negative-going band at 3745 cm\(^{-1}\). The (CH) bands of ethanol, which are stronger in the presence of gas phase ethanol than in the stepwise temperature programmed desorption spectra of Figure 2-7 (main text), make identification of ethoxide species more difficult, even at the highest reaction temperature of 673 K. However, the presence of a weak peak at 3680 cm\(^{-1}\), shown in the inset at the frequency observed by Taifan et al.,\(^{205}\) and assigned to the hydroxyl group on magnesium silicates, suggests that the model catalyst prepared here may have sites similar to those present on MgO-SiO\(_2\) catalysts synthesized by wet kneading. This peak is not present on pure MgO or bare SBA-15.

\[ \text{Figure 2-7. DRIFT spectra showing the stepwise temperature-programmed desorption of ethanol collected at (a) 373 K, (b) 523 K, and (c) 673 K in (A) the CH stretching region and (B) the expanded hydroxyl–CH stretching region. Vertical bars indicate the position of the ethoxide and ethanol } \nu(\text{CH}) \text{ modes, as reported by Birky et al.}\(^ {244}\) \text{ on a MgO catalyst.} \]
The spectra shown in Figure 2-8 B confirm the production of acetaldehyde which desorbs and is observed in the gas phase, with the P, Q, and R branches centered at 1775, 1750, and 1725 cm\(^{-1}\), whose relative intensities suggest that the molecules are rotationally hot. The bands between

![Graph](image)

**Figure 2-8.** operando DRIFT spectra during continuous feed of Ar/ethanol to the environmental chamber at a) 573 K, b) 623 K and c) 673 K, referenced to the clean MgO/SBA-15 surface at the same temperature. A) Hydroxyl and (CH) stretching regions showing the interaction of ethanol with silanol groups, and a weak positive-going peak at 3680 cm\(^{-1}\) (shown in the inset) that may correspond to formation of hydroxyls on magnesium-silicates under reaction conditions. B) Spectra in the 1350 – 1800 cm\(^{-1}\) range are dominated by gas phase acetaldehyde and molecularly adsorbed ethanol

1350 and 1500 cm\(^{-1}\) have contributions from both ethanol and acetaldehyde. The production of acetaldehyde indicates that the operando measurements reveal catalytic behavior consistent with that of the catalyst under our flow reactor conditions where detailed kinetic information has been obtained. Unfortunately, further experiments were not possible at this time due to closing of the laboratory during the COVID-19 pandemic.
2.5 Discussion

The measured acetaldehyde formation rates are fractional order with respect to ethanol at 723 K but do not reach saturation even at the highest pressures used here; the reaction order decreases with decreasing temperature to zero-order at 648 K. This behavior suggests that the surface is covered by either ethanol or ethoxide (vide supra). In contrast, the ethylene formation rates, while also fractional-order with respect to ethanol at 723 K, approach zero-order behavior at higher pressures; the reaction order also decreases to zero-order at low temperature. No ethylene production was observed at 643 K. This behavior suggests that, at the conditions employed here, the MgO-SiO₂ catalyst is highly covered by adsorbed species, the identity of which is not immediately clear, although they must be ethanol-related. That both the ethylene and acetaldehyde production rates behave similarly at 723 K is consistent with a single common species inhibiting both reactions. For alcohol dehydration over γ-Al₂O₃, Knözinger et al.²²⁰ used a combination of reaction kinetics measurements, estimation of alcohol surface concentrations, and transition state theory calculations to suggest that, in the zero-order regime, the catalyst surface is covered by adsorbed alcohol. This conclusion is in agreement with the kinetics data obtained by Chokkaram et al.,²⁴⁵ which also suggest that the surface of the same catalyst is saturated by alcohol. Moreover, Ivanova et al.²⁰⁶ have used transmission FTIR to observe that molecularly adsorbed ethanol is abundant on SiO₂ surfaces under similar reaction conditions. However, Hanspal et al.²²⁵ have used DRIFTS coupled with stepwise temperature-programmed desorption of adsorbed ethanol to identify ethoxide as the abundant species on MgO and Hydroxyapatite surfaces. This observation is consistent with the reaction kinetics measurements of Bhan and coworkers,²²²,²²⁵,²⁴⁶ which suggest that ethoxide species are abundant on γ-Al₂O₃ surfaces at reaction conditions. In all cases,
over the range of ethanol pressures we have studied, the literature concludes that abundant surface species on MgO-derived surfaces are monomeric ethanol or ethoxide species (as opposed to ethanol-ethanol dimers\textsuperscript{221,247} or ethanol-water dimers,\textsuperscript{222} as seen both on Al\textsubscript{2}O\textsubscript{3} and zeolites); this behavior is consistent with our measured ethanol reaction orders, which vary between 0 and 1.

In the case of the recent DFT calculations of Christiansen \textit{et al.},\textsuperscript{223} ethoxide adsorption on \(\gamma\)-Al\textsubscript{2}O\textsubscript{3} is energetically favorable, with a \(\Delta E\textsubscript{ads}\) of -92 kJ mol\(^{-1}\) when co-adsorbed with a proton, which suggests an ethoxide-covered surface. Interestingly, this value is comparable to the dissociative adsorption of ethanol to form ethoxide species on MgO calculated by Taifan \textit{et al.},\textsuperscript{227} who predict adsorption free energies of between -44 and -56 kJ mol\(^{-1}\), also suggesting an ethoxide-covered surface. It may be possible that on predominantly Lewis acidic surfaces, the surface is covered by molecularly-adsorbed ethanol, while ethoxide dominates basic surfaces. The intrinsic activation energy for dehydration of adsorbed ethanol was calculated by Christiansen \textit{et al.}\textsuperscript{223} to be 155 kJ mol\(^{-1}\), where the initial state was molecularly adsorbed ethanol. This barrier, coupled with the likelihood that the surface is covered by ethoxide (which would have to convert back to ethanol prior to dehydrating), leads to an apparent barrier of 63 kJ mol\(^{-1}\), which is in remarkable agreement with our measured barrier of 67±8 kJ mol\(^{-1}\). On this basis, it is reasonable to conclude that dehydration over MgO-SiO\textsubscript{2} proceeds according to the same mechanism that occurs over \(\gamma\)-Al\textsubscript{2}O\textsubscript{3}, with the surface covered by adsorbed ethoxide but with adsorbed ethanol as the initial state for the rate-controlling elimination.

Notably, Christiansen \textit{et al.}\textsuperscript{223} suggest that ethoxide co-adsorbed with a proton binds more strongly to \(\gamma\)-Al\textsubscript{2}O\textsubscript{3} surfaces than molecularly adsorbed ethanol (by about 13 kJ mol\(^{-1}\)), which is consistent with the calculations of Taifan \textit{et al.}\textsuperscript{227} and the FTIR spectroscopy of Hanspal \textit{et al.}\textsuperscript{225} Given that both reactions occur on the same surface, it is likely there is a shared intermediate
species bound to the surface that we suggest is ethoxide, although rigorously speaking ethoxide is a spectator species in the dehydration mechanism. DeWilde et al.\textsuperscript{222} observed that $\gamma$-Al$_2$O$_3$ was inhibited to the same extent by pyridine for acetaldehyde and ethylene production, leading to the conclusion that the reaction occurs at the same acidic surface site. Our kinetics and pyridine inhibition measurements over MgO-SiO$_2$ are also consistent with this observation (see Figure 2-4).

The rate of ethylene formation exhibits a primary KIE for cleavage of the C-H bond but not for cleavage of the O-H bond, which indicates that the rate-controlling step in this mechanism should be C-H bond scission. This observation would be consistent with the E$_2$ mechanism that predominates over Lewis acidic catalysts (e.g., $\gamma$-Al$_2$O$_3$, whereby the C-H and C-O bonds are cleaved simultaneously in a concerted transition state).\textsuperscript{220} However, dehydration over pure MgO is reported to follow a stepwise E$_{1cb}$ mechanism,\textsuperscript{248} the first step in which is abstraction of a proton from the $\beta$-C.\textsuperscript{249} For an E$_{1cb}$ dehydration mechanism to be consistent with our KIE measurements, heterolytic $\beta$-C-H cleavage must be rate-controlling followed by rapid loss of the hydroxyl leading to ethylene formation (whereas dehydrogenation should occur if the O-H bond is cleaved first).\textsuperscript{248} The presence of Lewis acidity likely moves the reaction along the spectrum of elimination mechanisms from an E$_{1cb}$ mechanism to something closer to an E$_2$ mechanism, similar to the continuum suggested by Bordwell,\textsuperscript{250} and our pyridine/DTBP inhibition experiments confirm the participation of Lewis acid sites in the dehydration. Indirect evidence for an E$_2$-type mechanism is provided by the remarkably good agreement between our apparent activation barrier and the DFT predictions of both Christiansen et al.\textsuperscript{223} and Taifan et al.\textsuperscript{227} While Taifan et al. did not consider an E$_{1cb}$ mechanism, the E$_{1cb}$ barrier predicted by Christiansen would be substantially higher than what was observed here.
For acetaldehyde formation, a small isotope effect was observed for O-H bond scission, while a primary KIE was observed for C-H bond scission. Both De Wilde et al.\textsuperscript{222} and Knözinger et al.\textsuperscript{220} propose that the dehydrogenation and dehydration reactions share a common intermediate that is bound to a Lewis acid site which is inhibited by pyridine adsorption. That the acid sites present on our catalyst are inhibited by pyridine but not 2,6-di-tert-butylpyridine (see Figure 4) indicates that only Lewis acid sites are present on the MgO-SiO\textsubscript{2} surface and not Brønsted sites, and that both reactions are inhibited to the same degree indicates that the same Lewis acid sites are involved in both pathways.\textsuperscript{214} Because of the similarity between our observations and those reported in the literature for Lewis-acid-catalyzed dehydrogenation, we propose that quasi-equilibrated heterolytic O-H bond scission establishes ethoxide species on the surface, which subsequently undergo rate-controlling C-H bond scission leading to acetaldehyde. However, the mechanism must differ from that which occurs over γ-Al\textsubscript{2}O\textsubscript{3} because no ethane is observed in the outlet of our reactor, implying that surface H species cannot be removed from the oxide surface via indirect transfer to ethylene.\textsuperscript{222} A contrasting mechanism was recently invoked by Moteki and Flaherty\textsuperscript{226} whereby H species on the surfaces of Ca- and Sr-hydroxyapatites recombine to desorb as molecular H\textsubscript{2} in a kinetically-insignificant step, which would be consistent with our isotope effect observations. Similarly, Di Cosimo \textit{et al.}\textsuperscript{214} evaluated ethanol dehydrogenation over MgO and MgO-Al\textsubscript{2}O\textsubscript{3} hydroxyapatites, and they suggest the direct formation of H\textsubscript{2} from surface H species. Diez \textit{et al.}\textsuperscript{215} propose the same mechanism for dehydrogenation of \textit{i}-propanol. Another possibility is the mechanism proposed by both Taifan \textit{et al.}\textsuperscript{227} and Chieregato \textit{et al.},\textsuperscript{207} wherein a proton (from O-H bond cleavage) assists in breaking the C-H bond. This transition state can be considered to be a Lewis acid-base interaction between the electron-poor surface proton generated during ethanol dissociation and the electron-rich hydride bound to the α-carbon of the surface.
ethoxide. If the principle vibration of the activated complex as it crosses the activation barrier is that of C-H bond cleavage, then a primary kinetic isotope should be observed for ethanol-d_6 but not for ethanol-OD. However, if the principle vibration of the activated complex is H-H bond formation, then a KIE should be observed for both ethanol-OD and ethanol-d_6; our measurements lie somewhere between these two extremes. Chieregato et al.\textsuperscript{207} show a transition state that involves both C-H bond scission and H-H bond formation, but it is not clear which of these events dominates. Taifan et al.\textsuperscript{227} show a similar transition state, but they also specify that the proton has moved away from the surface and that the ethoxide more closely resembles acetaldehyde, all of which suggests that this transition state is dominated by H-H bond formation. The observation of a modest isotope effect ($r_{\text{H}}/r_{\text{D}} = 1.58$) would be consistent with some participation in the transition state of the surface proton generated during ethanol dissociation, though whether the rate-controlling event is $\alpha$-C-H bond cleavage or H-H bond formation is hard to determine definitively from these measurements.

Scheme 2-3 shows the acetaldehyde ($k_3$) and ethylene ($k_5$) production pathways that are consistent with the above discussion. Notably, both pathways require an acid-base site pair, wherein the ethanol molecule dissociates to form an ethoxide bound to the Lewis acidic Mg$^{2+}$ center and a proton bound to a basic O$^2-$ center. The FTIR spectra for CO$_2$ adsorption in Figure 2-5 show that Mg$^{2+}$-O$^{2-}$ site pairs predominate on the MgO-SiO$_2$, which are those proposed as necessary for dehydrogenation by Di Cosimo et al.\textsuperscript{214} and Diez et al.\textsuperscript{215} That both mechanisms require Lewis acid sites is demonstrated by the in situ 2,4-DTBP inhibition experiment shown in Figure 2-4. Kozlowski and Davis\textsuperscript{224} have suggested that MgO surfaces are covered with ethanol and ethoxide under the conditions required for Guerbet coupling, consistent with our observation that an ethanol-related species inhibits the reaction at high ethanol pressures. In the case of Mg-
Al hydrotalcites,

increasing the amount of Al₂O₃ leads to an increase in the amount of acid-base site pairs, which in turn increases the selectivity for dehydrogenation. However, these materials can also possess substantial amounts of isolated Al³⁺ sites that catalyze bimolecular ethanol dehydration to yield diethyl ether, which we do not observe over MgO-SiO₂. TPD studies by Di Cosimo et al. show the relationship between increasing the NH₃ uptake with rising Al content, confirming the presence of significant numbers of Lewis acid sites in the high-Al materials. It thus appears that for MgO-SiO₂ catalysts, SiO₂ plays a role similar to Al insofar as it increases the number of Mg²⁺-O²⁻ site pairs available for catalysis, but because SiO₂ is not a strong Lewis acid on its own, the catalyst is not active for bimolecular dehydration to form diethyl ether and only minimally active for E₂-dehydration to form ethylene.

![Scheme 2-3](image)

**Scheme 2-3.** Proposed mechanism for acetaldehyde and ethylene production from ethanol over MgO-SiO₂ catalysts. (a) Overall reaction scheme. (b) Transition state for step 3. (c) Transition state for Step 5.

From the mechanism shown in Scheme 2-3, we can derive rate expressions for the production of acetaldehyde and ethylene. For acetaldehyde production, we begin by postulating that the dissociative adsorption of ethanol (the combination of steps 1 and 2) and the desorption of acetaldehyde (step 4) are quasi-equilibrated, denoted by ovals in Scheme 3 according to Boudart notation.

We further postulate that C-H bond cleavage (step 3) is irreversible and rate-controlling, consistent with our KIE observations (*vide supra*), denoted by a carat. For ethylene
production, we postulate that simultaneous scission of the C-H and C-O bonds is irreversible and rate-controlling (step 5) while the associative desorption of OH and H fragments is quasi-equilibrated. Thus, for both reactions, the kinetic term of the rate expression is first-order with respect to ethanol. As discussed above, it is likely that the surface is covered by ethoxide species, which leads to the rate expressions shown in Equations 2 and 3 for acetaldehyde and ethylene production, respectively, that are consistent with our kinetics observations.

\[
\begin{align*}
    r_{CH CHO} &= \frac{k_3K_1K_2P_{CH CHO}}{1 + K_1K_2P_{CH CHO}} \\
    r_{C2H4} &= \frac{k_4K_1P_{CH CHO}}{1 + K_1K_2P_{CH CHO}}
\end{align*}
\]

To evaluate the above assumptions about the mechanisms of dehydrogenation and dehydration, we have fit our experimental data to a microkinetic model based on the DFT calculations of Taifan et al.\textsuperscript{227} for the conversion of ethanol over pure MgO. In our model, we have considered only the elementary steps that lead to ethanol dehydrogenation and dehydration, as shown in Scheme 2-3. The thermodynamic parameters for these steps were obtained using the Gibbs free energies reported by Taifan et al.\textsuperscript{227} coupled with entropy data from the NIST Chemistry WebBook.\textsuperscript{253} The reaction conditions were matched to our experimental conditions. Without any modification to the thermodynamic parameters, the model predicts an ethylene selectivity of 90% and an acetaldehyde selectivity of 10%. These results are reasonably consistent with results that we have obtained using a pure MgO catalyst (see Figure 2-9), when extrapolated to zero time-on-stream to account for deactivation due to carbon deposition.
That the model correctly predicts our observations for selectivity over pure MgO suggests that the thermodynamic and kinetic parameters can be adjusted to provide insight into the differences between pure MgO and MgO-SiO$_2$ mixed oxides. Using the \textit{nlinfit} function in MATLAB, four fitting parameters were employed to fit the model to the data: the enthalpies of adsorbed ethanol (increased by 23 kcal mol$^{-1}$), ethoxide (decreased by 3 kcal mol$^{-1}$), and hydrogen (increased by 12 kcal mol$^{-1}$), as well as to the enthalpy of activation for step 3 in Scheme 2-3 (decreased by 22 kcal mol$^{-1}$). All the thermodynamic parameters for the microkinetic model are listed in Table 3, including their values after fitting the above parameters. The result of the fit is shown in Figure 2-10. While some of these modifications are substantial, we justify such large deviations as being driven by electronic and geometric interactions of MgO with SiO$_2$ that are plainly needed to achieve enhanced selectivity not only for dehydrogenation but also for the entire network of reactions in the Lebedev process.$^{204}$

\textbf{Figure 2-9.} Acetaldehyde (▲) ethylene (●) selectivity obtained using an undoped MgO catalyst. Dashed lines are used to guide the eye and do not correspond to any fit to this data. Reaction conditions: catalyst weight 0.04g, WHSV 0.02 min$^{-1}$, reaction temperature 698 K, ethanol partial pressure 3.67 kPa, and total pressure 101 kPa.
Table 2-3. Thermodynamic and kinetic parameters used in the microkinetic model.

<table>
<thead>
<tr>
<th>Step</th>
<th>ΔH</th>
<th>ΔS</th>
<th>ΔG</th>
<th>ΔG</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(kcal mol⁻¹)ᵃ</td>
<td>(cal mol⁻¹ K⁻¹)ᵃ</td>
<td>(kcal mol⁻¹)ᵇ</td>
<td>(kcal mol⁻¹)ᵇ after fitting</td>
</tr>
<tr>
<td>1</td>
<td>-29.9</td>
<td>-26.8</td>
<td>-10.5</td>
<td>10.6</td>
</tr>
<tr>
<td>2</td>
<td>5.1</td>
<td>9.9</td>
<td>-3.0</td>
<td>-15.9</td>
</tr>
<tr>
<td>3 (TS)</td>
<td>30.8 (51.4)</td>
<td>15.9 (15.9)</td>
<td>19.1 (39.7)</td>
<td>11.2 (27.7)</td>
</tr>
<tr>
<td>4</td>
<td>9.3</td>
<td>24.5</td>
<td>-8.3</td>
<td>-6.5</td>
</tr>
<tr>
<td>5 (TS)</td>
<td>34.8 (70.1)</td>
<td>48.5 (48.5)</td>
<td>-1.8 (33.5)</td>
<td>-8.7 (14.4)</td>
</tr>
<tr>
<td>6</td>
<td>9</td>
<td>8.3</td>
<td>1.7</td>
<td>-9.5</td>
</tr>
</tbody>
</table>

a.) Enthalpies and entropies reported at 298 K and 1 bar.  b.) Gibbs free energies reported at 723 K and 1 bar.

The large magnitude of the adjustments to adsorbed ethanol, hydrogen, and the transition state for step 3 can be justified based on the Lewis acid-base interactions that occur on this surface, as described recently by Metiu et al.²⁵⁴ The MgO-SiO₂ surface consists initially of Lewis acid-base site pairs that are modified by the dissociative adsorption of ethanol. Under reaction

Figure 2-10. Parity plots showing the agreement of the experimental and predicted rates for (a) acetaldehyde and (b) ethylene formation.
conditions, the microkinetic model reveals that the \( \text{Mg}^{2+}-\text{O}^{2-} \) site pairs are covered by ethoxide and protons \((\theta=0.05-0.49)\). In contrast, these site pairs on the MgO surface are covered not only by ethoxide/protons \((\theta=0.73)\) but also by molecularly adsorbed ethanol \((\theta=0.25)\). Notably, the proton that is cleaved during ethanol dissociation should act as a Lewis acid, bound to the Lewis basic \( \text{O}^{2-} \) site; correspondingly, ethoxide acts as a Lewis base, bound to the Lewis acidic \( \text{Mg}^{2+} \) site. Importantly, Metiu et al.\(^{254}\) suggest that Lewis acid-base interactions can occur through oxide surfaces, leading to effects in binding strength on the order of 23 kcal mol\(^{-1}\), in remarkable agreement with the empirical fitting performed here. On this basis, we suggest that the presence of the \( \text{SiO}_2 \) has the effect of eliminating the strong basic sites described by Di Cosimo et al.\(^{214}\) while increasing the number of acid-base site pairs, which in turn decreases the surface coverage by ethoxide and hydrogen. This change in surface coverage by Lewis acid-base pairs leads to a decrease in the barrier for dehydrogenation of nearly 23 kcal mol\(^{-1}\) in accordance with the description of Metiu et al.\(^{254}\)

### 2.6 Conclusions

We have proposed a mechanism for the catalytic transformation of ethanol into acetaldehyde and ethylene over mixed MgO-SiO\(_2\) catalysts based on the reaction kinetics measured over a model catalyst. Steady state measurements of ethanol conversion at several temperatures reveal that the formation rates of acetaldehyde and ethylene depend only weakly on the partial pressure of ethanol. Primary kinetic isotope effects were observed for ethylene formation when \( \text{C}_2\text{D}_5\text{OD} \) was employed but not for \( \text{C}_2\text{H}_5\text{OD} \), indicating that the cleavage of C-H bond is the rate limiting step for ethylene synthesis. A small primary kinetic isotope effect was observed for acetaldehyde formation only for \( \text{C}_2\text{D}_5\text{OD} \), indicating that the rate controlling step involves C-H cleavage. Both
the acetaldehyde and ethylene formation rates were inhibited by the presence of pyridine but not 2,6-diterbutylpyridine, demonstrating that Lewis acid sites are required for these reactions, in addition to basic sites. FTIR spectroscopy of adsorbed CO$_2$ reveals that the MgO-SiO$_2$ catalyst contains only Lewis acid-base site pairs consisting of Mg$^{2+}$-O$^2-$ sites. These observations were coupled with a microkinetic model based on the DFT literature for ethanol conversion over MgO. Based on our model, we conclude that the sites on the MgO-SiO$_2$ catalyst are less covered by ethoxide and hydrogen than the MgO catalyst, and that the transition state for dehydrogenation on the MgO-SiO$_2$ surface is stabilized by $\sim$23 kcal mol$^{-1}$ relative to that on the MgO surface, thereby explaining the improvement in selectivity observed generally for MgO-SiO$_2$ catalysts.

2.7 Supporting Information

2.7.1 Butadiene Production

![Graphs showing butadiene production over 0.08% MgO/SBA-15.](a) Linearized data used to obtain initial selectivity. (b) Selectivity to butadiene at 100% ethanol conversion, showing extrapolation to zero-time. Reaction conditions: 0.5g of catalyst, 698 K, WHSV = 0.017 hr$^{-1}$, ethanol partial pressure 2.27 kPa, and total pressure 101 kPa.

Figure 2-11. Butadiene production over 0.08% MgO/SBA-15. (a) Linearized data used to obtain the initial selectivity, (b) Selectivity to butadiene at 100% ethanol conversion, showing extrapolation to zero-time. Reaction conditions: 0.5g of catalyst, 698 K, WHSV = 0.017 hr$^{-1}$, ethanol partial pressure 2.27 kPa, and total pressure 101 kPa.
2.7.2 Catalyst Deactivation

The production rates of ethylene and acetaldehyde exhibited continuous deactivation with respect to the time on stream as shown in Figures 2-12 and 2-13. Time zero in Figure 2-12 corresponds to the completion of the 8 hours aging process described in the main text. We hypothesize that this deactivation is due to blocking of the active sites on the surface of catalyst coupled with eventual blocking of the catalyst pores.

![Figure 2-12](image1.png)

**Figure 2-12.** Catalyst deactivation during acetaldehyde (▲) and ethylene (●) production. Reaction conditions: 0.0067g catalyst, WHSV 0.16-0.55 min⁻¹, ethanol partial pressure 3.92-5.25 kPa, 723 K, total pressure 101 kPa.

![Figure 2-13](image2.png)

**Figure 2-13.** Catalyst deactivation during acetaldehyde (▲) and ethylene (●) production. Reaction conditions: 0.0067g catalyst, WHSV 0.41-0.55 min⁻¹, ethanol partial pressure 3.93-5.25 kPa, 723 K, total pressure 101 kPa.
2.7.3 Deactivation Correction

The observed ethylene and acetaldehyde production rates were corrected for deactivation. The data shown in Figure 2-14 were fit by assuming two parallel first-order deactivation processes. We hypothesize that these correspond to deposition of carbon on the catalyst surface and eventual blocking of the catalyst pores. Attempts to fit the data to either a single first-order or second-order deactivation process were unsuccessful.

Figure 2-14. Correction of the deactivation for acetaldehyde (a) and ethylene (b) production rates (red ▲ is the observed rate, blue line is the predicted rate, and black ▲ is the corrected rate) Reaction conditions: 0.0067g catalyst, WHSV 0.41-0.55 min⁻¹, ethanol partial pressure 3.93 kPa, 723 K, total pressure 101 kPa.
2.7.4 Catalyst Characterization Data

Figure 2-15. Pore size distributions for 0.08 wt% MgO/SBA-15 (●), calcined SBA-15 (▲), and non-calcined SBA-15 (■) catalysts based on the adsorption branch of N2 adsorption isotherms collected at 77 K (see Section 2.2.3 in the main text).

Figure 2-16. X-ray diffractogram for 0.08% MgO/SBA-15. No reflections corresponding to MgO were observed.
3.1 Introduction

The increasing concern about climate change tied to global energy consumption and CO₂ production has put attention on the thermal conversion of lignocellulosic biomass to bio-oil. The abundance of lignocellulosic biomass and compatibility of its refining, distribution, and consumption with the current technology and infrastructures developed based on crude oil consumption makes this approach a rational choice and realistic strategy to phase out the dependence on crude oil and fossil fuel sources. Thermal conversion of lignocellulosic biomass through fast pyrolysis involves the degradation of biomass with rapid heating of the organic materials in an oxygen-free process. This is followed by subsequent condensation of transformed organic compounds to produce bio-oil. Further, this product can be refined and upgraded through various methods to produce liquid fuels similar in characteristics to diesel or gasoline. Bio-oils produced by fast pyrolysis are composed of a complicated mixture of oxygenated compounds including carboxylic acids, aldehydes, ketones, alcohols, and phenols. The high presence of oxygen-containing compounds in bio-oil indicates low thermal and storage stability, high corrosive power, and low calorific value. In addition, other properties differentiate it from petroleum-based fuels and hinder its co-feeding ability in conventional refineries: higher viscosity and density, the difficulty of distillation at atmospheric pressure, and the presence of polar compounds and water, the latter usually representing between 25 and 30 wt %. Furthermore, bio-oil composition, rich in polar compounds, causes low miscibility compared with petroleum-based transportation fuels.
The catalytic oxygen removal from bio-oil products through hydrodeoxygentation (HDO) processes have been studied to increase the energy density and the stability and improve the overall quality of this product to create a liquid hydrocarbon blend similar to the current transportation fossil fuel blends. Bio-oil HDO is a process carried out at elevated pressure (15–352 bar) and moderate temperature (80–500 °C) using H₂ gas or hydrogen-donor compounds in the presence of a catalyst. In this process oxygen content is removed from the organic compounds of bio-oil in the form of H₂O, CO₂, and CO. However, the efficient and selective cleavage of C-O bonds in bio-oil compounds is difficult. Usually, an effective catalyst requires providing a combination of metal sites and acidic supports. The most frequently studied catalysts are those based on supported noble metals such as Ru/γ-Al₂O₃, Ru/TiO₂, Pt/C, and Pd/C.

Newman et al. showed that Ru/TiO₂ (P25) shows excellent selectivity and activity for DDO of phenol to benzene. However, the excellent selectivity and activity of the catalyst depends on the treatment procedure performed following Ru deposition. When Ru/TiO₂ catalysts were calcined after Ru deposition, catalysts were more selective toward hydrogenation products. When catalysts were reduced after Ru deposition, they were more selective toward the DDO reaction. Reductive treatment of the catalyst makes small Ru particles while oxidative treatment of the catalyst makes large Ru particles. As a result, hydrogenation of the ring is the preferred pathway when Ru particles are large while DDO of phenol is the preferred pathway when Ru particles are small. Based their mechanistic study, the reducibility of the support does not play a role, since creation of oxygen vacancies is too costly and on the surface of this catalyst H₂ dissociates heterolytically between the metal nanoparticle and a surface hydroxyl. The titania surface hydroxyls at the metal particle interface were proposed to be amphoteric, accepting a proton during the heterolytic dissociation of hydrogen, and then acting as a Brønsted acid to polarize the C-O
bond of phenol which adsorbs at the Ru-support interface, leading to water and benzene. The activation energy is lower than for oxygen vacancy creation and water in the solvent was shown to play a catalytic role.

Phan et al. have investigated the effect of metal oxide supports on C-O bond cleavage and shown that C–O bond elongation of adsorbed phenol is associated positively with the increased oxyphilicity: Ni < Fe ≈ Co ≈ Mn < Re < Mo ≈ Cr < W ≈ V ≈ Sc < Ti, which further confirms the significance of oxyphilicity in the C–O cleavage. The deoxygenation rate may depend on the relative strength of the C-O bond compared to the metal oxygen bond.

To limit the use of precious metals and develop cost-effective processes, other approaches based on metal oxide catalysts have been studied. Inspired by the early works using hydrodesulfurization catalysts in petroleum refineries, such as Co–MoS₂/Al₂O₃ and Ni–MoS₂/Al₂O₃, oxyphilic metal oxides with strong Lewis acidity including Nb and Re oxides, MoO₃, TiO₂, WO₃, Ta₂O₅, and V₂O₅ have attracted intensive attention for HDO processes.

Metal oxides have been studied in depth as selective oxidation catalysts. In selective oxidation, a metal oxide catalyst abstracts hydrogen from the adsorbed organic adsorbate and donates oxygen from the catalyst surface. In general, these types of catalytic mechanisms upon which lattice oxygen (or Nitrides, Hydrides, sulfides, and halides) enter the products is known as the Mars-van Krevelen mechanism. The metal oxide catalytic activity is influenced most strongly by the strength of M-O bond. Doornkamp and Ponec have reviewed the evidence for a Mars-van Krevelen mechanism in the deoxygenation of organic compounds, including nitrobenzene to nitrosobenzene, and carboxylic acids to aldehydes on transition metal oxide surfaces. The relationships between deoxygenation rate and the metal oxygen bond strength have been discussed and the “volcano plot” behavior was demonstrated clearly for the hydrogenation (i.e.
hydrogenolysis) of acetic acid to acetaldehyde. Pestman, et al. found that iron oxide had the highest activity after pretreatment in hydrogen and gave further evidence for the role of lattice oxygen vacancies in the mechanism.

According to Hoang-Van and Zegaoui, MoO₃ and WO₃, as reducible metal oxide catalysts, facilitate hydrogenation of the carbonyl group of acrolein to allyl alcohol. Building on that work, Thibodeau et al. confirmed that WO₃ hydrogen bronze is an effective hydrogenation catalyst by reporting quantitative production of allyl alcohol by reducing the C=O bond to a C-O bond at 50 °C. They have demonstrated that at higher temperatures allyl alcohol can be deoxygenated to propene. They described a Mars–van Krevelen mechanism in which alcohol adsorbs on an oxygen vacancy, forming a tungsten–oxygen bond and breaking the carbon-oxygen bond. This catalytic mechanism (Figure 3-1) was developed based on three main observations; first, Thibodeau et al. found that the active catalyst is formed by heating WO₃ in H₂ for ten hours at 623 K producing a bronze: H₁.₂₉WO₂.₇₇. The second reaction step is reducing the C=O bond to a C-O bond. The catalyst was found to be selective to allyl alcohol formation (no reduction of the C=C bond). Finally, the hydrodeoxygenation of allyl alcohol was performed at higher temperatures (600 K) to show the conversion of allyl alcohol to propene as well as propanol and acrolein.

In parallel with experimental work on tungsten oxide, Moberg, Thibodeau et al. constructed a potential energy surface (PES) for the HDO of acrolein to propene, based on the Mo₃O₉ cluster model described in selective oxidation of propene by Goddard, extending it to include propanol. The barriers to oxygen vacancy creation and HDO were similar.
Prasomsri et al. demonstrated that several reducible metal oxides, including $\alpha$-MoO$_3$, are effective HDO catalysts capable of selectively cleaving C-O bonds in various bio-oil-derived oxygenates under mild reaction conditions and highlighting the role of oxygen vacancies in the deoxygenation process.\textsuperscript{291-292} Also, reports show cleavage of aliphatic and aromatic C-O bonds in carbohydrate/sugar-derived compounds, guaiacol, and syringol-type compounds using molybdenum oxide catalysts,\textsuperscript{293-294} as well as on Mo$_3$O$_9$ and W$_3$O$_9$ clusters.\textsuperscript{295-298} Also, theoretical studies support the deoxygenation of oxygen containing compounds to unsaturated products.\textsuperscript{295, 297, 299}

Following the experimental work demonstrating HDO of allyl alcohol on the hydrogen WO$_3$ bronze, the surface mechanisms for the hydrogenation and hydrodeoxygentation steps on a model W$_3$O$_9$ cluster were investigated to determine whether the rate controlling step is oxygen
vacancy formation or breaking of the C-O bond and the factors controlling the selectivity between propene (HDO) and propanol (hydrogenation). However, the limitation of the W$_3$O$_9$ cluster model precluded theoretical treatment of the bulk bronze formation.

According to Thibodeau, WO$_3$ HDO catalysts have two types of acid sites of mechanistic importance. Oxygen vacancy sites are Lewis acids, which are sites for selective adsorption of carbonyl and alcohol moieties. The Brønsted acidity of the catalyst determines proton transfer from surface hydroxyls to the surface intermediate. Thus, adsorption and desorption energies are controlled by the Lewis acidity of oxygen vacancy sites, while the ease of proton donation is dependent on the Brønsted acidity. Comparison of previous calculations for W$_3$O$_9$ with Mo$_3$O$_9$ suggests that the metal-oxygen bond strength and Brønsted acidity are larger for WO$_3$, while the Lewis acidity is significantly less. Each of these factors plays a significant role in the greater ability of WO$_3$ to achieve substantial hydrodeoxygenation yields. For the hydrogenation of acrolein to allyl alcohol at 50°C, dissociation of hydrogen was sufficiently facile that complete conversion was observed under the conditions of 2.0 – 2.4 (g acrolein)/(h g WO$_3$) weight hourly space velocity. In the experimental investigation by Thibodeau et al., the composition of the reduced WO$_3$ bronze was determined as a function of hydrogen pretreatment temperature, as shown in Table 3-1. The oxygen substoichiometry and hydrogen content at the highest hydrogenation rate was H$_{1.29}$WO$_{2.77}$ after a pretreatment temperature of 350 °C. Noting that negligible loss of mass was observed below 200 °C in TGA experiments, we expect that under hydrogenation conditions at 50 °C, the oxygen substoichiometry should not change, but the reservoir of bulk hydrogen may depend on the rates of hydrogen dissociation at the surface and diffusion between the surface and bulk. Previous experimental work has not determined the surface composition of the bronze after pretreatment, under reaction conditions where hydrogenation is efficient (50 °C), or at higher
temperatures (150 – 350 °C) where hydrodeoxygenation is observed. Because hydrodeoxygenation accumulates oxygen during C-O bond scission and eliminates surface oxygen vacancies, hydrogen in the feed must continuously reduce the surface as well as provide surface hydroxyls that act as Brønsted acids. Therefore, the hydrogen bronze composition, both at the surface and in the bulk, can be expected to change under reaction conditions until steady state is achieved. In fact, Martinez-Ruiz \(^{301-302}\) observed that under liquid phase conditions feeding hydrogen and guiacol into a packed bed reactor of stoichiometric WO\(_3\), reduction occurred during the initial start-up transient and hydrodeoxygenation occurred at a rate similar to that observed after pretreatment. The microkinetic model developed by Thibodeau\(^{180}\) pointed to the importance of the barriers to formation of bridging and terminal hydroxyls in controlling the selectivity between propene and propanol, but could not assess whether the rate of deoxygenation or vacancy creation ultimately controls the overall reactivity of the catalyst.

In this Chapter, we focus on the development of a microkinetic model to describe the bronze formation mechanism with the goal of exploring and understanding the factors that control the behavior of the mass loss as a function of time at different temperatures in pure hydrogen. A representative set of TGA experiments, as reported by Thibodeau, et al.,\(^{181}\) are reproduced in Figure 3-2. Qualitatively, when WO\(_3\) is heated in hydrogen during bronze formation, there is an induction period, after reaching the treatment temperature, before mass loss becomes measurable. Thibodeau et al.\(^{181}\) used mass spectrometry to confirm that the mass loss was associated with dehydroxylation and water production. With increasing pretreatment temperature, the induction period became longer at first, but then decreased again at higher temperatures. The mass loss over a 10 h period approached a limit that increased with temperature, until at 475 °C the material was reduced essentially to pure metal, corresponding to a mass remaining of 79%. The amount of
hydrogen that was absorbed into the bronze was determined by heating to 1000 °C under inert conditions during which water was evolved, further decreasing the mass. The mass loss in this step allowed the quantitation of the hydrogen in the bronze, \( H_xWO_{3-z} \), assuming all hydrogen desorbed as \( H_2O \). To confirm the total amount of oxygen removed, the samples were heated again in oxygen and the mass gain returned to 100 %, within an experimental uncertainty of <1%. As the UM WO\(_3\) material was active both for hydrogenation and hydrodeoxygenation, we have focused the development of microkinetic models for both hydrogenation of acrolein and hydrodeoxygenation of allyl alcohol on that material, which was synthesized by Lu, Kanan, and

![Illustration of the TGA and MS data during bronze formation, and a two-step method to determine composition. A) Percent weight change on a ceramic pan loaded with the nano-WO\(_3\) (9 m\(^2\)/g) at a) 300, b) 350, c) 400, and d) 475 °C bronze formation temperatures. Illustration of B) temperature profile and C) mass spectral intensities for a) hydrogen (2 amu), b) water (18 amu), and c) oxygen (32 amu) vs. time for 350 °C bronze formation temperature. Reproduced from Thibodeau, et al. (Reprinted with permission by Elsevier.)](image-url)
Tripp\textsuperscript{303} by emulsion polymerization. The calculated composition from the analysis of TGA experiments similar to those shown in Figure 3.2 are provided in Table 3.1 for convenience. In summary, the goal is to describe the physical and chemical kinetic processes that lead to the induction period and the reasons that the rate of mass loss approaches zero despite being at an elevated temperature in pure H\textsubscript{2}, with a final oxygen substoichiometry that increases with pretreatment temperature.

**Table 3-1.** Calculated composition of tungsten oxide bronzes by TGA. Composition of tungsten oxide bronzes, H\textsubscript{y}WO\textsubscript{3-z}, after hydrogen treatment as a function of temperature and further reduced WO\textsubscript{3-x} after hydrogen removal as water. Reproduced from Thibodeau, et al. (Reprinted with permission by Elsevier.)

<table>
<thead>
<tr>
<th>Catalyst (Surface Area)</th>
<th>Pan Material</th>
<th>Pretreatment Temperature / °C</th>
<th>y</th>
<th>z</th>
<th>Bronze</th>
<th>Reduced</th>
</tr>
</thead>
<tbody>
<tr>
<td>UM-WO\textsubscript{3} (3.0 m\textsuperscript{2}/g)</td>
<td>Ceramic 200</td>
<td>0.93</td>
<td>0.06</td>
<td>H\textsubscript{0.90}WO\textsubscript{2.94}</td>
<td>0.52</td>
<td>WO\textsubscript{2.48}</td>
</tr>
<tr>
<td>UM-WO\textsubscript{3} (3.0 m\textsuperscript{2}/g)</td>
<td>Ceramic 300</td>
<td>1.11</td>
<td>0.08</td>
<td>H\textsubscript{1.11}WO\textsubscript{2.92}</td>
<td>0.63</td>
<td>WO\textsubscript{2.37}</td>
</tr>
<tr>
<td>UM-WO\textsubscript{3} (3.0 m\textsuperscript{2}/g)</td>
<td>Ceramic 350</td>
<td>1.29</td>
<td>0.23</td>
<td>H\textsubscript{1.20}WO\textsubscript{2.77}</td>
<td>0.88</td>
<td>WO\textsubscript{2.12}</td>
</tr>
<tr>
<td>UM-WO\textsubscript{3} (3.0 m\textsuperscript{2}/g)</td>
<td>Ceramic 400</td>
<td>0.77</td>
<td>1.13</td>
<td>H\textsubscript{0.77}WO\textsubscript{1.87}</td>
<td>1.51</td>
<td>WO\textsubscript{1.49}</td>
</tr>
<tr>
<td>UM-WO\textsubscript{3} (3.0 m\textsuperscript{2}/g)</td>
<td>Ceramic 450</td>
<td>0.21</td>
<td>2.84</td>
<td>H\textsubscript{0.21}WO\textsubscript{0.16}</td>
<td>2.95</td>
<td>WO\textsubscript{0.05}</td>
</tr>
<tr>
<td>UM-WO\textsubscript{3} (3.0 m\textsuperscript{2}/g)</td>
<td>Ceramic 475</td>
<td>0.29</td>
<td>2.80</td>
<td>H\textsubscript{0.29}WO\textsubscript{0.20}</td>
<td>2.95</td>
<td>WO\textsubscript{0.05}</td>
</tr>
</tbody>
</table>

\textsuperscript{a}At lower temperatures, the uncertainties are y(±0.05), z(±0.01), x(±0.02); at higher temperatures they are y(±0.3), z(±0.1), x(±0.05.)

3.2 **Formulation of a microkinetic model to describe bronze formation**

The term microkinetics was defined to denote reaction kinetics analyses that attempt to incorporate into the kinetic model the basic surface chemistry involved in the catalytic reaction. Therefore, the kinetic model is established on a description of the catalytic process in terms of
information and/or assumptions about the active sites and the nature of the elementary steps that comprise the reaction scheme.\textsuperscript{304} The first step in developing a microkinetic model is to write down a possible reaction network that contains all elementary surface transformations that can happen during the catalytic conversion of reactants to products. In the case of bronze formation, these include the dissociation of H\textsubscript{2} on the WO\textsubscript{3} surface, diffusion of protons on the surface or to the bulk, and dehydroxylation of the surface to form water and oxygen vacancies, which can diffuse between the surface and the bulk. The second step is to evaluate the thermodynamic characteristics of all involved species and calculate or estimate the kinetic parameters for all elementary surface reactions. Ultimately, the model is specified by a set of differential rate equations which are constrained by the material balance. This set of material balance equations are solved to determine the extent of reaction over a period of time and calculate the surface coverage of all species present. Analysis of the forward and reverse rates of all elementary steps for a range of reaction conditions can be carried out to determine which steps control the rate of the reaction.\textsuperscript{305-306}

We developed our kinetic model for WO\textsubscript{3} bronze formation within the mean-field approximation. In mean-field microkinetic modeling, all the surface species and active sites are assumed to be uniformly distributed at the nanometer scale, and rate constants depend on the “mean,” i.e., the average coverage, rather than accounting for the microscopic distribution of adsorbates and catalyst sites. However, this does not preclude the ability to define different catalyst sites or transfer of intermediates from one site to another; rather, this is done based on the average density of each site type.\textsuperscript{307}

To properly treat the non-spatially uniform system requires solving both diffusion and chemical kinetic equations simultaneously, which is intractable for this system’s complexity. The early work on WO\textsubscript{3} established that oxygen vacancy diffusion is rapid compared to the rate of
LeGore et al. estimated an oxygen vacancy diffusion constant at 300 °C between $2 \times 10^{-12}$ and $2 \times 10^{-13}$ cm$^2$/s from a vacuum reduction experiment on WO$_3$ epitaxially grown films and experiments involving reactions with H$_2$S.$^{309-310}$ In metal oxide sensors, the changes in the bulk conductivity, which is generating the signal, is due to competition between surface reactions that create or annihilate oxygen vacancies. The vacancies diffuse into the bulk and increase the electron concentration in the n-type semiconductor. Reghu et al. showed that in the limit that diffusion is fast compared to the surface reactions, solving the differential equation for the spatial distribution of vacancies (i.e. Fick’s 1st law) was not necessary.$^{310}$ Vacancies generated at the surface by oxidation and reduction reactions were coupled to the bulk in terms of a flux that increases the bulk vacancy concentration, assuming that the vacancies are instantaneously dispersed throughout the bulk. Only the surface to volume ratio is required. The agreement between theory and experiment that was attained by the model within the reaction limited case (i.e rapid diffusion) justifies using a mean-field method to describe bronze formation where the oxygen vacancies are homogeneously distributed in bulk.

Based on extensive literature, as well as the TGA and mass spectrometry results reported by Thibodeau et al. on hydrogen WO$_3$ bronze formation, the mass loss is due to the desorption of H$_2$O.$^{140}$ Therefore, the dehydroxylation reaction (to produce H$_2$O and vacancies) requires a second order elementary reaction step between hydroxyls, which could be bridging, terminal, or a combination of a bridging and terminal hydroxyl. According to the theoretical work by Rellañ-Piñeiro and López on MoO$_3$, the formation of water molecules is possible by recombining two neighboring hydroxyl groups on a terminal and bridging site during proton transfer on lattice oxygen.$^{311}$ Alternatively, Pacchioni et al. concluded from a thermodynamic point of view that H$_2$O desorption from a terminal site is favorable when two protons are on the same terminal oxygen.$^{312}$
Thus, there is no clear agreement regarding which hydroxyls are involved in the dehydroxylation process on WO₃.

Clearly surface diffusion of protons is necessary, and implementing a mean field model implies that diffusion is fast compared to the rate controlling dehydroxylation step. Ma et al. implemented kinetic Monte Carlo (kMC) models to analyze the interaction of ethanol and 2-propanol with oxidized and reduced WO₃(001) thin-film surfaces under UHV conditions. The alcohols adsorbed dissociatively on the reduced surface and coupling the hydroxyls to desorb as water requires the diffusion of surface hydrogens (i.e., hydroxyls). The kMC models compared the effects of surface diffusion and heterogeneity of adsorbate-adsorbate interactions on the coverage-dependent shape of thermal desorption spectra. Heterogeneity appeared to be more important than diffusion limitations in describing the TPD spectra. On the basis of the previous work of Ma et al., we suggest that a mean-field approximation is justified for proton diffusion in this situation, and if not, it is a practical limiting case.

3.2.1 Elementary reaction network and associated rate equations

Our approach to developing a network of elementary steps is to divide the possible interactions into five major categories. 1) H₂ dissociation on an oxygen vacancy site and formation of hydroxyls, 2) diffusion of protons between oxygens on the surface, 3) dehydroxylation of the surface and creation of oxygen vacancies by desorption of water, 4) diffusion of oxygen vacancies between terminal and bridging sites in the surface layer, and 5) diffusion of protons and oxygen vacancies between the surface and the bulk.

We have explored several possible scenarios, which differ both in the potential energy surface and in the rate laws for the elementary reaction step. For hydrogen dissociation, we
considered oxygen vacancies to be the active sites, based on previous work by Moberg et al., and the formation of either two bridging hydroxyls or two terminal hydroxyls. The potential energy surfaces differ but the rate law, which depends on the probability of having two unoccupied sites for hydroxyl formation, leads to different rate equations and results in quite different behavior. Therefore, we present results for the dissociative adsorption of hydrogen to form bridging hydroxyls and show that, within a 2-D model that includes only the surface layer, this scenario is able to predict behavior qualitatively similar to the experimental TGA data. Extending the model to a 3-D model, including diffusion of hydrogen and vacancies into the bulk, introduces additional complexity in the enthalpic and entropic terms, which will require further research. These models can form the basis for treating oxygen vacancy formation under reaction conditions in a more explicit way in the future.

We assume the WO₃ bronze formation reaction mechanism could be modeled by defining two gas-phase chemical species (H₂ and H₂O) and six surface moieties. As shown in Figure 3-3, depending on the position, terminal, or bridging, we can imagine six different surface moieties, three on terminal positions and three on bridging positions. The labels WOT, WOTH, and W denote a terminal oxygen, a terminal hydroxyl, and an oxygen vacancy on a terminal position, respectively. Similarly, OB, OBH, and OVB denote a bridging oxygen, a bridging hydroxyl, and an oxygen vacancy on the bridging position, respectively.

Figure 3-3. Surface moieties defined for developing a 2-D WO₃ bronze formation kinetic model.
The bronze formation mechanism for the 2-D model included these eight species in four elementary steps as shown in Table 3-2. Step 1 describes the dissociation of H₂ on a terminal oxygen vacancy and the formation of two hydroxyls on bridging positions. Step 2 describes the proton transfer from bridging sites to terminal sites and the reverse reaction. In steps 3, an oxygen vacancy is formed on a terminal or bridging position by formation of a H₂O molecule, respectively. Finally, in step 4, the oxygen vacancy transfer from the bridging position to the terminal (and reverse reaction) is illustrated.

**Table 3-2.** Sequence of reactions describing WO₃ bronze formation and rate equations.

<table>
<thead>
<tr>
<th>Steps</th>
<th>Reaction</th>
<th>Rate equations (mole m⁻² s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step 1: Hydrogen dissociation</td>
<td>H₂ + W + 2OB → 2OBH + W</td>
<td>( Rate_i = k_{f_i} \theta_W \phi_O )</td>
</tr>
<tr>
<td>Step 2: Proton migration</td>
<td>OBH + WOT ↔ OB + WOTH</td>
<td>( Rate_2 = k_{f_2} \theta_{WOT} \phi_{OB} - k_{r_2} \phi_{WOTH} \phi_{OB} )</td>
</tr>
<tr>
<td>Step 3: Oxygen vacancy formation (Terminal)</td>
<td>WOTH + OBH ↔ W + OB + H₂O</td>
<td>( Rate_3 = k_{f_3} \theta_{WOT} \phi_{OBH} - k_{r_3} \phi_{W} \phi_{OB} \phi_{H₂O} )</td>
</tr>
<tr>
<td>Step 4: Oxygen vacancy migration</td>
<td>WOT + OVB ↔ OB + W + OB</td>
<td>( Rate_4 = k_{f_4} \theta_{WOT} \phi_{OVB} - k_{r_4} \phi_{W} \phi_{OB} )</td>
</tr>
</tbody>
</table>

\( k_{fi} \): rate constant of forward reaction in step i  
\( k_{ri} \): rate constant of reverse reaction in step i  
\( \theta_i \), refers to surface concentration at terminal sites of moiety i (mole/m²)  
\( \phi_i \), refers to surface concentration at bridging sites of moiety i (mole/m²)

**3.2.1.1 Step 1, H₂ Dissociation**

The slow induction period before mass loss begins suggests that dissociative adsorption of hydrogen occurs at under coordinated tungsten sites, which we refer to as surface oxygen vacancies. These sites are thought to be the active site for hydrodeoxygenation, as surface oxygen vacancy sites should selectively adsorb alcohols. Based on experimental catalytic experiments,¹⁴⁰ we expect surface vacancies to be created during heating under a hydrogen environment at 625 K. According to previous work,¹³⁹ we anticipate formation of vacancies to occur in two steps. First, the dissociative gas phase adsorption of hydrogen forms surface hydroxyls. Then, dehydroxylation leads to formation of surface oxygen vacancies and desorption of water. Kim and Regalbuto described a similar mechanism for studying the effect of calcination of Pt/MoO₃ on H₂ spillover reaction.³¹⁵ Moberg et al.³¹⁶ described the process of H-atom production on the Mo₃O₈ cluster at a
coordinatively unsaturated site. They calculated the energy change for molecular adsorption of a 
H₂ molecule on the undercoordinated Mo site as -51.3 kJ/mol, with no barrier, leading to an 
elongated H-H bond. Similarly, Song et al. have shown that the addition of a H₂ molecule to 
exposed W atoms in substoichiometric WO₃ results in elongation of the H-H bond and dissociation 
to form surface hydroxyls.³¹⁷

Here we describe the dissociative adsorption of H₂ on a combination of a terminal oxygen 
vacancy and two bridging oxygens as the first step in our model. The dissociation of H₂ over 
oxygen vacancy is barrierless (H₂ + W + 2OB → 2OBH + W), so we assumed that the activation 
energy for this step is zero. Therefore, the forward rate equation for this step is proportional to the 
surface coverage of bridging oxygens squared (φₒ₂) and terminal oxygen vacancies (θₒ). The 
dependence on the H₂ pressure is implemented in the rate constant, which according to collision 
theory, is the flux of H₂ colliding with the surface per unit area per second and is calculated based 
on the impingement rate equation,

\[ k_f = \frac{p_{H₂}}{\sqrt{2\pi m k T}} \]

where \( k_f \) is the rate constant for the forward reaction of H₂ dissociation (m²s⁻¹), \( P_{H₂} \) is the 
H₂ pressure, \( m \) is the H₂ molecular weight, \( k \) is the Boltzmann constant, and \( T \) is temperature.

### 3.2.1.2 Step 2, H surface diffusion

The hydrogen diffusion on the tungsten oxide surface and bulk has been extensively 
studied.³¹⁸⁻³²⁴ Xi et al.³²⁴ have conducted a comprehensive theoretical mechanistic study of 
hydrogen spillover on WO₃ (001) and the formation of hydrogen bronze. They have addressed the 
mechanisms of hydrogen spillover from a Pt catalyst to a WO₃ surface and diffusion into the bulk 
by performing DFT calculations and mapping out the energy profiles of several prescribed
hydrogen spillover pathways. In the case of the proton's surface diffusion, there are three plausible H migration routes, terminal–terminal (WOTH⇄WOT), bridging–bridging (OBH⇄OB), and terminal–bridging (WOTH⇄OB). Among these diffusion pathways, the latter one, terminal–bridging, plays a critical step in our model, since as described in the first step, the product of H₂ dissociation is two bridging hydroxyls, and according to the third step, two neighboring hydroxyl groups at a bridging and terminal position is necessary for oxygen vacancy creation via desorption of water. This pathway is necessary to simulate the propagation of protons over surface oxygen sites. According to the calculated thermodynamic and activation energies by Xi et al. 324, this step has a relatively high energy barrier of 0.99 eV. Interestingly the presence of water on the surface catalyzes the diffusion process and reduces the energy barrier to 0.51 eV. In other computational studies, similar energy barriers between 0.3-0.7 eV were calculated for proton diffusion in surface and bulk WO₃. 322 Here we will adopted a 0.99 eV energy barrier for step 2, since at elevated temperature (>300 °C) the surface is more likely dehydrated. Assuming this step is a second-order reaction (OBH + WOT ⇄ OB + WOTH), a pre-exponential coefficient of 1x10¹³ s⁻¹ was used. 304

3.2.1.3 Step 3, Dehydroxylation and H₂O desorption

Previously Thibodeau et al. have shown that water is produced during oxygen vacancy creation. 140 Therefore, we have imagined that the oxygen vacancy formation could be done through two different elementary steps, resulting in the creation of vacancies in bridging or terminal positions. This step require the proximity of two hydroxyls on a bridging and a terminal site (OBH and WOTH, respectively), which are provided through the diffusion mechanism of protons between the lattice oxygens upon forming hydroxyl groups in step one. According to the theoretical work by Rellań-Piñeiro and López on MoO₃, the formation of water molecules by
recombining two neighboring hydroxyl groups on a terminal and bridging site during proton transfer on lattice oxygen has a low energy barrier of 0.20 eV, which results in the production of coordinated water binding to the Mo site. The energy required for water molecules to desorb is 1.22 eV with a reverse adsorption energy barrier of zero eV. \(^{311}\) Kim et al. described a mechanism for 2-Propanol dehydration reaction on (WO\(_3\))\(_3\) clusters on TiO\(_2\)(110). \(^{296}\) In their kinetic model, the last step of the dehydration involves the creation of a hydroxylated cluster with adjacent hydroxyls on bridging and terminal sites, resulting in a coordinated water molecule. A relatively low energy barrier of 0.6 eV for water desorption from these structures was reported. \(^{296}\) For the forward reaction in step 3, the energy for dehydroxylation was 103 kJ/mol, including zero point corrections. We set the reverse adsorption activation energy as an adjustable parameter and assuming the reactions are second order, a pre-exponential factor of 1\times10^{13} \text{s}^{-1} was used. \(^{304}\)

### 3.2.1.4 Step 4, oxygen vacancy diffusion on surface

Diffusion of oxygen vacancies on the surface and bulk WO\(_3\) has been studied experimentally and theoretically. \(^{325-326}\) Hung et al. \(^{326}\) have employed DFT calculations to examine the migration mechanism of a mono-oxygen vacancy within the WO\(_3\) monoclinic structure. They have investigated the energy barrier of directional V\(_O\) migration in-plane and out of the plane at different oxygen vacancy concentrations. According to their analysis, at WO\(_{2.875}\), the migration of an oxygen vacancy from a position analogous to a terminal position in our model to bridging sites in the x and y direction (W⇄OB) gives two different energy barriers of 0.37 eV and 0.44 eV. We note that because of the nonlinearity of the -O-W-O- chains, the a and b lattice vectors are not equivalent. The tilting of the octahedral structural units in the WO\(_3\) structure leads to a distorted monoclinic unit cell. This difference between the barrier energy for x- and y-directions arises from
the anisotropy in the W-O-W bonding. These energy barriers for more oxidized structures (WO$_{2.984}$) are slightly different, 0.23 eV and 0.51 eV for the terminal to bridging sites and 0.68 for bridging to bridging migration.

In our microkinetic model, the transfer of an oxygen vacancy between the terminal and bridging position is important since, in step 3 oxygen vacancies are generated at the terminal sites. For extension of the 2-D to the 3-D model (not included in this chapter), the elementary step describing oxygen vacancy diffusion to the bulk requires oxygen vacancies in the bridging position. This step is also important because H$_2$ dissociation is assumed to happen on terminal oxygen vacancies and the equilibrium between them will affect the terminal surface hydroxyl and terminal oxygen vacancy coverage. In addition, this step provides the mechanism for extending the vacancy creation to the bridging oxygen content on the monolayer. For simplicity we did not try to distinguish between vacancies in the x and y directions, given the mean-field approach for modeling this reaction. Therefore, we used the lowest energy barrier for oxygen vacancy diffusion. The barrier energies for the WO$_{2.984}$ condition, 0.23 eV, which is closer to the initial state of the oxidized surface in our TGA experiments was adopted in our model. Assuming these steps are second-order reactions, a pre-exponential coefficient of $1 \times 10^{13}$ s$^{-1}$ was used.\textsuperscript{304}

### 3.2.2 Thermodynamic evaluation of the reaction network

For the calculation of enthalpies and entropies of the proposed reaction network at elevated temperatures, we have adopted the DFT calculation results of W$_3$O$_9$ cluster system that has been reported by Thibodeau et al.\textsuperscript{180} We made zero point energy (ZPE) corrections to the electronic minimum energies to establish the potential energy surface at zero Kelvin. To calculate the thermodynamic parameters for each step, we used translational, rotational, vibrational and
electronic partition functions. The partition functions were calculated using vibrational frequencies and rotational temperatures extracted from DFT calculation results of geometry optimized structures of the clusters. For the single point minimum electronic energy, a higher level of theory was used as described in Thibodeau’s PhD thesis.\textsuperscript{327}

The thermodynamic enthalpy and entropy of step 1 were determined from the DFT derived energies, vibrational frequencies, and rotational constants of the \( \text{W}_3\text{O}_9 \) cluster plus gas phase hydrogen converting to the \( \text{W}_3\text{O}_9 \) cluster with two hydroxyl groups on bridging positions, according to the reaction,

\[
\text{H}_2 + \text{W}_3\text{O}_9 \rightarrow \text{W}_3\text{O}_9\text{H}_2(bb). \tag{2}\]

The calculated \( \Delta H \) of this reaction at 0 K was 118 kJ/mol.

For step two, to illustrate the migration of a hydrogen at a bridging site to a terminal site we used \( \text{W}_3\text{O}_9\text{H}_2(bb) \) cluster as the reactant and calculated the energy changes for conversion of this cluster to \( \text{W}_3\text{O}_9\text{H}_2(bt) \) as,

\[
\text{W}_3\text{O}_9\text{H}(b) \rightarrow \text{W}_3\text{O}_9\text{H}(t). \tag{3}\]

The calculated \( \Delta H \) of this reaction at 0 K was -73 kJ/mol.

Similarly, we used the \( \text{W}_3\text{O}_9 \) cluster to evaluate step 3. As described earlier, the dehydroxylation steps include depend on the presence of bridging and terminal hydroxyls which results in \( \text{H}_2\text{O} \) formation/desorption, creating an oxygen vacancy at a terminal site. The associated reaction describing this step based on \( \text{W}_3\text{O}_9 \) clusters is

\[
\text{W}_3\text{O}_9\text{H}_2(bt) \rightarrow \text{W}_3\text{O}_9(T) + \text{H}_2\text{O}(g). \tag{4}\]

The calculated \( \Delta H \) of this reaction at 0 K was 146 kJ/mol.
To estimate the oxygen vacancy transfer in step 4, we calculated the energy changes during transferring a terminal oxygen to a vacancy at a bridging site \((W_3O_8(B))\), which results in creation of a terminal oxygen vacancy \((W_3O_8(T))\) as,

\[
W_3O_8(b) \rightarrow W_3O_8(t).
\] (5)

The calculated \(\Delta H\) of this reaction at 0 K was -45 kJ/mol.

In Figure 3-4, the enthalpy changes at 0K are reported as a potential energy surface (PES). To evaluate the thermodynamic consistency of described reaction sequence, we coupled the sum of the enthalpies of each steps with the calculated enthalpy of adding \(\frac{1}{2} O_{2(g)}\) to a \(W_3O_8(B)\) cluster (equation 6). The sum of these reaction enthalpies should be equal to the enthalpy of formation of \(H_2O\), which also was calculated using DFT results at the same level of theory.

\[
\begin{align*}
H_{2(g)} + W_3O_8 & \rightarrow W_3O_8(B) + H_2O_{(g)} \\
W_3O_8(B) + 0.5 O_{2(g)} & \rightarrow W_3O_9 \\
H_{2(g)} + 0.5 O_{2(g)} & \rightarrow H_2O_{(g)}
\end{align*}
\] (6)

The net value for addition of the sum of the enthalpies and vacancy filling reaction was -270 kJ/mol, which can be compared to the calculated \(\Delta H_f\) (\(H_2O\)) (-245 kJ/mol), indicating that the thermodynamic consistency of the cluster model is typical for DFT calculations at this level of theory.\(^{328}\)

**Figure 3-4.** PES of the proposed reaction network for 2D model.
3.2.3 Material balance equations and MATLAB code

The rate equation of each step is shown in Table 3-2. The surface concentration of each surface moiety is defined as the number of moles of the specific moiety per unit of area. The total number of terminal sites (WOT+WOTH+W) is equivalent to the total number of W atoms on the surface, which depends on the mass of catalyst and specific surface area. Based on the m-WO$_3$ (100) surface orientation, and a bulk density of 7.16 g/ml, the idealized cubic WO$_3$ lattice parameter was 3.77 Å and the tungsten site density was set to 7.018x10$^{18}$ W atoms/m$^2$. The total number of the bridging sites (OB+OBH+OVB) was taken to be twice the total number of terminal sites. As shown in Table 3-3, the differential equations of each surface moiety and gas-phase chemical species are constructed using the material balance and are written based on the rate equations of the five steps mentioned above (Table 3-2).

In our model we integrate the rate equations for a continuous flow stirred tank reactor (CSTR) model. The key assumption for the CSTR is that the reactor contents are well mixed and the concentration of any species in the reactor is uniformly distributed through the effluent stream. The governing equations for a CSTR are the material balances for reactants and products of the reaction. In general, one term in each material balance equation must be written for each independent reaction in which the species participates. A material balance written around species $i$ is given by:

$$\text{accumulation} = \text{input} - \text{output} + \text{generation} - \text{consumption} \quad (8)$$

In the case of gas-phase species the input and output molar flow rates are denoted as $F_i^\circ$ and $F_i$ describing the feed and exit molar flow rates in mol/s. The surface moieties only exist in the reactor, so the input and output terms are zero.
Table 3-3. Differential equation describing changes in concentration of surface moieties and gas phase species molar flow rate based on material balance relations.

\[
\frac{dF_{\text{H}_2}}{dt} = F'_{\text{H}_2} - F_{\text{H}_2} - \text{Rate}_4 \\
\frac{dF_{\text{H}_2O}}{dt} = F'_{\text{H}_2O} - F_{\text{H}_2O} + \text{Rate}_3 \\
\frac{d[\theta_W]}{dt} = \text{Rate}_3 + \text{Rate}_4 \\
\frac{d[\theta_{\text{WOTH}}]}{dt} = -\text{Rate}_2 - \text{Rate}_4 \\
\frac{d[\theta_{\text{WOTH}}]}{dt} = \text{Rate}_2 - \text{Rate}_3 \\
\frac{d[\phi_{\text{OBH}}]}{dt} = \text{Rate}_2 + \text{Rate}_3 + \text{Rate}_4 - 2\text{Rate}_1 \\
\frac{d[\phi_{\text{OH}}]}{dt} = 2\text{Rate}_1 - \text{Rate}_2 - \text{Rate}_3 \\
\frac{d[\phi_{\text{OVB}}]}{dt} = -\text{Rate}_4 \\
\frac{d[\phi_{\text{OH}}]}{dt} = \text{Rate}_2 + \text{Rate}_3 + \text{Rate}_4 - 2\text{Rate}_1 \\
\frac{d[\phi_{\text{OVB}}]}{dt} = 2\text{Rate}_1 - \text{Rate}_2 - \text{Rate}_3 \\
\frac{d[\phi_{\text{OBH}}]}{dt} = -\text{Rate}_4
\]

The steady-state operation of an ideal CSTR was combined with a series of forward and reverse rate equations driven by mass-action kinetics according to the proposed mechanism. These rate equations were set up in MATLAB as ordinary differential equations (ODE) and were solved using MATLAB’s ode23t ODE solver algorithm. In microkinetic modeling, the system of ODEs is usually stiff, and its solution requires an implicit numerical method.\textsuperscript{307}

Our MATLAB code consists of a 4-module structure that allows for simple troubleshooting. The first module of the MATLAB code in our calculation starts with a description of general reaction conditions and the definition of physical constants. This module sets the total pressure, the total gas phase flow rate, the partial pressure of gas-phase species (H\textsubscript{2}, H\textsubscript{2}O, and inert gas), catalyst mass, and specific surface area. The second module provides necessary input to the ODE solver, defining the surface concentration of defects and the surface hydroxyls (W, OVB, WOTH, and OBH\textsubscript{n}) along with terminal and bridging oxygen concentrations on surface and in bulk (WOT, and OB) as the initial conditions for the ODE solver. The third module performs calculations of
the thermodynamic and kinetic parameters based on the cluster calculations and periodic boundary condition values published in the literature, as described in the previous section. The final module contains the ODE solver and differential rate equations written for each gas-phase species and the surface moieties.

From the solution of the MKM, the concentration of gaseous species, coverages of surface species, reaction rates, conversion, and selectivity were calculated. In addition, analysis of the MKM results provided significant insights into the mechanism. The following is a qualitative analysis of the solution of the 2-D model for WO$_3$ bronze formation at different temperatures and starting configurations of the surface.

### 3.3 Results and discussion

As shown in Figure 3-5, we have investigated the influence of the temperature on the extent of WO$_3$ bronze formation reaction according to our 2D model. In this simulation, we set the initial mass of the catalyst at 30 mg, with 3 m$^2$/g specific surface area. The gas flow was set at 100 standard cm$^3$/min (sccm) of pure H$_2$ with 1 bar pressure. The terminal oxygen vacancy defect (W) concentration was set to 1x10$^{-3}$ of the total number of surface tungsten atoms.

![Figure 3-5](image.png)

Figure 3-5. Influence of the temperature on the simulated TGA experiment.
The model simulates the extent of mass loss as a function of temperature from the mass of oxygen removed from bridging and terminal sites relative to the total oxygen and tungsten mass. This 2D model qualitatively predict the dependence of the mass loss on temperature, showing an initial induction period which grows autocatalytically, but then limits to a slow rate of mass loss at longer times. The model shows that the relative mass remaining in the final time region decreases with increasing temperature. Although the behavior is qualitatively similar to the experimental data, this 2D model neglects diffusion of hydrogen and oxygen vacancies between the surface and the bulk which can be expected to affect both the timescale and temperature regime significantly.

According to the TGA results reported by Thibodeau et al.\textsuperscript{140} (Figure 3-2), bulk WO\textsubscript{3} powder material does not reduce significantly below 200 °C and fully reduces to W metal at temperatures >400 °C. In the 2-D model with the chosen parameters, the extent of the mass loss for 120 °C and 140 °C limits at a relative mass of 0.92-0.93. The removal of all oxygen from our 2D model corresponds to a relative mass remaining of 0.29, which happens at a much lower temperature, 240 °C. Because mass loss occurs through dehydroxylation, diffusion of hydrogen from the surface to the bulk should decrease the coverage of surface hydroxyl groups and reduce the desorption rate. However, the timescale to reach the point where mass loss has limited is of order 100 times longer than in experiment. Increasing pre-exponential factors from $10^{13}$ s\(^{-1}\) to $10^{15}$ s\(^{-1}\) could bring the model into better agreement; however, without a fundamental basis for choosing them and strictly 2-D experimental data to compare to, we have not explored varying those parameters. There could be errors both in the thermodynamic and kinetic parameters that lead to a scaling issue in our model, caused by calculating them from W\(_3\)O\(_9\) cluster models for each step. However, the potential energy surface for the elementary steps included in the model, and particularly the activation...
energy for dehydroxylation, appear reasonable based on experimental data. Several other mechanisms were not able to describe the limiting mass loss behavior, and were therefore inconsistent with experiment. Therefore, we analyze the kinetic processes that account for the changes in surface concentrations and qualitatively evaluate this set of elementary steps as a possible hydrogen bronze formation mechanism.

The sigmoidal shape of the relative mass loss in Figure 3-5 is typical for autocatalytic reactions. These chemical reactions proceed slowly at the start (the induction period) because there is little catalyst present; the terminal oxygen vacancy sites (W) can be created by dehydroxylation if the initial state of the surface is hydroxylated but otherwise there must be an initial finite coverage of surface vacancies. In the autocatalytic phase, the reaction rate increases exponentially as the reaction proceeds, because each water molecule desorbed (step3) creates an additional site for H$_2$ dissociation (step 1) which can then populate the reactants, terminal and bridging hydroxyls, needed for further dehydroxylation in step 3. The number of terminal oxygen vacancies, which are proposed to be the catalytic sites for H$_2$ dissociation increases exponentially in time until one or both reactants (terminal and bridging hydroxyls) limits the rate of dehydroxylation. Here we study the changes in the concentration of surface moieties in these three phases and study the effect of stability of hydroxyls and oxygen vacancies at the terminal and bridging positions on this mechanism. We found that for initial conditions that include terminal or bridging hydroxyls, dehydroxylation occurred rapidly and resulted in an equivalent coverage of terminal oxygen vacancies (W). Therefore, the kinetics of the autocatalytic phase was studied directly by varying the initial W site coverage.

The length of the autocatalytic period is directly related to the concentration of W moieties, which are assumed as the active site for H$_2$ dissociation. As shown in Figure 3-6, at constant
temperature, by increasing the number of terminal oxygen vacancies on the surface, the length of the autocatalytic period decreases, as expected.

The end of the autocatalytic period is coincidental with a decrease in terminal oxygens (WOT, open circles) and an increase in terminal oxygen vacancies (W, *), as shown in Figure 3-7. Relative concentrations are defined as the concentration (moles/m²) relative to the concentration of initial tungstens. Although the concentration of W does not reach 1 (removal of all the WOT moieties), a small but finite terminal oxygen concentration ($10^{-4} - 10^{-7}$) is maintained by the reverse of equilibrium $K_4$, which limits the terminal hydroxyls needed for dehydroxylation.

![Figure 3-6](image)

**Figure 3-6.** The effect of concentration of terminal oxygen vacancies (W moieties) as the active site for H₂ dissociation at 210 °C on the length of the induction period.
Notice that the bridging hydroxyl concentration (OBH, diamonds) is large compared to

Figure 3-8. Changes in the Partial Pressure of water as the result of dehydroxylation of the surface.

Notice that the bridging hydroxyl concentration (OBH, diamonds) is large compared to
terminal hydroxyls (WOTH, triangles) at low temperature, but the ratio inverts at the highest temperature. The fast reduction in mass while the reaction accelerates exponentially results in an increase in the water pressure as shown in Figure 3-8. The desorption of water peaks right at the end of the exponential phase.

In the autocatalytic stage, the mass-loss rate for all temperatures appears to be limited by the \( \text{H}_2 \) dissociation on the limited number of W sites. However, desorption can only occur in Step 3 from coupling of a bridging and terminal hydroxyl. Dissociation of hydrogen, within this mechanism, only populates bridging hydroxyls and the reversible reaction step 2 is necessary for migration of bridging hydroxyls to form terminal hydroxyls, which is thermodynamically favorable, as shown in Figure 3-9 for \( \text{K}_2 \). Comparison of the forward rate constants for steps 2 and 3 shows that \( k_2 \) is 100x smaller than \( k_3 \), suggesting that as soon as hydroxyls are formed on terminal sites, they are intermediates that react with bridging hydroxyls and desorb as water. Comparing the concentration of terminal hydroxyls (WOTH, open triangles, Figure 3-7A) and bridging hydroxyls (OBH, diamonds, Figure 3-7B) shows that the terminal/bridging ratio at low temperature is less than unity, approaches unity at intermediate temperatures, but only reaches 500 at 240 °C, which is still well below the value of the equilibrium constant of \( \text{K}_2 = 10^7 \) at 240°C. The rate of dehydroxylation is clearly limited by the rate of step 2; however writing a steady state approximation expression is complicated by the reverse of step 3 and coupling of the terminal hydroxyl concentration to bridging oxygen vacancies in Step 5.
At temperatures \( \leq 140 \, ^\circ\text{C} \), the mass lost corresponds to depletion of terminal oxygen but negligible loss of bridging oxygens. For higher temperatures (170 \(^\circ\text{C}\) and above in Figure 3-5) the mass loss did not stop at the relative mass of 0.93 at the end of the autocatalytic phase, but continues into the third phase. In the conditions studied, the maximum concentration for OVB was achieved at 240 \(^\circ\text{C}\) with a relative concentration close to 1; however, within the surface 2-D model, the stoichiometric ratio of bridging oxygen sites to terminal oxygens is 2:1, so roughly half of the bridging oxygens remained. In the TGA data (Figure 3-1) a similar behavior is observed, and for temperatures higher than 350 \(^\circ\text{C}\), the mass loss extends beyond 0.93 relative mass. The relative mass loss in case of removal of all the oxygens from the monolayer is 0.79. As shown in Figure 3-6 the maximum relative mass loss achieved in our model was 0.81 at 240 \(^\circ\text{C}\).

As shown in Figure 3-7B, the concentration of the bridging oxygen vacancies (OVB, x’s) increases by four orders of magnitude over the range of temperatures studied, while the terminal oxygen vacancy (W *’s) concentration is close to unity. Because within the proposed mechanism, dehydroxylation requires both terminal and bridging hydroxyls, and the terminal hydroxyl

![Figure 3-9. Changes in the equilibrium constant of step 2-4.](image-url)
concentration (WOTH, circles Figure 3-7A) is very low, their concentration limits the rate of desorption. Tracking the concentrations of moieties on bridging sites (Figure 3-7B) indicates that the major concentration of moieties at this position are hydroxyl groups at a lower temperature, while at higher temperatures, the number of oxygen vacancies (OVB, X) increases and the bridging hydroxyl (OBH, diamonds) concentration depletes. At 240 °C, the OVB concentration exceeds the OBH concentration and reaches 1.6 by the end of the time span of the simulation. For terminal hydroxyls to form, bridging oxygens must migrate to terminal positions via the reverse of step 4, which is thermodynamically unfavorable. Then it is thermodynamically favorable for protons to transfer from the bridging hydroxyls (OBH) to create terminal hydroxyls (WOTH) via step 2. At all temperatures studied, the removal of the terminal oxygens can happen to the same extent. However, the determining factor for the higher amount of mass loss is the extent of conversion of OB moieties to OVB, which becomes less thermodynamically unfavorable since K₄ decreases with temperature. As shown in Figure 3-9, the equilibrium constant for step 3 also increases due to the increase in the entropy term at higher temperatures.

Figure 3-10. Changes in concentration of oxygen vacancies on terminal (W) and bridging sites (OVB). The vertical axis is in logarithmic scale.
To further evaluate the effect of the stability of oxygen vacancies and hydroxyls on bridging and terminal sites, the equilibrium constants for step 4 and step 2 were altered by a specific amount at different temperatures. As shown in Figure 3-11, in the simulation at 140 °C (Figure 3-11A),

**Figure 3-11.** The effect of variation of equilibrium constant of step 2 and step 4 on the extent of mass loss at A)140 °C, B)190 °C and C) 240 °C.
the variation of $K_4$ and $K_2$ by ±50% did not affect the extent of the mass loss. At this temperature, only terminal oxygens are removed.

At 190 °C, changing $K_2$ by ±50% did not affect the extent of the mass loss and all of the simulated TGA curves overlapped with the reference curve. On the other hand, increasing the $K_4$ by 10% and 50% resulted in a decrease in the mass loss. According to the proposed reaction network (Table 3-2), by increasing $K_4$, the stability of terminal oxygen vacancies (W) are increased relative to bridging oxygen vacancies. This results in the consumption of the limited numbers of the remaining WOT moieties and makes creation of bridging oxygen vacancies less favorable on the surface during the third phase. A smaller number of the WOT moieties consequently results in fewer sites, which are necessary for transferring H through step 2. Consequently, the smaller concentration of WOTH moieties decreases the rate of step 3. In the case of decreasing the value of $K_4$ by 10% and 50%, the extent of the mass loss increases. This can be explained based on the reverse of the scenario described.

As expected, a similar behavior was observed for the simulation at 240 °C with an even bigger effect. Here, by decreasing the stability of the W moieties, a larger number of WOT and, consequently, WOTH would form as transient intermediates on the surface, which increases the rate of water desorption and the extent of mass loss.

Interestingly, the changes in the stability of hydroxyls on bridging and terminal did not affect the extent of mass loss similar to the 140 °C simulations. This is consistent with our earlier conclusions that step 2 in the model is not equilibrium limited. Also, these results indicate that the induction period and exponential phase are not equilibrated, but is kinetically significant, limiting the rate of dihydroxylation in the autocatalytic phase.
This conclusion is further supported by simulation results that indicate that the length of the induction period is sensitive to variation of the energy barrier of step 2 ($E_{a2}$). As shown in Figure 3-12, by varying the value of $E_{a2}$ by ±5%, the slope of the exponential phase changes. This further confirms that the autocatalytic phase is kinetically limited by the transfer of protons from bridging oxygens to the terminal sites.

\[ \text{Figure 3-12.} \] The effect of variation of the $E_{a2}$ on the rate of the mass loss.

We used the calculated concentrations for terminal hydroxyls (WOTH) and bridging hydroxyls (OBH) to calculate the 2-D monolayer's hydrogen content at each temperature. Similarly, we used the concentrations of bridging oxygen vacancies (OVB) and terminal oxygen vacancies (W) to calculate the amount of oxygen lost and ultimately calculate the chemical formula of the simulated non-stoichiometric hydrogen WO$_3$ bronze. As shown in Table 3-4, the hydrogen content reaches a maximum at 140 °C. Interestingly, based on the TGA and MS analysis of
Thibodeau et al.\textsuperscript{140}, a similar trend was observed for the composition of hydrogen in the final chemical formula of hydrogen bronze (Table 3-1).

**Table 3-4.** Simulated stoichiometric coefficient and chemical formula of hydrogen \( \text{WO}_3 \) bronze.

<table>
<thead>
<tr>
<th>Temperature ((^\circ\text{C}))</th>
<th>(y)</th>
<th>(3-x)</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>1.48</td>
<td>2.32</td>
<td>(\text{H}<em>{1.48}\text{WO}</em>{2.32})</td>
</tr>
<tr>
<td>140</td>
<td>1.90</td>
<td>1.99</td>
<td>(\text{H}<em>{1.90}\text{WO}</em>{1.99})</td>
</tr>
<tr>
<td>170</td>
<td>1.86</td>
<td>1.94</td>
<td>(\text{H}<em>{1.86}\text{WO}</em>{1.94})</td>
</tr>
<tr>
<td>190</td>
<td>1.71</td>
<td>1.81</td>
<td>(\text{H}<em>{1.71}\text{WO}</em>{1.81})</td>
</tr>
<tr>
<td>210</td>
<td>1.34</td>
<td>1.47</td>
<td>(\text{H}<em>{1.34}\text{WO}</em>{1.47})</td>
</tr>
<tr>
<td>240</td>
<td>0.34</td>
<td>0.53</td>
<td>(\text{H}<em>{0.34}\text{WO}</em>{0.53})</td>
</tr>
<tr>
<td>270</td>
<td>0.02</td>
<td>0.20</td>
<td>(\text{H}<em>{0.02}\text{WO}</em>{0.20})</td>
</tr>
</tbody>
</table>

3.4 **Conclusion**

We developed a 2-D model describing solid-state kinetics of hydrogen \( \text{WO}_3 \) bronze formation with just 5 elementary steps. Although the developed simple 2-D model predicts mass loss at lower temperature and over longer time scales, it successfully simulates the dependence of the extent of mass loss on \( \text{H}_2 \) pretreatment temperature. By simulating the bronze formation reaction at different temperatures and using the concentration of the assumed surface moieties, we calculated the stoichiometric composition of H and O. The hydrogen content increases with temperature and at 170 \(^\circ\text{C}\) peaks and then decreases similarly to the trend observed by Thibodeau et al.\textsuperscript{140} According to their report, the optimum condition for pretreatment of \( \text{WO}_3 \) catalysts for
hydrogenation was achieved at 350 °C, in which the hydrogen content of the catalyst was at maximum. The equivalent point for the optimum point in our model was achieved at 170 °C.

In addition, according to the proposed reaction network, the overall bronze formation includes three phases, induction period, an autocatalytic (exponential) phase, and a slow-down phase. These stages are typical for autocatalytic systems in which the product of the catalytic cycle is itself acting as a catalyst site. Our analysis shows that the length of the induction period is a function of the pre-set terminal vacancy concentration. Here in our model, the terminal oxygen vacancies are active sites for H₂ dissociation. A mechanism involving 4 elementary steps results in the desorption of water and creation of new W moieties as an active site for further H₂ dissociation. The rate limiting step in the dehydroxylation process is transfer of hydrogen from the bridging hydroxyl positions, that are populated during hydrogen dissociation, to form terminal hydroxyls. The terminal hydroxyls concentration remains small and limits the rate of dihydroxylation. In addition, the sensitivity of the slope of the exponential phase to the variation of the energy barrier of step 2 confirms that this phase of the reaction is kinetically limited by transferring the proton from the bridging position to terminal sites. The analysis of the surface moieties concentration suggests that in the temperature range of 120-170 °C, the mass loss is mainly due to the removal of terminal oxygens. At higher temperature, the additional mass lost is due to the creation of bridging oxygen vacancies. The extent of the mass loss at elevated temperature is controlled by the equilibrium between W and OVB moieties.
SULFUR-INDUCED DEEP ELECTRON AND HOLE TRAPS IN TITANIA

4.1 Abstract

Numerous studies have shown that sulfating titania narrows the band gap and improves photocatalytic activity for oxidation of contaminants in water, which can proceed via electron or hole mediated pathways. Although deep electron traps have been suggested to increase hole lifetimes and quantum efficiency, there is no clear evidence for unoccupied states deep in the band gap. By contrast, transient absorption indicates sulfur induces hole traps. We present experiments on sulfur-free and sulfated titania in which dissociation of hydrogen generates electrons that fill the lowest unoccupied states. Their energy below the conduction band minimum (CBM) is measured directly from changes in diffuse reflectance spectroscopy in the infrared and UV-vis ranges. For all commercial sulfur-containing anatase materials, we show that conversion of tridentate sulfate species into sulfur substituted on lattice sites occurs under highly oxidizing conditions above 400 °C and leads to partially unoccupied states ~2.8 eV below the CBM. The deep trap state observed is assigned to sulfur atoms substituted on a titanium lattice site with a formal charge of $S^{5+}$ in non-stoichiometric TiO$_{2+x}$ created under highly oxidizing conditions. Our UV-vis spectrum after reduction of these deep trap states to a $S^{4+}$ formal oxidation state is in remarkable agreement with the predicted spectrum of Harb, Sautet and Raybaud, using HSE06 density functional perturbation theory. Our band structure calculations demonstrate that titanium vacancies (or excess oxygen) are necessary for creation of partially unoccupied states. Titanium vacancies were confirmed by XRD Reitveld analysis. The partial occupancy of these states and the ability of sulfur to switch between oxidation states explains their role as both electron ($S^{5+} + e^- \rightarrow S^{4+}$) and hole ($S^{5+} + h^+ \rightarrow S^{6+}$) traps. Therefore, the electronic structure model
we present reconciles previous (unsubstantiated) proposals that sulfur could induce electron traps with transient absorption data that indicates sulfur induces hole traps.

4.2 Introduction

Titania is one of the most promising, widely available photocatalysts.\textsuperscript{330-333} However, its photocatalytic activity is limited by its wide band gap (ca. 3 eV), because only 5\% of the natural solar spectrum contains UV photons with energy greater than the absorption edge.\textsuperscript{334} Thus, dopants (e.g., boron, sulfur, nitrogen, carbon, fluorine and phosphorous), have been used to shift the absorption spectrum into the visible region,\textsuperscript{335-338} which is generally understood to occur by creating new states within the gap, effectively red shifting the absorption edge.\textsuperscript{338} However, the relationship between the presence of dopants and their effect on photocatalysis remains widely debated.\textsuperscript{337}

Several studies have directly compared pure and sulfated anatase TiO\textsubscript{2} and provided direct experimental evidence that sulfation improves photocatalytic activity both in the gas\textsuperscript{188, 339} and liquid\textsuperscript{189, 340-342} phase. A number of factors have been considered, including increased surface acidity,\textsuperscript{343} greater structural stability\textsuperscript{188, 344} and more efficient electron-hole separation.\textsuperscript{187, 189, 341, 345-347} However, the fundamental role of sulfur remains unclear because most commercial anatase contains sulfur.\textsuperscript{348} Most studies have focused on photooxidation, which can involve either reactions with holes (h\textsuperscript{+}) or indirect reaction of electrons in the conduction band (CB) to produce hydroxyl radicals.\textsuperscript{349-350} If sulfur can act as either an electron or hole trap then recombination could be suppressed and improve the photocatalytic efficiency. Whether the electron or hole mediated pathway dominates is influenced by the lifetime and mobility of the un-trapped particle. In sulfated TiO\textsubscript{2} samples the absorption onset is reported at ~500 – 800 nm (2.4 – 1.5 eV, varying by synthesis method), showing that sulfur doping narrows the band gap\textsuperscript{182, 186, 351}, which is clearly a significant
factor. Absorption in the visible region could, in principle, be explained by either new filled states above the valence band maximum (VBM) or new empty states below the conduction band minimum (CBM). The creation of new states above the VBM was clearly demonstrated in XPS valence band measurements,\textsuperscript{335} and theoretical electronic structure calculations generally predict sulfur induced states above the valence band (VB).\textsuperscript{352-357}

For many years, dynamical effects have been proposed in which the sulfating process induces deep electron traps that, after electron-hole pair creation, could scavenge the electrons and increase the hole (h\textsuperscript{+}) lifetime.\textsuperscript{187-189} To our knowledge there is no clear evidence for deep electron traps. Such traps would require unoccupied states above the VBM. Although occupied states attributed to sulfur 3p orbitals are well known from XPS valence band measurements,\textsuperscript{335} XPS only probes occupied states and therefore cannot detect the existence of unoccupied states. Moreover, band structure calculations generally indicate that the sulfur-derived bands are completely filled.\textsuperscript{352-353, 357-358}

The strongest experimental evidence for unoccupied states deep in the band gap is a pre-edge resonance (~2473 eV) observed in sulfur K-edge X-ray absorption studies for both SO\textsubscript{2} adsorption on the rutile TiO\textsubscript{2} (110) surface\textsuperscript{359} and amorphous titania synthesized with sulfate.\textsuperscript{360-361} While a pre-edge resonance could be assigned to an empty state above the VBM, many body explanations are possible and the energy of the state is uncertain because of limitations of both spectral resolution (~3 eV) and accurate determination of the work function.

A decrease in the direct recombination signal in photoluminescence with sulfur doping has been interpreted to be evidence for electron traps,\textsuperscript{189, 362-363} but does not distinguish between electron and hole trapping mechanisms. Transient absorption (TA) measurements provide more specific insight regarding the charge carrier dynamics in sulfur-doped TiO\textsubscript{2}.\textsuperscript{349, 364} Interpreting the decay in
TA spectra after e/h+ pair creation with UV light is challenging because the lifetime may be affected by recombination, trapping of CB electrons, or trapping of VB holes. Since the TA spectra of electrons and holes overlap, chemical scavengers (e.g. O2 or methanol) are often used. Tachikawa et al. found that the contribution from hole absorption decays faster in sulfur-doped TiO2 than in pure TiO2, which is consistent with a trapping mechanism in which electrons in occupied sulfur states fill the VB h+ and effectively trap the h+ onto sulfur derived states. Takeshita et al. demonstrated that, unlike VB h+, the holes trapped on sulfur do not have sufficient oxidizing potential to oxidize water. Rockafellow et al. interpret the low activity of these trapped h+ on sulfur induced states as due to their S 3p nature and being higher energy orbitals compared to the O 2p orbitals in the VB183. While these studies provide evidence for h+ traps, there is no evidence in the electron dynamics literature, either, that sulfur derived states in TiO2 can act as electron traps.

We exploit a unique approach to probe unoccupied electronic states without creating e/h+ pairs. Yates et al. have shown that n-type doping of pure titania with atomic hydrogen supplies electrons that fill empty states. Electrons that are inserted into CB states in defect-free materials (like P25 and P90) can be excited using IR spectroscopy, and the increase in absorbance has a characteristic power law, \( \sim \omega^{-p} \) (with \( p = 1.5 - 1.7 \)). If unoccupied states exist at energies within 1 eV of the CBM, generally known as shallow traps (ST), a broad electronic absorption with a threshold is observed in the IR difference spectrum. The shape and the energy of the new electronic absorption features in the spectra directly probes the lowest unoccupied states.

In this work, we exploited this strategy using both UV-vis and IR spectroscopy to identify the lowest unoccupied states spanning the energy range of the band gap and compared sulfated,
calcined anatase with sulfur-free titania. Dissociative adsorption of molecular hydrogen on surface oxygen sites of anatase produces surface hydroxyls,

\[ H_2 + 2O^\xi_0 \rightarrow 2H^\xi_0, \]  
(1)

which then dehydroxylate to form oxygen vacancies, H\(_2\)O and electrons,\(^{367}\)

\[ 2H^\xi_0 \rightarrow O^{\bullet\bullet}_0 + V^{\bullet\bullet}_0 + H_2O + 2e', \]  
(2)

where Kröger-Vink notation is used.\(^{368}\)

For sulfur-free titania, the deepest unoccupied states occur in the conduction band and in shallow traps, as others have observed.\(^{365-366}\) In contrast, for sulfated and calcined anatase we present direct evidence that electrons can fill sulfur-induced states deep in the band gap. Because XPS VB measurements are sensitive only to occupied states and band narrowing is observed in UV-vis, these states must be only partially filled. We show that sulfate dehydrates first to tridentate sulfate, but the deep traps are not formed until sulfur is incorporated into the titania lattice. The agreement between measured UV-vis spectra and previous predictions of Harb et. al\(^{357}\) uniquely assigns the deep traps to sulfur atoms occupying titanium lattice sites in a formal S\(^{5+}\) oxidation state that are reduced to S\(^{4+}\) by addition of electrons from reaction 1 and 2. Conversely, because the sulfur induced states are partially filled, in a formal S\(^{5+}\) oxidation state, they can also trap a valence band hole and be oxidized to S\(^{6+}\). Therefore, they can act both as electron and hole traps. We attribute this dual nature to sulfur’s facile redox behavior. The partial occupancy is induced by formation of oxygen rich non-stoichiometric titania during calcination. Our DFT calculations show that either excess oxygen, TiO\(_{2+x}\), or equivalently titanium vacancies, Ti\(_{1-y}\)O\(_2\), partially depopulates the sulfur-induced defect states. The presence of titanium vacancies was confirmed with Reitveld analysis of x-ray diffraction measurements.
4.3 Results and discussion

Identification of the lowest unoccupied energy states: Figure 4-1 shows combined diffuse reflectance UV-vis and Infrared Fourier Transform (DRIFTS) spectra of three TiO₂ samples, P90 (pure pyrogenic anatase–rutile mixture, Evonik), “BC” (pure anatase, synthesized at Barnard College), and “USR” (Sulfur-containing commercial anatase, US Research Nanomaterials), obtained in experiments performed under H₂, Ar and O₂ gas flow at 300 °C after rigorously cleaning the surface (vide infra) using methods described previously. Additional data for rutile and other commercial anatase materials are given in section 4.4.

Pyrogenic titania. We first discuss results (Figure 4-1A) for P90, which is a sulfur-free, low-defect-density material, to establish that the hydrogen dissociation reaction produces electrons that accumulate in the conduction band, as a basis for comparison to the sulfur free and sulfated titania, where unoccupied electronic states exist in the band gap. Pyrogenic TiO₂ (i.e., P90) contains 10 wt% rutile and 90 wt% anatase phases and is synthesized from vaporized TiCl₄ at temperatures between 1000 and 2400 °C, yielding a sulfur-free, low-defect-density material. Exposure of P90 to H₂ leads to vibrational and broad electronic absorbance (BEA) features in the IR region of the spectra. The vibrational bands at 3697 cm⁻¹ and 3668 cm⁻¹ (Figure 4-1A, inset a) are due to isolated hydroxyls, while a wide band in the 3000-3400 cm⁻¹ range is assigned to hydrogen-bonded hydroxyl groups, and the behavior of these bands confirm the role of hydroxyl groups as intermediates in the H₂ dissociation reaction (see Figure 4-1A, inset b). Subsequently, a BEA feature appeared in the IR region of the spectra. The BEA intensity increases continuously from 7000 to 1000 cm⁻¹, where it is cut off by bulk phonon absorption below 1000 cm⁻¹. Excitation of CB electrons by IR light to higher-energy, unoccupied states (as illustrated in the schematic band diagram in Figure 4-1A) generates a broad featureless absorbance which increases toward
lower wavenumbers according to a power law form, \( i.e., A \propto \omega^{-p} \) (with \( p = 1.5 - 1.7 \)).\textsuperscript{366} In supporting information section (SI), Figure 4-11 shows that the spectrum collected under H\(_2\) can be described by a power function with a \( p \) value of 1.5. The BEA intensity, measured at 2000 cm\(^{-1}\) (Figure 4-1A, inset b), continues to grow under the H\(_2\) environment, as expected under steady state conditions. Because the rate of dehydroxylation (reaction 2) is fast compared to the first step (reaction 1), the hydroxyl peak intensities remain small while electrons are populating the CB. The BEA feature assigned to electrons in the CB is direct evidence that there are no lower lying empty states and that P90 has a low defect density. In particular, there is no significant absorption observed in the 17500-26000 cm\(^{-1}\) region of the UV-vis spectrum.

Immediately after the gas flow was switched to Ar (red spectra in Figure 4-1A), the hydroxyl bands decreased as dehydroxylation and oxygen vacancy formation depleted hydroxyl intermediates (reaction 2) and led to a slight increase in the BEA intensity. Thereafter, the BEA intensity stayed constant for several hours. The stability of the BEA feature under the dry Ar environment shows that there are no available holes or any empty mid-gap states available below the CBM. It also shows that the environment is extremely dry and oxygen free.

That this BEA feature is electronic in origin (and consistent with a ST state) was confirmed by its persistence after switching the gas to Ar (red spectra), shown in the IR region in figure 4-1A, the BEA quenches rapidly under a dry O\(_2\) environment (blue spectra). This is due to the
removal of electrons from the CB upon re-oxidizing the surface vacancy sites generated during the e-
VB
e-
e-
e- IR photons CB
~ 0.2 eV IR photons UV-Vis photons ~ 2.8 eV

Figure 4-1. Absorbance difference spectra in the UV-vis (16500-26500 cm-1), and IR (1000-7000 cm-1) regions, relative to the clean, oxidized surface of A) pyrogenic titania, B) pure anatase, and C) sulfated anatase. Reaction with H2 produces hydroxyls (inset a) that dehydroxylate to form oxygen vacancies and electrons. The broad electronic absorbance (BEA) is observed in P90 at low wavenumbers due to excitation of CB electrons (shown in schematic band diagram); in pure anatase with a threshold of ~0.2 eV due to shallow traps, and in sulfated calcined anatase revealing deep traps at ~2.8 eV. Integrated OH and BEA area (inset b) confirm the hydroxyls are intermediates in reactions 1 and 2 (see text). Hydroxyl bands decrease but BEA features persist after switching to Ar (red curves); and finally, BEA features decay after switching to O2 (blue curves). The indicated times for each spectrum represent the time after switching to each gas flow environment.
H$_2$ dissociation reaction.$^{366, 370-371}$

**Sulfur-free anatase.** Since commercially available anatase samples contain sulfate impurities,$^{348}$ we synthesized sulfate-free anatase (BC sample) using a modified sol-gel method described elsewhere.$^{257, 348}$ Exposure of the clean, oxidized surfaces to H$_2$ at 300 °C leads to both vibrational and electronic spectral features, as shown in Figure 4-1B. Relative to P90, the spectra of the sulfate-free anatase shows stronger hydrogen-bonded OH modes (2900-3600 cm$^{-1}$) as well as the water band (1620 cm$^{-1}$) during the reaction with H$_2$, which is attributed to the more hydrophilic nature of low temperature synthesized anatase.$^{372}$ The frequencies of the isolated hydroxyls (3703, 3663, and 3625 cm$^{-1}$) are similar to those observed in P90 at 300 °C,$^{242}$ which indicates that the reactions are taking place on the same facets as on P90. The appearance of IR signals for isolated hydroxyl groups that reach a plateau under H$_2$ flow confirms that the reaction reaches steady state (Figure 4-1B, inset b). Like P90, a strong and continuously growing BEA feature (Figure 4-1B, inset b) was observed in the IR range of the spectrum during the H$_2$ dissociation reaction. However, the general shape of the BEA feature of sulfate-free anatase is different from that of P90. The step-like shape of the BEA observed in the IR region of the BC spectra has been previously attributed to excitation of electrons from shallow traps.$^{365-366}$ Evaluation of the BEA shape observed in the BC spectra reveals that the electronic absorption feature has an absorption edge of ~0.2 eV (Figure 4-1B and Figure 4-11). As illustrated in the schematic band diagram in Figure 4-1B, IR photons have sufficient energy to excite accumulated electrons in the ST states, 0.2 eV below the CBM to the manifold of higher energy unoccupied states in the CB. Litke et al. have reported that the presence of water and the extent of hydroxylation of the surface increases the density of trap states and prevents the delocalization of electrons in the CB.$^{373-374}$ Therefore, the observed difference between P90 and our sulfate-free
anatase is not intrinsic to the anatase TiO$_2$ crystal structure, but rather is due to a higher density of defects. Di Valentin et al. explored defects in n-doped anatase titania and found defect states below the CBM for 6-coordinated Ti$^{3+}$ interstitial sites at 0.3 eV (2150 cm$^{-1}$), 6-coordinated Ti$^{3+}$-OH sites at 0.4 eV (3226 cm$^{-1}$), 5-coordinated Ti$^{3+}$ species of O-vacancies at 0.7 eV (5646 cm$^{-1}$), and the 5-coordinated Ti$^{3+}$ interstitial sites at 0.8 eV (6452 cm$^{-1}$).

That this BEA feature is electronic in origin (and consistent with a ST state) was confirmed by its persistence after switching the gas to Ar (red spectra), with the simultaneous removal of isolated hydroxyl modes, and also that it was eliminated immediately after exposure to O$_2$ (blue spectra), similar to the P90 case. There was no significant absorption observable in the 17500-26000 cm$^{-1}$ region of the spectra. The lack of electronic absorption in the UV-vis region, along with the observation of a strong BEA feature with a threshold in the IR range, demonstrate clearly that these ST states in the sulfur-free anatase are the lowest unoccupied states present and there are no empty or partially occupied mid-gap states available.

**Sulfated anatase.** In contrast to P90 and BC, exposure of calcined, sulfur-containing anatase (USR) to H$_2$ showed no electronic features in the IR range (Figure 4-1C). Instead, a broad and strong peak, centered at 23000 cm$^{-1}$ (~2.8 eV) in the UV-vis region of the spectra appeared during H$_2$ flow. The narrow bands at 3670 and 3655 cm$^{-1}$ (Figure 1C, inset a) along with wider hydrogen bonded modes at 3000-3700 cm$^{-1}$ confirms the surface is covered with hydroxyl intermediates. Similar to the previous cases, the intensity of the OH bands plateau as the BEA continues to increase (Figure 4-1C, inset b). The appearance of this strong absorption in the UV-vis region together with the absence of the BEA feature in the IR energy range indicates that electrons produced by the surface reaction accumulate into electronic states, located ~2.8 eV below the CBM, demonstrating that, under the oxidizing conditions used to activate the sulfated titania,
these states are only *partially filled*. The absorption edge of sulfated, calcined titania (as shown in the SI) has an onset below 435 nm (2.85 eV), consistent with numerous reports\textsuperscript{182, 186, 335, 351, 376} of sulfur-induced, at least partially occupied states above the pure TiO\textsubscript{2} VB. These electrons are energetically too deep in the band gap to be excited to the CB by IR photons, but UV-vis photons can excite them into empty CB states, as illustrated in the schematic band diagram in Figure 4-1C. Similar to the other cases, the intensity of the BEA increased slightly after switching to an Ar environment (red spectra) due to the consumption of remaining hydroxyls on the surface, and decayed quickly after switching to O\textsubscript{2} (blue spectra). We observed similar behavior for other commercial sulfur-containing anatase samples, including those from Sigma Aldrich, Alfa Aesar, and Nanographi (see the SI). These results are the first experimental evidence revealing that the sulfur-induced states above the VB, after calcination, are partially empty. Since these states are not fully occupied, they can accept photoexcited electrons (e.g. from higher energy CB and/or ST states) and act as deep electron trap (DT) states. On the other hand, because these states are partially filled, they can also donate electrons to fill holes generated in the VB (e.g. by UV photoexcitation), meaning that they can function as either electron traps or hole traps depending on the electronic state of the sulfated TiO\textsubscript{2}.

To further confirm that the BEA features are electronic in origin and to distinguish them from vibrational features, the surfaces of P90, sulfate-free anatase (BC) and a commercial sulfur-containing anatase (USR) were exposed to D\textsubscript{2} gas flow, instead of H\textsubscript{2}. Upon exposure to D\textsubscript{2}, the bands related to surface OD groups appeared at lower frequencies as expected based on their isotope shifts (SI). Comparison of the shape and thresholds of the BEA features in the D\textsubscript{2}- with the H\textsubscript{2}-reaction spectra makes identification of the electronic features clear because the electronic
contribution remains while the vibrational modes shift to lower frequency. A more detailed description of the D₂ experiment results is provided in the next section.

**Chemical species:** Having established the presence of deep electron trap states, we looked more closely at the chemical changes happening during calcination prior to the spectra measured during the H₂ reaction shown in Figure 4-1C. The fact that these DT states have been observed in multiple sulfated titania samples, but not in pure titania, suggests that the presence of sulfur is in some way responsible for the creation of these DT states. Previous studies show that the photocatalytic activity goes through a maximum during calcination at temperatures between 300 and 600 °C, while simultaneously the sulfur content decreases.¹⁸⁸, ³⁵¹, ³⁷⁶

Figure 4-2A shows the DRIFT spectra monitored *in situ* during a stepwise temperature-programmed calcination of a sulfated anatase (AA) from 30 °C to 400 °C to identify sulfur related transformations. The samples were maintained at each temperature for at least 8 h under rigorously dry oxygen flow. The DRIFT spectrum recorded at 30 °C shows several impurities (Figure 4-2A). Isolated hydroxyl groups and hydrogen bonding modes occur between 2500-3800 cm⁻¹. The 1622 cm⁻¹ band is assigned to the water bending mode.²⁴², ³⁷⁷-³⁷⁸ At 100 °C, as dehydration occurs, carbonate bands become resolved at 1444 cm⁻¹ (Figure 4-2A, inset a)²⁴², and the well known sulfate band²⁵⁶ appears at 1320 cm⁻¹. By 200 °C, the surface is dehydrated, as evidenced by the disappearance of the water bending mode, which is consistent with previous reports.³⁷⁷, ³⁷⁹ Heating to 200 °C eliminates carbonate bands, while the sulfate band persists and continues to shift as the surface is dehydrated (Figure 4-2A, inset b).²⁵⁶, ³⁸⁰ The sulfate species undergo a dehydration reaction to form a tridentate sulfate species,²⁵⁶ characterized by the band at 1360 cm⁻¹ assigned to the S=O group, as illustrated in Figure 4-2A, inset b. During calcination at 400 °C the 1360 cm⁻¹ band of the tridentate species disappears.
Figure 4-2B presents a set of difference spectra from the beginning to the end point of the 400 °C calcination step that reveal the formation of a new band at 1150 cm\(^{-1}\) as the tridentate species disappears. Spectra a-d are difference spectra for which the last spectrum recorded at 400 °C was subtracted from the first spectrum recorded at the same temperature. No changes are observed for the sulfur free materials (a and b). For USR and AA (c and d), the negative going band at \(\sim 1360\) cm\(^{-1}\) shows disappearance of tridentate sulfate, which is coincidental with developing a new wide band centered at 1160 cm\(^{-1}\). Devi, et al. report bands in the 1120-1180 cm\(^{-1}\) region of sulfur doped titania to Ti-S, S-O and Ti-O-S bonds.\(^{363}\) We observed similar behavior for all other sulfated anatase samples investigated (See SI).

Although some sulfur was incorporated into the titania lattice, parallel experiments showed that significant desorption of sulfur also occurred. Calcination of larger quantities of anatase, prepared for ICP analysis under similar conditions at 400 °C, reduced the sulfur content from 1300 ppm to about 80 ppm. For the AA material analyzed by ICP, we confirmed the removal of the tridentate species, formation of lattice modes at 1160 cm\(^{-1}\) and appearance of the DT states upon reaction with H\(_2\) (See SI). These changes are not reversible and the S=O mode does not reappear after reducing the temperature to 300 °C under dry or humid conditions prior to the H\(_2\) dissociation reaction (See SI).
Electronic Origin of the Sulfur induced DT states: To determine whether the tridentate sulfate species or lattice-incorporated sulfur species are responsible for the creation of DT states, we repeated the H\textsubscript{2} dissociation reaction over the AA sample while the S=O mode was still present in

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4-2.png}
\caption{A) DRIFT spectra of sulfated anatase (AA) sample referenced to KBr powder revealing surface evolution through stepwise temperature-programmed calcination from 30 °C to 400 °C. Carbonate species' bands disappeared completely at 200 °C (inset a). The characteristic blue shift of the sulfate v(S=O) mode due to reconfiguration of sulfate-like species from a bidentate to tridentate structure is shown beside inset b. The v(S=O) mode was removed completely at 400 °C (inset b). B) Difference spectra of both sulfated and sulfur-free samples showing changes in the surface condition during v(S=O) mode disappearance from the beginning to the end point of the 400 °C calcination step and control experiments for calcination at 300°C and washing. The negative going band at \textasciitilde1360 cm\textsuperscript{-1} is coincidental with developing a new wide band centered at 1160 cm\textsuperscript{-1}.}
\end{figure}
DRIFT spectra, by ending the stepwise temperature-programmed calcination at 300 °C. As shown in the SI, electrons accumulate in the conduction band, similarly to P90’s BEA, showing that neither shallow nor deep traps were formed. Clearly, sulfate-like species were not responsible for DT states. We emphasize that during calcination at 300 °C, new bands did not appear at 1150 cm$^{-1}$ (Figure 4-2B, curve e).

Figure 4-3 compares DFT calculations for a tridentate sulfate-like species on anatase TiO$_2$ (101) with the clean surface to identify sulfur derived bands (details of calculations are given in SI.). The total density of states (DOS) and the Ti and O partial density of states (PDOS), shown in Figure 4-3A, are consistent with previous calculations using the PBE functional and underestimate the bandgap, as expected.$^{184, 352-353, 356}$ For the anatase surface decorated with a tridentate sulfate-like structure (Figure 4-3B), the sulfur derived bands at -6 eV are below the titania valence band and there are no mid-gap states. This is consistent with our experimental observations reported in the SI that sulfate-like structures do not create deep traps.
Because sulfate species can be removed by dissolving them in water,\textsuperscript{381} we also repeated the H$_2$ dissociation reaction on washed material (Figure 4-2B, curve f). The DRIFT difference spectra show loss of tridentate sulfate but no evidence for incorporation of sulfur into the lattice with washing (Figure 4-2B, curve f) Again, there was no electron accumulation in DT states at 2.85 eV below the CBM (24500 cm$^{-1}$) and only accumulation of electrons in the CB (See SI). The fact that DT states are not observed when sulfate species are present and only appear when the 1150 cm$^{-1}$ lattice modes are present is evidence that sulfur atoms occupying titania lattice sites are the origin of DT states.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4-3.png}
\caption{Total density of states (DOS) and partial density of states (PDOS) for A) the pure anatase TiO$_2$(101) surface; B) with a tridentate sulfate leading to sulfur derived bands deep in the VB; C) with a sulfur substituted on a surface bridging oxygen inducing fully occupied states above the VB; D) with a sulfur substituted on a surface titanium site inducing fully occupied states above the VB; and the effect E) and F) of a hydroxyl acting as a Lewis acid to partially depopulate the sulfur derived state.}
\end{figure}
The electronic structure of sulfur depends on the location within the titania lattice as well as its (formal) oxidation state. Extensive experimental studies have considered anionic sulfur ($S^{2-}$) on oxygen sites and cationic sulfur ($S^{6+}$ and $S^{4+}$) substituted on titanium sites, based on XPS spectra. Our calculations for oxygen substituted on a surface bridging oxygen ($S_{O}$) show occupied states located about 0.2 eV above the pure TiO$_2$ VBM derived from S 3p orbitals, as shown in the PDOS of Figure 4-3C. These results are consistent with previous calculations by Tian et al., Harb et al. and Chen et al. and have a formal oxidation state of $S^{2-}$. Substitution of sulfur on titanium sites ($S_{Ti}$) also lead to fully occupied states about 0.15 eV above the VBM (Figure 4-3D) with a formal oxidation state of $S^{4+}$, consistent with work by Ohno et al., Long et al., and Harb et al. Both isolated and dimerized interstitial sulfurs have been predicted to create fully occupied states higher in the gap. Although these states can account for band narrowing, the similarity in the PDOS does not allow us to distinguish which site is the deep trap state.

Predictions of the UV-vis spectra for 13 different isolated and dimerized configurations by Harb et al. show distinct differences and provide a clear basis for identifying both the site and the oxidation state of sulfur. Figure 4-4 compares our UV-vis spectrum of the deep trap state with spectra calculated from the difference between their spectra for sulfur on titanium, oxygen, and interstitial sites and their spectrum for pure anatase. The position, peak width, and asymmetry of our DT state agrees remarkably well with their prediction for sulfur on a titanium site in a formal $S^{4+}$ oxidation state ($S^{4+}@Ti$). Their prediction for sulfur in the $S^{6+}$ oxidation state shows no absorption within the gap ($S^{6+}@Ti$). Anionic sulfur substituted on oxygen sites leads to ($S^{2-}@O$) an absorption closer to the band edge near 350 nm. Sulfur dimers substituted on a pair of oxygen sites gives an absorption at 600 nm.
Comparison of our spectroscopic evidence with their simulated UV-vis difference spectra shows that during the H₂ dissociation reaction, sulfur atoms must be reduced from higher oxidation states to produce sulfur atoms in the final oxidation state with a formal charge of S⁴⁺. Furthermore, for the sulfur induced states to act both as electron and hole traps, they must be at an intermediate oxidation state between S⁴⁺ and S⁶⁺ (Figure 4-3).

To produce a formal S⁶⁺ state, Harb et al. introduced two sulfurs on titanium sites with an additional titanium vacancy, which fully depletes the sulfur-induced band. However, the presence of titanium vacancies is stoichiometrically equivalent to excess oxygen. Experimentally, we found that to remove the tridentate species and create deep traps it was necessary to have a high oxygen flow rate (~100 sccm) during calcination at 400 °C; the DT states were not formed.
under 10 and 20 sccm O₂ flow. Based on the necessity of strongly oxidizing conditions, we suggest that the post-treated TiO₂ lattice may be non-stoichiometric, either with a deficiency of titanium or equivalently with excess oxygen. Addition of one excess oxygen will fully deplete the sulfur-induced band to give a formal S⁵⁺ oxidation state, because the O 2p orbitals are lower in energy and contribute to the TiO₂ VB. To simulate a formal S⁵⁺ state, we modified the structures in Figure 4-4C and D by adding one surface hydroxyl group, which results in a half-filled sulfur-derived band. In the low concentration limit the sulfur derived defect states have no periodicity and a localized description of the state with a formal S⁵⁺ oxidation state is more physically relevant.

We view the OH adsorbed on a surface Ti atom as acting as a Lewis acid and partially depopulating the S-induced states. In the case of S₇Ti, the S atom initially has a formal charge of 4⁺ charge. However, by adding the OH_ads, it loses one electron and is oxidized to a formal charge of 5+. In the case of S₇O, the formal oxidation state is 2⁻, and addition of the Lewis acid withdraws one electron yielding a formal charge of 1⁻. The change in the electron density induced by addition of an OH can be assessed qualitatively by the Bader charges on the sulfur, having a value of, +2.12e for S₇Ti (Figure 4-3D) increasing to +2.70e (Figure 4-3F), which can be referenced to a Bader charge of +2.20e on Ti in the 4⁺ oxidation state. For S₇O, the Bader charge is -0.80e (Figure 4-3C), which can be compared to a Bader charge of -1.1e for lattice oxygen.

Although sulfur may be present and substituted on Ti sites, O sites, and interstitials at the surface and in the bulk, the higher-level calculations and calculated UV-vis spectra by Harb et al.³⁵⁷ strongly suggest that only sulfur on titanium sites in a higher oxidation state (S⁵⁺) a non-stoichiometric oxygen rich titania matrix can act as the deep electron traps we observed.

We confirmed that the post-treated TiO₂ lattice is non-stoichiometric, and has either a titanium-deficiency or, equivalently, excess oxygen. The V₇Ti concentration can be measured using
X-ray diffraction (XRD) together with a Rietveld refinement analysis, following the methods of Wang et al.\textsuperscript{384} As shown in the SI, the $V_{\text{Ti}}$ concentration in as-received and pretreated sulfur-free and sulfur-containing materials was consistently between 4 and 5\%. The increasing vacancy concentration is consistent with decreases in the $c$ lattice constant and unit cell volume, similar to Bokhimi et al.\textsuperscript{385}

**Broader implications:**

There are contradictory arguments about whether sulfated titania enhances photocatalytic activity or not. The narrowing of the band gap clearly leads to enhanced activity under visible light, however, some reports demonstrate higher photocatalytic activity under UV light for sulfur-doped titania,\textsuperscript{187,363,386} while others show less photooxidation activity under UV light compared to pure titania.\textsuperscript{182-184,186,349,351,364} The ability of sulfur atoms substituted on Ti sites in an oxygen-rich titania lattice to act both as electron and hole traps brings new perspectives to electron and hole dynamics in the photocatalysis of sulfated titania. As illustrated in the center of Figure 4-5, electron-hole pair formation can occur with UV light from the VB into the CB, leaving behind a hole in the valence band, or with visible light from partially filled sulfur derived states into the CB, creating a hole in the sulfur states. Charge carriers can be created with UV light at the surface or in the bulk, while the location of carriers created with visible light can be near the surface if the sulfur atoms are localized at the surface. It is widely understood that photooxidation reactions of organic compounds over titania can take place either through a hole mediated mechanism by charge transfer from the organic molecule directly to the VB holes (h$^+$), as shown on the left side of Figure 4-5, or by an electron mediated pathway, as shown on the right side of Figure 4-5, in which the CB electron reacts with dissolved oxygen, producing $O_2^-$ species which then undergo...
secondary reactions leading to HO₂• and OH• radicals. These radical species degrade organic compounds. The use of electron or hole scavengers have been widely used to distinguish between the direct (hole mediated) and indirect (electron mediated) pathways. In addition, the decomposition products of these pathways differ and provide qualitative insight to the rates of each pathway. If trapping is fast, it can compete with the rate of e⁻-h⁺ pair recombination and increase the lifetime of these charge carriers, which is a key parameter in determining the quantum efficiency of the photocatalysis reaction.

*Effect of electron trapping.* As previously proposed, sulfur can act as electron traps. Photoluminescence measurements show a decrease in the intensity of the recombination peak as a

![Figure 4-5](image.png)

*Figure 4-5.* Schematic mechanism of sulfur induced partially occupied states, formally in S⁵⁺ oxidation state, able to act both as an electron and a hole trap. Trapping of holes (left) could increase the electron lifetime and improve the efficiency of water-mediated radical pathways, while trapping of electrons (right) could increase the hole lifetime and enhance direct oxidation by holes that exist deeper in the VB and have greater oxidation potential.
function of sulfur content, which is consistent with rapid trapping of electrons formally reducing \( \text{S}^{5+} \) to \( \text{S}^{4+} \), as illustrated in the left side of Figure 4-5. Zhang et al.\(^{362} \) reported a correlation between enhanced photocatalytic degradation of glyphosate with the sulfur concentration under UV irradiation and a decrease in the recombination signal in photoluminescence. Their XPS measurements indicated that sulfur is incorporated in the lattice in the form of \( \text{S}^{6+} \) cation. If the electron is localized on sulfur-induced electronic states, it cannot participate in the electron mediated pathway, but charge separation can increase the lifetime of the VB hole. The VB hole has a greater oxidation potential (as illustrated in the color coded bar at right) than holes localized on sulfur derived states. To return to steady state, the electron trapped on sulfur may be photoexcited into the CB or be scavenged by \( \text{O}_2 \) at the surface as observed in our experiments.

The direct evidence provided in Figure 4-1 for the existence of electron traps in sulfated titania substantiates this electron trapping mechanism, as previously invoked by a number of workers. Bakar et al.\(^{182} \) found that sulfur doping enhances the photodegradation of methyl orange and attributed the effect to sulfur capturing the photoexcited electron and decreasing the recombination rate. Importantly, they showed that the presence of isopropanol, which is a hole scavenger, shuts down the degradation reaction, showing that the dominant pathway for methyl orange degradation is through the hole-mediated pathway. The insights from our study also explain the work of Naik et al.,\(^{189} \) who studied the photocatalytic degradation of methyl orange with sulfur and nitrogen-doped titania in the aqueous phase. They showed a three-fold enhancement of the photocatalytic activity of sulfur-doped titania over P25. Interestingly the UV visible spectra of their sulfur- (and nitrogen-) containing titania show an absorbance at 430 nm, very similar to the trap state of Figure 4-1 and predicted by Harb et al.,\(^{357} \) for cationic sulfur on a titanium site in a \( \text{S}^{4+} \) oxidation state. (Figure 4-4). In addition, their XPS results provide evidence
of the presence of sulfur in a high (S$^{5+}$/S$^{6+}$) oxidation state. Although other factors could account for the enhanced activity besides electron traps, work by Lin et al.\textsuperscript{187} on the degradation of organic pollutants found that the surface area and Bronsted acidity did not correlate with the enhanced photocatalytic activity of their sulfated titania under UV light. In addition, the enhanced photocatalytic activity compared to pure titania was only observed for sulfur concentrations less than 5%. According to the calculations of Harb et al.\textsuperscript{357} at concentrations of 2%, formation of sulfur dimers is thermodynamically favored compared to isolated sulfurs on titanium sites, explaining the drop in photocatalytic activity at higher concentrations.

For UV excitation, the proposed model suggests that the electron trapping mechanism enhances the direct (hole oxidation) pathway by reducing the recombination rate and increasing the hole lifetime. In addition, it retains the greater oxidation potential of the deeper VB holes. On the contrary, we note that if electron hole pair formation is induced with visible light from the partially filled sulfur-derived states into the CB, trapping of the CB electron into the sulfur-derived trap states is essentially recombination and provides no clear enhancement in quantum efficiency.

\textit{Hole trapping mechanism.} Considering excitation with UV light, as illustrated in the right side of Figure 4-5, donation of an electron from the partially occupied sulfur-derived states to the VB hole corresponds to trapping of the hole into the sulfur derived state, formally oxidizing the sulfur from S$^{5+}$ to S$^{6+}$. Transient absorption experiments for sulfated titania provide direct evidence for trapping of holes, although the atomistic level identity of the traps was not known.\textsuperscript{183, 349, 364} Filling the VB hole should reduce the recombination rate and increase the lifetime of the CB electron. However, the oxidation potential of the hole trapped on sulfur will be considerably less than the original VB hole, and must de-trap before diffusing to the surface to react in a direct hole mediated reaction. This scenario can explain decreased photocatalytic activity in the UV
compared to sulfur free titania, particularly if the dominant decomposition mechanism requires holes with greater oxidation potential.

In contrast to the enhancement observed by Naik et al.,\textsuperscript{189} Zhang et al.,\textsuperscript{362} and Bakar et al.,\textsuperscript{182} Rockafellow et al.,\textsuperscript{183} found that on pure TiO\textsubscript{2}, under UV irradiation, quinoline decomposes 2.5 times faster at pH 6 than on sulfated titania. They analyzed the degradation products of quinoline at pH 6 to assess the selectivity between the electron mediated (“hydroxyl”) vs. hole mediated (“SET”) pathways. Their assumption was that the sulfur derived states were completely filled and could act as hole traps; in fact the UV-vis spectrum of the sulfated anatase synthesized with thiophene is in excellent agreement with the absorption spectra for S\textsuperscript{4+} on a titanium site, although material doped with S\textsubscript{8} is more similar to the predictions by Harb et al.\textsuperscript{357} for sulfur dimers. Both materials showed an XPS S 2p peak at high oxidation state after calcination. At pH6, they observed that the degradation reaction mainly occurs through the hole-mediated pathway. The hole-mediated pathway for this reaction on sulfur-doped material is reduced under UV light. Rockafellow et al. attributed this decrease in the hole-mediated mechanism by trapping VB holes onto sulfur and the inability of the sulfur holes to oxidize quinoline. Under visible light, the holes created on sulfur-derived trap states do not have sufficient oxidation potential to oxidize quinoline. Thus, it is important to mention that hole-mediated pathways can be anticipated to be molecule-specific and depend on the ease of oxidizing the organic compounds.

The picture in Figure 4-5 is consistent with the conclusions of Rockafellow et al.\textsuperscript{183} who analyzed the degradation products in the decomposition of p-Anisyl-1-neopentanol (AN) over pure titania with UV light. Both the direct and indirect pathways contribute equally. However, for sulfated titania under UV light, the electron-mediated pathway is 10 times more effective than the hole-mediated pathway. They conclude that CB electrons were solely responsible for degradation of
AN, and that the trapped holes in the sulfur-induced states do not have enough oxidation potential to activate the hole-mediated pathway. There was not significant activity under visible light.

The overall improvement in quantum efficiency of the electron- vs. hole-trapping mechanism for a particular oxidation reaction will depend on both the difference in oxidation potential of VB h\textsuperscript{+}'s compared to h\textsuperscript{+}'s trapped on sulfur derived states and the mobility of CB electrons vs. VB holes. The spatial extent of the S\textsubscript{Ti} electron trap state as shown in the work of Harb et al.\textsuperscript{357} and its position in the gap suggest that it is a relatively isolated localized state, which would enhance hole lifetimes. The mobilities of holes, which may involve hopping of small polarons or thermal ionization, is a difficult challenging many-body problem of current interest, which has recently been investigated in anatase by Carey et al.\textsuperscript{388} More detailed TA studies on sulfur-doped titania could be used to create a clearer picture about the dynamics of charge carriers related to these DT states. Complementary to TA studies, determination of the chemical environment, structural and geometrical location of sulfur atoms in the TiO\textsubscript{2} lattice using ESR, XAFS, XPS and quantum calculation would provide valuable information regarding further support for this picture and the dynamics of charge mobility through electron photoexcitation events.

4.4 Supporting information and Experimental and Theoretical Methods

4.4.1 Materials and methods

Pyrogenic TiO\textsubscript{2} (P90) was purchased from Evonik and used as received. Rutile was purchased from US Research Nanomaterials and used as received. TiO\textsubscript{2} anatase (Sigma Aldrich, denoted “SA”), TiO\textsubscript{2} anatase (US Research Nanomaterials, denoted “USR”), TiO\textsubscript{2} anatase (Alfa Aesar, denoted “AA”) were all purchased from their respective manufacturers. Since commercially
available anatase samples contain sulfate impurities, which complicates the interpretation of spectral results, we synthesized sulfate-free anatase using a modified sol-gel method described elsewhere. Briefly, to 50 ml 100% ethanol in a 100 ml three-neck round-bottom flask in ice, we added 2.89 ml of TiCl$_4$ dropwise with a pressure equalized addition funnel. Once addition of TiCl$_4$ was completed, the reaction was stirred at ambient condition for 2 hours. The reaction mixture was placed in an oven at 87 °C and heated for three days. The powder was rinsed by addition of milli-Q water and centrifuged at 20,000 rpm for 30 minutes, several times every day for 30 days until the pH of the supernatant was around 7.

4.4.2 In situ DRIFT and UV-vis DRS

Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectra were recorded using a Nicolet 6700 Fourier Transform Infrared (FTIR) spectrometer equipped with a Praying Mantis™ (Harrick Scientific Production, IBC) accessory for DRIFTS applications. KBr powder was placed in the sample cup inside a Harrick Scientific high temperature reaction chamber (HVC). The HVC sample cup is located on a temperature-controlled sample stage equipped with a cartridge heater and a chromel-alumel (K-type) thermocouple. The temperature of the sample cup is controlled by a Harrick Scientific Automatic Temperature controller (ATC-024-1). All DRIFTS spectra were recorded under gas flow by accumulation of 512 scans at 8 cm$^{-1}$ resolution using a DTGS detector.

In situ UV-Vis Diffuse Reflectance Spectroscopy (DRS) measurements were done with a home-made UV-Vis DRS system. The UV-Vis probe light was emitted from a 75 W Xe lamp (Edmund Scientific) and dispersed in a scanning Czerny-Turner monochromator (HORIBA Scientific). The monochromatic output was focused on the entrance of the Praying Mantis™ (Harrick Scientific Production, IBC) accessory. The reflected light from the sample surface was
detected with a silicon detector (Edmund Scientific). The detector output was amplified in low noise amplifiers (MODEL 181, Princeton Applied Research) and accumulated in a digital multimeter (Keithley 2000, Keithley Instruments) with a computer interface. The UV-vis spectrometer was arranged above the FTIR spectrometer so that we could interchange the position of the Praying MantisTM accessory with HVC between the FTIR and UV-Vis optical benches without opening it to air or altering the environmental condition.

The TiO$_2$ samples were spread over the KBr powder in the sample cup for spectroscopic measurements. Water and carbon dioxide impurities in the O$_2$ were removed using a molecular sieve trap (13X, 4 to 8 mesh, Acros Organic, degassed at 200 °C for at least one day) immersed in a dry ice-acetone bath.

Prior to H$_2$ (or D$_2$) dissociation reaction all samples were pretreated with a similar temperature programmed calcination. After loading into HVC at 30 °C, over dry and cleaned KBr powder, temperature was increased stepwise to 100 °C, 200 °C, 300 °C and 400 °C, holding for a minimum of 8 h at each temperature, during which time multiple DRIFT spectra were recorded. All of the pretreatment procedure was done under a rigorously dry O$_2$ environment.

The H$_2$ (or D$_2$) dissociation reaction was carried out after cooling down the sample in HVC to 300 °C under Ar flow for 1 h to properly flush out O$_2$. A single beam background correction spectrum was collected as the reference condition of the sample ahead of the H$_2$ (or D$_2$) dissociation reaction. Samples were kept at 300 °C for the entire time during H$_2$ (or D$_2$) dissociation reaction. To avoid potential explosion, before switching H$_2$ (or D$_2$) gas flow to O$_2$ flow, a minimum 1 h Ar flushing step was performed. We performed multiple spectroscopic measurements under Ar environment to study the behavior of the BEA. Usually, the holding time under Ar flow after switching from the H$_2$ environment was hours or days.
4.4.3 Computational methods

All calculations were performed using density functional theory (DFT) and the plane-wave projector augmented-wave (PAW) method$^{389-390}$ as implemented in the VASP code.$^{391}$ Spin-nonpolarized approaches with PBE exchange-correlation functional were adopted.$^{392}$ A kinetic energy cutoff of 400 eV was used for the plane-wave expansion. Anatase surfaces are modeled through 108-atom (110) slabs with three Ti layers and O-terminated surfaces. The periodic supercell includes a 15 Å vacuum space in the direction normal to the surface (cf. Fig.4-3), separating the slabs. The dipole correction$^{393}$ was applied in order to remove the artificial dipole interaction caused by using the slab supercell method for surface calculations. A 4×4×1 k-point mesh was used to sample the Brillouin zone during structure relaxation and electronic structure calculations. All atoms were fully relaxed until their atomic forces were less than 0.02 eVÅ$^{-1}$.

4.4.4 Additional experimental results

4.4.4.1 Material Characterization

4.4.4.1.1 X-ray diffraction

As previously reported$^{348}$ for all materials further investigated in this work, and shown in Figure 4-6 the commercial anatase samples showed powder diffraction lines assigned to anatase, commercial rutile showed lines assigned to the rutile phase, while P90 contains a mixture of anatase and rutile similar to the larger particle size pyrogenic material P25. Further analysis of P90 using total scattering measurements and pair distribution analysis has been reported previously.$^{369}$
XPS survey spectra

Figure 4-6. X-ray diffractograms of P90, P25, rutile, SA, USR, and Nanografi anatase samples. The backgrounds were adjusted and the diffractograms of Nanografi anatase was scaled by a factor of 4 for clarity. Lines on the top of the figure show the expected reflections for anatase (black) and rutile (red).

4.4.4.2 XPS survey spectra

Figure 4-7. XPS analysis of the as-received TiO₂ samples. Survey scans were performed with 1 scan and 100 pass energy.

TiO₂ samples were placed on carbon tape for XPS analysis. Samples were outgassed at room temperature and pressures < 10⁻⁸ torr for 3 h before the analyses. XPS analyses were performed using a SPECS PHOIBUS 100 MCD plus analyzer at a pass energy of 100 eV with an Al Kα X-ray source working at 240 W and 20 mA. Figure 4-7 shows XPS survey spectra, as reported
previously,\textsuperscript{348} for all of the materials further investigated here. Details of the calculations of the sulfur composition has been given previously.\textsuperscript{348}

### 4.4.4.3 BET analysis

Nitrogen adsorption isotherms were measured at 77 K using a Micromeritics ASAP-2020 instrument. Samples were degassed at 350 °C for 4 h prior to the measurements. The pore size distributions were calculated using the BJH method,\textsuperscript{235, 394} and surface areas were calculated using the BET method,\textsuperscript{395} as reported previously for these materials,\textsuperscript{348} which were further investigated in this work.

**Table 4-1. Elemental and BET analysis of the as-received TiO\textsubscript{2} samples**

<table>
<thead>
<tr>
<th>Material</th>
<th>S-content by XPS (S atoms nm\textsuperscript{2})</th>
<th>S-content by ICP-OES (ppm)</th>
<th>Surface area (m\textsuperscript{2} g\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrogenic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P90</td>
<td>ND\textsuperscript{b}</td>
<td>&lt;500</td>
<td>100</td>
</tr>
<tr>
<td>P25</td>
<td>ND\textsuperscript{b}</td>
<td>&lt;500</td>
<td>55</td>
</tr>
<tr>
<td>Anatase</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SA</td>
<td>1.5</td>
<td>3660</td>
<td>97</td>
</tr>
<tr>
<td>AA</td>
<td>0.5</td>
<td>1361</td>
<td>136</td>
</tr>
<tr>
<td>USR</td>
<td>0.5</td>
<td>782</td>
<td>97</td>
</tr>
<tr>
<td>NG</td>
<td>0.15</td>
<td>1310</td>
<td>280</td>
</tr>
<tr>
<td>BC</td>
<td>ND\textsuperscript{b}</td>
<td>NA\textsuperscript{c}</td>
<td>159</td>
</tr>
<tr>
<td>Rutile</td>
<td>US research</td>
<td>ND\textsuperscript{b}</td>
<td>&lt;500</td>
</tr>
</tbody>
</table>

1. \textsuperscript{a} Information on how the surface sulfur coverage was determined is provided in the supplemental information of previous work by Mahdavi et al.\textsuperscript{348}
2. \textsuperscript{b} None Detected
3. \textsuperscript{c} Not Available
4.4.4.4 ICP-OES analysis of as-received materials

ICP-OES analyses were performed using an iCUP 6000 ICP-OES ThermoFisher instrument. Around 0.1 gram of the TiO$_2$ samples were digested in 2 mL HCl, 2 mL HNO$_3$, and 5 mL HF solution at room temperature in Teflon vials until dissolved. HF was neutralized with a saturated solution of boric acid before analysis. Intensities were converted to sulfur content from experimental calibration curves and reported as ppm on a mass basis (mg S/kg sample). The sulfur content is also provided in Table 4-1, as reported previously for these materials,$^{348}$ which were further investigated in this work.

4.4.5 Additional DRIFTS characterization during Pretreatment

![Figure 4-8](image)

**Figure 4-8.** DRIFTS spectra of anatase SA recorded during the step-wise calcination. Sample was heated at each temperature overnight before increasing the temperature. Spectra are off set for clarity.

DRIFTS spectra of USR Anatase recorded during the temperature programed calcination is shown in Figure 2A. Figures 4-8, 4-9, and 4-10 show the spectra for the SA, Rutile and BC anatase samples, respectively.
Figure 4-9. DRIFTS spectra of anatase SA recorded during the step-wise calcination. Sample was heated at each temperature overnight before increasing the temperature. Spectra are off set for clarity.

Figure 4-10. DRIFTS spectra of anatase BC recorded during the step-wise calcination. Sample was heated at each temperature at least overnight before increasing the temperature. Sample was heated at 400 °C for several days. This sample unlike other samples did not dehydroxylate after calcination at 400 °C.
4.4.6 Measurement of BEA features on additional materials

4.4.6.1 P90 and sulfate-free anatase

The DRIFTS difference spectra for P90 and sulfate-free (BC) titania after reaction in $\text{H}_2$ are shown in Figure 4-11. In addition to vibrational features, a broad electronic absorption (BEA) feature is observed. Sensitivity to oxygen, and generation of a similar feature regardless of using $\text{H}_2$ or $\text{D}_2$ (see below) shows that the BEA feature is electronic in origin; however, the general shape of the BEA feature of sulfate-free anatase is different from that of P90. As shown in Figure 4-11, the BEA features of P90 were fitted with a power-function. On the other hand, the BEA feature of anatase BC was fitted with a combination of a power-function (same as that of P90) and a sigmoid function.

\textbf{Figure 4-11.} Spectral analysis of the BEA features. The spectrum shape of P90 samples under $\text{H}_2$ environment at 300 °C has been fitted with a power function ($\text{Absorbance} \propto \omega^p$). The p value for the fit was calculated to be $p=1.5$. The shape of the BC spectrum under $\text{H}_2$ flow at 300 °C was fitted with a linear combination of a sigmoid function (85%) and the power function which was used for the P90 spectrum (15%).
Based on spectra presented in Figure 4-11, we conclude that the BEA feature of P90 originated from intraband transitions of CB electrons, while the BEA feature of anatase BC originated from transition of shallow trap (ST) electrons to the CBM. It is reported that hydroxylated anatase samples contain a high density of ST states and the prevalence of such states prevents the addition of electrons to the CB states. Since ST states are generally referred to as being less than 1eV from the CBM, the IR photon energy range of the mid-IR spectrometer is sufficient to excite the ST electrons to CB states, which results in the shape of the anatase BC spectrum with a threshold energy associated with the energy difference between the STs and the CBM.

4.4.6.2 Rutile

Because the prototypical photocatalysts, P25 and P90, contain both rutile and anatase phases, we performed similar experiments to determine the rutile contribution in the observed BEA of P90. Exposure of rutile TiO$_2$ to H$_2$ (Figure 4-12) led to the formation of two isolated hydroxyls at 3655 and 3683 cm$^{-1}$, a broad H-bonded hydroxyl band (3000-3600 cm$^{-1}$), and a water bending mode at 1620 cm$^{-1}$. All of these vibrational features associated with surface hydroxyls and water are immediately eliminated once the H$_2$ supply is switched to Ar. These results are all consistent with surface dehydroxylation and dehydration. Therefore, reduction of the sample and electron addition to the lowest available empty states is expected.
Figure 4-12. Difference DRIFTS spectra recorded during the reaction of the rutile sample with H$_2$. The Green spectrum is recorded under Ar, prior to the H$_2$ environment. Black spectra were recorded under H$_2$ and red spectra were recorded under Ar. Blue spectra are recorded at 300 °C under O$_2$ flow. The indicated times for each spectrum represent the time after switching to each gas flow environment.

Consistently, we observed a BEA feature for rutile as shown in Figure 4-12. The electronic nature of this feature is evident because it is sensitive to O$_2$ and is independent of the isotope used (H$_2$ or D$_2$), see below. However, in contrast to the BEA feature observed for P90 and anatase BC, the intensity of the rutile BEA feature increases toward higher wavenumber. This suggests that the electrons are added to ST states of rutile, which are deeper in the band gap compared to that of anatase. This observation is consistent with the previous reports; the absence of CB electrons when rutile TiO$_2$ is n-doped by photoexcitation $^{370, 397-400}$ electrochemical excitation $^{396, 401}$ and exposure to atomic hydrogen $^{397}$ has been attributed to the greater depth of the trap states in rutile compared to anatase $^{370, 398}$.

4.4.6.3 Sulfated Anatase samples

We studied four sulfated anatase samples in this work (SA, AA, USR, and NG). These materials were purchased as anatase samples; however, we confirmed the presence of sulfur
contaminants in these commercial anatase samples using FTIR, XPS, and ICP-OES analysis. Using the method presented in this work, we have probed the mid gap states of these samples during the H₂ dissociation reaction. This method is particularly useful because some mid-gaps states might have polaronic nature, meaning that they are formed only in the presence of electrons. Therefore, such states can be observed only upon in situ generation of electrons.

We did not observe a BEA feature in the IR region for any of the sulfated anatase samples. The vibrational features observed, as described in the main text, confirms that upon exposure to H₂, hydroxylation, dehydroxylation, and water formation occurs. Therefore, electrons must be accumulated somewhere in the sample. The lack of a BEA in the IR region suggests that the added electrons reside in traps deeper than the ~ 1eV range of the mid-IR spectrometer.

To find the location of these electrons in the band gap, we performed a set of experiments that probes both IR and UV-vis absorption by TiO₂ during the H₂ dissociation. As presented in Figures 4-13 for NG and 4-14 for SA and AA, the BEA is not present in the IR region for any of the commercial sulfur containing anatase samples (NG, SA and AA), similarly to the results for the USR samples shown in Figure 4-1 of the main text. In contrast, there is a strong absorption in the UV-vis region centered at 23000 cm⁻¹ (435nm or ~ 2.8 eV) for SA and AA (NG sample has not been studied under UV-vis region.), consistent with the results shown in the main text for USR anatase (Figure 4-1C). This is confirming that there is a direct correlation between absence of the BEA in the IR region and the presence of the strong absorbance in the UV-vis region. These observations demonstrate that the electrons produced during the H₂ dissociation reaction populate unoccupied electronic states deep in the band gap and not the CB or ST. Note that we did not observe the strong absorbance in the UV-vis region for sulfur-free BC and P90 samples (see the main text). Therefore, the presence of these deep trap states is clearly sulfate related because we
observed similar behavior for all the sulfated samples (SA, AA, USR, and NG) and none of the sulfate free samples (P90 and anatase BC).

Figure 4-13. Absorbance spectra in the UV-vis (16500-26500 cm⁻¹), and IR (1000-7000 cm⁻¹) regions, relative to the clean, oxidized surface of SA (Top) and AA (Bottom).
4.4.7 Reactions with D₂ (instead of H₂)

To distinguish electronic absorbance features from vibrational features, the pretreated titania surfaces were exposed to D₂ as well as H₂ and DRIFT spectra were recorded during the reaction at 300 °C. The spectra in Figure 4-15 A for P90 during the D₂ reaction showed a similar background increase to that recorded under H₂ (Figure 4-15 B). The intensity of the BEA feature increased with time under both H₂ and D₂ atmospheres. Once the gas flow was switched to Ar, the O-H and O-D bands disappeared rapidly due to dehydroxylation and oxygen vacancy formation while the intensity of the BEA decreased gradually. Comparison of the frequencies of the modes confirms their origin by the isotope shift to lower frequencies by a factor of $2^{-1/2}$. A broad band in the 2100-2700 cm⁻¹ region and two distinct bands at 2703 and 2779 cm⁻¹ were observed as peaks.
superimposed on the smooth electronic background in the D₂ spectra. The band at 2703 cm⁻¹ is the deuterated equivalent of the 3671 cm⁻¹ band, which is assigned to the bridging hydroxyls of the anatase (101) surface.²⁴² The 2779 cm⁻¹ band is assigned to silica impurities,²⁴² consistent with silica impurities observed by XPS. The BEA features disappeared rapidly upon exposure of the sample to O₂, further supporting the assignment to electronic features because O₂ is a known electron scavenger and re-oxidizes the vacancies formed by reaction 2 (see the main text)³⁹⁸.

As shown in Figures 4-15 (C-H), similar experiments were performed on the NG, SA, and USR samples, all of which contain sulfur. In contrast with the behavior of P90, no BEA features were observed under either the D₂ or H₂ environment. For the reactions occurring in H₂, new vibrational bands appear. Isolated hydroxyl groups and hydrogen bonding modes occur between 2500-3800 cm⁻¹. The 1622 cm⁻¹ band is assigned to the water bending mode.²⁴², ³⁷⁷⁻³⁷⁸ For the reactions occurring in D₂, the surfaces following pretreatment at 400 °C still have some isolated hydroxyls and hydrogen bonded modes, which illustrates the more hydrophilic nature of the lower temperature synthesized anatase materials. Therefore, when the reaction is started at 300 °C in D₂, there are negative absorbance feature in the 2500-3600 cm⁻¹ region that show exchange of OH with OD. Positive isolated OD bands appear at 2731 and 2703 cm⁻¹, while the wide peaks at 2400-1600 cm⁻¹ are due to hydrogen bonded OD interactions. This confirms that the D₂ reaction occurs on the surface. The absence of the BEA suggests that electrons are trapped in deeper available electronic states, out of reach of the IR photon energy. Some spectra were recorded out to 7000 cm⁻¹, showing that the baseline was zero within detection limits over the range of the mid-IR instrument. The similarity of the D₂ and H₂ spectra for all four commercial anatase materials, all of which contain sulfur, demonstrates the generality of our conclusions.
The DRIFT spectra for the sulfur-free anatase (BC) are perhaps more complicated to understand due to the superposition of both a BEA feature and vibrational modes, but comparison of results using D$_2$ and H$_2$ reactions is helpful. As reported in Figure 4-15 (I and J) right after exposing the dehydroxylated surface of sulfur-free anatase (BC) to D$_2$ or H$_2$ at 300 °C, the BEA feature started to grow, as electrons populate the ST states in the band gap. These spectra were recorded out to 7000 cm$^{-1}$ and clearly show that the baseline rises substantially in the region beyond 4000 cm$^{-1}$, which is well resolved from vibrational modes. For the DRIFTS spectra during the H$_2$ reaction, isolated hydroxyl bands at 3678 cm$^{-1}$ and hydrogen bonded modes in the 2500-3600 cm$^{-1}$ region are superimposed on the BEA. For the reaction in D$_2$, because the surface after pretreatment at 400°C still has some surface hydroxyls, the vibrational features are similar to those observed for the sulfated titania samples but are again superimposed on the BEA, which has a sigmoid shape associated with the 0.2 eV threshold. The positive-going bands located at 2731 and
2700 cm$^{-1}$ and the broad absorption in 2400-1600 cm$^{-1}$ are assigned to surface OD groups and
confirm dissociation of D$_2$. The negative-going isolated and hydrogen bonded hydroxyl features, relative to the BEA background, clearly illustrate that the surface was covered with OH groups to some extent after pretreatment at 400 °C and that, upon D$_2$ exposure, H/D exchange happened. Similar to the H$_2$ dissociation reaction observed on the BC sample, the BEA was stable under the Ar environment. As observed for P90, exposure to O$_2$ quenched the BEA, and for the H$_2$ reaction on BC, the remaining spectrum is the pure vibrational spectrum of the surface hydroxyls and hydrogen bonded OH and water.

4.4.8 Sulfur-free and sulfated sample absorption edge position

In multiple places in the main text, we have referred to the sulfur induced states as partially occupied or partially unoccupied. Since these states are partially filled, there are electrons in these states prior to the H$_2$ (or D$_2$) reaction. One way to confirm the presence of electrons in these sulfur-induced states under oxidizing conditions is to compare the absorption edge of sulfur-free and

Figure 4-16. UV-vis spectra of calcined BC (sulfur-free anatase) and AA (commercial sulfur containing anatase) under O$_2$ flow at 300°C.
sulfur containing materials under oxidizing conditions. As shown in Figure 4-16, the absorption edge of sulfated, calcined titania has an onset below 435 nm (2.85 eV), confirming that at least partially occupied states exist at energy levels above the pure (BC) TiO$_2$ VB. This observation is consistent with numerous reports of sulfur doped TiO$_2$ materials$^{182, 184, 383}$.

**4.4.9 Appearance of new bands assigned to lattice incorporated sulfur**

Similarly to the changes shown in Figure 4-2A during calcination at 400 °C for the AA and USR samples, Figure 4-17 shows results for the other sulfated anatase materials SA and NG. We again observed a negative band at 1360 cm$^{-1}$ assigned to the disappearance of the S=O stretching mode of sulfate like species on the TiO$_2$ surface$^{256}$ and positive broad band centered at 1150 cm$^{-1}$ assigned to lattice incorporated sulfurs.$^{363}$ These findings show the reproducibility of the reconfiguration of sulfate-like species on the surface. Since we observed appearance of new lattice

![Figure 4-17](image-url)  
**Figure 4-17.** Difference spectra of SA and NG samples showing changes in the surface condition during ν(S=O) mode disappearance from the beginning to the end point of the 400 °C calcination step. The negative going band at ~1360 cm$^{-1}$ is coincidental with developing a new broad band centered at 1160 cm$^{-1}$.  

164
modes for all four commercial anatase materials, which correlates with the appearance of the deep traps during the H\textsubscript{2} dissociation reactions, this strengthens the argument that the DT states originated from lattice incorporated sulfur atoms. In addition, as mentioned in the main text, To determine whether the tridentate sulfate species or lattice incorporated sulfur species are responsible for the creation of DT states, we repeated the H\textsubscript{2} dissociation reaction over the AA sample while the S=O mode was still present in DRIFT spectra, by ending the stepwise temperature-programmed calcination at 300 °C. As reported in Figure 4-18A, the shape of the BEA was comparable to P90’s BEA, showing that neither shallow nor deep traps were formed. Clearly, sulfate-like species were not responsible for DT states. We also repeated the H\textsubscript{2} dissociation reaction on washed material and found very similar results to the case when tridentate

![Figure 4-18](image)

**Figure 4-18.** A) DRS spectra of AA sample in IR and UV-vis regions during H\textsubscript{2} reaction when the S=O mode was not removed during calcination. B) DRS spectra of AA sample in IR and UV-vis regions during H\textsubscript{2} reaction after the S=O mode was removed by washing.

sulfate was present. As shown in 4-18B, there was no electron accumulation in DT states at 2.85 eV below the CBM (24500 cm\textsuperscript{-1}) and only accumulation of electrons in the CB.
4.4.10 Stability of sulfur lattice modes and deep traps to water

Sulfated titania have shown enhanced photoactivity in both gas and liquid phase. Therefore, we tested the stability of the deep traps formed under oxidizing conditions to exposure to water. The sulfate-like species at room temperature are assigned as bidentate structures, which during pretreatment under rigorously dry O₂ environment dehydrate and form tridentate structures with the signature S=O mode at 1360 cm⁻¹. Although the tridentate species can be rehydrated to the sulfate-like species, if sulfur is converted to a sulfur substituted in the titania lattice, it should have greater stability in an aqueous environment. Figure 4-19 shows the surface condition of the AA sample pre-calcination and during calcination at 400 °C. The S=O mode was completely removed at the end of the pretreatment at 400 °C. The sample was then exposed to humidity for 24 hr at room temperature. A multilayer of water formed on the surface obscuring surface vibrational modes, but heating under dry conditions at 100 °C shows that the lattice modes at 1150 cm⁻¹ remain while no sulfate bands reappear. This shows that reconfiguration

![Figure 4-19](image_url). Surface condition of the AA anatase sample before, after calcination at 400 °C, and following exposure to humidity for 24 hours at room temperature prior to measurement at 100°C.
of the sulfate-like structure to lattice-incorporated sulfur atoms is not reversible under these conditions. Furthermore, we repeated the H₂ dissociation reaction at 300 °C and verified the existence of the deep traps. The spectra before and after exposure to humidity were similar to that shown in Figure 4-1C. This suggests that the deep trap states that we have identified can account for the photocatalytic activity observed in both gas and liquid phase conditions.

4.4.11 Sulfate removal with washing

As noted in the main text, there are reports that sulfate species can be removed by dissolving them in water. Figure 4-20 shows the surface of the 300 °C pretreated AA material before and after removal of sulfate-like species by solely washing the sample with DI water in room temperature. For the washing process, we soaked an adequate amount of material pretreated at 300 °C in 100 ml of DI water with pH of 7 for 48hr, followed by excessive rinsing of the sample.

![Figure 4-20](image.png)

**Figure 4-20.** Surface condition of the AA anatase, calcined to 300 °C, before and after washing process for sulfate removal.
with cold water during filtration. The sample was dried at 90 °C for 12 hr before loading onto KBr in the environmental chamber prior to DRIFTS measurement. As shown in Figure 4-2B, our difference spectra show loss of tridentate sulfate but no evidence for incorporation of sulfur into the lattice with washing.

4.4.11.1 Determination of Sulfur concentration after deep trap formation.

We performed a set of experiments to determine the order of magnitude of the sulfur concentration in titania after the transformation from the tridentate species to sulfur incorporated in lattice sites and assess their ability to accommodate the electrons produced during the H₂ reaction. As reported previously and shown in Table 4-1 for these materials which were further investigated in this work, the sulfur in the as-received commercial materials (AA, SA, USR, NG) content varied between 782 and 3660 ppm. The following experiments were performed only with AA, since that material was investigated in the greatest detail for other aspects of this work, and the concentration of lattice-incorporated sulfur will certainly vary with the original concentration and the calcination conditions.

To quantify the sulfur concentration at levels of 100 ppm by ICP-OES, a 1 g sample of TiO₂ was required. The ICP-OES analysis was performed for all samples together with calibration standards after the materials were prepared as described below and characterized by DRIFTS. Initially, a 2 g sample of AA was placed on the glass frit of a glass calcination cell and heated for 1 day at each temperature (100, 200, 300°C) under a flow rate of 120 sccm of dry O₂. Following that treatment, 1 g was removed for analysis and the remaining material was transferred to a stainless-steel tube reactor supported by a plug of glass wool and the calcination was continued to 400 °C under the same oxygen flow. Following these treatments, a milligram sample of the
material was placed on top of KBr powder in the HVC environmental chamber and analyzed by DRIFTS. A background spectrum was collected for pure KBr degassed up to 300 °C, prior to loading the calcined material. As shown in Figure 4-21A, the material calcined at 300 °C showed the tridentate sulfate band at 1360 cm⁻¹ and no lattice modes in the 1150 cm⁻¹ region, as expected. Using UV-visible DRS, we confirmed that no DT states were populated during the H₂ dissociation reaction. (results not shown) However, as shown in Figure 4-21A, for the materials calcined at 400 °C, the tridentate sulfate band at 1360 cm⁻¹ was still present and no lattice modes in the 1150 cm⁻¹ region were observed. As shown in Table 4-2, the sulfur content in the as-received AA material, 1207 ppm, was similar to that reported previously, but did not change significantly after calcination at 300 °C and decreased to 967 ppm after calcination at 400 °C, presumably due to loss of some sulfate.

Although the purpose of KBr in DRIFTS experiments was simply intended to provide a reflective support for single beam reference spectra, we discovered that in fact it plays a catalytic role in the transformation of tridentate sulfate to the lattice incorporated sulfur. A 2 g 1:1 mixture of AA and KBr was loaded into the stainless-steel tube reactor and heated for 1 day at each temperature from 100 °C to 400 °C. Analysis of this material by DRIFTS, placed on KBr in the environmental chamber, confirmed that at 300 °C the tridentate sulfate modes were absent and the lattice modes at 1150 cm⁻¹ had formed (Figure 4-21A). A 1 g sample of this material was retained and analyzed by ICP-OES analysis, which showed that most of the sulfur (1192 ppm) was present somewhere within the TiO₂-KBr mixture, raising the question of whether the deep traps should be associated with lattice incorporated sulfur or some other chemical species in the KBr phase. To resolve this question, the remaining mixed material was washed to dissolve the KBr. Then 1 mg
of the washed material was placed on KBr in the DRIFTS environmental chamber. Similarly to
the 1:1 mixture, we confirmed the absence of the tridentate sulfate modes and conversion to the
lattice modes at 1150 cm$^{-1}$. Importantly, the H$_2$ dissociation reaction showed the absorption at

Figure 4-21. A) DRIFT spectra of AA materials investigated for sulfur level determination by ICP-OES. Each
spectrum was recorded from the surface after completion of pretreatment of samples prepared in bulk quantities.
B) UV-Vis spectrum recorded during the H$_2$ dissociation reaction on the post-washed surface of the AA anatase
calcined with KBr at 400 °C. Inset shows the removal of the tridentate species and the presence of the lattice
sulfur mode after the pretreatment step, referenced to the AA spectrum pretreated at 300 °C in part A. C) DRIFT
spectra of the AA surface after calcination at 400 °C after 1 week and calcination at 500 °C after an additional
three days demonstrating that the transformation occurs, but much more slowly, in the absence of KBr.
2.85 eV in the UV-vis spectrum confirming the presence of deep traps, with an intensity similar to that observed for the AA materials (Figure 4-13B) within the reproducibility of the calcination process and loading onto the KBr support. The growth of the DT state under H₂, persistence in Ar, and disappearance in oxygen was all consistent with previous behavior (Figure 4-21B). The ICP analysis of the washed material, as shown in Table 4-2, confirmed that the KBr was removed (based on the reduction of the potassium from 386,035 ppm in the 1:1 mixture to 6711 ppm in the washed material) while the sulfur content per mass of TiO₂ was 82 ppm. Although the major portion of the sulfur content was washed away with KBr, we attribute the remaining sulfur to sulfur incorporated into the TiO₂ lattice. Compared to dopant levels in semiconductors, defect concentrations of order 100 ppm are quite large and can certainly result in detectable electronic defect states.

Table 4-2. Sulfur concentration in AA measured by ICP-OES

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sulfur content (mg/kg TiO₂)</th>
<th>Potassium content (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As received</td>
<td>1207</td>
<td>39.6</td>
</tr>
<tr>
<td>Calcined 300 C without KBr</td>
<td>1214</td>
<td>116</td>
</tr>
<tr>
<td>Calcined 400 C without KBr</td>
<td>967</td>
<td>29.8</td>
</tr>
<tr>
<td>1:1 Mixture of AA and KBr calcined at 400 C</td>
<td>1192</td>
<td>386,035</td>
</tr>
<tr>
<td>1:1 Mixture of AA and KBr calcined at 400 C and washed</td>
<td>82.2</td>
<td>6711</td>
</tr>
</tbody>
</table>

To unequivocally show that the deep traps are not related to a product of a reaction between KBr and sulfate, we carried out the calcination process in the environmental chamber of the DRIFTS cell using pure AA anatase, as shown in Figure 4-21C. After reaching 400 °C, the tridentate species was present. Further calcination for an additional week did not remove the
sulfate band at 1360 cm$^{-1}$. After increasing the temperature to 500 °C, however, the 1360 cm$^{-1}$ band was removed and the lattice modes appeared over the course of an additional 3 days, as shown in the inset of Figure 4-21C.

Clearly, the presence of KBr plays a catalytic role in the transformation of sulfate to substitution onto lattice sites. Since water is a by-product of the surface oxygen vacancy formation, the hygroscopic nature of KBr may play a role in removing water from the titania surface and drive vacancy formation forward. In turn, oxygen vacancy formation could play an important role in the process of incorporating sulfur into the lattice. The exact effect of KBr to catalyze the deep trap formation and a detailed mechanistic explanation of the possible role of oxygen vacancy formation in the sulfate reconfiguration mechanism is beyond the scope of this paper and needs more theoretical and experimental studies.

As an alternative and independent means of estimating the sulfur concentration, we considered the number of reducible oxygens available and the observation that at sufficiently long H$_2$ reaction times, electrons begin to accumulate in shallow traps. A plot of the absorbance as a function of time is shown in Figure 4-22A for the AA sample. In the IR region at 67 minutes, only hydroxyl and water modes are observed, but for 180 minutes the characteristic threshold for excitation of electrons from shallow trap (ST) states into the conduction band was observed. Rekoske and Barteau $^{367}$ determined, on the basis of gravimetric measurements for reduction of titania, that there is a limit of 1.9 reducible surface oxygens per square nanometer for anatase. Based on the BET surface area of the AA anatase of 136 m$^2$/g, the number of reducible surface oxygen atoms is of order 2.5x10$^{20}$ per gram TiO$_2$. According to reaction (2), the number of electrons produced would be twice this amount, or 5x10$^{20}$ e$/g$ TiO$_2$. For comparison, a sulfur concentration of 30 ppm corresponds to 5x10$^{20}$ S/g TiO$_2$. Thus, this back-of-the-envelope estimate
gives a deep trap density that is on the same order of magnitude as the sulfur concentration determined from the ICP-OES experiments.

Figure 4-22. Plot of the intensity of the BEA as a function of time for the AA anatase during the H₂ reduction reaction, showing a fit to a sequential reaction kinetics model (Top). The growth of the BEA in the UV region saturated between 1 and 3 hours, resulting in accumulation of electrons in shallow traps, as shown in the IR region (Bottom).
4.4.12 Ti vacancy concentration determination

To determine the average concentration of Ti vacancies and the possible effect of calcination step on creation of $V_{Ti}$ in sulfated and sulfur-free materials we used X-ray diffraction technique together with Rietveld refinement method based on the work of Bokhimi and Morales. X-ray powder diffraction was done at room temperature using a PANalytical X-PertPro diffractometer with Cu Kα radiation in a parallel beam optical configuration equipped with a multichannel PIXcel detector. The X-ray light beam was filtered with a Ni film for removal of Cu Kβ irradiation. Powder samples were placed on a quartz zero-background plate for the XRD analysis. The reflected X-ray beam intensity was measured by step scanning in the $2\theta$ range between 20° and 80° with a step size of 0.005°. We used a LaB$_6$ standard (NIST SRM-640c, Gem Dugout, State College, Pennsylvania, USA) to evaluate and confirm the accuracy and reproducibility of the goniometer alignment by mixing it with the anatase materials as an internal standard for three consecutive measurements. The XRD of titania samples were refined by using the General Structure Analysis Software-II (GSAS II) program. The instrument parameters contributing to line shapes for refinement were determined from measurements of the pure LaB$_6$ standard. Diffraction patterns of the anatase-LaB$_6$ materials were refined with a superposition of the two phases to accurately determine the sample carrier alignment and apply very small corrections to accurately align the LaB$_6$ diffraction lines and therefore accurately determine the $2\theta$ positions of the anatase lines. Then, for refinement of the pure anatase samples, the sample carrier offset could be applied to make (very small) corrections to the $2\theta$ positions of the pure anatase diffraction pattern. Thus, both the relative intensity of the diffraction lines and the accuracy of the line positions was ensured in the patterns analyzed during Rietveld refinement.
In addition to the unit cell parameters, we particularly refined the cation occupancies in the anatase crystal structures for the AA and BC materials to compare the vacancy concentration in sulfur-free and sulfur-containing samples for the as-received and after calcination in a dry oxygen flow. Figure 4-23 shows the Rietveld refinement plots. The residual (wR) and goodness of fit ratio (GOF) values along with Ti occupancy and crystal unit parameters are reported in Table 4-3. The Ti vacancy concentrations were determined based on Ti site occupancy value calculated with the fitted model and stochiometric value of 0.125.

As discussed in the main text, the vacancy concentration in the sol-gel synthesized sulfur-free anatase (BC) is relatively high, reflecting the low temperature synthesis conditions, but decreases after calcination. The as-received AA material had a vacancy concentration of 4.1%, which decreased slightly and was not significantly different from that of the calcined BC material. Given the fact that no deep traps were present in the sulfur free BC material and were present in the AA material, while both materials had similar Ti vacancy concentrations, we conclude that the Ti vacancies are not the electronic origin of the deep traps.

Table 4-3. Ti site occupancy, Ti vacancy concentration, unit cell parameter and parameters describing refinement accuracy of studied samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>Ti site Occupancy</th>
<th>Ti vacancy %</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>wR</th>
<th>GOF</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA as received</td>
<td>0.119875</td>
<td>4.1</td>
<td>3.785121</td>
<td>9.515707</td>
<td>4.92%</td>
<td>1.29</td>
</tr>
<tr>
<td>AA calcined at 300 °C</td>
<td>0.1211</td>
<td>3.12</td>
<td>3.78119</td>
<td>9.50801</td>
<td>7.213%</td>
<td>1.09</td>
</tr>
<tr>
<td>AA calcined at 400 °C</td>
<td>0.1202625</td>
<td>3.79</td>
<td>3.78496</td>
<td>9.51311</td>
<td>7.441%</td>
<td>1.16</td>
</tr>
<tr>
<td>BC as received</td>
<td>0.1055</td>
<td>15.6</td>
<td>3.792919</td>
<td>9.497997</td>
<td>5.55%</td>
<td>1.13</td>
</tr>
<tr>
<td>BC calcined at 400 °C</td>
<td>0.121</td>
<td>3.2</td>
<td>3.785834</td>
<td>9.512815</td>
<td>5.69%</td>
<td>1.16</td>
</tr>
</tbody>
</table>
As shown in Figure 4-24, the correlation between the Ti vacancy concentration and (A) the $c$ parameter and (B) the unit cell volume is consistent with previously reported data by Bokhimi and Morales \textsuperscript{385}. As the vacancy concentration increases, the cell volume decreases and the lattice parameter in the $c$ direction decreases. The changes in the unit cell size, based on the diffraction line positions, provide further support for the analysis of the vacancy concentrations which are controlled predominantly by relative line intensities.
Figure 4-23. Rietveld refinement plots for AA and BC samples pre- and post-calcination.
Figure 4-24. Correlation between the Ti vacancy concentration and A) the c lattice parameter, and B) unit cell volume, for materials studied in this work and those reported by Bokhimi and Morales.
FUTURE WORKS

Here, we described extensive studies about the implication of experimental analysis and computational approaches to studying surface reactions and catalyst properties. Interesting conclusions were obtained during these studies. However, more experimental work is needed to understand the reactions on solid surfaces. In the following, there are some suggestions that could be used to expand the studies described in this thesis.

5.1 Future work for Chapter 2

Direct conversion of gaseous ethanol to butadiene over multifunctional catalysts based on the Lebedev process has been extensively studied. The utilized catalyst for this process plays an essential role in terms of developing a selective pathway towards butadiene. Different loadings of magnesia on SBA-15 are required to examine the effect of increasing magnesia loading on butadiene production rate and other products. The studies conducted on the key step of the Lebedev reaction have emphasized the challenges related to this process and identified the required type of the active sites on the catalyst surface to execute high selectivity towards butadiene. Although we have thoroughly investigated the surface properties, utilizing surface characterization techniques such as XPS and SEM could create more detailed pictures that complement our FTIR spectroscopic studies.

Through the use of high-resolution scanning electron microscopy, we can study the fine details of the intricate pore structure of SBA-15. According to our DRIFT findings, the possible location of the deposited Mg$^{2+}$-O$^{2-}$ pairs are either the entrance of the SBA-15 channels or the
boundary regions of the crystallites. Using EDS detectors could give a clear picture of the surface distribution of MgO pairs. The feedback of these studies could be used for developing a process to synthesize more efficient catalysts for this reaction.

5.2 Future work for Chapter 3

As future work, the first activity for microkinetic modeling should be extending the 2-D model to a functioning 3-D model. As mentioned in the main text of Chapter 3, there is a scaling issue that needs to be addressed. Although, the DFT calculations on the small clusters (MO$_3$O$_9$ and W$_3$O$_9$) have been shown to capture essential features in the surface reaction thermodynamics and energy barriers for selective oxidation of propene to acrolein and hydrodeoxygenation of acrolein to allyl alcohol, propanol, and propene, several properties of the cluster do not make it possible to model the mechanism of reactions of the tungsten oxide bronze formation. For example, as noted by Thibodeau et al.\textsuperscript{140}, when adding multiple hydroxyls to the cluster, large distortions are probably unrealistic compared to bulk catalysts, resulting in unrealistic thermodynamic values for proposed steps. This issue could be addressed by using scaling factors for each step. The correct combination of the scaling factors could be achieved by fitting the model with the experimental results. However, the 2-D model is based on W$_3$O$_9$ clusters, and it is impossible to extract thermodynamic and energy barriers for the diffusion of hydrogen and oxygen vacancy to/from the bulk.

A practical approach is to perform more accurate calculations using slab and periodic bulk calculations or larger clusters. Deriving thermodynamic and energy barrier for the solid-state kinetic model described in this chapter from comprehensive periodic slab calculations could solve the scaling issue since, in our model, we adopted the energy barriers of each step from literature...
with a different computational level of theory and accuracy compared to Thibodeau et al.\textsuperscript{140} DFT calculations on cluster models.

In addition to the computational aspect of this study, a further surface analysis could provide information that can complete our knowledge of the surface composition during bronze formation. Utilizing XPS and Ion Scattering Spectroscopy coupled with Hall effect measurements on pretreated epitaxially grown WO\textsubscript{3} films in a UHV preparation chamber can provide information about the surface and bulk composition at different pretreatment regimes. Eventually, these measurements could provide information to measure the ratio of different types of vacancies and hydroxyls and evaluate their distribution between surface and bulk. DRIFT techniques also can provide information about water evolution from reactions of hydrogen in the bronze with the lattice oxygen to desorption of water on the surface by designing a temperature-programmed desorption experiment under UHV conditions.

Ultimately, the computational and experimental results would be used to develop a microkinetic model that simultaneously includes the bronze formation reactions with the hydrogenation and HDO reactions of the organic compounds on the surface. Additional experimental analysis of the hydrogenation and HDO reactions based on an operando type experiment using DRIFT and residual gas analysis can provide mechanistic insights into the reaction. This information could be used to adjust the proposed steps or the addition of new pathways to the microkinetic model.
5.3 Future work for Chapter 4

Based on our findings and previous reports in the literature, we have described that sulfur induces states in anatase doped with cationic sulfur that can act as both electron and hole traps. This is due to sulfur atoms' ability to exist in different oxidation states and get involved with redox reactions by accepting electrons from CB and donating electrons to holes in the VB.

Studying these materials' surface in as-received, post pretreatment, and post H\textsubscript{2} dissociation conditions with XPS could provide solid complementary evidence for our findings. The pretreatment procedure could be done in a UHV preparation chamber, and the sample could be transferred to the analysis chamber without being exposed to the atmosphere. Later, the same sample could undergo H\textsubscript{2} dissociation in the preparation chamber for injection of electrons or could be bombarded with electrons in the analysis chamber to fill the electron traps. Adding electrons and exposing the surface to electron scavengers (e.g., O\textsubscript{2}) to evacuate the electron traps could induce shifts in the oxidation state of sulfur, which is direct evidence of these states acting as electron traps.

In addition, utilizing an FTIR experimental set-up coupled with accurate dosing manifolds as described by Cybulskis et al.\textsuperscript{405} could be used to measure the amount of injected electrons to create a calibration curve for the BEA. This calibration curve could be used to evaluate sulfur-induced states quantitatively. As another analytical tool, the calibration of the BEA could be used to study the charge transfer between metal and support. By in-situ analyses of BEA changes during hydrogenation or HDO reaction, the effect of the electronic structure of the metal-oxide support and the metal nanoparticles on the reaction could be evaluated.


140. Thibodeau, T. J.; Canney, A. S.; DeSisto, W. J.; Wheeler, M. C.; Amar, F. G.; Frederick, B. G., Composition of Tungsten Oxide Bronzes Active for Hydrodeoxygenation. Applied Catalysis a-General 2010, 388, 86-95.
149. Ye, J.; Liu, C.; Mei, D.; Ge, Q., Active Oxygen Vacancy Site for Methanol Synthesis from Co2 Hydrogenation on In2O3 (110): A Dft Study. ACS Catalysis 2013, 3, 1296-1306.
156. Ting, L. R. L., et al., Electrochemical Reduction of Carbon Dioxide to 1-Butanol on Oxide-Derived Copper. Angewandte Chemie (International ed. in English) 2020, 59, 21072-21079.


238. Frontmatter. In Handbook of Heterogeneous Catalysis, 1997; pp I-XIX.
244. Branda, M. M.; Rodríguez, A. H.; Belelli, P. G.; Castellani, N. J., Ethanol Adsorption on Mgo Surface with and without Defects from a Theoretical Point of View. Surface Science 2009, 603, 1093-1098.
253. WebBook, N. C.


323. Xi, Y.; Zhang, Q.; Cheng, H., Mechanism of Hydrogen Spillover on Wo3(001) and Formation of Hxwo3 (X = 0.125, 0.25, 0.375, and 0.5). *J. Phy. Chem. C* 2014, 118, 494-501.
324. Xi, Y.; Zhang, Q.; Cheng, H., Mechanism of Hydrogen Spillover on Wo3 (001) and Formation of H X Wo3 (X= 0.125, 0.25, 0.375, and 0.5). *The Journal of Physical Chemistry C* 2014, 118, 494-501.


BIOGRAPHY OF THE AUTHOR

Amir Rahmani Chokanlu was born in Tehran, Iran, on March 21st, 1987. He attended the Sharif University of Technology and graduated in 2010 with a Bachelor’s degree in Chemistry. He continued his education in chemistry and entered the Analytical Chemistry graduate program at Tehran University in the fall of 2010.

Amir started his chemistry Ph.D. program at the University of Maine in 2016 under the supervision of Dr. Brian Frederick, Dr. François Amar, and Dr. within the multidisciplinary UMaine Catalysis Group. His research field of interest is experimental physical chemistry focusing on surface chemistry, solid-state physics, and microkinetic modeling. Amir’s research activities could be described in two main categories. (1) Thermocatalytic and photocatalytic reactions, and (2) Surface chemistry and material characterization. Amir is a candidate for the Ph.D. degree in Chemistry from the University of Maine in December 2021.