

Spectroscopic Studies of Small Molecule Oxidation Mechanisms on Cu/TiO₂ Aerogel
Surfaces

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Dissertation submitted to the faculty of the Virginia Polytechnic Institute and State
University in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

In

Chemistry

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April 20, 2022

Blacksburg, Virginia

Keywords: surface chemistry, infrared spectroscopy, heterogeneous catalysis, CO
oxidation, methanol oxidation, chemical warfare agent decomposition

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Abstract

The targeted design of new catalyst materials can only be accomplished once a fundamental understanding of the interactions between material surfaces and adsorbed molecules is developed. *In situ* infrared spectroscopy and mass spectrometry methods were employed to probe interactions at the gas-surface interface of oxide-supported metal nanoparticle materials. High vacuum conditions allowed for systematic investigations to describe detailed reaction mechanisms. Specifically, variable temperature infrared spectroscopy was utilized to uncover the binding energetics of CO to the oxide surface of TiO₂-based materials. As binding energetics are related to the electronic structure of the adsorption site, differences in evaluated binding enthalpies are hypothesized to probe electronic metal-support interactions that describe charge transfer between the supported metal nanoparticles and TiO₂. Cu/TiO₂ aerogels were identified as a candidate for more in-depth studies. Flow reactor methods in combination with the surface-based infrared spectroscopy were utilized to elucidate the CO oxidation reaction mechanism over Cu/TiO₂ aerogels. Bridging oxygen atoms on TiO₂ regions of the material were identified as the active site for catalysis in a Cu-assisted Mars-van Krevelen lattice extraction mechanism. Methanol oxidation was then studied with similar methods to show the complete conversion to CO₂ and H₂O at high temperatures through the reduction of titania and formation of a formate intermediate. Higher-order carbonaceous alcohols were probed for adsorption and reactivity on Cu/TiO₂ aerogels and were observed to follow a similar reaction pathway. The higher-order alcohols, however, were shown to undergo a partial oxidation pathway in the absence of gaseous O₂ that is hypothesized to originate from enhanced binding to Cu sites. The decomposition of the chemical warfare agent simulant dimethyl chlorophosphate was also investigated. A hydrolysis pathway to form the significantly less toxic molecule CH₃Cl was observed, highlighting the unique promotional effects and chemistry on Cu/TiO₂ aerogels. The results presented exemplify both the influence of electronic metal-support interactions on catalysis and the versatile reactivity of Cu/TiO₂ aerogels.

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General Audience Abstract

Interactions between small gaseous molecules and material surfaces have very important implications for applications regarding the environment, industry, and military/public safety. The mechanisms in which gases interact with a solid surface can determine how the material can be functionally used as catalysts. Scientists and engineers start to build a fundamental understanding of what makes a catalyst successful for different applications by understanding the location and strength of interactions. A catalyst's surface acts to lower activation barriers and provide low-energy pathways for interacting molecules to chemically change, by breaking bonds for molecular decomposition and/or forming new bonds. The vibrations of chemical bonds that break and form on surfaces are probed with infrared spectroscopy at the gas-surface interface to study molecular adsorption and reactivity. In addition, a flow cell reactor is used to characterize reaction progress and identify products in real-time. A class of reactive nanoparticulate materials is utilized as a model system on which to study various chemical reactions for important applications including small molecule oxidation for industrial detoxification and clean energy applications, as well as the decomposition of chemical warfare agents. Reaction mechanisms for the oxidation of carbon monoxide and alcohols were elucidated through the utilization of the methods described above. In addition, the decomposition of a chemical warfare agent simulant is characterized. The discoveries and understanding of important chemical properties presented in this dissertation will aid in the synthesis of effective next-generation catalyst materials.

Acknowledgments

Nothing is ever accomplished alone, and even the most individualized accomplishments are built on the foundation laid by family, friends, teachers, and mentors. Though I am the sole author of this dissertation, its completion would not be possible without the help of some great people.

I would like to thank my groupmates and good friends, Harrison and Nick. My time at Virginia Tech would have been significantly more challenging and challenging without you. Being a sounding board when I needed to bounce ideas off another scientist, providing fun distractions when I needed to step away from the lab, and being there for support when I needed it most is what got me through some of the biggest challenges in graduate school.

I would like to thank my advisor, John Morris, who was instrumental in my development as a scientist and as a thinker. His teachings helped to make me a more patient and critical analyzer of results, an avid reader of scientific literature, and a successful instructor and communicator. As a mentor and a role model, I also thank former group member Darren for showing me the ropes on the workings of the lab and assisting my development in my first year in the group.

To my Ph.D. committee members including David Cox, Feng Lin, Nicholas Mayhall, and Diego Troya, I thank you for your insights and guidance throughout the progression of my graduate career.

I would like to thank the family and friends that have supported me throughout the daily challenges of graduate school. In the depths of dark winters, my father and sister always reminded me that there is more to life than research, and were able to get me out on ski trips to give the mind and body a break and some time to reflect. Lastly, I would like to thank Sasha, for always being a friendly face and enthusiastic companion every day I returned home.

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Attributions

Portions of the work in Chapter 3 and 4 of this dissertation has been published previously in the Journal of Physical Chemistry C with the following reference:

Maynes, A. J.; Driscoll, D. M.; DeSario, P. A.; Pietron, J. J.; Pennington, A. M.; Rolison, D. R.; Morris, J. R. Electronic Metal–Support Interactions in the Activation of CO Oxidation over a Cu/TiO₂ Aerogel Catalyst. *J. Phys. Chem. C* **2020**, *124*, 21491–21501.

In this multi-author work, Andrew Maynes performed and conducted all the vacuum-based and flow cell experiments, performed the analysis, and constructed the manuscript with guidance from J. Morris. P. Desario, J. Pietron, A. Pennington, and D. Rolison synthesized the Cu/TiO₂ and TiO₂ aerogel materials that were the focus of the studies, in addition to the Au/TiO₂ aerogel and Cu/P25 materials. Kristin Knight performed the study relating change in adsorption enthalpy to CO pressure in Chapter 3.

Chapter 5 of this dissertation is in manuscript preparation with the following reference:

Maynes, A. J.; DeSario, P. A.; Pietron, J. J.; Rolison, D. R.; Morris, J. R. Mechanistic Insights into the Catalytic Oxidation of Methanol on Cu/TiO₂ Aerogels. *In Preparation*

In this multi-author work, Andrew Maynes performed and conducted all the vacuum-based and flow cell experiments, performed the analysis, and constructed the manuscript with guidance from J. Morris. P. DeSario and D. Rolison synthesized the materials that were the focus of the study.

In Chapter 6, Andrew Maynes collected the infrared spectra for the adsorption and reaction of alcohols. Mikaela Boyanich assisted in the collection of flow cell data for the anaerobic oxidation of ethanol, 1-propanol, 2-propanol, and 1-butanol. Paul DeSario and Debra Rolison synthesized the TiO₂-based materials for this study.

In Chapter 7, Andrew Maynes collected all the infrared spectra describing DMCP adsorption and reaction and analyzed the data. Nathan Jones and Harrison Siegal assisted in the collection of the flow cell mass spectrometry data. Paul DeSario and Debra Rolison synthesized the TiO₂-based materials for this study.

Publications

Maynes, A. J.; DeSario, P. A.; Pietron, J. J.; Rolison, D. R.; Morris, J. R. Mechanistic Insights into the Catalytic Oxidation of Methanol on Cu/TiO₂ Aerogels. *In Preparation*

Troya, D.; Johnson, E.; Maynes, A. J.; Karim, A.; Morris, A.; Morris, J. Catalytic CO Oxidation by Cu Single Atoms on the UiO-66 Metal-Organic Framework: The Role of the Oxidation State. *In Preparation*

Maynes, A. J.; Driscoll, D. M.; DeSario, P. A.; Pietron, J. J.; Pennington, A. M.; Rolison, D. R.; Morris, J. R. Electronic Metal–Support Interactions in the Activation of CO Oxidation over a Cu/TiO₂ Aerogel Catalyst. *J. Phys. Chem. C* **2020**, *124*, 21491–21501.

DeSario, P. A.; Pitman, C. L.; Delia, D. J.; Driscoll, D. M.; Maynes, A. J.; Morris, J. R.; Pennington, A. M.; Brintlinger, T. H.; Rolison, D. R.; Pietron, J. J. Low-Temperature CO Oxidation at Persistent Low-Valent Cu Nanoparticles on TiO₂ Aerogels. *Appl. Catal. B Environ.* **2019**, *252*, 205–213.

Driscoll, D. M.; Troya, D.; Usov, P. M.; Maynes, A. J.; Morris, A. J.; Morris, J. R. Geometry and Energetics of CO Adsorption on Hydroxylated UiO-66. *Phys. Chem. Chem. Phys.* **2019**, *21*, 5078–5085.

Driscoll, D. M.; Troya, D.; Usov, P. M.; Maynes, A. J.; Morris, A. J.; Morris, J. R. Characterization of Undercoordinated Zr Defect Sites in UiO-66 with Vibrational Spectroscopy of Adsorbed CO. *J. Phys. Chem. C* **2018**, *122*, 14582–14589.

Chapter 1

Introduction: Fundamental Studies of Heterogeneous Catalysts

Thesis Statement

This research aimed to elucidate reaction mechanisms through a fundamental understanding of electronic and atomic dynamics on the surface of a novel catalyst. *In situ* infrared spectroscopy was utilized to find the underlying drivers of catalysis to develop new strategies in the synthesis and implementation of a more effective class of catalysts made with abundant materials.

1.1 Motivation

The underlying motivation for the scientific research presented in this dissertation is to provide a fundamental understanding of interfacial reaction mechanisms on novel materials to aid in the engineering of effective next-generation catalysts. High surface area nanomaterials can be synthesized to maximize the concentration of more reactive surface sites relative to inaccessible bulk atoms. Surface atoms often have a high chemical potential relative to bulk atoms (due to the low atomic coordination) and provide a specific accessible site for interaction with gaseous adsorbates and reaction intermediates. The characterization of these surface sites while monitoring reactions at these locations is crucial for the understanding of what drives catalysis on novel material surfaces. Therefore, I focus on why certain high surface nanomaterials exhibit catalytic properties, utilizing experimental techniques that probe atomic processes as they occur. The insights gained through these pursuits can then be utilized to develop new synthetic strategies for more active heterogeneous catalyst materials.

1.2 Heterogeneous Catalysis and the Use of Supported Metal Nanoparticles

1.2.1 *d*-Band Theory and the Nanoscale Reactivity of Gold

Gold is valuable and sought after due to its inert properties: it does not react or tarnish over time. Researchers however have shown that when the Au particle size is reduced to the nanoscale, specifically about 1-5 nm in diameter, the inert material becomes highly reactive.¹⁻³ In 1985, Hutchings was the first to propose the use of gold for catalysis, specifically acetylene hydrogenation, when a correlation between conversion and standard reduction potential of metal cations in supported metal chloride catalysts was revealed.¹ Then in 1987, Haruta et al. published a groundbreaking study that showed catalytic CO oxidation to CO₂ could be performed by 3d transition metal oxide supported gold nanoparticles (NPs).² Further explorations indicated that the performance of metal oxide supported AuNPs was so effective that the particles on a Fe₂O₃ support oxidized CO at temperatures as low as 203 K and converted 100% of the reactant gas at 273 K.³ Observing catalysis on a material as famously inert as gold led researchers to uncover why nanoparticulate gold is reactive.

To understand why gold is reactive at the nanoscale, Hammer and Nørskov began studying the noble nature of gold in 1995.⁴ Investigating the energy of the highest occupied molecular orbital and the lowest unoccupied molecular orbital relative to the Fermi level (E_F , where no electrons can occupy states higher in energy at 0 K) can provide insights to whether or not a gaseous molecule will adsorb to the metal surface. Along these lines, the width and position of the Au metal density of states (DOS), or *d*-band energies, within the band structure relative to the Fermi level were assessed with density functional theory (DFT) calculations.^{5,6}

The d -band position of a metal relative to the Fermi level can be predicted by the electronic configuration of the metal in question. Metals with more filled d -orbitals like Au ($5d^{10}6s^1$) are pushed below the Fermi level due to fully occupied d -orbitals while metals like Mn ($3d^54s^2$) have a d -band that lies partially above the Fermi level due to lower d -occupancy. Hammer and Nørskov postulated that because the d -band of gold lies entirely below the Fermi level, the hybridization through interaction with an adsorbate results in populated high energy d -states (antibonding-like states) leading to an unfavorable interaction and an inert surface.⁷ Interaction between an adsorbate and a coinage metal with low-lying d -bands is shown schematically in Figure 1.1b.⁸ If the hybridized d -coupling between an adsorbate and an early transition metal with higher energy d -states overlaps with the Fermi level, the high energy d -states above E_F will be unoccupied while the lower energy d -states will be occupied upon adsorption (Figure 1.1a).⁸ The combination of unoccupied high energy states and occupied low energy states describes a favorable interaction of chemisorbed adsorbates. Metal d -bands higher in energy, as measured by the d -band center, result in hybridized adsorbate states with favorable bonding and antibonding regions that do not appear when the metal d -bands are lower in energy and high energy antibonding-like states are occupied.⁵

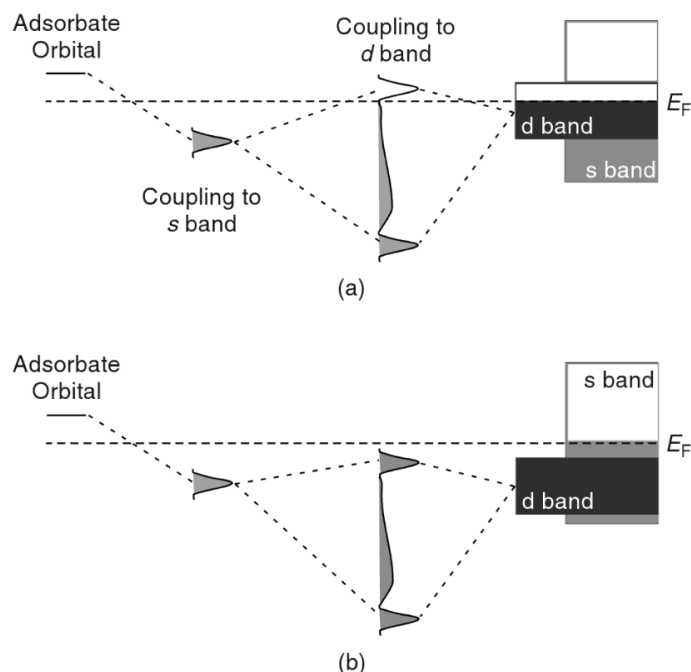


Figure 1.1 Schematic diagram of the interaction between an adsorbate electronic valence orbital and the *s*-states and *d*-states of a transition metal surface with either an early transition metal with higher *d*-states (a) or with a coinage metal with lower energy *d*-states (b). Adapted from Kolasinski, K. *Surface Science: Foundations of Catalysis and Nanoscience*, 4th Edition; John Wiley and Sons, 2019 with permission from John Wiley and Sons.⁸

Similar *d*-band studies were explored on a broader scale to evaluate whether the position of the *d*-band center is relevant for the catalytic activity of various transition metals.⁷ Here, nitrogen chemisorption energies were calculated for different 3d transition metals. The electronic coupling between the N atom (valence 2p electrons) and the metal occurs through the lower energy states first, via the free-electron-like *s*-states of the metal. The energetic coupling to the *s*-states remains relatively constant upon changing the identity of the metal (as most metals have half-filled *s*-bands). The lack of a change in the

s-states indicates that the differences in the band structure of 3d transition metals lie largely within the *d*-states of the metals. Focusing on just the *d*-band center, calculated results show that the adsorption strength of an adsorbate (N, CO, O) increases as the *d*-band center increases in energy relative to the Fermi level (i.e. as $E_d - E_F$ approaches zero),⁵ in agreement with previous discussion. In practice, it is the shift of the highest energy hybridized *d*-states above E_F that matters most for increasing the adsorption strength of a molecule.

The discussed findings have implied a connection between catalytic activity and the position of the *d*-band due to its correlation with a molecule's adsorption strength, the first significant step for catalysis. This is the basis of *d*-band theory. The *d*-band model was experimentally supported in a 2005 study that compared theoretical X-ray absorption spectroscopy and X-ray emission spectroscopy of N adsorbed onto a Ni(100) surface and a Cu(100) surface with experimental results.⁷ With several studies supporting the described relationship between *d*-states and adsorption, *d*-band theory has been widely accepted as a predictive model for adsorption strength and as a descriptor for catalytic screening/modeling.⁹

The *d*-band model can be applied to gold to explain catalytic activity at the nanoscale. Nørskov used the model and explored CO adsorption strength on both gold and platinum surfaces.¹⁰ The DFT calculations showed that Au (111), (211), and (532) extended surfaces bound CO and O₂ weakly to the surface and had a predicted *d*-band center of about -3.3 eV. When the same calculations were performed on a 12 atom Au cluster, which has an overall lower coordination number than the extended gold surfaces, the adsorbates bound stronger to the undercoordinated metal and had a corresponding *d*-band shift to -2.4 eV. The increased *d*-band center was very similar to the extended surfaces

of Pt, a known catalyst for CO oxidation. The result suggested that the catalytic activity of Au at the nanoscale could be largely attributed to the coordination number of the atoms and the altered *d*-band center of those low coordination number sites. The similar results observed on Pt clusters suggested both the model and the size-dependent electronic structure of the metal can apply to nearby transition metals in the periodic table. DFT calculations revealed that undercoordinated Au atoms have *d*-states of higher energy than fully coordinated gold atoms (bulk gold).¹¹ Thus the uncoordinated atoms bind adsorbates stronger than fully coordinated sites. This relationship can be attributed to undercoordinated metal sites possessing a relatively high surface energy, and interacting with an adsorbate will lower the surface energy. Similarly, the DOS of differently sized Au clusters was calculated by Andersson et al. and showed the increasing shift of the *d*-band center as particle size decreased down to a four atom cluster.¹²

In all, *d*-band theory has shown why AuNPs are reactive and why small particles can enhance or induce catalysis. The applications of this model for catalysis are not limited to Au. Metals with a similar density of states to Au can get similar promotional effects when confined to nanoscale size. Pd, Pt, Cu, and Ag all have comparable DOS to Au,¹³ and therefore make excellent candidates to study for potential catalysts. These groups of metals however are often low in abundance, leading to high materials cost which limits scalability and long-term impact/usage. The exception to abundancy, however, is Cu.¹⁴ Extrapolation of the favorable adsorbate binding strength for reactions based on *d*-band center for Cu suggests a potential nanoparticulate metal catalyst that is needed to bring down material costs in heterogeneous catalysis.

1.2.2 Catalyst Properties and Particle Size Effects

With the adsorption interactions and activity of AuNPs attributed to the *d*-band center, which depends on particle size and coordination number, catalyst parameters can be tuned and adjusted to make the most use of the phenomena. Valden Lai and Goodman sought to uncover the Au particle size dependence on activity in 1998, before *d*-band theory was fully developed, using scanning tunneling microscopy/spectroscopy (STM/STS) for AuNPs supported on TiO₂ films.¹⁵ Their experiments concluded that activity for CO oxidation was highest for AuNPs that are about 3.5 nm in diameter, with both smaller and larger nanoparticles having diminished activity. The field has since used 3.5 nm Au as the standard for catalytic studies, with a Au loading below 3% to prevent nanoparticle agglomeration.¹⁶ From previous discussion, a particle size of 3.5 nm is likely to have the optimal *d*-band center from the relatively high proportion of low-coordination number sites.¹² While Au particles smaller than 3.5 nm might possess a more favorable *d*-band center, the amount of activated oxygen available on a Au/TiO₂ catalyst is proportional to the circumference of the Au nanoparticle (the number of interfacial perimeter sites between Au and the TiO₂ support); fewer sites for activated reactants results in lower catalytic activity.¹⁷ More information on oxygen activation is discussed in section 1.4.2. Reinecke et al. also determined that valence band changes in Au are dependent on average coordination number, indicating that electronic structure also plays an important role in the activity of AuNPs.¹⁸

With electronic structure showing importance in the catalytic activity of Au/TiO₂, researchers expanded the studies further to investigate how the oxidation state of Au affected reactivity. Wei and coauthors used spectroscopic methods to determine that Au⁰

sites in AuNPs are more reactive for CO oxidation than $\text{Au}^{\delta+}$ sites.¹⁹ Other studies disagreed, claiming that the initial reduction of $\text{Au}^{\delta+}$ to Au^0 by CO is what makes the cationic sites more active due to a stronger binding energy, which allows a Au-CO triatomic complex to diffuse across the AuNP towards active sites on the TiO_2 support.^{20,21} Cationic $\text{Au}^{\delta+}$ is also favorable for the stability of negatively charged active intermediates (OH^- or OOH^-).²² While a consensus for all reactions may never be met, the importance of metal oxidation state on Au/ TiO_2 catalysts cannot be understated.

Similar oxidation state dependency for reactivity can be found on Cu nanoparticles as well. Jernigan and Somorjai discovered that Cu thin films had increasing CO oxidation activity as the Cu state was more metallic, that is activity went as $\text{Cu} > \text{Cu}_2\text{O} > \text{CuO}$.²³ Similarly, they also observed that the apparent activation energy ($E_{a,\text{app}}$) increased with increasing Cu oxidation state: Cu with an $E_{a,\text{app}} = 37.7$ kJ/mol, Cu_2O showing an $E_{a,\text{app}} = 58.6$ kJ/mol, and CuO with an $E_{a,\text{app}} = 71.1$ kJ/mol.²³ Other investigations have shown that Cu^{2+} needs to be reduced before the metal is active for CO oxidation.^{24,25} Perhaps vital to the ability for Cu to be an effective catalyst, given the dependency on oxidation state, is the relative stability of those oxidation states. The oxidation states of Cu, particularly low-valent Cu (Cu^0 or Cu^{1+}) are unstable and readily oxidize to Cu^{2+} . Cu has even been observed to completely oxidize from metallic Cu^0 to Cu^{2+} in only one hour at 548 K in a 2:1 $\text{CO}:\text{O}_2$ reaction mixture.²³ These mild temperatures for oxidation as well as the more extreme calcination temperatures needed to obtain unstable low-valent Cu particles present a unique challenge for the synthesis of Cu-based catalysts.^{24–29}

1.2.3 Aerogels and Nanostructuring Support Oxides

Conventional surface decorated metal NPs on oxide supports are the focus of much of the literature in the metal NP catalysis field. Researchers have observed promotional effects when nanostructuring the support oxide of a catalytic system.^{30–35} The specific style of nanostructuring can take various forms. For example, Carrettin et al. simply decreased the particle size of the CeO₂ support in a Au/CeO₂ catalyst and observed an increase in CO oxidation activity by two orders of magnitude.³¹ Si and Flytzani-Stephanopoulos synthesized ceria in nanorods, nanocubes, and nanopolyhedra to support Au NPs and studied the effects that the oxide nanostructure had on water-gas shift activity.³² A significant correlation was found between the lattice strain in the ceria nanostructure and the catalytic activity of the Au/CeO₂ system. Specifically, nanorods were found to be the most active and contained the highest lattice microstrain in the (111), (200), and (220) crystal planes. The ceria nanopolyhedra support was closely followed in terms of both activity and lattice strain, while the nanocubes displayed poor activity and very low strain parameters. Introduction of a dopant/co-oxide,³⁰ and use of oxide/carbon nanostructures (i.e. quantum dots, graphene, carbon nanotubes) also had promotional effects on catalysis.³⁵

Nanostructuring through the use of aerogels has been of particular interest recently.^{33,34,36} Aerogels are highly porous materials prepared by a sol-gel synthetic procedure and supercritical drying, and possess a low density (0.05 g/cm³), high surface area (1000 m²/g), and high pore volume (18 cm³/g).³⁷ While these materials have been around for many decades, their use in heterogeneous catalysis has not been widespread.

SiO₂ aerogels are the most utilized aerogel as a sorbent material for their high surface area and surface functionality.^{38–40} TiO₂ aerogels have seen higher usage as of late as a catalytic support, as deposition of metal NPs onto conventional TiO₂ compromises the surface area and pore size of the support.^{41,42} The use of an oxide support with high surface area and pore size allows for those losses during NP deposition to be less impactful on the material. A graphic representing the different profiles for surface-decorated and aerogel materials is shown in Figure 1.2. Debra Rolison and co-workers have been implementing TiO₂ and CeO₂ aerogels as supports for Au and Cu NPs that show enhanced catalytic activity for water splitting,⁴³ CO oxidation,^{36,44,45} methanol oxidation,⁴⁶ and chemical warfare agent decomposition.^{47–49}

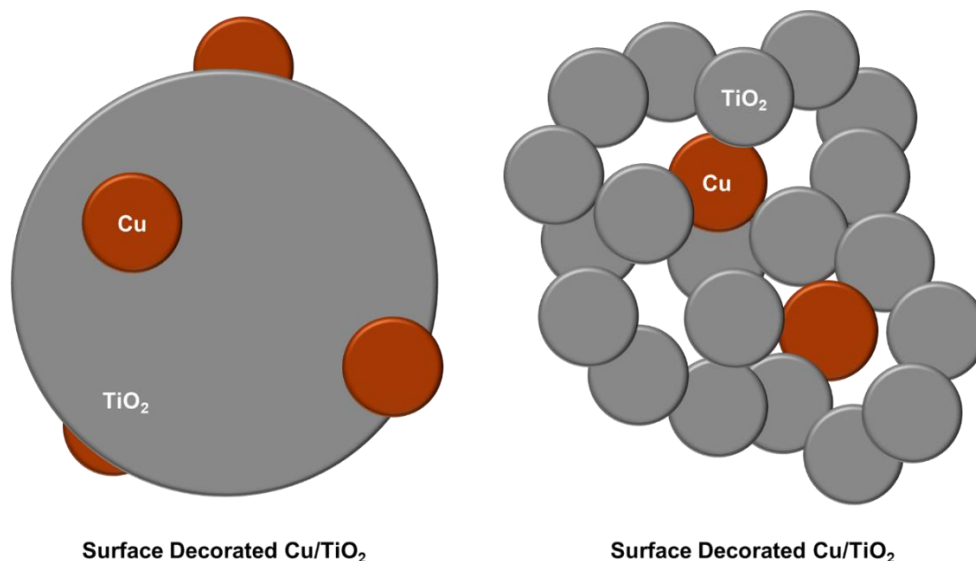


Figure 1.2 Structural profiles of a conventional surface-decorated Cu/TiO₂ material (left) and a Cu/TiO₂ aerogel (right).

The promotional effects of the aerogel support are clear, yet not fully understood. The aerogel nanostructure is suggested to increase the number of junctions, or points of interfacial contact, between the oxide and supported NPs and may play a role in the overall

catalytic activity of the materials.^{36,44,48,50} These multiple points of oxide/NP interfacial contact can also provide sinter-resistance and metal-NP stability that surface-decorated materials cannot, as metal NPs have high surface energy and are likely to agglomerate and sinter at elevated temperatures.^{51,52} This sintering process becomes inhibited when the metal NPs do not have a clear path to one another.

1.2.4 Cu/TiO₂ Aerogel Materials

As suggested, the combination of potentially reactive copper nanoparticles (CuNPs) with a nanostructured TiO₂ aerogel support may strike a balance between high reactivity, high stability, and low cost for a catalyst. The Cu/TiO₂ aerogel materials studied throughout this work were described in detail by DeSario et al.³⁶ The TiO₂ aerogel is primarily of anatase phase but some evidence could suggest there are small regions of brookite and amorphous titania in the support. Through the sol-gel synthesis and supercritical drying process, the TiO₂ aerogel support has an average diameter of 9.0 nm. This particle size is significantly lower than the 60 nm of conventionally used commercial TiO₂ powders from sources such as Evonik or the American Instrument Company, Inc. Additionally, the surface area of the Cu/TiO₂ aerogel after Cu photodeposition remained very high at 131 m²/g, an order of magnitude higher than surface decorated Cu/TiO₂ at 10.6 m²/g. A pore size distribution plot of the two materials indicated that the surface decorated material did not contain any pores, but a minimal void volume was calculated to be 0.055 cm³/g. The Cu/TiO₂ aerogel has a pore volume of 0.53 cm³/g, again an order of magnitude higher than the non-networked material. Scanning electron microscopy images of the

surface decorated Cu/TiO₂ and networked aerogel material displaying the difference in support particle size are shown in Figure 1.3.

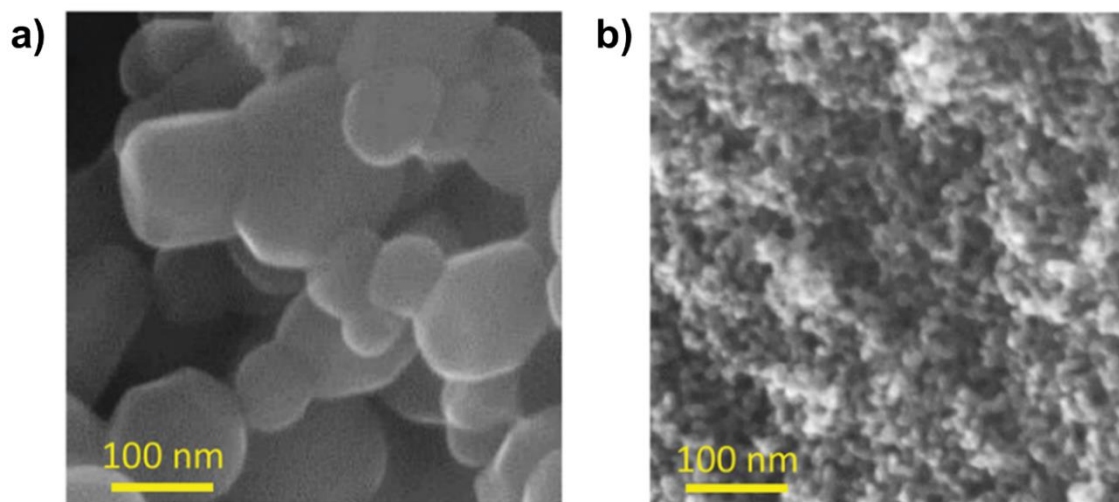


Figure 1.3 Scanning electron microscopy images of (a) conventional surface decorated Cu/TiO₂ and (b) the networked Cu/TiO₂ aerogel materials. Reprinted from *Nanoscale*, 9, DeSario, P. A. et al., Oxidation-Stable Plasmonic Copper Nanoparticles in Photocatalytic TiO₂ Nanoarchitectures, 11720–11729, 2017 with permission from the Royal Society of Chemistry.³⁶

Diffuse UV-visible spectroscopy of the Cu/TiO₂ materials showed that the structure of the support oxide has a dramatic impact on the Cu speciation, with the mesoporous aerogel stabilizing low-valent reduced Cu sites. Copper speciation is often determined through X-ray photoelectron spectroscopy (XPS), but the Cu LMM Auger peak that is usually used to differentiate Cu oxidation states overlaps with the binding energy of Ti 2s in the spectra. Despite the inability to specifically determine the Cu oxidation state, XPS can differentiate Cu(II) from Cu(I) and Cu(0). XPS measurements confirmed the diffuse UV-visible spectroscopic results of the aerogel stabilizing low-valent Cu species.

Confirmation of the low-valent Cu oxidation states was shown through measurements of the relative ratios of Cu(I) and Cu(0), denoted as Cu_{red}, relative to Cu(II). The ratio of Cu_{red}/Cu(II) for the Cu/TiO₂ aerogel was measured to be 3.1 while the surface decorated Cu/TiO₂ sample had a Cu_{red}/Cu(II) ratio of 1.2. While these material parameters were able to be measured, a more nuanced view of the chemical structure of the Cu NPs is needed for more detailed mechanistic understandings.

From the measured particle sizes provided in the work and assuming the CuNPs are of the same size for the materials with different supports,³⁶ the surface decorated Cu/TiO₂ should have about 65 CuNPs on each TiO₂ particle, as opposed to the 0.3 CuNPs per TiO₂ particle on the aerogel. The ability for Cu to interact with more than one TiO₂ particle in the Cu/TiO₂ aerogel could correspond to enhanced sinter resistance. However, it is important to note that the Cu/TiO₂ aerogels are not entirely resistant to nanoparticle agglomeration. A Scherrer analysis of XRD measurements before and after a 4-hour exposure to a flowing atmosphere of 5% H₂/95% Ar at 573 K indicated that metallic Cu(111) reflections grew from 7 to 16 nm after the heated exposure.⁴⁴ While this growth relates to twelve 7 nm particles agglomerating, the overall CuNP size is only increased by a factor of 2.3. With 65 CuNPs on the surface decorated Cu/TiO₂, it is reasonable to assume that more agglomeration and NP sintering would occur than on the Cu/TiO₂ aerogels, in lieu of a direct experimental comparison.

1.3 CO as a Probe Molecule for the Characterization of Surface Sites

Gaseous carbon monoxide has been employed as a highly effective molecular probe over many decades.^{53–55} The high sensitivity of the infrared (IR) stretching frequency of

CO to the electronic structure of adsorption sites can be used to help characterize the surfaces. The molecular orbital diagram for CO is shown in Figure 1.2. Polarization and charge transfer, both from the metal to CO and CO to the metal, affect the vibrational frequency of adsorbed CO molecules.^{53,56} Cations with the electron configuration of a group 18 element, like Ti^{4+} , are void of d shell electrons, thus they do not exhibit π -electron back bonding to the adsorbate. Interactions between CO and low electron density surface sites occur through electrostatic and σ -bonding interactions. Charge transfer occurs from the C-end lone pair of CO to the metal cation in a σ -coordination. Specifically, the high energy 5σ orbital donates electrons to the e^- deficient surface site, and the loss of high energy electrons, despite its identity as a bonding orbital, stabilizes the C-O bond in carbon monoxide. The strengthened intramolecular interaction causes the $\nu(\text{CO})$ stretching frequency to increase relative to that of gas-phase CO (at 2143 cm^{-1}), as shown in the blue trace of the sample IR spectrum in Figure 1.4. Conversely, metal cations with partially filled d orbitals can contribute charge to the $2\pi^*$ orbitals of CO. The higher the d -filling a metal site has, the greater amount of charge it can contribute to the lowest unoccupied molecular orbital of CO. The increase in electron density in the antibonding orbitals of CO causes the C-O bond force constant to decrease and the C-O bond length to increase. These changes result in a decreased $\nu(\text{CO})$ stretching frequency relative to gas-phase CO as displayed in the sample IR spectrum (red trace) in Figure 1.4. Metal sites often display a synergistic effect between the two charge transfer mechanisms.⁵³ The IR spectral frequency of a CO upon adsorption to a metal site is commonly a compromise between σ -(CO to M^{n+}) and π -(M^{n+} to CO) interactions. Polarization effects caused by electric fields at binding sites also contribute to the CO-metal spectral frequency.^{53–55} The high sensitivity of the IR

stretching frequency of CO to a specific surface site to which the adsorbate is coordinated can be used to help characterize surface sites.

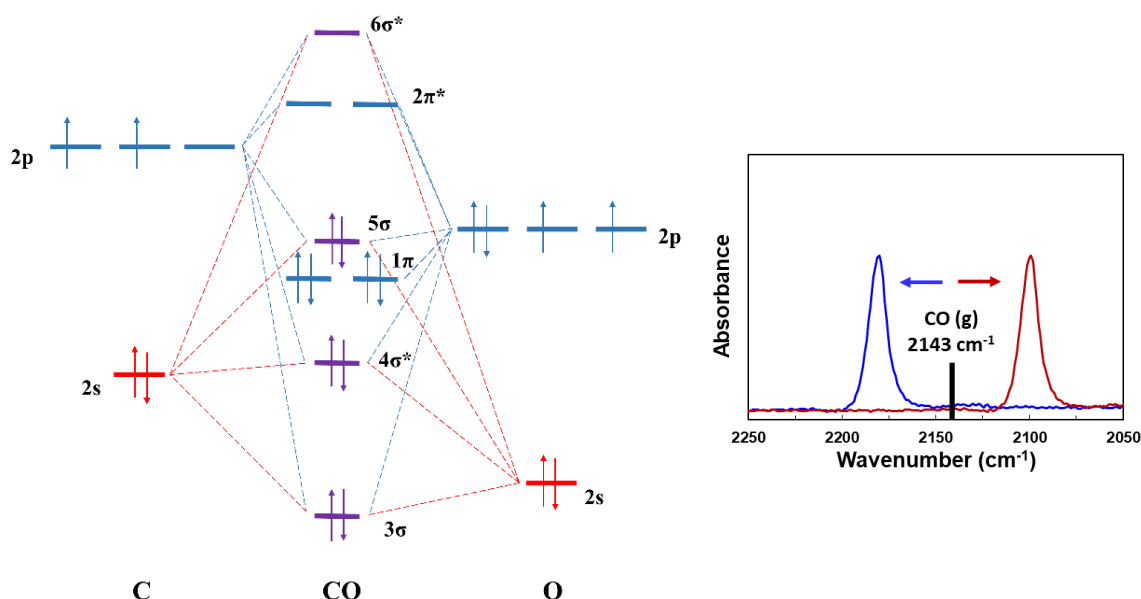


Figure 1.4 Molecular orbital diagram of carbon monoxide (left) and spectroscopic effects of CO adsorption (right) onto surface sites with high (red trace) and low electron density (blue trace).

1.4 CO Oxidation on TiO₂-Based Materials

1.4.1 The Significance of CO Oxidation

CO oxidation is a simple model system for the exploration of reaction mechanisms on complex materials.^{57–59} It allows researchers to investigate adsorption sites and energetics in addition to oxygen activation, one of the most important steps in oxidative catalysis. A single-atom oxidation from reactant (CO) to product (CO₂) allows for a material's reactivity to be closely analyzed to monitor changes to surface sites, identify catalytic active sites, and elucidate atomic movement of adsorbates without being hindered by spectroscopic complexity. The importance of CO oxidation is also shown in areas such

as exhaust stream treatment, energy conversion/storage, and industrial applications.^{60,61} CO oxidation is most studied for next-generation materials to be used in automobile catalytic converters, to reduce the amount of incomplete combustion products that have an adverse environmental and toxic impact. Most materials used for catalytic converters are precious metals with low Earth-abundancy like Pt, Pd, and Rh, which significantly raises the cost. Therefore, cheaper, more Earth-abundant materials for these catalysts are attractive.

1.4.2 Interfacial Reaction Mechanisms on Au/TiO₂

While Au/TiO₂ catalysts have been a focus of studies since the discovery of their catalytic properties, consistent mechanistic understandings for CO oxidation have not been achieved in the field.² In 2011, Yates and coauthors aimed to unravel this shortcoming in their pioneering 2011 low-temperature surface science study which identified O₂ dual-perimeter sites on the Au/TiO₂ catalyst as the active site for CO oxidation.⁵⁸ IR spectroscopy and DFT calculations showed that between 113 K and 133 K, CO adsorbed to Ti⁴⁺ sites at the interface of a metal nanoparticle and metal oxide support. An IR peak at 2179 cm⁻¹ is attributed to CO binding to support metal cation sites and a peak at 2102 cm⁻¹ is attributed to CO binding to metallic gold. Once O₂ is added to the reaction chamber, CO₂ was formed on the catalyst surface with an IR feature appearing in the spectrum at 2341 cm⁻¹. The only CO feature to decrease was the 2179 cm⁻¹ peak attributed to CO on the TiO₂ support, evidence that only CO bound to TiO₂ contributed to the oxidation reaction at the low temperatures studied. DFT calculations attributed the reactive CO on TiO₂ to the relatively high diffusion barrier of CO on Au (>0.5 eV) compared to that on TiO₂ (0.3 eV). The gold nanoparticles are necessary for the activation of the molecular

oxygen at the Au/TiO₂ interface as the reaction does not proceed with pure TiO₂. The results suggest a Langmuir-Hinshelwood mechanism (Figure 1.5A) where both CO and O₂ are adsorbed onto the catalyst before a reaction can occur. Common reaction mechanisms on surfaces are depicted in Figure 1.5.

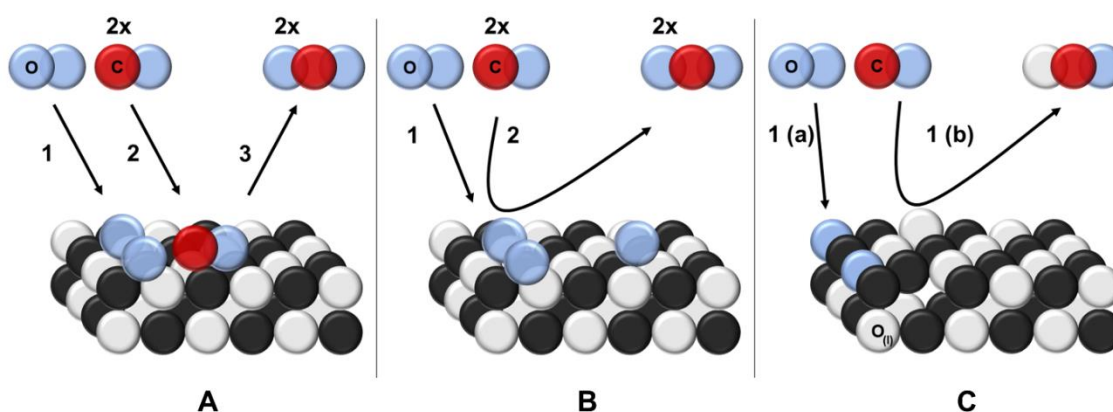


Figure 1.5 (A) Langmuir-Hinshelwood mechanism with adsorbed molecules reacting with one another on a surface, (B) Eley-Rideal mechanism with a gaseous molecule, 2, reacting directly with an adsorbed molecule, 1, on the surface, (C) Mars-van Krevelen Mechanism where a gaseous or adsorbed molecule, 1b, reacts with a molecule incorporated into the surface lattice structure.

While the preceding experiment yielded a critical discovery for the understanding of the CO oxidation mechanism, the study by Yates and coauthors was narrow in terms of thermal range. Widmann and Behm also made an important discovery in 2011 indicating that in an anaerobic environment at 353 K, the CO oxidation reaction proceeds through lattice extraction of oxygen atoms within TiO₂ regions of the material, a Mars-van Krevelen mechanism (Figure 1.5C).¹⁷ Experiments were performed under anoxic conditions monitored by temporal analysis of products (TAP) mass spectrometry. In TAP experiments, a small, well-defined pulse of gaseous reactant molecules is exposed to a

catalyst material and the effluent stream is sampled via mass spectrometry before being removed from the system by high vacuum pumps. The shape and size of the effluent pulse (related to number of molecules) yield information about the dynamics, mechanism, and kinetics of the reaction.⁶² Results indicated that a Au/TiO₂ catalyst exposed to pure CO was able to react and form CO₂. The catalyst that had just undergone 673 K calcination had active oxygen species on the surface that produced more CO₂ upon CO exposure to Au/TiO₂ than subsequent CO doses where the active molecular oxygen was already consumed. Replenishable oxygen was present in the TiO₂ lattice near Au perimeter sites that contributed to the reaction. At high enough temperature, lattice oxygen migration/extraction can replenish some of the perimeter vacancies with an activation barrier of 0.97 eV.⁶³

The highlighted CO oxidation mechanism studies showed a disagreement of determined reaction mechanism depending on the temperature, due to many different activation barriers. In 2016, Widmann and Behm performed further studies to determine a relationship between reaction temperature and mechanism.⁵⁷ Using the same TAP methods as the previous discovery at 353 K,¹⁷ they performed complementary reactions at 393 K, 253 K, and 183 K. At 393 K, electron paramagnetic resonance spectra showed that lattice oxygen was removed, as suggested previously, via the formation of Ti³⁺ sites. Ti³⁺ sites are attributed to new features appearing in the spectra upon CO dosage at $g_L = 1.958$ and $g_I = 1.976$. At the lower temperatures, no Ti³⁺ sites were formed as it is an activated process, and CO could only adsorb to the Au/TiO₂ catalyst without undergoing anaerobic oxidation.

Combining the three studies above can develop a complete understanding of the CO oxidation reaction mechanism on Au/TiO₂. At elevated temperatures, CO binds to Au,

diffuses towards dual perimeter sites of the Au/TiO₂ catalyst, and reacts with either adsorbed molecular oxygen or TiO₂ lattice oxygen to form CO₂ that desorbs from the catalyst surface.^{17,57,58} It is likely that both Mars-van Krevelen and Langmuir-Hinshelwood reactions occur simultaneously, depending on the nearest form of reactive oxygen.⁶⁴ When the temperature is decreased from 253 K to 133 K, CO can bind to TiO₂ and undergo the same reaction at perimeter sites with only molecularly adsorbed oxygen, as lattice extraction from TiO₂ has too large an activation barrier. However, at temperatures lower than 123 K, CO diffusion on Au is an activated process and the reaction only utilizes CO bound to the support.

1.4.3 CO Oxidation on Cu Nanoparticles

The studies of CO oxidation on Cu-based catalysts in the literature are quite controversial. CO oxidation, as mentioned previously, appears to depend strongly on the oxidation state of Cu. However, the specific active form of Cu for reactivity is debated among researchers, even with most in agreement that low-valent Cu is generally preferred.^{24–29} Jernigan and Somorjai studied Cu thin films with different oxidation levels and found that metallic Cu had a higher rate for CO oxidation and lower activation energies than Cu₂O and CuO thin films.²³ Boccuzzi et al. later investigated Cu particles on ZnO and TiO₂ supports.²⁹ They found that certain metallic sites were able to adsorb O atoms and CO simultaneously, and had two independent routes for CO oxidation. One pathway involved gaseous oxygen reacting with CO adsorbed at either terrace or perimeter Cu sites and the other involved CO interacting with lattice O to form a carbonaceous intermediate prior to complete oxidation to CO₂. Interestingly, the presence of O₂(g) was necessary for

the formation of the formate intermediate, indicating an inductive effect of $O_2(g)$. In the work of Chen et al., Cu/TiO₂ was employed for CO oxidation and found that Cu²⁺ was the main factor in determining activity at 473 K.²⁶ The activity of Cu/TiO₂ was not enhanced by increasing the Cu surface area (1.22-3.19 m²/g) or the Cu content (3.7-10.3 wt%). Another study by the same authors then investigated the role of Ti³⁺ on the oxidation state of Cu and CO oxidation activity.²⁴ Chen et al. proposed that calcination of the Cu/TiO₂ catalyst induced electronic interactions between the metal NP and the support oxide, with Ti³⁺ reducing Cu sites in the following charge transfer: $Cu^{2+} + Ti^{3+} \rightarrow Cu^{1+} + Ti^{4+}$. The charge transfer was observed to occur with increasing temperature, with Cu²⁺ sites agglomerating into CuO particles at 438 K and then reducing to Cu₂O at 498 K. The formed Cu¹⁺ and its reduction is a major contributor towards CO oxidation.

Wu et al. then synthesized Cu/TiO₂ with varying techniques including wet impregnation and photodeposition.²⁸ They claimed that photodeposition of Cu left the surface with native Cu¹⁺ and Cu⁰ sites, while the impregnation method left surface Cu²⁺ that were later reduced to Cu⁰. A Langmuir-Hinshelwood mechanism was proposed where cooperation between Cu₂O and Cu⁰ was necessary for the stabilization of adsorbed CO and O. Additionally, H₂O was shown to deactivate the catalyst for CO oxidation through competitive adsorption with reactants.

Studies of a Cu(111) surface by Eren et al. concluded that the reduction of the model catalyst to the form of a partial surface Cu₂O layer enhanced the CO oxidation activity.²⁵ Significantly, no CuO was observed, and Cu⁰ sites suffered oxygen poisoning due to a stronger implied adsorption energy compared to CO. The introduction of Ce into Cu/TiO₂ catalysts was determined to increase the turnover frequency and decrease the E_a for CO

oxidation through interactions with high electron density Ce^{3+} .²⁷ The authors proposed that Cu-CeO₂ interactions increased the Ce^{3+} concentration and number of oxygen vacancies present, resulting in increased catalytic rate by activation of O₂ as the O supplier for oxidation of CO. Cu^{1+} is also likely to be stabilized by the electronic interactions with CeO₂ regions of the catalyst. In all, the works of CO oxidation on Cu and Cu/TiO₂ show complex results that often conflict with one another.

To try and solve some of the issues of unstable low-valent Cu species, DeSario et al. synthesized a Cu/TiO₂ aerogel catalyst material that utilized extended nanoscale junctions through multiple points of interfacial contact between the Cu and TiO₂ for oxidation state stability.³⁶ The material was analyzed for CO oxidation and was determined to be active for CO oxidation at temperatures below 373 K, but had higher activation energies than previous Cu-based materials ($E_a = 61.2\text{-}63.9$ kJ/mol).⁴⁴ Cu-based catalysts with the stability of low valent oxidation states and low temperatures of activity are rarely reported in the literature and are therefore a prime candidate to probe the activity of the catalyst in depth.

1.5 Effect of Water on Au/TiO₂ Catalytic Activity

After exploring how structure and morphology impact catalysis on gold, the focus was expanded to examine how co-dosed molecules can affect reactivity on TiO₂-supported NPs. Water is an extremely important molecule in almost every field of study, and heterogeneous catalysis is not excluded. Early studies were able to show that the amount of water in the reactant gas mixture affected the rate and conversion of the CO oxidation reaction on Au/TiO₂.⁶⁵ The discovery of the promotional effects of water during catalytic

oxidation reactions opened the field to study how water affects the reactivity of metal oxide supported AuNPs. A previous review on the topic determined that the key roles of water in the enhancement of catalytic activity include both assisting in the activation of molecular oxygen and the creation (and prolonged lifetime) of charged cationic gold species.⁶⁶

CO oxidation on Au/TiO₂ was found to produce more CO₂ with water (up to 200 ppm) present in the reactant stream.⁶⁷ Daté and Haruta studied concentrations ranging from 1 to 6,000 ppm and discovered that water concentrations above 200 ppm would inhibit CO₂ production compared to a reference absent water. The authors attributed the increased activity to moisture activating molecular oxygen at dual perimeter sites, where activation occurred specifically at oxygen vacancies of the support oxide. The small concentrations of adsorbed water were determined to be the limiting reagent, as only surface-bound water (not vaporous) modifies the catalyst surface and influences the activity. Temperature programmed reduction and microreactor flow cell studies also detected exclusively adsorbed moisture affecting reactivity, adding to the understanding that adsorbed water affects the electronic state of the AuNPs.²² Authors attributed the observed electronic structure effects to H₂O and OH⁻ preventing the reduction of Au, maintaining the noble metal in its partially cationic state.

Hydroperoxy intermediates have also been proposed as the active oxygen on the Au/TiO₂ catalyst.^{68,69} Isotopic and kinetic measurements clarified a potential mechanism where only on the AuNPs does adsorbed H₂O interact with adsorbed O₂ and form active -OOH to react with CO to form adsorbed CO₂ and OH. Two hydroxyls then interact to form a surface-bound water molecule available to undergo activation again and a reactive oxygen atom that can oxidize CO.⁶⁸ Later DFT calculations provided evidence supporting

the above mechanism, where increased binding and activation of O₂ on Au clusters was determined through modeling co-adsorption of H₂O with CO and O₂.⁶⁹ The weakened O-O bond showed peroxy-like characteristics and could react by either Eley-Rideal or Langmuir-Hinshelwood type mechanisms (depicted in Figure 1.5).

Further investigations have shown that the water-assisted creation of cationic gold species plays a key role in the enhanced catalytic activity on oxide-supported gold nanoparticles.^{21,70} XPS measurements coupled with reaction data revealed that oxidized Au was more active than metallic Au for CO oxidation.⁷⁰ Without water present, the AuNPs were reduced to metallic gold during the reaction. Conversely, cationic gold species like Au(OH)₃ and Au₂O₃ persisted after the reaction when water was present. The authors concluded that water on the catalyst surface contributed toward suppression of Au reduction throughout the oxidation reaction. A similar study on Au/CeO₂ came to the same conclusion, adding that the generated Au⁺ site is more energetically favorable for CO adsorption.²¹ The active Au⁺ species can then preferentially bind CO and the mobile Au-CO complex can more readily diffuse to and across perimeter sites to react with active oxygen.²⁰ Hare et al. also discovered hindered activity on metal NPs (a Pt/ γ -Al₂O₃ system) due to the presence of water.⁷¹

1.6 Alcohol Oxidation on Supported Gold Nanoparticles

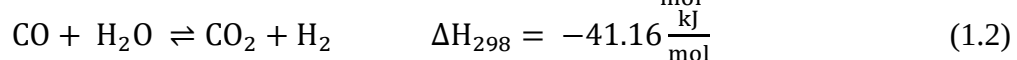
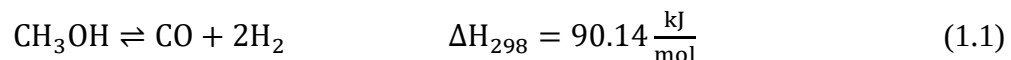
Methanol reactivity is important for both industrial applications and green processes (production of H₂ for fuel cells) and in the gas phase for CWA decomposition, with many chemical simulants containing methoxy groups (see Chapter 1.7). As the oxidative reactant molecule increases in complexity, from CO to methanol, studies start to

show inconsistent results in a very complex picture. Methanol oxidation was studied using DFT calculations, high-resolution electron energy loss spectroscopy (HREELS), and thermal desorption spectroscopy (TDS) on Au/TiO₂.⁷² The adsorption of O₂ changes the electronic structure of the surface via a charge transfer to molecular O₂ from a perimeter gold atom. CO was used to as a probe to characterize the catalyst with HREELS, and showed agreement with previously discussed results. CO is highly sensitive to the electronic structure of the material it is adsorbed to, making it an excellent probe molecule. HREELS spectra before and after O₂ adsorption to a CO-saturated surface resulted in a peak shift from 2104 to 2136 cm⁻¹, indicating a charge transfer from the 5σ orbital of CO to Au. The charge transfer occurred when Au donated electron density to the co-adsorbed O₂ and the CO molecule was sensitive to that electronic structural change. TDS data from the same study revealed that the oxidation of methanol is highly selective towards formaldehyde and water production, and only proceeds when O₂ is adsorbed prior to catalyst exposure to methanol. Without pre-adsorbed O₂, methanol binds to dual perimeter sites at the Au-TiO₂ interface and prevents the adsorption of oxygen for activation. No reaction occurs as lattice oxygen removal from TiO₂ is too activated (0.97 eV) to occur at 95 K.⁶³ Thus, the authors proposed a mechanism that begins with the adsorption of O₂ to dual perimeter sites. Methanol then co-adsorbs to react directly on top of molecular oxygen on the metal oxide support to form a Au-stabilized CH₃OH-O₂ intermediate, via an Eley-Rideal mechanism (depicted in Figure 1.5b). Subsequent oxidation forms formaldehyde from CH₃O, where Au acts as a hydrogen storage material to accept H atoms from methanol. Lastly, H atoms migrate on the AuNP until they encounter an activated O atom

to form OH, which can react with another adsorbed hydroxyl to both form water and regenerate the active O atom.

Another study that investigated methanol reactions over different gold loadings of Au/TiO₂ found that instead of formaldehyde and water selectivity, the reaction was very selective towards CO production and, to a lesser extent, CO₂ at high temperature (573 K).⁷³ Au/ZrO₂ and Au/ZrO₂-TiO₂ catalysts were also studied and were conversely selective towards H₂ and CH₄ production. 3% wt loading of Au on Au/TiO₂ was the second-highest performing catalyst in terms of methanol conversion at most temperatures.

Related studies have shown that the change of textural properties and surface chemistry account for many of the differences in product selectivity, and gold loading and particle size play a less significant role.⁷⁴ The work of Ramírez et al. similarly revealed different selectivities after the catalysts were shown to have different bandgap energies, BET surface areas, and pore size and volume as characterized by UV-VIS spectroscopy and N₂ adsorption-desorption, respectively. The authors claim that the methanol oxidation over Au/TiO₂ undergoes different mechanisms with changing temperatures, similar to results discussed for CO oxidation.⁵⁷ At temperatures below 513 K, mainly dissociatively adsorbed surface methoxy species and unreacted adsorbed methanol were observed. Upon increasing temperature to 543 K, Lewis acid sites were the main active sites for the water shift reaction to produce CO₂. At temperatures approaching 573 K, a combination of methanol decomposition (Equation 1.1) and the water-gas shift reaction (Equation 1.2) leads to the highest conversion of methanol to CO and CO₂.

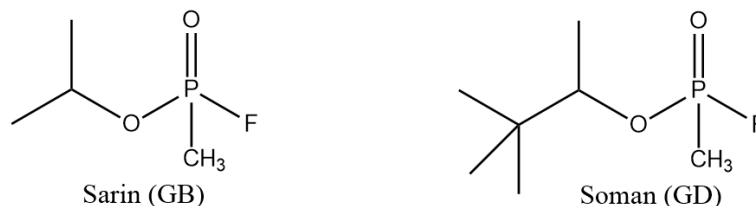


Unlike the study from Camellone et al.,⁷² there were no detectable quantities of formaldehyde formed, nor the byproduct methyl formate. Significantly, neither spectroscopic methods nor temperature programmed desorption experiments were performed to determine surface-bound products in these studies.

1.7 Decomposition of Chemical Warfare Agents on TiO₂-Based Materials

Despite the numerous studies on TiO₂-based catalysts as described, there are very few studies that use the material for the decomposition of chemical warfare agents, like sarin gas, despite promising results. The oxidative activity alone indicates Au/TiO₂ is an interesting catalyst to study CWA decomposition reactions, as oxidative processes are the main decomposition pathway for many compounds.⁷⁵ In addition, the role of water previously discussed might allow for methanolysis/hydrolysis to occur for certain CWAs. Because of the toxicity of CWAs, chemical simulants that pose much less of a safety hazard are often used in studies. These simulants have a very similar structure to the CWA while being far less toxic, as shown in Figure 1.6. Multiple simulants can even be used to generate a structure-function relationship to predict the interactions that a material will have for the CWA.

Chemical Warfare Agents (CWAs)



Common Chemical Simulants

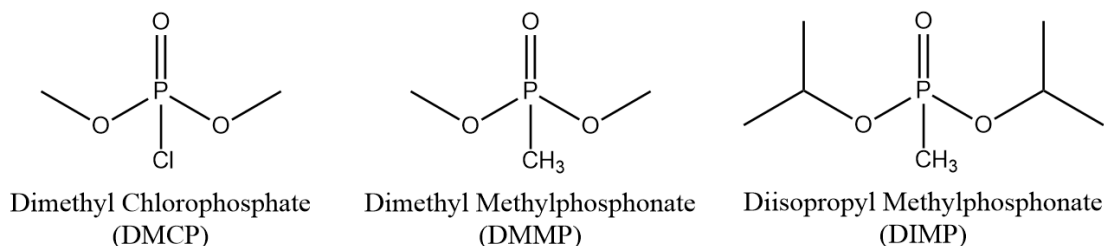


Figure 1.6 Structure of the nerve agent sarin and soman, with some commonly studied chemical simulants.

Panayotov and Morris studied the adsorption and reaction of the sarin simulant dimethyl methylphosphonate (DMMP) on anatase TiO_2 ^{76,77} and Au/TiO_2 .⁷⁸ In the first principal adsorption studies of DMMP on commercially available TiO_2 , Panayotov and Morris used FTIR spectroscopy to determine that two adsorption processes occur. Thermally reversible physisorption occurred via an interaction between surface hydroxyls and the P=O group in DMMP, and reactive chemisorption then occurred via interaction between coordinatively unsaturated Ti Lewis acid sites (Ti^{4+} , Ti^{3+} , Ti^{2+}) and the same P=O group. The reactive chemisorption resulted in a poisoned catalyst, however.⁷⁶ In addition, the main adsorption site was found to depend on the degree of hydroxylation of the surface. The main reaction pathway at moderate temperatures of 295 K to 400 K involved nucleophilic attack of an adsorbed DMMP molecule from adjacent oxygen in the TiO_2

lattice.⁷⁷ The reaction results in a surface-bound methoxy species (to a Ti atom) as well as various surface-bound P-O_x groups including methyl methylphosphate (MMP) and methylphosphate (MP) above 413 K.

A study by the same authors then used Au/TiO₂ to investigate DMMP decomposition.⁷⁸ Similar results to pure TiO₂ were observed, but key differences appeared in the further decomposition of carbon-containing DMMP breakdown products. Where pure TiO₂ stopped at the production of surface-bound methanol, Au/TiO₂ could further oxidize these species to form CO and CO₂. Under anaerobic conditions, lattice oxygen around the periphery of AuNPs was the active species for reaction, which happened upon adsorption to form mainly CO and various P-containing products. Hydrolysis also occurred along the perimeter of Au to form surface-bound methanol. The formation of CO and formate oxidation products suggested that Au promotes lattice oxygen extraction, and oxidation proceeds until accessible surface oxygen is depleted. Aerobically, a charge transfer from Au to an adsorbed O₂ molecule generates the active oxygen species to react with DMMP physisorbed on TiO₂ to fully oxidize carbon-containing species to CO₂. The charge transfer was experimentally determined using CO as a probe molecule to track spectroscopic changes in the electronic structure of Au. An IR blueshift from 2086 cm⁻¹ to 2130 cm⁻¹ shows the change from Au⁰ to Au^{δ+} as more electron density is donated from the CO molecule to Au^{δ+}.

Working with the actual CWAs instead of simulants, a DFT study of sarin adsorption onto TiO₂ showed a strong relationship between the interacting surface facet and binding strength, as (001) surfaces showed much stronger binding than the (101) surface of TiO₂.⁷⁹ Reversibility of binding is generally required for catalysis, and the work

by Le et al. provided an important preference for surface facets that improve synthetic methods of the TiO_2 containing catalysts. Also utilizing pure agents, Petrea et al. mixed the heterogeneous Au/TiO_2 catalyst with a homogeneous La^{3+} catalyst to decompose sarin and soman nerve agents in the liquid phase.⁸⁰ The La^{3+} - Au/TiO_2 mixed catalyst method outperformed both La^{3+} and Au/TiO_2 alone for the visible light irradiated defluorination of soman and sarin under low basic conditions. Importantly, the defluorinated decomposition products are much less toxic than their parent compounds.

In similar materials with a nanostructured support oxide, Cu/TiO_2 aerogels were directly compared to both TiO_2 and Au/TiO_2 aerogels for the decomposition of DMMP by McEntee et al.⁸¹ The Cu/TiO_2 aerogel exhibited enhanced hydrolytic activity for adsorbed DMMP compared to the other materials, and that the unique interface between the aerogel and Cu stabilizes active OH sites through a NP-support charge transfer pathway. Reaction products include bound OCH_3 groups and the singly and doubly hydrolyzed DMMP, as well as a bidentate phosphoryl species. Au/TiO_2 aerogels were not able to stabilize terminal OH (OH_t) groups as effectively as the Cu analog. The basic OH_t groups were observed to be responsible for the nucleophilic attack on DMMP through an OH_t/OH_b (or terminal-to-bridging OH) loss ratio of 3-4:1 for Cu/TiO_2 aerogels compared to a 2.5:1 loss ratio for Au/TiO_2 aerogels. The enhanced ability for Cu/TiO_2 to activate OH at the NP-oxide interface was explored, while the researchers also found evidence that the Au/TiO_2 interface does not dissociate molecular H_2O to the active OH_t groups. The extent of H_2O dissociation was reduced after Au NPs replaced Cu on TiO_2 , as shown in other investigations.⁸²

Similar hydrolytic decomposition pathways on Cu/TiO₂ aerogel surfaces were observed with the full CWA sarin in recent studies through the reactive loss of both terminal and bridging OH groups.⁸³ DRIFTS data indicated the loss of the P-F bond in sarin, leading to initial decomposition products IMPA or MPA. Hydrolysis also occurred to leave surface isopropoxides on the catalyst surface. In an O₂-containing atmosphere, removal of the P=O moiety of adsorbed sarin for O-P-O or PO_x species is enhanced relative to an inert atmosphere. The addition of broadband (BB, UV, and visible) light caused the Cu/TiO₂ aerogels to become more active for sarin decomposition. Rates of P-CH₃ and P=O removal were increased with the introduction of the BB light. More complete removal of P=O suggested more mineralized phosphorus-containing products on the surface as they were oxidized to O-P-O or PO_x. Additional reaction products including CO, CO₂, acetone, and other carbonaceous species (formates, carbonates, and/or carboxylates) were also observed, underscoring the complex reactivity of the Cu/TiO₂ aerogels. These pathways are not well understood, however. Focused surface-based experiments are needed to elucidate the mechanisms of oxidation and hydrolysis of these surface species. Only with mechanistic understandings can the underlying causes of catalytic activity be exploited through targeted synthetic materials design.

1.8 Specific Aims and Overview

Oxidative heterogeneous catalysis at the gas-surface interface can be carefully studied through the utilization of *in situ* spectroscopic and spectrometric techniques. This thesis focuses on uncovering the underlying mechanisms that drive oxidative catalysis on a Cu/TiO₂ aerogel material. Experimental approaches and the instrumentation utilized are

described in detail in Chapter 2. Most of the studies presented were performed in a stainless-steel high vacuum chamber equipped with infrared spectroscopy. However, a custom-built ambient pressure packed-bed reactor was designed and coupled with both mass spectrometric and IR spectroscopic detection methods for real-time product analysis is also described.

Chapter 3 explores investigations of electronic interactions at the nanoparticle/support interface with variable-temperature infrared spectroscopy (VTIR). VTIR is described in detail and used on several TiO_2 -based materials to elucidate the role of the supported metal nanoparticles as well as the nanostructure of the support, and how they influence interfacial charge transfer. Cu/TiO_2 aerogels are identified as a candidate for further investigations.

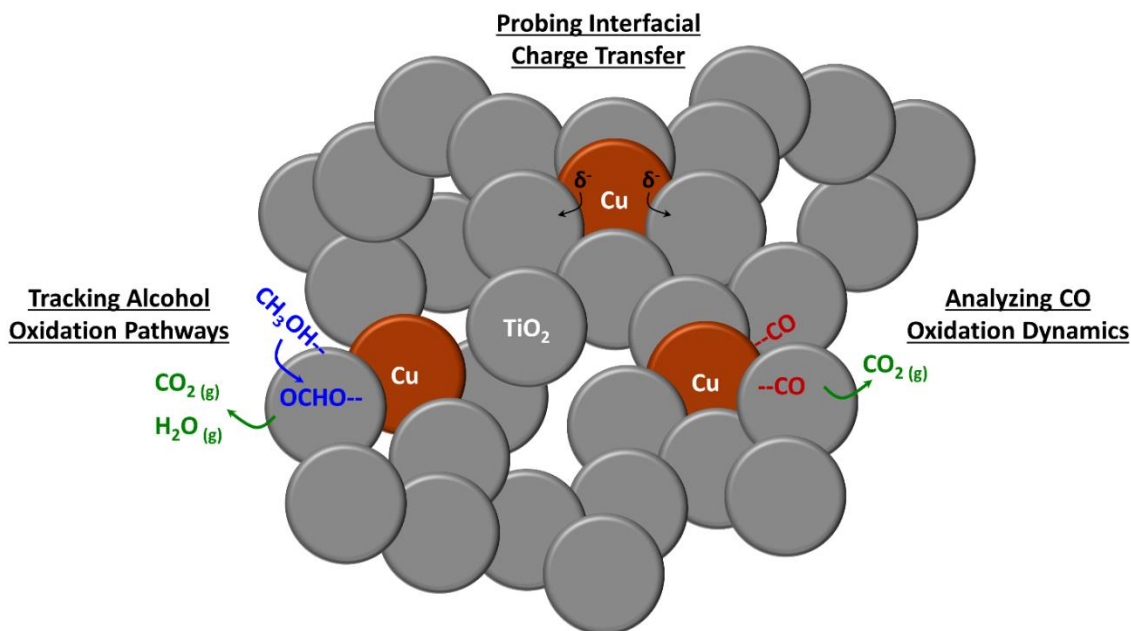


Figure 1.7 Schematic description of Chapters 3-5 including the probing of interfacial charge transfer, the analysis of CO oxidation, and the tracking of methanol oxidation on Cu/TiO_2 aerogels

Chapter 4 aims to both characterize the complex mixture of surface sites and elucidate the CO oxidation mechanism on the Cu/TiO₂ aerogel materials. Here, IR spectroscopy is used to identify various distinct Cu and Ti surface sites, and the packed-bed reactor indicates that the material is active for CO oxidation. Further surface studies are performed to find out where the CO oxidation reaction takes place and how the catalyst material is affected by the reaction.

A more complex oxidation mechanism is then analyzed in Chapter 5, focusing on methanol oxidation. With the previous chapter describing how a simple oxidation mechanism proceeds on Cu/TiO₂ aerogels, this chapter looks for similarities and differences in the reactivity of an alcohol and tracks the surface species in addition to gaseous products.

Chapter 6 builds upon the insights gained in Chapter 5 by examining the 2-propanol (and other alcohols) partial and complete oxidation on Cu/TiO₂ aerogels. Here, further studies are performed focusing on the Cu-localized binding of various alcohols and linking a stronger adsorption strength on Cu to a partial oxidation pathway that is not available to alcohols with weaker binding interactions with the Cu NPs.

Chapter 7 then describes the adsorption and reaction of the chemical warfare agent simulant dimethyl chlorophosphate (DMCP) over the same CuTiO₂ aerogel material. Surface-based studies investigate the promotional effects Cu has on the dissociative adsorption towards decomposition products including CH₃Cl, CO₂, and surface formates.

Finally, Chapter 8 summarizes the results and conclusions of the dissertation and provides future directions for the expansion of the works presented. Each of these goals

aided in the development of a fundamental understanding of surface-based reaction mechanisms and molecular processes on oxide-supported metal nanoparticles that are important for defense, industrial, and environmental applications. The key findings can be important in the synthesis and development of effective next-generation catalysts.

Chapter 2

Experimental Approach for Studying Interactions and Catalysis at the Gas-Surface Interface

2.1 Experimental Considerations

The overall objective of this research is to analyze how different properties and materials affect fundamental gas-surface interactions including adsorption and reactivity. A key component to studying these interactions is the use of ultra-high vacuum (UHV)-based surface science instrumentation. Instruments that allow for UHV environments have provided important information to scientists that involve the characterization and tracking of molecules at surfaces and interfaces.⁸⁴⁻⁸⁷ Fourier transform infrared spectroscopy (FTIR) and quadrupole mass spectrometry (QMS) are powerful tools that will be used in these environments to study the relevant gas-surface interactions. As the “pressure gap” between UHV and more relevant ambient pressures is large and can lead to inconsistent experimental findings between the two environments, custom-built instrumentation is utilized to bridge the gap and understand the important fundamental interactions. Briefly, a UHV chamber is used to provide *in situ* spectroscopic characterization of both surface-adsorbed species and gaseous species, while allowing for a variable pressure environment and a wide range of available temperatures. In addition, an ambient pressure packed-bed flow reactor was developed to monitor gas streams and track both reactants and products in real-time as they interact with a material or catalyst of interest. The goal of this chapter is to provide the relevant information for the techniques that are utilized throughout this dissertation.

2.2 Ultra-High Vacuum Chamber and Sample Mount

The UHV chamber utilized for most of the studies presented in this work is represented schematically in Figure 2.1. The main reaction chamber is a 9 cm diameter spherical stainless-steel vessel (Kimball Physics) that includes 14 Conflat® (CF) flange ports (6x 4.5” flange, 8x 1.33” mini flange) for the introduction of gas/vapor molecules, samples, vacuum pumps, and other instrumentation. A magnetically levitated turbomolecular pump (400 L/s, Pfeiffer HiPace 80) rests underneath the main chamber and is separated by a pneumatic gate valve to separate the sample and gas/vapor molecules from the vacuum pump. The pressure of the chamber is monitored via a cold cathode ionization gauge (Pfeiffer FullRange) located between the spherical chamber and the pneumatic gate valve. It is important to note that the gauge can ionize gases that can go on to do chemistry within the chamber, so it must be turned off before any gases are introduced to ensure that observations are due to gas-surface chemistry and not from the ionization gauge. An additional small auxiliary chamber is directly connected to the main chamber to house the quadrupole mass spectrometer (SRS300 residual gas analyzer) to allow for line-of-sight detection of gas-phase species that desorb from the sample surface. The auxiliary mass spectrometer chamber is separated from the main chamber by a manual gate valve (VAT Valve). While the instrument has the RGA analyzer, it was not used in the studies presented in this work. An aluminum framework (80/20 Inc.) is used to mount the apparatus. Details of the UHV cell can be found in previous work.⁸⁸

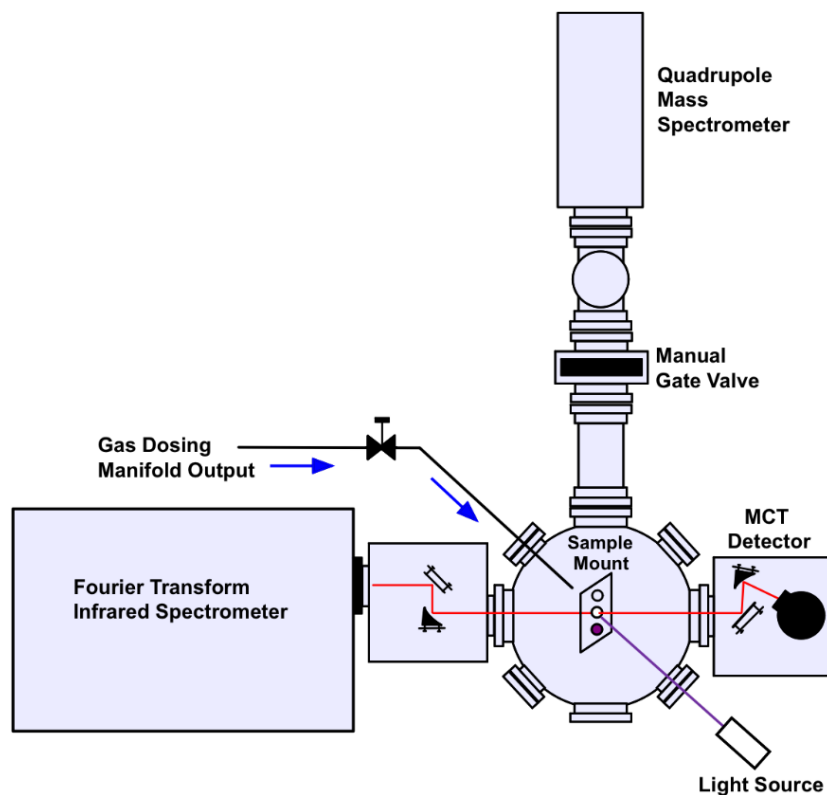


Figure 2.1 Schematic of the ultra-high vacuum chamber. The main chamber contains the sample. The FTIR and optics enclosures are not held under vacuum.

A custom-designed sample mount utilizes stainless steel clamps to secure a 0.050 mm thick tungsten mesh. Samples are pressed as 7 mm discs into the voids of the W grid (Tech-Etch, 0.20 mm square holes spaced 0.254 mm apart). Methods such as aerosol deposition or drop-casting can also be used to introduce samples onto the W mesh. A K-type thermocouple is spot-welded onto the mesh directly above the samples to monitor the sample temperature and used as a feedback loop to an external power source. The stainless-steel support clamps are attached to Cu leads, which allow for resistive heating with an applied current from the external power source to provide temperature control. Cooling of the copper leads and mesh can be provided by the addition of liquid nitrogen to an insulated reservoir that acts as a heat sink. A working temperature range of the sample lies between

95 K and 1000 K when using the liquid nitrogen cooling and resistive heating. The sample holder is mounted onto an external precision manipulator (McAllister) for vertical alignment with the infrared beam and translation for detection of both samples and the blank mesh under the same conditions.⁸⁹ A pinhole aperture that is located below the W grid and in line with the sample position (not pictured) is used to align the infrared light by locating the path of the beam within the chamber. A schematic representation of the sample mount is provided in Figure 2.2.

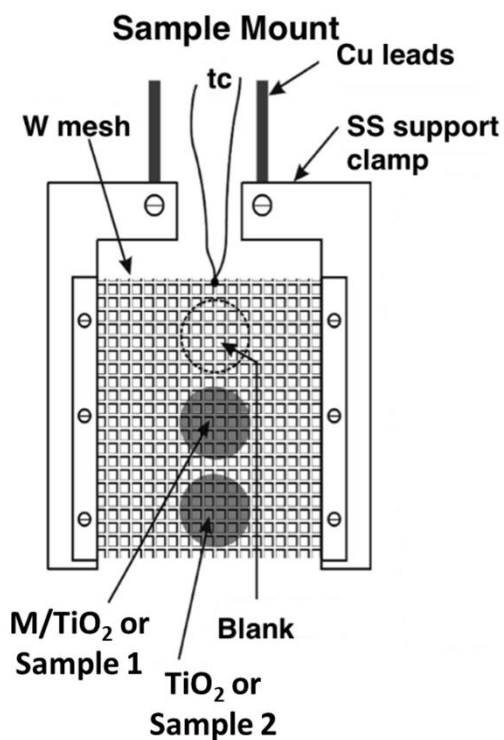


Figure 2.2 Schematic representation of the sample mount used within the vacuum chamber.

2.3 Infrared Spectroscopy

Fourier transform infrared spectroscopy (FTIR) is incorporated in the apparatus for the detection of surface species as well as gaseous compounds during experimental operation. FTIR is capable of characterizing solids, liquids, and gases based on characteristic vibrational frequencies of chemical functional groups. FTIR can also effectively elucidate atomic-level vibrational features on/in materials to evaluate changes in a chemical system. Specifically, bond formation and cleavage events can be detected and characterized at the gas-surface interface with infrared spectroscopy. Spectra are acquired before, during, and after the exposure of gas molecules onto the sample to observe the chemical events occurring.

A Thermo Nicolet Nexus 470 FTIR spectrometer is affixed to the UHV chamber system (see Figure 2.1). Two of the 4.5" CF flanges are equipped with KBr windows (International Crystal Laboratories) to allow for the transmission of infrared light through the chamber. The infrared light is originated from a SiC source, progresses through the interferometer, and is focused through a set of mirrors toward the KBr window and into the vacuum chamber. The entrance optics enclosure contains one parabolic mirror (Thor Labs, 228.6 mm focal length) and one flat mirror (Edmund Optics) that are attached to micrometer stages (Newport) for fine focusing adjustments. The IR light then transmits through the thin W grid (either through the pressed sample or the blank spot in the mesh), through the other KBr window, and into another set of mirrors within the exit optics enclosure that directs the beam into an external mid-range ($650\text{-}4000\text{ cm}^{-1}$) mercury-cadmium-telluride (MCT) detector that is liquid-nitrogen cooled. The exit optics enclosure contains another Edmund Optics flat mirror and a parabolic mirror (Thor Labs, 152.4 mm

focal length) to reflect and focus the light onto the MCT-A detector. Both optics components and the FTIR spectrometer are dry-air purged (Parker Balston Spectra 30) to remove residual gaseous and vapor molecules in the path of the IR beam outside of the UHV chamber. Representative spectra for Cu/TiO₂ and TiO₂ aerogel materials are shown in Figure 2.3.

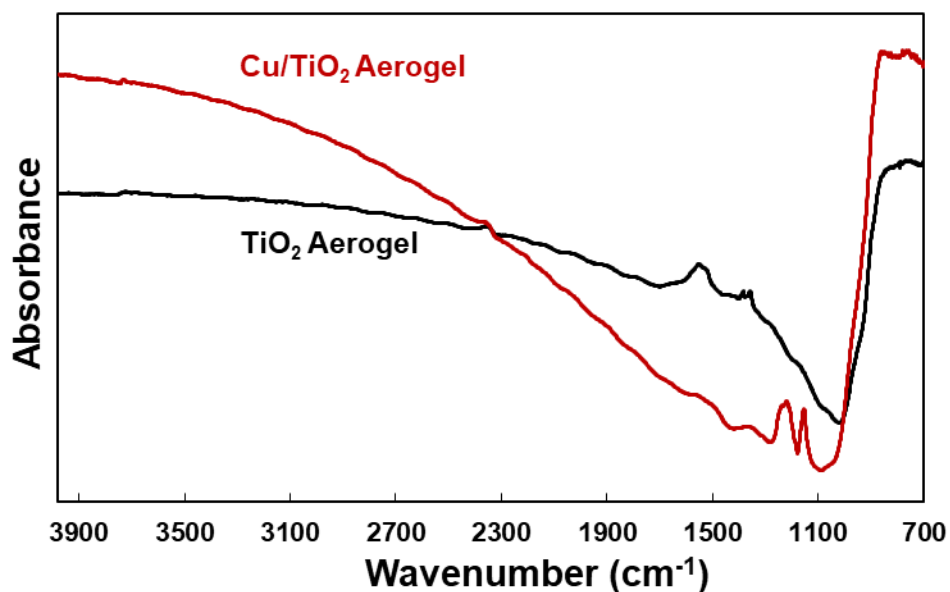


Figure 2.3 FTIR spectra of Cu/TiO₂ (red) and TiO₂ (black) aerogels after thermal treatment in O₂.

2.4 Variable-Temperature Infrared Spectroscopy

Defining and quantifying the adsorption energetics of gas molecules to different surface sites is crucial to understanding site-dependent characteristics of adsorption. Variable-temperature infrared spectroscopy (VTIR) measurements analyze gas-surface interaction energetics to yield adsorption enthalpies at discrete binding sites.⁹⁰ VTIR requires a fixed partial pressure of gas molecules interacting with a sample material within

a closed vacuum system. A consistent number of gaseous molecules in the chamber is needed to evaluate the equilibrium between free gas molecules and surface adsorbed molecules with infrared spectroscopy. Indicative infrared absorbance bands monitored at discrete temperatures give the relative number of adsorbed molecules, as per Beer-Lambert's Law shown in Eq. 2.1

$$A = bN \text{ and } A_M = bN_M \quad (2.1)$$

where A is the integrated absorbance of the IR absorbance band, A_M is the integrated absorbance of the IR absorbance band at full coverage, N is the number of adsorbed molecules, N_M is the number of adsorbed molecules at full coverage, and b is the proportionality constant related to the path length and molar absorptivity. IR absorbance bands need to fall within the Beer-Lambert's law regime for the relation to hold. The van't Hoff equation relates the equilibrium constant for gaseous adsorption to temperature, as follows in Eq. 2.2

$$\ln K(T) = \left(-\frac{\Delta H_{ads}^o}{RT} \right) + \left(\frac{\Delta S_{ads}^o}{R} \right) \quad (2.2)$$

where R is the gas constant, T is the temperature, ΔH_{ads}^o is the standard adsorption enthalpy, and ΔS_{ads}^o is the standard adsorption entropy. Further, the Langmuir equation relates the equilibrium constant to surface coverage of the adsorbed molecules (N/N_M), and the pressure of the gas (P) as shown in Eq. 2.3.

$$\frac{N}{N_M} = \frac{K_{eq}(T)P}{1 + K_{eq}(T)P} \quad (2.3)$$

Combining equations 2.1, 2.2, and 2.3 gives Eq. 2.4 relating the infrared absorbance to the enthalpy and entropy of adsorption to a discrete binding site at a specific temperature.

$$\frac{A}{A_M} = \frac{\exp\left(-\frac{\Delta H_{ads}^o}{RT}\right) \exp\left(\frac{\Delta S_{ads}^o}{R}\right) P}{1 + \exp\left(-\frac{\Delta H_{ads}^o}{RT}\right) \exp\left(\frac{\Delta S_{ads}^o}{R}\right) P} \quad (2.4)$$

Assuming the ideal gas law ($P=N_{Total}RT/V_g$), that P is low ($A_M \gg A$), and that the ΔH_{ads}^o is constant over the evaluated temperature range, the integrated absorbance A can be related to the adsorption enthalpy at each temperature as shown in Eq 2.5.

$$\ln\left(\frac{A}{T}\right) \approx A_M \left(\frac{N_{Total}RT}{V_g}\right) \exp\left(\frac{\Delta S_{ads}^o}{R}\right) \exp\left(-\frac{\Delta H_{ads}^o}{RT}\right) \quad (2.5)$$

To simplify, constant terms can be combined to yield the proportionality of Eq. 2.6 that is used to evaluate the ΔH_{ads}^o .

$$\ln\left(\frac{A}{T}\right) \propto \left(-\frac{\Delta H_{ads}^o}{RT}\right) \quad (2.6)$$

2.5 Ambient Pressure Packed-Bed Flow Reactor

An ambient pressure packed-bed flow reactor was developed to conduct real-time characterization of gas streams flowing over a catalyst bed under controlled conditions. The flow cell methodology acts as a complementary method to the variable pressure chamber, where a potential catalyst can be exposed to a constant stream of reactants to track metrics like conversion and selectivity while identifying all gaseous compounds (reactants and products) that interact with the sample material. Two different reactor systems were used in the following works. One was a custom-built system utilized in the studies presented in Chapter 4, while a commercially available system was used in Chapters 5, 6, and 7. The reactors perform the same fundamental task but differ mainly in the temperature control methods and vapor introduction cells. The custom-built system will

be described herein, as the commercial system (Altamira Instruments, μ BenchCAT) is very similar (just without the mixing cell and second sample cell). The detection methods are the same for both reactors. Figure 2.4 shows a schematic for the custom-built reactor system.

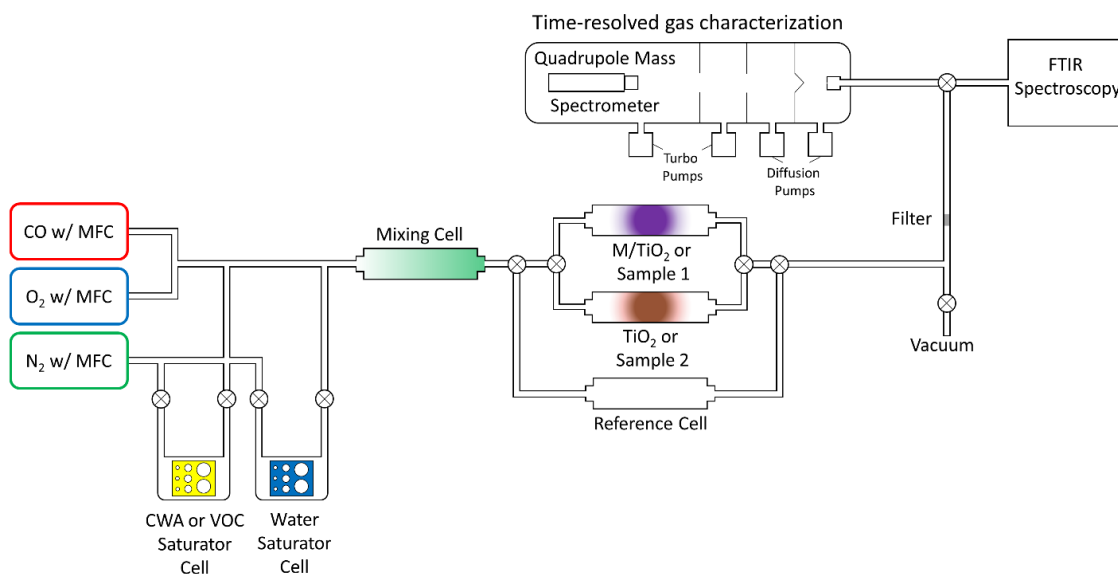


Figure 2.4 Schematic of the custom-built ambient pressure packed-bed flow reactor with two detection methods.

The custom-built reactor controls gaseous reactant flow into the system with mass flow controllers (50 SCCM MKS, 100 SCCM MKS). Stainless steel tubing (1/4" OD) fitted with Swagelok® connections are used to carry the gas streams between components in the flow cell. Glass saturator cells (Glassblowers.com, 30 mm x 50 mm) are used to saturate the gas stream with a vapor such as a CWA or volatile organic compounds. The saturator cells are held at consistent temperatures with circulating water chillers (Polyscience 1160A, 6L). Adjusting the temperature of the liquid in the saturator cell affects the amount of vapor that will make up the gas stream. A glass vapor mixing cell was added in line to

allow for gases and vapors to thoroughly mix prior to sample exposure. The packed catalyst bed is placed in a 1/4" diameter quartz tube and secured with quartz wool on both sides. Temperature is monitored with a K-type thermocouple. The quartz reaction cells are surrounded by a coil of nichrome wire to adjust sample temperature, backed by a VARIAC transformer to supply power and a PID controller (Omega, platinum series) to adjust the applied current to the wires for stable cell temperatures. A diaphragm vacuum pump (Vacuubrand, 1 L/s) is available for evacuation of parts of the gas handling and sample system to assist in sample pretreatments and purging of the lines. Two different detection methods are utilized in the flow reactor; a differentially pumped QMS (ABB Extrel MEXM) is available for m/z scanning and single ion monitoring of the effluent gas stream and an FTIR spectrometer (Thermo, Nicolet Nexus 870 FTIR) is available for spectroscopic detection of the gas mixture.

The reactor system coupled to the QMS has been benchmarked by analyzing the conversion of CO oxidatively to CO₂ over a Cu/TiO₂ aerogel material as was first shown to be active by DeSario et al.³⁶ Figure 2.5 displays the QMS data for O₂, CO, and CO₂ gas after a 50/50 mixture of CO and O₂ flowed through a packed bed of Cu/TiO₂ aerogel at different temperatures. O₂ data points come from the integrated 32 m/z signal in the QMS, CO data points are from the 28 m/z signal (that also contains ambient N₂), and the CO₂ points are from the 44 m/z signal. Between increases in temperature, the Cu/TiO₂ sample was activated at high temperatures in pure O₂ (omitted from the plot). Acquiring signal at the reference cell before each reactive exposure conveys the relative conversion/formation of reactants/products. At 433 K, little conversion of CO or O₂ is observed and only small amounts of CO₂ are formed. As the temperature of the catalyst bed is increased up to 573

K, CO conversion increases and larger amounts of the CO₂ product are detected. This method of experimentation allows for the screening of potential catalyst materials and the collection of important reaction information like kinetics and mechanistic insights. It is important to note that full mass scans are attainable but not shown in Figure 2.6.

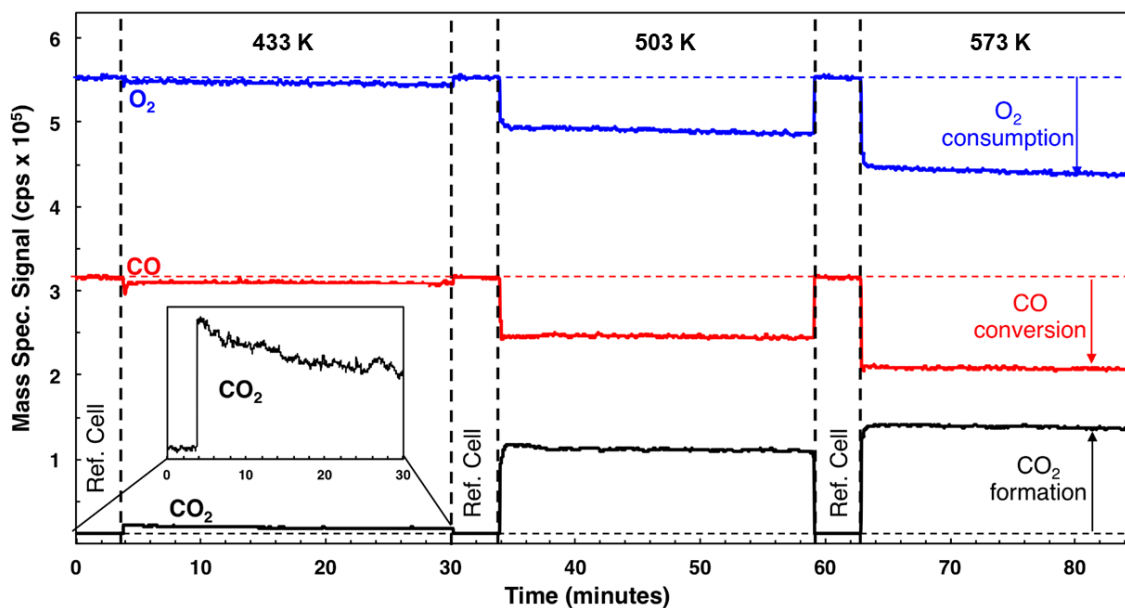


Figure 2.5 QMS data of CO oxidation over Cu/TiO₂ aerogels at different temperatures.

The inset provides a zoomed-in look at the CO₂ production at 433 K.

2.6 Summary

The instrumentation described in this chapter provides *in situ* monitoring of gaseous adsorption, reaction, and desorption events of molecules at material surfaces. The UHV chamber system both maintains clean sample surfaces from ambient gases and allows for precise measurement of gas-surface interactions while allowing for a high degree of control of exposure conditions. The infrared spectroscopic measurements provide valuable

information about binding energetics and the molecular bonds that are ruptured or formed on the surface. Coupled with surface IR instrumentation is an *in-situ* flow reactor system that monitors the makeup of gas streams after they interact with a surface of interest. The instruments described combine to gain a more complete understanding of catalysis and reaction dynamics under both UHV and ambient/industrially relevant experimental conditions.

Chapter 3

Variable-Temperature Infrared Spectroscopy as an Experimental Probe of Electronic Metal-Support Interactions

Adapted with permission from Maynes et al., Electronic Metal-Support Interactions in the Activation of CO oxidation over a Cu/TiO₂ Aerogel Catalyst. *Journal of Physical Chemistry C*, 2020, 124, 21491-21501. Copyright 2020 American Chemical Society.

3.1 Introduction

The overall goal of this work is to describe surface reaction mechanisms and the underlying dynamics that drive heterogeneous catalysts to aid in catalyst design for lower cost/more effective materials. Characterizing the adsorption and binding energetics of important molecules on surfaces of interest provides a fundamental understanding that can be built upon to describe more complex interactions and catalysis. Binding energetics are also very important in applications such as gas storage, separation, and sensing. Scientists looking for new catalyst materials often use reactant binding enthalpies or free energies as descriptors relating to catalytic activity in “volcano curves”.^{5,9,13} Understanding the binding energetics for a key reactant or product is necessary to ensure that reactants adsorb strong enough to a surface to undergo a reaction, but not too strong so that they cannot be removed from the surface, restoring the catalyst to its original state and replenishing the active site. Temperature-programmed desorption (TPD) and calorimetry are most commonly used to evaluate binding energetics at the gas-surface interface.^{91,92} These methods, however, are expensive and burdensome to perform when evaluating weak interactions and operating at a low temperature. Scientists have found ways to overcome

the issues that TPD and calorimetry have at low temperature/binding energetics by developing IR-based methods like variable-temperature infrared spectroscopy (VTIR).^{90,93} This technique is uniquely powerful in that it is the only method that can evaluate site-specific energies within a heterogeneous material. As the electronic structure of the surface and the adsorbate are key factors regarding adsorption and binding strength, a systematic evaluation of the binding energetics could yield insights into relative electronic structure differences between materials.

The chemical and electronic interactions at the nanoparticle (NP)/oxide interface play a critical role in heterogeneous catalysis.^{17,58,94} However, the field lacks a comprehensive understanding of how the physical and electronic structure of the metal/oxide interface affects subsequent chemistry. TiO₂ decorated with metal NPs is known to alter the overall material work function due to charge transfer at the interface.⁹⁵ Despite the number of experimental and computational works on NP/TiO₂ (where NPs are often Cu, Au, and Pt) and similar catalytic systems, little attention is focused on how the interfacial charge transfer impacts surface adsorption.

Charge transfer from a low work function material to a high work function material upon contact is a well-known phenomenon.^{96–99} While many efforts have been dedicated to showing how oxygen vacancies in a metal-oxide support stabilize deposited metal nanoparticles,^{100–105} much less focus has been given to the idea that the deposited NPs can play a role in the generation of those oxygen vacancies through support reduction.¹⁰⁶ Such a hypothesis can be made when analyzing metal-assisted Mars-van Krevelen mechanisms as described in Chapter 1.4.2 and in the works of Widmann and Behm.^{17,57,63}

Enhanced reducibility of the oxide can be driven by charge transfer between the metal and the support. In many cases, the lattice oxygen atoms around the periphery of the metal NP/oxide interface may be easily extracted by a reactant to produce an oxygen vacancy (V_O).^{94,106} Many have suggested that metals may stabilize the V_O defect sites by providing a sink for redistribution of the excess charge when oxygen is removed from the lattice.^{102–105,107,108} Alternatively, low work function metals deposited on oxides with relatively high electron affinities can directly reduce the oxide via electron transfer, potentially activating oxygen extraction.^{109–112} In some cases, the oxygen has been shown to spill over onto the metal particle itself.^{99,113} Specific to Cu, Chen et al. reported a significant electronic interaction within a decorated Cu/TiO₂ catalyst, where synthetically generated Ti³⁺ sites reduced Cu²⁺ to Cu¹⁺ via electron transfer, stabilizing the active form of copper and oxidizing Ti in the process.²⁴ Theoretical investigations into Cu/TiO₂ describe charge transfer preferentially from Cu to the oxygen atoms within TiO₂, thereby increasing the reducibility of the oxide support.¹¹⁴ These studies notwithstanding, the overall understanding of how charge transfer affects catalytic reaction pathways remains limited due to a lack of systematic experimental and theoretical studies.^{24,26,108}

The studies herein aim to understand changes in the electronic structure of TiO₂ due to the presence of metal nanoparticles, and alterations to the support oxide by evaluation of the binding energetics of CO interactions with Ti⁴⁺ sites. CO binding to Ti⁴⁺ has a unique spectroscopic signature that does not overlap with any other IR features in the materials studied (Cu/TiO₂, Au/TiO₂, and Pt/TiO₂). Ti⁴⁺ sites are also present on all the studied materials and make a simplistic comparison point while studying the energetic influence of the oxide nanostructure or identity of the metal NP. The nature of CO as an IR

probe molecule (see section 1.3) also allows this method to provide information about vibrational frequencies, another descriptor that depends upon electronic structure.

3.2 Procedural Methods

3.2.1 Materials

Synthetic procedures for most materials were performed by Dr. Debra Rolison's research group at the Naval Research Laboratory. Further information about the synthetic procedure is provided in a previously published work.³⁶ Briefly, Cu/TiO₂ and Au/TiO₂ aerogels were prepared by photodepositing Cu nanoparticles onto TiO₂ aerogels.^{36,81,115} First, TiO₂ aerogels were prepared using a sol-gel method.³⁷ A wet gel is formed by adding a solution of Ti(*i*OPr)₄ (Alfa Aesar, 97+%) in 3.9 g of ethanol (absolute ethanol, Warner-Graham) to a mixture of H₂O (0.39 g), ethanol (4.0 g), and nitric acid (78 mg of 70% HNO₃, Fisher). After aging for 24 h, the wet gel was rinsed 10× with acetone over multiple days. The wet gels were loaded under acetone into a supercritical dryer and rinsed with liquid CO₂ at 283 K before heating the dryer to 314 K and then venting to atmospheric pressure. The TiO₂ aerogels were calcined in air at 698 K (2 K min⁻¹ heating and cooling ramp, 4 h dwell) to produce nanocrystalline anatase aerogels.

Following an established method,²⁸ Cu nanoparticles were photodeposited onto either the synthesized TiO₂ aerogels or a commercially available P25 TiO₂ (Evonik) by illuminating slurries containing ~150 mg TiO₂ suspended in a solution of 110 mL of 2 mM Cu(NO₃)₂ (Sigma-Aldrich, 98%) in 9:1 (vol:vol) H₂O:CH₃CH₂OH (adjusted to pH 9.5 ± 0.5) for a period of 24 h with a 500 W Xe arc lamp (Newport Oriel). The Cu/TiO₂ aerogels were collected by centrifugation followed by re-suspension in Ultrapure 18 MΩ

cm water (Barnstead Micropure) for 10 cycles. The Cu/TiO₂ materials were then dried in air at 373 K overnight. The Cu/TiO₂ aerogel had a weight loading was 10.4% while the Cu/P25 was about 1%.

The Au/TiO₂ composite aerogels were synthesized in a manner described by Pietron et al.^{33,81,116} First, decanethiolate-stabilized Au nanoparticles were synthesized by a method developed by Brust et al.¹¹⁷ One-third of the decanethiolate monolayer on the ligand-stabilized nanoparticles was then chemically exchanged with mercaptoundecanoic acid, creating mixed methyl/carboxy-terminated, monolayer-stabilized Au nanoparticles that are soluble in the ethanol solvent used in the sol-gel synthesis. The synthesis of Au/TiO₂ aerogels follows the same procedure as that described for TiO₂ aerogels with the additional step of first dissolving mixed alkanethiolate-stabilized Au nanoparticles in the ethanol solvent used in the TiO₂ gel synthesis to create composite gels. The Au/TiO₂ composite aerogels were rinsed, supercritically dried, and calcined in air in the same manner as that described for TiO₂ aerogels.

Au/P25 and Pt/P25 TiO₂ materials are 1% wt. loading commercially available samples purchased from STREM (7440-57-5 and 7440-06-4, respectively). Na-ZSM-5 zeolite material was a commercially available sample purchased from Riogen (#0276-ZSNaA100-Powder).

3.2.2 Vacuum Studies with Infrared Spectroscopy

Systematic studies were performed in a stainless-steel high-vacuum reactor cell with a base pressure of 1×10^{-8} Torr (see Chapter 2). NP/TiO₂ and analogous pure TiO₂ support samples were pressed (at 5000 psi) as 7 mm disks into the voids of a tungsten mesh,

which was secured onto a stainless-steel sample holder. The tungsten mesh sample holder allows for both samples to be exposed to the same gaseous and thermal environments, enabling direct comparisons between the materials.⁸⁹ A K-type thermocouple was attached directly to the tungsten mesh to monitor sample temperature. The tungsten mesh is resistively heated using copper rods attached to an external power supply. A liquid nitrogen cold trap cools the entire sample manipulator for low-temperature adsorption experiments. Details of the high-vacuum cell can be found in previous work and in Chapter 2.2.⁸⁵ An FTIR spectrometer with an external MCT-A detector (Thermo, Nicolet Nexus 470 FTIR, resolution 2 cm^{-1} , optical velocity 1.8988 cm/s) couples to the vacuum chamber to provide the *in situ* infrared spectroscopic measurements.

Samples were pretreated in the vacuum chamber under two sets of conditions. Oxidizing treatment exposed the aerogel samples for 1 hour in 673 K (573 K for P25 TiO_2) in 10 Torr of O_2 followed by 30 minutes at 673 K (or 573 K) in vacuum. Reductive treatment held the aerogel samples at 673 K (or 573 K) in vacuum for 2 hours. These procedures effectively remove weakly-bound organic species on the surface, as confirmed by infrared spectroscopy of the samples. For exposures of O_2 (99.994% purity, Airgas Ultra High Purity) and CO (99.3% purity, Airgas CP300, a gas manifold affixed to the vacuum chamber allowed for quantifiable amounts of each gas to be introduced into the chamber and exposed to each material.

3.2.3 Variable-Temperature Infrared Spectroscopy Studies in a Vacuum Chamber

VTIR was employed to analyze CO–surface interaction energetics. The VTIR method to determine gaseous adsorption enthalpies at discrete binding sites has been

described in previous reports and in Chapter 2.⁹⁰ In short, VTIR requires a fixed pressure of CO interacting with the Cu/TiO₂ sample within a closed system. A van't Hoff analysis was used to relate the adsorption equilibrium constant, K , to the standard adsorption enthalpy, $\Delta H_{\text{ads}}^{\circ}$ (see Eq. 2.2). With the assumptions of Langmuirian adsorption for CO on the studied surfaces, low CO surface coverages, and a constant $\Delta H_{\text{ads}}^{\circ}$ over the evaluated temperature range, the integrated absorbance of a characteristic CO-surface bound IR band at each studied temperature can be related to the standard adsorption enthalpy (see Eq 2.6).⁹⁰ The CO-surface interaction studies began by introducing 1 Torr of CO to the vacuum chamber at 173 K and sealed. The system was allowed to equilibrate for 5-10 minutes at each temperature before data collection. Infrared spectra were acquired over a range of surface temperatures (193 K to 263 K or higher) and were composed of an average of 250 scans.

3.3 Results and Discussion

3.3.1 Validation of the VTIR Method with the Vacuum Cell

After describing and deriving the VTIR method,⁹⁰ Garrone et al. evaluated the CO binding enthalpy on a Na-ZSM-5 zeolite material. In the study, 0.8 Torr of CO was exposed to the Na-ZSM-5 material at 234.7 K and IR spectra were taken as the temperature of the system increased to 304 K. Linearization of the integrated intensity of the Na(CO)⁺ spectral feature vs. $10^3/T$ resulted in an evaluated adsorption enthalpy (ΔH_{ads}) of -27.6 ± 0.8 kJ/mol. The VTIR experiment by Garrone et al. was re-created to validate the VTIR method on the UHV cell described in Chapter 2. For these studies, a fixed partial pressure of CO (1 Torr) in a closed system was employed to establish equilibrium between adsorbed CO and

CO(g). This pressure of CO was chosen to both replicate a similar exposure as performed by Garrone et al., and to ensure that the surface and gaseous CO molecules immediately surrounding the sample surface are in thermal equilibrium. If a lower pressure of CO were to be used, CO molecules in collisions with the outside of the chamber would be at a higher temperature than the surface, and not enough molecular collisions would occur to equilibrate the temperatures of the surface and the CO molecules immediately surrounding the surface and lead to error in the temperature measurement. A sample experiment run at a slightly higher CO pressure (1.2 Torr) did not result in a change to the ΔH_{ads} , so the thermal effects here were identified to be negligible at 1 Torr. The surface temperature was used to shift the equilibrium between bound and gaseous CO. A van't Hoff analysis was performed to determine binding enthalpy by relating the IR absorbance intensity for surface-bound CO as a function of relative concentration.⁹⁰ The results of this validation study are displayed in Figure 3.1.

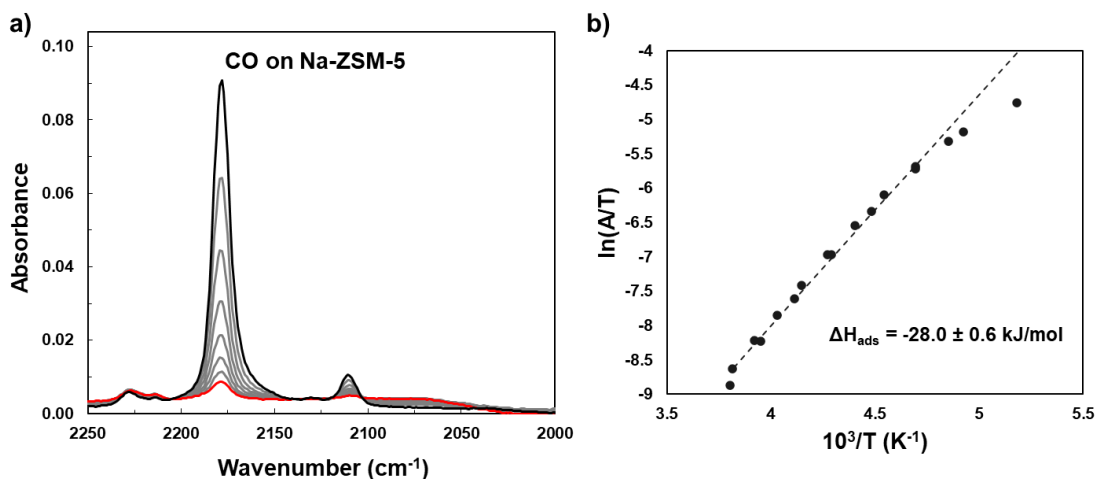


Figure 3.1 CO adsorption on a Na-ZSM-5 zeolite is monitored to validate the VTIR method. (a) FTIR difference spectra of CO on the Na-ZSM-5 zeolite at temperatures starting from 193 K and increasing to 263 K. (b) Arrhenius plot of VTIR data to evaluate ΔH_{ads} of CO on the zeolite.

Figure 3.1 shows both the IR scans of CO exposed to Na-ZSM-5 between 193 K and 263 K and the linearized integrated IR data as per the van't Hoff equation. The infrared band of 2178 cm^{-1} describes the CO molecule bound to the zeolite while the lower intensity feature at 2110 cm^{-1} is characteristic of the isocarbonyl (binding through the O atom in CO).⁹⁰ The same characteristics of binding are observed in the recreated experiment and the original work, with the lowest temperatures (and therefore highest coverages) showing progressive deviation from linearity due to the lateral interactions between adsorbate molecules. These lowest temperature data points were omitted from the analysis due to the necessary assumption of no lateral interactions between adsorbates. Integrating the area under the 2178 cm^{-1} IR feature and using the van't Hoff analysis yields an evaluated ΔH_{ads} of $-28.0 \pm 0.6\text{ kJ/mol}$ for CO on the zeolite, consistent with both the measurement by Garrone et al. ($-27.6 \pm 0.8\text{ kJ/mol}$) and direct calorimetric measurements (-28 kJ/mol).⁹⁰ Consistency between measured binding enthalpies in separate experimental systems indicates the reproducibility of the VTIR method.

3.3.2 VTIR to Evaluate CO-Ti⁴⁺ ΔH_{ads} in Cu/TiO₂ Aerogels

The VTIR method has been shown to be a particularly effective approach for studying weak reversible interactions, as is the case for CO interacting with Ti⁴⁺. The measurements were first performed on an oxidized Cu/TiO₂ aerogel sample, where the material was exposed to 10 Torr of O₂ for 1 hour at 673 K, followed by 30 minutes under vacuum at the same temperature after gaseous O₂ was removed. Figure 3.2a shows the infrared spectrum for CO bound to various sites on the Cu/TiO₂ aerogel. A more rigorous analysis of the identity of the surface sites, including Cu^{(2-x)+}, will be discussed in Chapter

4. As CO is first introduced to the aerogel at 193 K, a wide variety of surface sites are observed. With rising surface temperature, changes beyond pure desorption of CO from weak-interacting surface sites are observed. The CO features on Cu^{1+} and Cu^0 increase in intensity as the temperature rises from 193 to 263 K while Cu^{2+} and Ti^{4+} decrease. A surface reaction during the VTIR experiment will result in the failure of the van't Hoff analysis, where a non-linear relationship between $\ln(A/T)$ and $10^3/T$ is observed. This alteration of oxidation states in the presence of CO implies a reaction is occurring. The reactivity of this system is also observed by cooling the sample (still exposed to CO) back down to previous exposure temperatures after reaching the maximum of 263 K. This return to colder temperatures is shown in Figure 3.2b. Upon return to 203 and 233 K, Cu sites are observed to have been reduced; Cu^{2+} is consumed and relative concentrations of low valent Cu states increase. To prevent the failure of the van't Hoff analysis on Cu/TiO₂ aerogels, experimental changes should be made to stabilize the oxidation states of Cu.

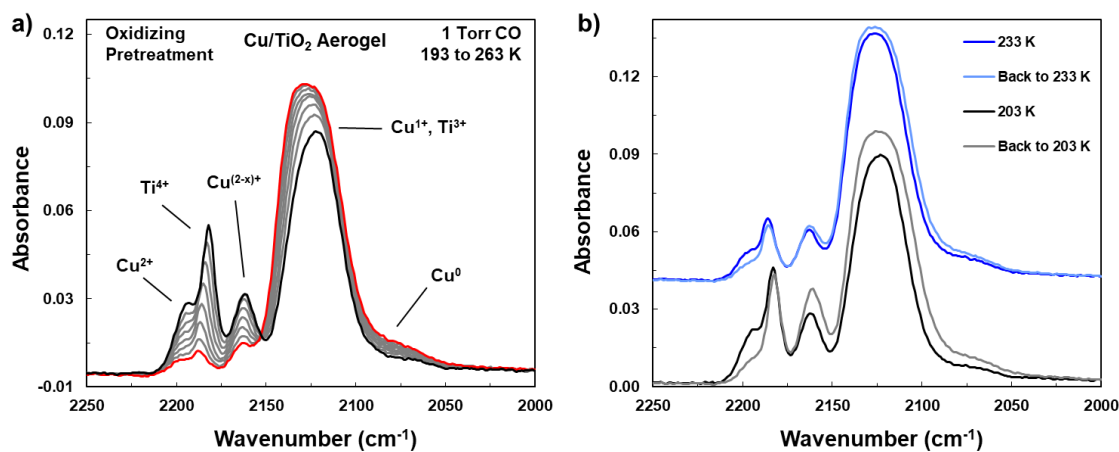


Figure 3.2 (a) FTIR difference spectra of CO on oxidatively pretreated Cu/TiO₂ aerogel at temperatures starting from 193 K (black) and increasing to 263 K (red). (b) Spectra were collected upon returning to 233 and 203 K after reaching the maximum temperature. Spectra are referenced to a clean Cu/TiO₂ aerogel before CO exposure at 193 K. In the

$\text{Cu}^{(2-x)+}$ feature, $0 < x < 1$.

The Cu/TiO₂ aerogel was then subjected to a reducing pretreatment, which was necessary to stabilize the oxidation state of the Cu nanoparticles in the presence of CO that otherwise serves as a reductant under our experimental conditions. The reducing pretreatment was a simple temperature elevation for the sample to 673 K while under vacuum for 2.5 hours. Figure 3.3 shows the infrared spectrum for CO bound to the reduced Cu/TiO₂ sample (panel a) and the TiO₂ sample (panel b) at a surface temperature of 193 K and how the band intensities change at elevated temperatures. In contrast to the experiments performed on a pre-oxidized sample, these changes were found to be reversible (Figure 3.3c). Here, the stability of the oxidation states of Cu is clearly observed in the IR spectra of Cu/TiO₂ interacting with CO upon heating from 193 to 263 K and upon cooling from 263 K back down to 203 K. Due to the reversible nature of CO interacting with the reduced TiO₂-supported nanoparticle sample, reductive pretreatments will be used for all VTIR samples for the remainder of this study.

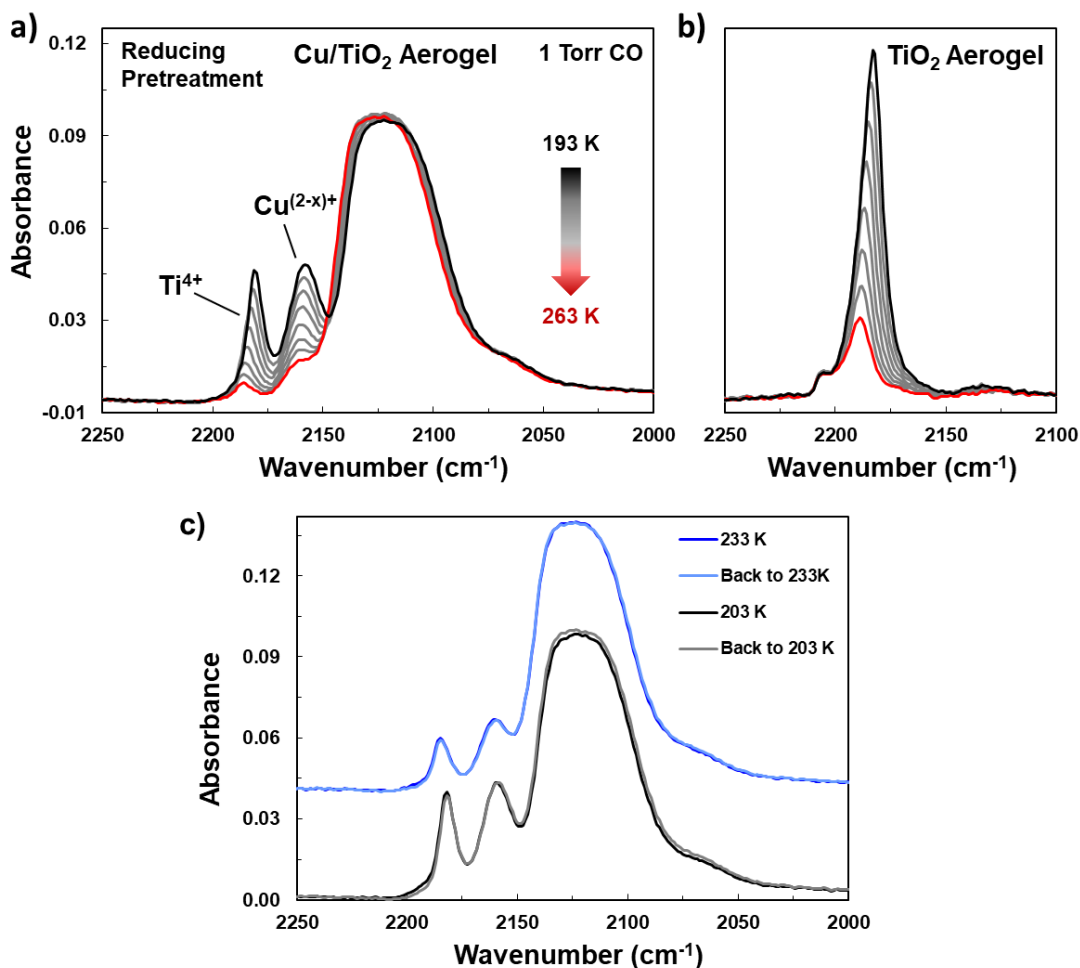


Figure 3.3 FTIR difference spectra of CO on reductively pretreated Cu/TiO₂ (a) and TiO₂ aerogel (b) at temperatures ranging from 193 to 263 K. Spectra were taken upon returning to 203 and 233 K to probe the reversible nature of CO interacting with the reductively pretreated sample (c). Spectra are referenced to clean Cu/TiO₂ and clean TiO₂ aerogel, respectively, at 193 K.

From the IR spectra in Figure 3.3a, it can be observed that the number of unique surface sites decreases, as Cu²⁺ is completely reduced to low-valent Cu oxidation states from the reducing pretreatment conditions. By integrating the area of the component peaks that decrease over the increasing temperature range (Ti⁴⁺ and the mixed Cu oxide, Cu^{(2-x)+}),

we can utilize the van't Hoff analysis and determine adsorption enthalpies for CO coordinating to weak-interacting surface sites as shown in Figure 3.4a. The ΔH_{ads} of CO bound to Ti^{4+} sites within the Cu/ TiO_2 aerogel is determined to be -19.3 ± 1.7 kJ/mol using the van't Hoff analysis, which is more exothermic by 7.5 kJ/mol compared to the ΔH_{ads} of CO bound to Ti^{4+} sites within the metal-free TiO_2 aerogel. The difference in ΔH_{ads} of CO on Ti^{4+} sites for these two materials details the role of electronic metal-support interactions (EMSI).^{118,119} The Cu particles likely provide additional electron density to TiO_2 , which results in a larger adsorption enthalpy for CO. This observation is consistent with the flow of electrons from low work-function metals to supports of higher work function.⁹⁶⁻⁹⁹ The reported work function of copper particles is 4.21 ± 0.02 eV,¹²⁰ which is significantly below that of TiO_2 (> 5.4 eV).¹²¹⁻¹²³ The charge redistribution also affects the vibrational frequency of the adsorbed CO. Specifically, the peak wavenumber of the CO- Ti^{4+} infrared band is red-shifted in the presence of the Cu particles, clearly observed in Figure 3.4b.

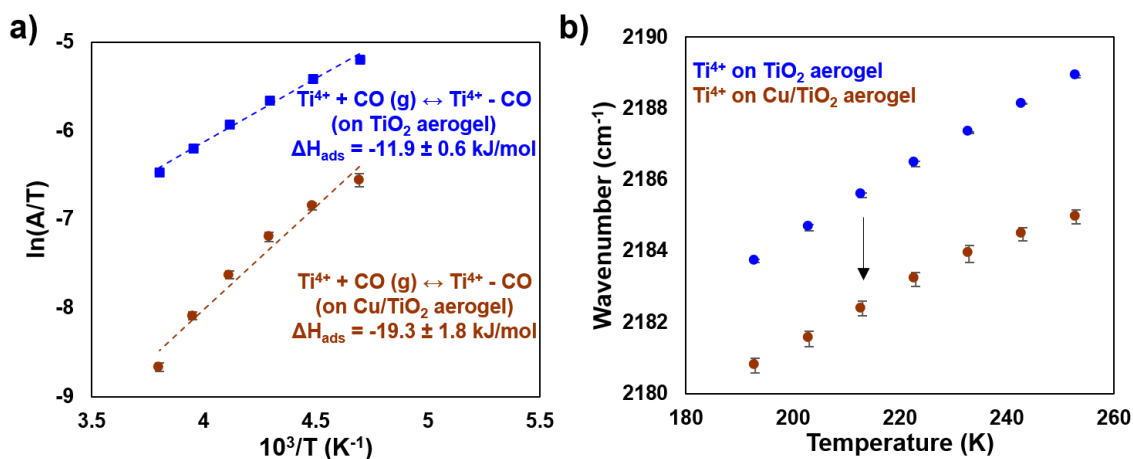


Figure 3.4 (a) Arrhenius plot of VTIR data from Figure 3.3 to evaluate ΔH_{ads} of CO on Ti^{4+} for TiO_2 aerogel support (blue circles) and Cu/ TiO_2 aerogel (brown squares). (b) center of CO- Ti^{4+} IR peak (in cm⁻¹) vs temperature in VTIR experiment for both Cu/ TiO_2 and TiO_2 aerogels. Error bars indicate 1 standard deviation from triplicate measurements. Error

bars smaller than the symbols are not visible.

The increase in the ΔH_{ads} of CO at Ti^{4+} sites highlights the additional charge that TiO_2 regions of the material have due to the presence of Cu. Specifically, the additional charge increases the ability for Ti^{4+} sites to back-donate charge to the $2\pi^*$ orbital of the CO molecule, resulting in the observed redshift and increased adsorption enthalpy. Charge transfer between metal nanoparticles and a TiO_2 support is widely reported. Often, conduction band electrons in TiO_2 are generated by UV light exposure and transfer to Au (serving as an electron sink) for increased electron-hole separation.^{124–126} The specific metal-to-support transfer as described above, however, has been shown only for a few cases.^{111,112,127–129} Wang and co-authors observed this behavior in Au/ZnO nanorods, where electrons from the metal nanoparticle were donated to the oxide support.⁹⁶ Liu et al. also observed a similar phenomenon on the same material, but only after an oxidizing pretreatment.¹³⁰ McEntee et al. published similar studies but utilized an adsorbed donor/acceptor molecule to induce charge transfer between Au and TiO_2 .¹³¹ To date, charge transfer has not previously been demonstrated through the use of CO as a probe to directly compare metal oxides in the presence and absence of metal nanoparticles. However, structural effects have also been shown to play a major role in the electronic nature of TiO_2 .^{106,132} As such, subtle differences in the structure of the Cu/ TiO_2 and pure TiO_2 aerogels may also affect the character of adsorbed CO.

3.3.3 Pressure Dependence to Evaluated ΔH_{ads}

The evaluated adsorption enthalpy of CO on Ti^{4+} sites within metal-free TiO_2 materials is not itself a novel discovery, as it has been reported in the literature numerous times. However, there is a wide discrepancy between evaluated ΔH_{ads} depending on the method used, computational technique (if used), specific Ti^{4+} site being evaluated, and surface coverage/exposure pressure. The ΔH_{ads} values for CO on Ti^{4+} reported in the literature are compiled in Table 3.1.

Table 3.1 Compiled results of CO $-\Delta H_{\text{ads}}$ on TiO_2 (in kJ/mol) from literature. A ‘*’ denotes a computationally derived $-\Delta H_{\text{ads}}$, while the others are experimentally evaluated.

CO- Ti^{4+} $-\Delta H_{\text{ads}}$ (kJ/mol)	Site/System	CO Coverage [ML] or [Θ] / Pressure [Torr]	Reference
11.9	TiO_2 Aerogel	1 Torr	This work, ⁵⁰
19.50*	5-folded, 1 vacancy	$\Theta = 0.5$	133
20.3	Not reported	0.5-40 Torr	134
20.55*	Anatase stoichiometric (linear response method)	1 ML	135
21.23 - 26.05*	Anatase reduced V_O	0.125 ML	135
21.32*	Anatase stoichiometric (finite differences method)	1 ML	135
24.60*	Anatase stoichiometric (linear response method)	0.25 ML	135
25.28*	Anatase stoichiometric (finite differences method)	0.125 ML	135
25.31*	5 folded, all vacancies	$\Theta = 0.5$	133
26.05*	Anatase reduced 2xH (pos1)	0.25 ML	135
26.94*	5-folded	$\Theta = 1$	133
27.21*	Anatase reduced 2xH (pos4)	0.25 ML	135
27.5	Not reported	Modeled from ¹³⁶	134
30.96*	5-folded, at vacancy	$\Theta = 0.5$	133
36.82 – 38.49*	$\text{TiO}_2(110)$ w/ V_O	DFT, not given	137
37.82*	5-folded	$\Theta = 0.5$	133
40.52*	Anatase reduced V_O (on V_O)	0.125 ML	135
41.42	Defect-free $\text{TiO}_2(110)$	0 ML	138
42	Not reported	0.098 to 9.8 Torr	136

43.42*	Perfect surface Ti ₅	$\Theta = 1/3$	139,140
48.24*	Not reported	“Monolayer”	141
52	Not reported, low frequency (should be Ti ⁴⁺)	1-100 Torr	142
54	Not reported, low frequency (should be Ti ⁴⁺)	1-100 Torr	142
55	Not reported, low frequency (should be Ti ⁴⁺)	1-100 Torr	142
63.55*	Ti ⁴⁺	$\Theta = 1$	143
67.54 - 77.19*	Not reported	1 CO / Ti center	141
83.81*	Ti ⁴⁺	$\Theta = 1/2$	143
100.5*	4-folded, bridging site, all vacancies	$\Theta = 0.5$	133
112.0*	4-folded, all vacancies	$\Theta = 0.5$	133
150.5*	4-folded, tilted bridging site, all vacancies	$\Theta = 0.5$	133

The pressure of CO, or more explicitly the number of CO molecules per Ti center varies significantly in the evaluation of ΔH_{ads} in the compiled works. Based on the reported values in Table 3.1, it can be hypothesized that the coverage, or approximate number of CO molecules in proximity to Ti⁴⁺ affects the evaluated ΔH_{ads} . To test this hypothesis while maintaining the thermal equilibrium between the TiO₂ surface and the gaseous CO above the surface necessary to maintain a valid VTIR experiment,⁹⁰ low partial pressures of CO were supplemented by an inert gas, N₂ in this case, to reach a pressure suitable for thermal equilibrium, 1 Torr. The study with four different partial pressures of CO using the VTIR method to evaluate the ΔH_{ads} of CO on Ti⁴⁺ sites of non-networked TiO₂ is shown in Figure 3.5.

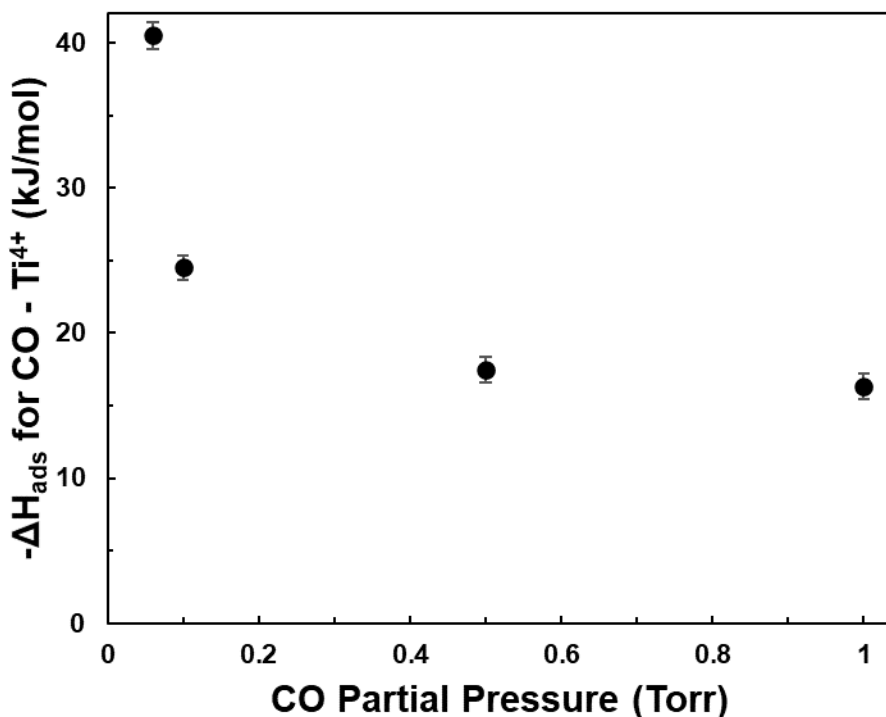


Figure 3.5 CO coverage effects on the evaluated ΔH_{ads} of CO on Ti^{4+} sites of pure anatase TiO_2 . Error bars indicate 1 standard deviation from the linear regression of the VTIR experiments, run in triplicate measurements. Data acquired by Kristin Knight

The data presented in Figure 3.5 confirms the hypothesized pressure dependence on CO-Ti^{4+} ΔH_{ads} , where the ΔH_{ads} becomes more negative with decreasing CO pressure. In addition, the evaluated ΔH_{ads} of CO bound to Ti^{4+} sites at the lowest experimental CO partial pressure of 0.06 Torr is more consistent with the literature values, particularly with the study by Linsebigler et al. evaluating the adsorption enthalpy of CO on the (110) facet of defect-free TiO_2 and found an adsorption enthalpy of 41.42 kJ/mol.¹³⁸ This validation study stresses the care that must be taken when comparing ΔH_{ads} values, as the coverage dependence to evaluated binding enthalpy is significant. Given the significant effect that pressure has on an evaluated ΔH_{ads} , comparisons to reported values in the literature do not

yield too many insights. Direct comparisons between different materials exposed to the same conditions, however, can provide valuable information about the change in the chemical/atomic systems of interest. These direct comparisons under consistent conditions ensure that the changing variables between the materials themselves are being evaluated instead of a pressure/coverage dependence.

3.3.4 Effect of Nanostructuring: VTIR of CO on Cu/P25 TiO₂

To analyze the effects of NP-support interfacial contact on the binding energetics of CO to Ti⁴⁺ sites, Cu NPs were supported onto commercially available P25 TiO₂ particles. These TiO₂ particles are well characterized and understood in the literature.^{95,144} Importantly, the P25 TiO₂ samples have a larger particle size than the TiO₂ aerogels (60 nm average for P25 vs 9 nm for the aerogel).^{36,144} Microscopy images of the different forms of TiO₂ show the difference in the degree of contact between particles, where a dramatic increase in TiO₂ contact is present in the aerogels (see Chapter 1.2.4).^{36,144} It is important to consider the weight loading of Cu in these two cases. The aerogels shown previously have been at a 10.4 wt% of Cu while the Cu/P25 is at only at about 1 wt%. The materials are made with these weight loadings to ensure the stability of the metal nanoparticles to sintering and agglomeration at high temperatures.¹⁴⁵ The multiple points of interfacial contact on the Cu/TiO₂ aerogels stabilize the particles at high temperatures that are catalytically relevant, while the surface-decorated Cu/P25 TiO₂ (see Figure 1.2) require smaller weight loadings to have larger average spacing between the Cu particles to prevent their growth at high temperatures. The same photodeposition process was utilized for Cu/P25 as was used for the Cu/TiO₂ aerogel materials, with the only difference being the

form of TiO_2 used and the weight loading.

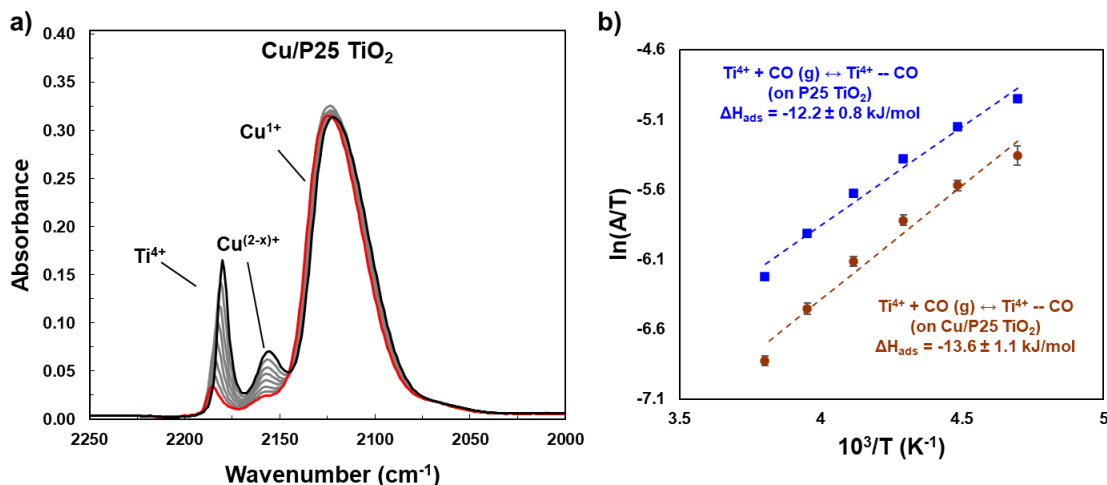


Figure 3.6 (a) FTIR difference spectra of CO on Cu/P25 TiO_2 following a reducing pretreatment at temperatures starting from 193 K and increasing to 263 K. (b) Arrhenius plot of VTIR data to evaluate ΔH_{ads} of CO on Ti^{4+} for TiO_2 aerogel support (blue circles) and Cu/ TiO_2 aerogel (brown squares). Error bars smaller than the symbols are not visible.

The results of an analogous VTIR experiment on the Cu/P25 sample (after reductive pretreatment of 573 K under vacuum) are shown in Figure 3.6. Upon initial review, the IR spectra of CO coordinating to the surface clearly shows significantly lower amounts of surface Cu^0 sites compared to the aerogel, exemplifying the importance of the networked support to stabilize the lower oxidation state of Cu. When analyzing the VTIR data, a significant difference between the aerogel and P25-supported Cu samples emerges in the evaluated adsorption enthalpy. The ΔH_{ads} of CO bound to Ti^{4+} sites within the Cu/P25 TiO_2 sample is evaluated to be -13.6 ± 1.1 kJ/mol. In comparison, a pure P25 sample analyzed is determined to have a $\text{CO} \leftrightarrow \text{Ti}^{4+}$ ΔH_{ads} of -12.2 ± 0.9 kJ/mol, a difference of only 1.4 kJ/mol more exothermic from the presence of Cu. It is evident that the

nanostructuring of the support or the NP loading affected the ΔH_{ads} , and therefore the degree of interfacial charge transfer, initiated by the presence of Cu NPs. However, it cannot be said whether the larger change present in the aerogel material is due to the weight loading or the multiple points of interfacial contact between the Cu NP and the support, or a combination of the two. The researchers that synthesized and characterized the Cu/TiO₂ aerogels also showed that the networked support led to a higher concentration of reduced Cu sites ($\text{Cu}^{1+} + \text{Cu}^0$) relative to a non-networked support.^{36,44} This crucial alteration of oxidation state can readily impact the overall work function of the Cu particles between the two materials, as shown in other systems.¹⁴⁶ But, it must be stated that the aerogel support allows for a relatively high stable loading of Cu NPs to exist without sintering at high temperatures, and the major difference could also be attributed to the overall metal loading of the system. These differences will be explored with the added perspective of more metals on similar TiO₂ supports.

3.3.5 Effect of Metal Identity and Support Nanostructure on ΔH_{ads}

Due to the phenomena observed, analogous VTIR experiments and analyses were performed on various TiO₂-based materials to compare the effects of metal nanoparticle identity and nanostructure of the support oxide on the degree of interfacial charge transfer (via $\text{CO} - \text{Ti}^{4+} \Delta H_{\text{ads}}$). The systems studied include a Au/TiO₂ aerogel, Au/P25 TiO₂, and Pt/P25 TiO₂ in addition to the previously discussed Cu/TiO₂ aerogel, Cu/P25 TiO₂, and metal-free TiO₂ standards of the aerogel and P25. Note that the Au and Cu/TiO₂ aerogels are all at approximately 10% metal weight loading while the P25-supported particles are all approximately 1% metal weight loading. All the reported values were evaluated from

samples that underwent a reducing pretreatment (673 K *in vacuo* for 2.5 hours for aerogel samples, 573 K *in vacuo*). The summarized results of the VTIR experiments along with the changes to the vibrational frequency ($\Delta\nu_{\text{CO}}$), in cm^{-1} , of CO coordinating to Ti^{4+} sites (to show another indicator of electronic effects on the character of adsorbed CO, see Chapter 1.3) are shown in Figure 3.7.

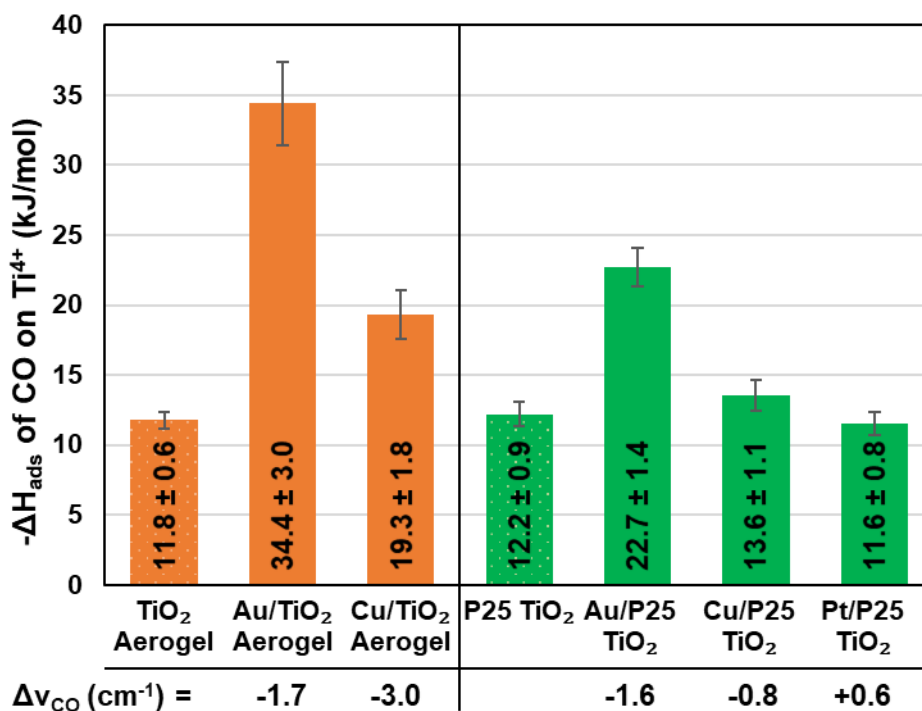


Figure 3.7 Summary of the evaluated adsorption enthalpies for CO on Ti^{4+} sites for various TiO_2 based materials, with TiO_2 aerogels in orange and surface decorated P25 TiO_2 in green. Error bars indicate 1 standard deviation from the linear regression of the VTIR experiments, run in triplicate measurements. The difference in Ti^{4+} vibrational frequencies for each material relative to their most similar support at 193 K are displayed below the chart.

From the compiled data in Figure 3.7, metal identity appears to be related to the CO adsorption enthalpy on the support oxide. As previously discussed, the differences can be largely attributed to the metal work functions relative to TiO₂. The EMSIs at the NP/TiO₂ interface are driven by differences in material work functions, with charge transfer occurring at the interface from the lower work function material to the higher work function material as Fermi levels align.^{96–99} With numerous factors affecting the work function of any metal or metal oxide, it is challenging to evaluate exact differences between the NP work functions and TiO₂. The literature is not consistent with work function values even for a system as heavily studied as TiO₂, where reported values range from 4.29 to 7.9 eV, with most works citing values above 5.4 eV.^{121–123,147} The work of Zhao et al. denotes the importance of calculated work functions and how they are reported. The authors calculated TiO₂ work functions on six separate crystal facets and found values between 3.5 eV and 6.6 eV that varied by facet and whether or not surface relaxation was applied.¹²³ The average work function from the subset of relaxed surfaces of TiO₂ was 5.4 eV, and as that is near the center of the range of reported values, will be estimated as the TiO₂ work function for this work. The variance in reported work functions for metals is similar, and that variance grows as the band structures change with decreasing particle size down to the nanoscale.¹² For consistency, the work function values for the bulk metals will be used to evaluate the degree of charge transfer. The work function of metals has been reported by several works,^{120,121,148–151} and include measurements for Cu (4.65 eV), Au (5.1 eV), and Pt (5.65 eV). The overall phenomena of charge transfer on the material work functions is shown in Figure 3.8.

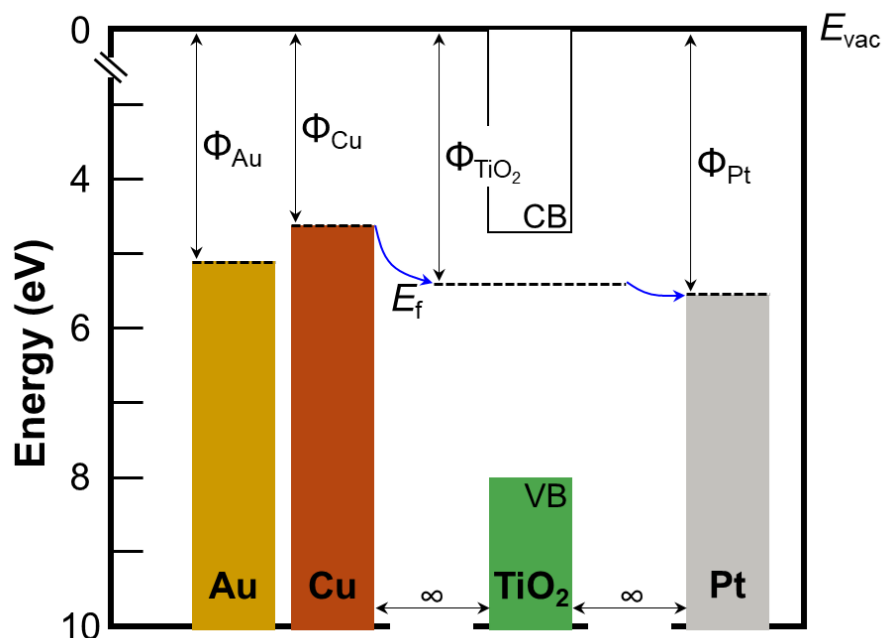


Figure 3.8 Band diagrams showing the band structures for Cu, Au, Pt, and TiO₂. Material work functions (Φ), Fermi levels (E_f), top of the valence band (VB), and bottom of the conduction band (CB) are all shown relative to the vacuum level (E_{vac}). Blue lines demonstrate the directional charge transfer when the separation of materials is brought from infinity to 0 (in contact) and the Fermi levels align. Values for work functions and band positions are all from bulk materials from the literature.^{120–123,147–151}

The metals shown in the left portion of Figure 3.8 have work functions lower than that of TiO₂ and would donate charge to TiO₂ upon contact to align Fermi levels with the TiO₂ support. Pt has a higher work function than TiO₂, and therefore would accept charge from TiO₂ for Fermi alignment. Both expected directions of charge transfer are explicitly observed whether through the change in vibrational frequency of CO on Ti⁴⁺ sites (in the case of Pt) or the change in CO-Ti⁴⁺ adsorption enthalpies on the different materials with and without metal nanoparticles present (Cu and Au, Figure 3.7). For example, negative

charge accumulates at the interface for Au and Cu-supported materials. The accumulated charge reduces the Ti^{4+} sites near the particles, which we hypothesize results in the increase in $\text{CO-Ti}^{4+} \Delta H_{\text{ads}}$ in the accumulation layer (the area of accumulated electron density on TiO_2 after NP-to-oxide charge transfer). The accumulation layer of TiO_2 is reported to extend to widths between 2 nm and 18 nm.^{152–154} The CO molecules interacting with Ti^{4+} sites within the accumulation regions are likely to be most affected. Regarding the change in $\text{CO} \Delta H_{\text{ads}}$, Au is the only metal nanoparticle that does not match the expected result that decreasing metal work function ($\text{Pt} > \text{Au} > \text{Cu}$) leads to a greater change in ΔH_{ads} .

The difference in Au/TiO_2 expected ΔH_{ads} based on work function could be attributed to different phenomena. First, the metal oxidation state is known to have an impact on its work function,^{121,146} with Cu_2O increasing to 4.9 eV and CuO increasing to 5.9 eV.¹²¹ Since we know from CO spectroscopy that the Cu oxidation states include Cu^{2+} (after oxidizing pretreatment), Cu^{1+} , Cu^0 , and a mixed oxide, the overall work function of the Cu particles will likely be different than that of bulk Cu^0 which can affect the degree of interfacial charge transfer. In lieu of calculated work functions for the studied metal NPs, the binding energy change to CO is indicative of the Lewis acidity of the Ti^{4+} sites. As adsorption enthalpy decreases, the acidity decreases. Second, the adsorption strength of the metal NP to CO influences the coverage of CO molecules on the NP, which can affect vibrational frequencies.¹⁵⁵ Undercoordinated Au can have binding energies with CO between -52 kJ/mol and -83 kJ/mol,²⁰ while Cu atoms have a significantly lower CO binding energy of -20 kJ/mol.^{156,157} The high binding energy of Au likely leads to a significantly higher surface coverage, which may impact the evaluated adsorption enthalpy on the oxide through repulsive interactions of NP adsorbates. Overall, the oxidation state

and CO coverage of the metal NPs likely contribute to the evaluated ΔH_{ads} and CO-Ti⁴⁺ vibrational frequency.

As coverage can impact the evaluated CO-Ti⁴⁺ ΔH_{ads} , a simple experiment can be proposed to find the coverage for any of these TiO₂-based materials. For example, with a gas doser aligned directly with the sample, CO can be introduced at very low temperatures and pressures (about 100-120 K and 1×10^{-6} Torr, respectively) while acquiring IR spectra until a maximum absorbance of CO on Ti⁴⁺ is reached, A_{max} . Once the maximum absorbance is reached and no further changes to CO-Ti⁴⁺ are observed in the spectra, the exposure to CO should stop and the A_{max} can be used as a comparison point during future exposures to CO. Coverage can be calculated for any subsequent exposure by just taking the absorbance, A_x , divided by A_{max} for the sample to function as a proxy for concentration via Beer's Law (provided that the experiment is operating within the linear Beer's Law regime).

The Ti⁴⁺ frequency shift is also affected by the charge transfer between NPs and TiO₂. Pt shows a blueshift of 0.6 cm^{-1} but cannot be considered significant due to experimental parameters limiting frequency resolution (data spacing is 0.96 cm^{-1}). Both Au/TiO₂ samples exhibit a $\Delta\nu(\text{CO})$ of CO-Ti⁴⁺ redshifted to a lesser degree than Cu aerogels. The frequency shift of Cu/P25, similar to Pt/P25, also cannot be considered significant. The change in weight loading of metal NPs may influence the observed $\Delta\nu(\text{CO})$ by extending the accumulation regions on TiO₂ and increasing the number of CO-Ti⁴⁺ complexes close to metal NPs. NPs interfacing with additional surface atoms on the support in an aerogel could allow for an increased number of interfaces for charge transfer to occur. The effect of the increased NP-oxide interfaces is observed with a more exothermic

adsorption enthalpy on Au and Cu aerogels relative to the surface-decorated analogs. Importantly, the change to the CO-Ti⁴⁺ vibrational frequency does not appear to be as sensitive as the change to the CO-Ti⁴⁺ ΔH_{ads} . The high sensitivity of ΔH_{ads} between TiO₂-based materials relative to the $\Delta\nu(\text{CO})$ demonstrates the powerful nature of this method of determining NP work functions relative to TiO₂.

The change in binding energy of the CO-metal bond can influence the CO-metal vibrational frequency through a change in coverage, as previously discussed. Wang et al. showed that the binding energy of CO on Au increased dramatically with decreasing coordination number (CN) of Au atoms, ranging from -3.9 kJ/mol (CN = 9) to -83 kJ/mol (CN = 3).²⁰ As the aerogel stabilized particles from agglomeration and has a lower overall Cu particle size, increased CO binding strength to undercoordinated metal sites could increase the coverage and influence the evaluated adsorption enthalpy and vibrational frequencies of CO-Ti⁴⁺ on the Cu/TiO₂ and Au/TiO₂ aerogel samples.¹⁵⁵ There are observed discrepancies in the data presented in Figure 3.7: Ti⁴⁺ $\Delta\nu(\text{CO})$ is consistent between Au/TiO₂ materials while the CO-Ti⁴⁺ ΔH_{ads} are significantly different. Discrepancies in the evaluated energetics and vibrational frequencies between the Au/TiO₂ materials cannot be elucidated with the data shown. The two Cu/TiO₂ materials, however, are consistent between the relative magnitudes of CO-Ti⁴⁺ adsorption enthalpy and CO-Ti⁴⁺ vibrational frequency. In summary, there are many complexities to the interfacial charge transfer between metal NP and TiO₂ observed through the behavior of the $\Delta\nu(\text{CO})$ and change in ΔH_{ads} , and further experimental studies in addition to computational models are needed to characterize the electronic structure of these materials. Despite the complexities, the novel application of the VTIR method for the characterization of relative

differences in electronic structure on oxide supports has been shown to be effective. The methods described may be the first to measure the work function of the metal nanoparticles, relative to TiO_2 . The CO-Ti^{4+} adsorption enthalpy acts as a sensor to measure the impact that charge transfer has on binding energetics.

3.3.6 Impact of Experimental Observations of Interfacial Charge Transfer

The discovery of an interfacial charge transfer affecting the ΔH_{ads} of CO on Ti^{4+} on oxide-supported metal nanoparticles has significant implications in the field of catalysis. Additional charge on TiO_2 regions of supported metal nanoparticle materials is likely to change the chemical potential of the support, particularly through the surface Ti-O bonds. Widman and Behm have shown in several works that CO oxidation proceeds via a Mars-van Krevelen type mechanism on Au/TiO_2 at elevated temperatures (above 353 K), with lattice O atoms from TiO_2 being the active site where extraction occurs.^{17,57,63} Charge transfer from Au to TiO_2 can be hypothesized to impact the Ti-O bonds closest to the NP, and ripens the bridging O atoms for extraction due to the additional electron density on the support observed in the above studies. It is well known that the presence of the Au NP acts to electronically stabilize any bridging O vacancies that form by accepting the additional electron density.^{63,158} The confluence of these two ideas would reveal a synergistic effect of Au/TiO_2 charge transfer on catalysis. First, the additional charge on TiO_2 from Au weakens Ti-O bonds and ripens O for extraction by CO, which results in a formed bridging O vacancy and reduced Ti^{3+} sites (with electrons in the conduction band). The high-energy electrons left on the TiO_2 support are then stabilized by back-donation to the relatively higher work function Au NP.

As a link between catalysis on Au/TiO₂ and the interfacial charge transfer between metal NP and support oxide is shown, one could look to rationally design a catalyst material to maximize the NP-to-oxide charge transfer to lower the oxygen vacancy formation energy of the oxide to the lowest possible value. With the model described, depositing very low work function metals onto TiO₂ would likely increase the amount of charge donated to TiO₂, and increase the reducibility of the oxide. Considerations in the choice of metals cannot simply stop at the lowest work function, however. Other factors like propensity to form an oxide, metal stability, and ability to function as a catalyst itself (instead of purely a dopant) should be considered. In addition, natural abundance and cost are major factors as well, as the catalysts for gas-phase reactions most commonly in use are group 7-9 metals with very low natural abundance (Ir, Pt, Pd, Au). Finally, tuning the effects of nanostructuring to maximize activity by adjusting the number of NP-oxide interfaces could play a major role as well. As shown with Au NPs, surface mechanisms on the NP can still occur and need to be accessible to gaseous reactants for catalysis to occur,⁵⁸ so complete coverage of NPs with the support oxide (as an overlayer) might not be ideal.

Although this work provides one of the first direct insights into charge transfer at the metal-metal oxide interface, the effect of metal identity on interfacial charge transfer needs to be studied further. Because Au/TiO₂ has been heavily studied and mechanisms have been determined for gas-phase reactions like CO oxidation,^{17,57,58} the works in this chapter have shown that Cu/TiO₂ aerogels might be able to capture similar reactivity to Au. Cu/TiO₂ aerogels have indeed already shown activity for CO oxidation,³⁶ and Cu is a far more abundant metal than Au, leading to a lower cost material. Analysis of the mechanism and comparison to the Au/TiO₂ system would yield valuable insights into the

overall impact of the interfacial charge transfer between the metal NP and oxide support. Therefore, CO oxidation on Cu/TiO₂ aerogels will be the focus of upcoming studies.

3.4 Conclusions

VTIR experiments showed distinct changes to the evaluated adsorption enthalpy of CO interacting with Ti⁴⁺ sites on TiO₂ when different metal nanoparticles were deposited on the metal oxide. Introduction of Cu and Au NPs to TiO₂ was observed to redshift the CO-Ti⁴⁺ vibrational frequency and result in a larger CO adsorption enthalpy that increased in magnitude with increasing weight loading and nanostructuring. This behavior is consistent with the understanding of interfacial charge transfer from the relatively low work function Cu and Au particles to that of TiO₂. Conversely, the Pt NPs were not shown to significantly impact the CO-Ti⁴⁺ vibrational frequency or adsorption enthalpy. Pressure effects on the evaluated ΔH_{ads} were also characterized and found to play a major role on the binding energetics, with lower pressure/coverage of CO on TiO₂ resulting in a lower observed adsorption enthalpy.

Chapter 4

Characterizing Active Sites and Elucidating the CO Oxidation Reaction Mechanism over a Cu/TiO₂ Aerogel Catalyst

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4.1 Introduction

Metal nanoparticles (NPs) supported on metal oxides have been shown to be effective catalysts for CO oxidation,^{2,23,58,159} methanol oxidation,^{73,160} and the decomposition of organophosphorus chemical warfare simulants/agents.^{78,80,81} The most commonly studied metal NPs are precious metals (Au, Pd, Pt, Ir) due to their high catalytic activity and selectivity toward desired products. However, more Earth-abundant metals are desirable. Copper nanoparticles are an attractive alternative to precious metals, but the active forms of nanoscale copper (both in terms of particle size and oxidation state) are typically unstable under operational conditions.¹⁶¹ Recent efforts have shown unprecedented stability of low-valent Cu when supported within a networked oxide support, like a TiO₂ aerogel.^{36,115} The TiO₂ aerogel supports provide multi-point, 3-dimensional interfacial contacts with supported Cu NPs that stabilize Cu⁰ and Cu¹⁺, and prevent sintering of particles at elevated temperatures. Novel Cu/TiO₂ aerogels (10.4 wt % Cu, 131 m²g⁻¹) have been previously characterized,¹¹ but lack a full understanding of the available surface sites for reaction.¹² Cu/TiO₂ aerogels exhibit activity towards low-temperature CO oxidation,¹¹⁵ and drive the hydrolytic decomposition of the chemical

warfare agent simulant dimethyl methylphosphonate.⁸¹ Yet, despite promising activity for these important reactions, the underlying mechanistic understanding of the promotional effects of Cu on TiO₂ is currently lacking

Uncovering reaction dynamics and mechanisms for a model reaction on new catalyst designs can yield insights into how the material will operate under more complex reactions. CO oxidation is a simple model system for the exploration of reaction mechanisms on complex materials.^{57–59} The importance of CO oxidation is also shown in areas such as exhaust stream treatment, energy conversion/storage, and industrial applications.^{60,61} Mechanistic studies involving supported-metal NP catalysis have shown that CO oxidation mechanisms can vary between materials. For example, low-temperature CO oxidation on Au/TiO₂ has been shown by Yates et al. to proceed by a Langmuir-Hinshelwood type mechanism with CO and O₂ adsorbed at the catalyst interface.⁵⁸ In contrast, Ir/MgAl₂O₃ was observed to react with CO in an Eley-Rideal type mechanism with Ir atoms activating adsorbed O₂ to react with gaseous CO.¹⁶² A single material can even catalyze different CO oxidation mechanisms depending on reaction temperature. Widmann and Behm, in contrast with the prior work by Yates et al., showed that Au/TiO₂ activates lattice oxygen in the titania support for extraction by CO in a Mars-van Krevelen (MvK) type mechanism above 80 °C.^{17,57} These studies demonstrate that the character of the metal and support greatly affect key reaction parameters such as reactant adsorption strength, interfacial chemistry, and stability of intermediates/products, which all combine to define the reaction pathways.

The chemical and electronic interactions at the NP/oxide interface play a critical role in heterogeneous catalysis.^{17,58,94} However, the field lacks a comprehensive

understanding of how the physical and electronic structure of the metal/oxide interface affects subsequent chemistry. TiO_2 decorated with metal NPs is known to alter the overall material work function due to charge transfer and band bending at the interface.⁹⁵ While many efforts have been dedicated to showing how oxygen vacancies in the support stabilize deposited metal nanoparticles,^{100–105} much less attention has been given to the fact that the deposited NPs can activate oxygen for catalysis by promoting reduction of the support oxide.¹⁰⁶

Enhanced reducibility of the oxide can be driven by charge transfer between the metal and the support. In many cases, the lattice oxygen atoms around the periphery of the metal NP/oxide interface may be easily extracted by a reactant to produce an oxygen vacancy (V_O).^{94,106} Many have suggested that metals may stabilize the V_O defect sites by providing a sink for redistribution of the excess charge when oxygen is removed from the lattice.^{102–105,107,108} Alternatively, low work-function metals deposited on oxides with relatively high electron affinities can directly reduce the oxide via electron transfer, thereby activating oxygen extraction.^{109–112} In some cases, the oxygen has been shown to spill over onto the metal particle itself.^{99,113} Specific to Cu, Chen et al. reported a significant electronic interaction within a typical (non-aerogel) decorated Cu/ TiO_2 catalyst, where Ti^{3+} sites reduced Cu^{2+} to Cu^{1+} via electron transfer, stabilizing the active form of copper.²⁴ Theoretical investigations into Cu/ TiO_2 describe charge transfer preferentially from Cu to the oxygen atoms within TiO_2 , thereby increasing the reducibility of the oxide support.¹¹⁴ These studies notwithstanding, the overall understanding of how charge transfer affects catalytic reaction pathways remains limited due to a lack of systematic experimental and theoretical studies.^{24,26,108} Studies in Chapter 3 of this work show aimed to clarify this

phenomenon, and charge transfer was observed to occur from CuNPs to TiO₂, resulting in a stronger observed CO-Ti⁴⁺ adsorption enthalpy in the presence of Cu. The role that this charge transfer has on catalysis, specifically how it relates to the ability for the support to form V_O sites, needs to be evaluated.

In situ vibrational spectroscopic studies of CO have been applied to track oxidation and to characterize surface sites within Cu/TiO₂ aerogels. Supported by packed-bed reactor studies, evidence is provided of lattice oxygen extraction by CO as the main mechanism for oxidation to CO₂. Copper nanoparticles suspended within the 3-dimensional architecture of the aerogel assist in the extraction of lattice oxygen.

4.2 Procedural Methods

4.2.1 Cu/TiO₂ Synthesis

Cu/TiO₂ aerogels were prepared by photodepositing Cu nanoparticles onto TiO₂ aerogels in a manner described previously.^{36,81,115} First, TiO₂ aerogels were prepared using a sol-gel method.³⁷ A wet gel is formed by adding a solution of Ti(ⁱOPr)₄ (Alfa Aesar, 97+%) in 3.9 g of ethanol (absolute ethanol, Warner-Graham) to a mixture of H₂O (0.39 g), ethanol (4.0 g), and nitric acid (78 mg of 70% HNO₃, Fisher). After aging for 24 h, the wet gel was rinsed 10 times with acetone over multiple days. The wet gels were loaded under acetone into a supercritical dryer and rinsed with liquid CO₂ at 283 K before heating the dryer to 314 K and then venting to atmospheric pressure. The TiO₂ aerogels were calcined in air at 698 K (2 K min⁻¹ heating and cooling ramp, 4 h dwell) to produce nanocrystalline anatase aerogels. Following an established method,²⁸ Cu nanoparticles were photodeposited onto the TiO₂ aerogels by illuminating slurries containing ~150 mg TiO₂

aerogel suspended in a solution of 110 mL of 2 mM $\text{Cu}(\text{NO}_3)_2$ (Sigma-Aldrich, 98%) in 9:1 (vol:vol) $\text{H}_2\text{O}:\text{CH}_3\text{CH}_2\text{OH}$ (adjusted to $\text{pH } 9.5 \pm 0.5$) for a period of 24 h with a 500 W Xe arc lamp (Newport Oriel). The Cu/TiO_2 aerogels were collected by centrifugation followed by re-suspension in Ultrapure 18 M Ω cm water (Barnstead Micropure) for 10 cycles. The Cu/TiO_2 aerogels were then dried in air at 373 K overnight.

4.2.2 Vacuum Studies with Infrared Spectroscopy

Systematic studies were performed in a stainless-steel high-vacuum reactor cell with a base pressure of 1×10^{-8} Torr (see Chapter 2). Cu/TiO_2 and TiO_2 aerogel samples were pressed (at 5000 psi) as 7 mm disks into the voids of a tungsten mesh, which was secured onto a stainless-steel sample holder. The tungsten mesh sample holder allows for both samples to be exposed to the same gaseous and thermal environments, enabling direct comparisons between the materials.⁸⁹ A K-type thermocouple was attached directly to the tungsten mesh, within 3 mm of the samples, to monitor sample temperature. The tungsten mesh was resistively heated using copper rods attached to an external power supply. A liquid nitrogen cold trap cools the entire sample manipulator for low-temperature adsorption experiments. Details of the high-vacuum cell can be found in previous work and in Chapter 2.2.⁸⁵ An FTIR spectrometer with an external MCT-A detector (Thermo, Nicolet Nexus 470 FTIR, resolution 2 cm^{-1} , optical velocity 1.8988 cm/s) couples to the vacuum chamber to provide the *in situ* infrared spectroscopic measurements.

Samples were pretreated in the vacuum chamber under two sets of conditions. Oxidizing treatment exposed the samples for 1 hour at 673 K in 10 Torr of O_2 followed by 30 minutes at 673 K in vacuum. Reductive treatment held the samples at 673 K in vacuum

for 2 hours. These procedures effectively remove weakly-bound organic species on the surface, as confirmed by infrared spectroscopy of the samples. For exposures of O₂ (99.994% purity, Airgas Ultra High Purity), CO (99.3% purity, Airgas CP300), and CO₂ (99.99% purity, Praxair), a gas manifold affixed to the vacuum chamber allowed for quantifiable amounts of each gas to be introduced into the chamber and exposed onto each material.

4.2.3 Ambient Pressure Packed-Bed Flow Reactor

Catalyst activity was screened with a custom-built packed-bed reactor coupled to a differentially pumped quadrupole mass spectrometer (ABB Extrel MEXM). 3 mg of Cu/TiO₂ aerogel catalyst was packed into a 0.25-inch diameter quartz tube and secured by quartz wool on both sides of the tube. Gaseous reactant flow into the cell was controlled with mass flow controllers (50 SCCM MKS, 100 SCCM MKS). Temperature was monitored with a K-type thermocouple. Quartz reaction cells were surrounded by a coil of nichrome wire to adjust sample temperature, backed by a VARIAC transformer to supply power and a PID controller (Omega, platinum series) to adjust the applied current to the wires for stable catalyst temperatures. Prior to each experiment, the Cu/TiO₂ sample was activated at 573 K under 10 SCCM flow of O₂ for 30 minutes.

4.3 Results and Discussion

Interactions of CO with Cu/TiO₂ aerogels have been investigated using infrared spectroscopic techniques and a packed-bed reactor. IR spectroscopic studies of adsorbed CO with gas-phase spectroscopy of CO₂ are applied to build a fundamental understanding

of the surface reactions on the novel aerogel-based catalyst. The objectives of this work include (1) evaluating the oxidative activity of a Cu/TiO₂ aerogel material, (2) characterizing surface sites present within the Cu-based catalyst, and (3) identifying the active site and determining the mechanism for CO oxidation on the Cu/TiO₂ aerogels.

4.3.1 Temperature-Dependent Catalytic CO Oxidation

The temperature dependence on CO oxidation efficiency over the Cu/TiO₂ aerogel catalyst was characterized within a packed-bed reactor. Following 573 K activation in O₂, a stable sample temperature was established (while maintaining oxygen flow) before adding 5 SCCM of CO to the stream. The time-dependent mass spectral signal of the effluent gas stream for $m/z = 44$ (CO₂), recorded at several sample temperatures from 393 to 573 K, is shown in Figure 4.1a. While little CO₂ production was observed below 433 K, the reaction rate and yield increased dramatically above 463 K. In fact, the total production plateaued after only a few seconds at 573 K, where near 85% CO conversion was sustained with no signs of abating after 80 minutes. No other gas-phase carbonaceous products were detected. Other reports of CO oxidation on similar Cu-based catalysts show significant reactivity below 373 K.^{24,26,28,115} However, for applications in exhaust stream treatment, lower-temperature activity is not as important as catalyst stability and avoiding nanoparticle agglomeration; Cu NPs in the aerogels have been shown to be stable to at least 673 K in the IR measurements.

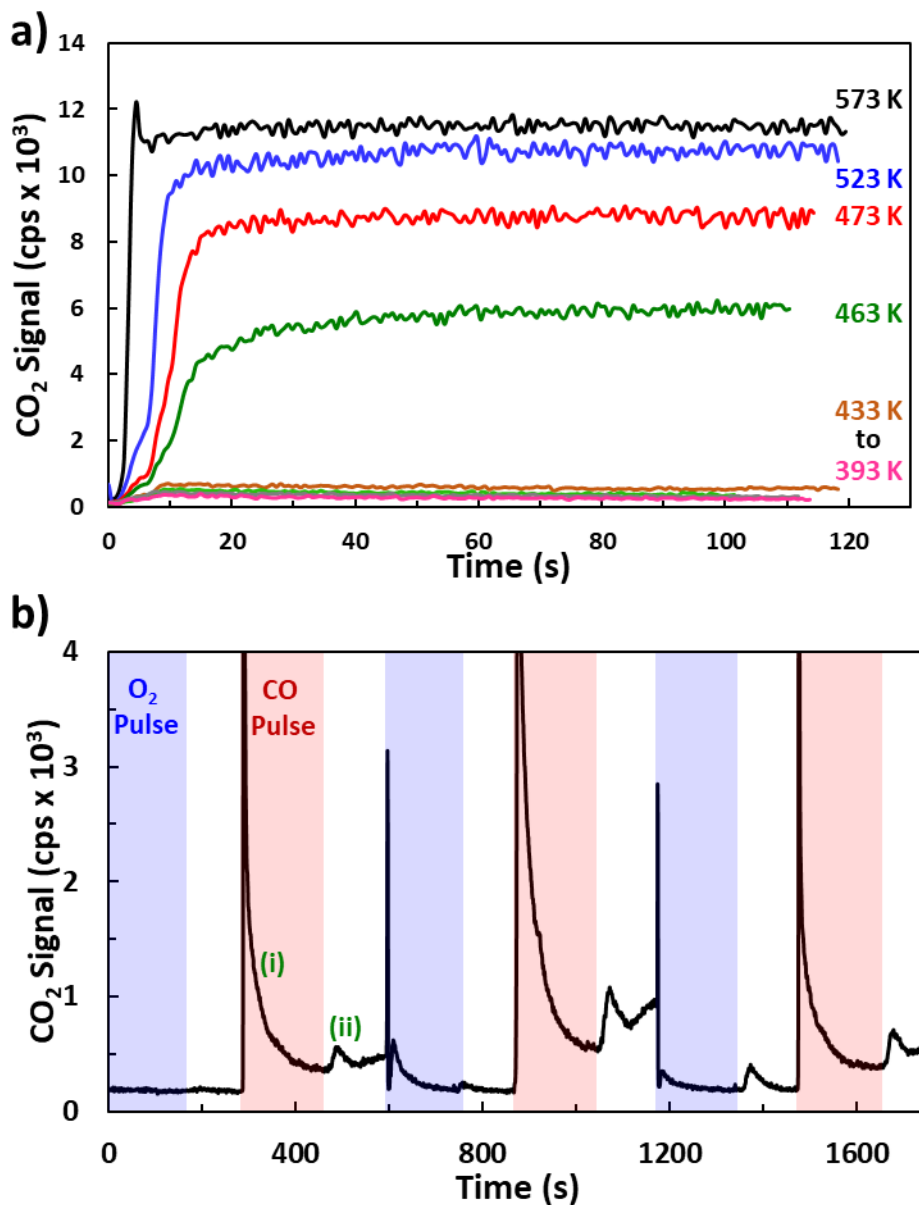


Figure 4.1 Downstream mass spectrometry of CO and O₂ flow over Cu/TiO₂, monitoring signal at 44 m/z at (a) different catalyst bed temperatures and (b) alternating activating O₂ and reactive CO pulses over at 573 K. Point (i) shows CO₂ production, point (ii) shows thermal desorption of CO₂ in vacuum.

Although others have observed efficient CO oxidation over Cu-based catalysts, there are few detailed studies into the overall mechanistic details of the

reaction.^{23,25,28,115,163,164} Here, insight into the role of gas-phase O₂ in the overall reaction is provided by exploring CO₂ production under anaerobic conditions. A Cu/TiO₂ sample was exposed to alternating, 5 min pulses of 10 SCCM pure O₂, to initially oxidize the catalyst, followed by exposure to CO in the absence of gas-phase oxygen (Figure 4.1b). Between each gas pulse, the reactor tube was evacuated for two minutes to remove residual and weakly bound O₂. Transient, but rapid, initial CO₂ production is observed at 573 K upon introduction of CO. However, CO₂ production decreased as the available active oxygen was consumed.

The mass spectrometry data detailing the oxidative ability of Cu/TiO₂ aerogels at various temperatures in Figure 4.1 can also be used to analyze the reaction kinetics. Initial rates of the oxidation to CO₂ can be taken and plotted as a function of 1/T in an Arrhenius-type plot to evaluate the apparent activation energy of reaction. The Arrhenius plot showing the linearity of the natural logarithm of the initial rates as a function of 1/T is shown in Figure 4.2. The $E_{a,app}$ is evaluated to be 51 ± 3 kJ/mol. The Cu/TiO₂ aerogel catalyst might not be as active as Au/TiO₂ with lower activation barriers for a Langmuir-Hinshelwood mechanism,¹⁶⁵ but the evaluated $E_{a,app}$ is consistent with the CO₂ desorption energy of the lattice extraction mechanism on Au/TiO₂, calculated to be about 52 kJ/mol by Schlexer et al.⁶³

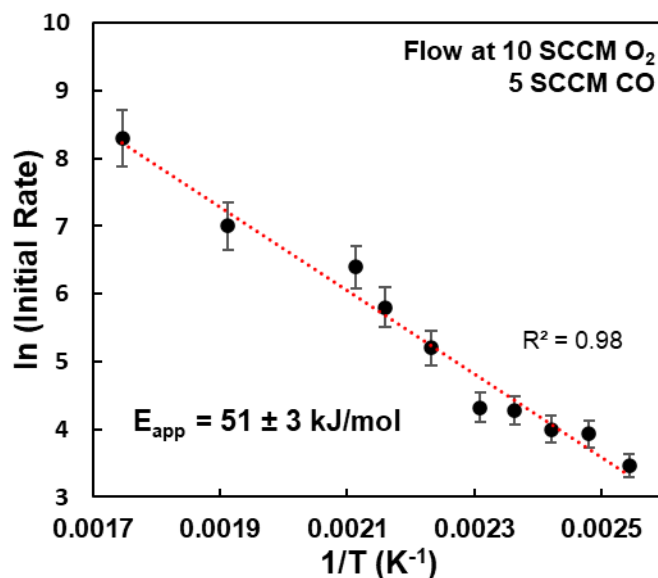


Figure 4.2 Arrhenius plot of the natural log of the initial rates for the CO oxidation reaction over Cu/TiO₂ as detected by m/z: 44 in the QMS as a function of reaction temperature to evaluate apparent activation energy. The raw data that makes up this plot comes from Figure 4.1a. Error bars represent 5% error of the evaluated rates.

Product formation in the absence of O₂ gas indicates either removal of oxygen within the Cu/TiO₂ lattice via a MvK mechanism,¹⁷ or reaction with adsorbed oxygen consistent with a Langmuir-Hinshelwood or an Eley-Rideal mechanistic pathway.^{58,159} The observation of a color change from white activated Cu/TiO₂ to black Cu/TiO₂, following the CO pulse, indicates the reduction of titania by CO.^{166–169} Similar studies on Au/TiO₂ proposed that the MvK mechanism controls CO₂ production, where the presence of Au played an important role in the overall chemistry.^{17,57,63} They referred to this phenomenon as a "Au-assisted MvK mechanism". One speculates that the copper particles within the TiO₂ aerogel samples explored here likewise assist in the activation of oxygen. Consistent apparent activation energies between systems also can suggest a similar reaction pathway.

Control studies ensured that pure TiO₂ aerogels are not active for CO oxidation from the packed-bed reactor studies. Copper, unlike gold, is often observed in a variety of oxidation states that likely influence the reactivity of the Cu/TiO₂ aerogel catalyst.^{115,163,170} To distinguish between these possible mechanisms, *in situ* IR characterization of CO oxidation is performed to characterize CO binding sites and determine how binding sites change in aerobic or anaerobic conditions.

4.3.2 CO(ads) as an Infrared Spectroscopic Probe of Surface Sites

Speciation of copper is often determined by X-ray photoelectron spectroscopy, specifically the Cu LMM Auger electrons.³⁶ However, the signal in this region is largely dominated by photoelectrons from the Ti 2s level due to the spectral overlap and large abundance of Ti in the material. Therefore, IR spectroscopic studies of the probe molecule CO have been employed to characterize the nature of sites that decorate the surface of Cu/TiO₂ aerogels.⁵³

Over the course of several decades, CO has been employed as a highly effective molecular probe.^{53–55} The high sensitivity of the IR stretching frequency of CO can be used to help characterize surface sites, such as those of the Cu/TiO₂ aerogel catalyst. Polarization and charge transfer (both from the metal to CO and CO to the metal) affect the vibrational frequency of adsorbed CO molecules.^{53,56} Interactions between CO and low electron density sites (i.e. Ti⁴⁺) occur through electrostatic and σ bonding interactions. Specifically, charge transfer occurs from the C-end lone pair of CO to the metal cation in a σ -coordination. The interaction causes the $\nu(\text{CO})$ stretching frequency to increase relative to that of gas-phase CO. Alternatively, metal cations with partially filled *d* orbitals can

contribute charge to the $2\pi^*$ orbital of CO. The increase in electron density in the antibonding orbitals of CO causes the C-O bond force constant to decrease and the C-O bond length to increase, resulting in a $\nu(\text{CO})$ stretching frequency decrease relative to the gas-phase molecule. The high sensitivity of the IR stretching frequency of CO to a specific surface site to which the adsorbate is coordinated can be used to help characterize surface sites, such as those of the Cu/TiO₂ aerogel catalyst.

Prior to CO characterization, the samples were pretreated under either oxidizing conditions (673 K, 10 Torr O₂, 1 hour) or under reducing conditions (673 K, in vacuum, 2 hours). The sample was then cooled in vacuum to 173 K before exposure to 600 mTorr of CO. Difference IR spectra (recorded before and after CO exposure) on the Cu/TiO₂ material are shown in Figure 4.3.

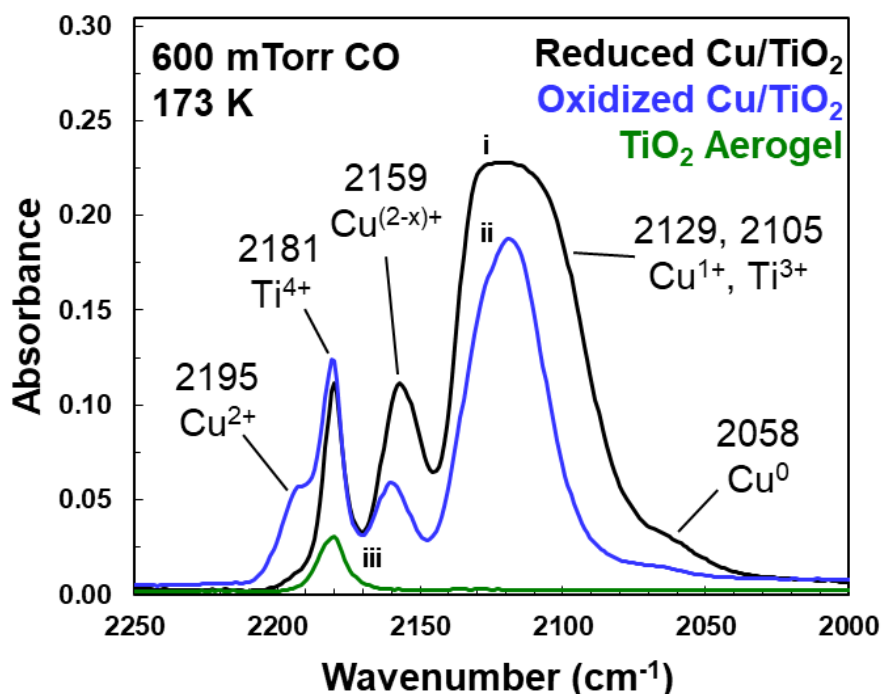


Figure 4.3 Infrared spectroscopy of CO adsorption at Cu/TiO₂ aerogels prepared by a reducing treatment (spectrum i, black trace) and oxidizing treatment (spectrum ii, blue

trace). TiO₂ aerogel standard shown (spectrum iii, green trace) underwent oxidizing pretreatment prior to CO adsorption. Each trace shown is a difference spectrum, referenced to the same pretreated sample prior to CO exposure.

The lowest frequency spectroscopic feature in Figure 4.3, which appears as a small shoulder at 2058 cm⁻¹, is attributed to CO adsorbed to metallic copper Cu⁰ sites.¹¹⁵ It has been established that CO bands below 2100 cm⁻¹ are characteristic of metallic copper sites while CO bands above 2100 cm⁻¹ are characteristic of oxidized Cu sites.^{29,171,172} The metallic copper is likely situated along the interface of the copper nanoparticle and the titania support.^{36,115} The most predominant spectral feature, spanning 2100 - 2130 cm⁻¹, is identified as CO adsorbed at both Cu¹⁺ and Ti³⁺ sites. The large spectral component at 2105 cm⁻¹ that emerges following reductive pretreatment is indicative of the formation of Ti³⁺ sites that back-donate *d*-electrons to the CO 2 π^* orbital.^{115,173-175} Reduction of the lattice is consistent with the observation that the TiO₂ changes from white to black during CO exposure (see text associated with Figure 4.1). No CO-Ti³⁺ is observed on the TiO₂ aerogel following an oxidizing pretreatment. While consistent with previous work, there is not definitive evidence that CO bound to Ti³⁺ sites yields an infrared band in this range and future studies may refine this band assignment. Adsorbed CO on Cu¹⁺ also contributes to signal in this spectral region. This assignment is consistent with other reports that identify an IR band centered at 2125 cm⁻¹, which is typically attributed to the vibrational signature of CO bound to Cu¹⁺.¹⁷⁰ The CO vibrational band at 2181 cm⁻¹, which can be assigned to CO at Ti⁴⁺ sites, is in agreement with literature values and matches the present measurements for CO adsorption on a TiO₂ aerogel standard.¹⁷⁰ CO coordinated to Cu²⁺

has previously been shown to yield a vibrational band 2195 cm^{-1} , in agreement with the assignment shown in Figure 4.3.¹⁷⁰

Beyond the infrared absorption bands identified above, the distinct feature at 2159 cm^{-1} cannot be unambiguously assigned to CO at a specific surface site. Previous studies on Cu/TiO₂ materials attribute an absorption band near 2159 cm^{-1} to hydrogen-bonded CO located at surface hydroxyl sites (TiOH).¹⁷⁰ However, this assignment is inconsistent with the Cu/TiO₂ aerogel employed here because the thermal pre-treatment effectively removes surface hydroxyl groups.¹⁷⁶ In fact, OH groups are not detected spectroscopically on the Cu/TiO₂ or TiO₂ aerogel surface following pre-treatment. Further, CO adsorption on the pure TiO₂ aerogel (void of Cu particles) does not lead to IR bands in this region. Previous investigations of CO adsorption onto Cu-containing zeolites (Cu-SSZ-13) reported a vibrational wavenumber for CO at 2154 cm^{-1} , which was assigned to a dicarbonyl species coordinating to Cu (albeit at significantly lower temperatures than the experimental procedure).¹⁷⁷ Dicarbonyls manifest infrared absorbance bands associated with symmetric and asymmetric motions;¹⁷⁰ however, such IR bands have not been observed in the present work. The intensity of the band at 2159 cm^{-1} is observed to increase as the sample is reduced and decreases as the sample is oxidized. Given that the CO vibrational frequency increases with the oxidation state of the copper site to which it is bound, and that the band appears between those assigned to CO at Cu²⁺ and Cu¹⁺, the 2159 cm^{-1} feature is assigned to CO bound to an intermediate oxidation state of copper: Cu^{(2-x)+}, where $0 < x < 1$.

4.3.3 CO Oxidation Mechanistic Studies

The mechanistic details of CO oxidation over Cu/TiO₂ were explored via infrared spectroscopic investigations of surface-bound and gas-phase product evolution by recording spectra during exposure of the catalyst to gaseous CO and O₂. Surface-bound species were probed by transmitting the IR beam through the sample (see above), while gas-phase product evolution (i.e., CO₂) was monitored by translating the sample out of the path of the IR beam.

Evidence that CO oxidation follows a MvK mechanism emerged from experiments performed under anaerobic conditions. Exposing an oxidatively pretreated Cu/TiO₂ sample to CO revealed that CO₂(g) was clearly generated in the absence of O₂(g) at concentrations that scaled with the partial pressure of CO(g) (410 mTorr to 5.50 Torr, Figure 4.4a). Under these anoxic reaction conditions, the oxidant is the solid material itself. That is, the oxygen is extracted either upon reduction of the Cu nanoparticles or the TiO₂ support.

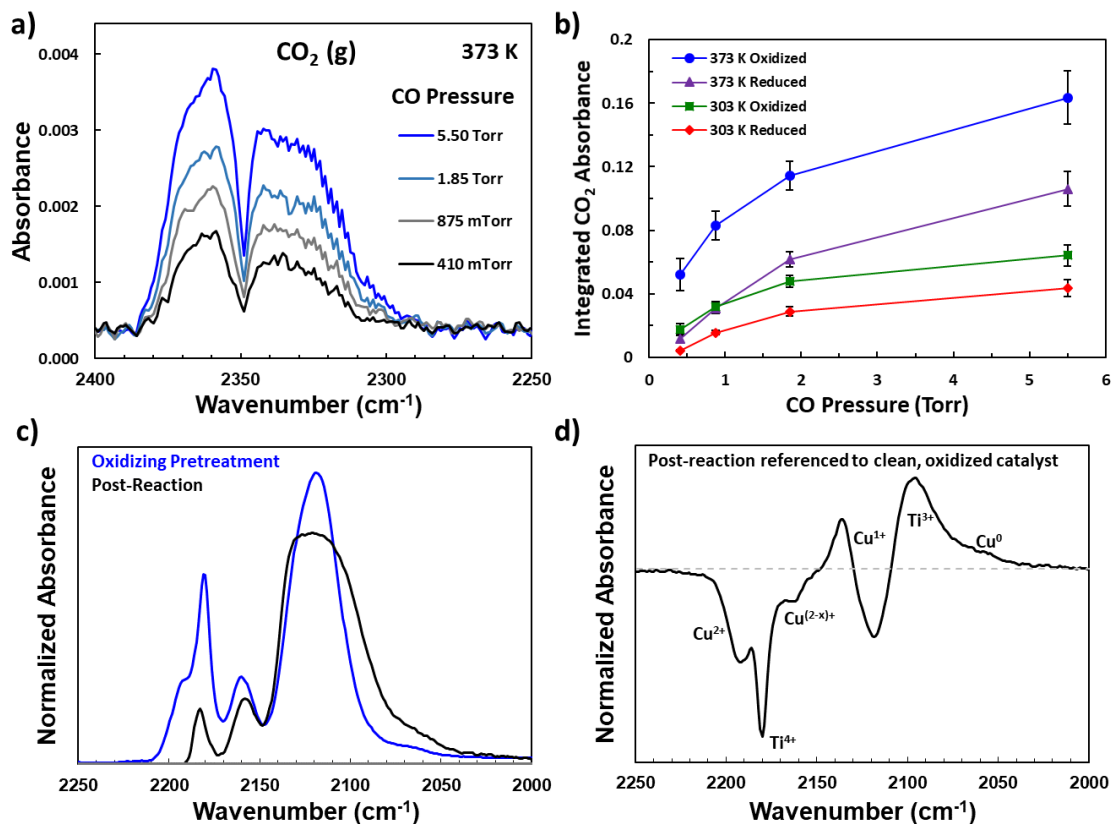


Figure 4.4 (a) Infrared spectra of the gas-phase species generated by the reaction of CO on Cu/TiO₂ at different pressures. Spectra were taken through the blank area of tungsten mesh. (b) Plot of integrated CO₂ absorbance vs CO pressure for Cu/TiO₂ reaction with pure CO. Traces show two different reaction temperatures and pretreatment conditions. Error bars indicate 1 standard deviation from the average of 5 reaction iterations. (c) Area-normalized low-temperature CO adsorption (183 K, 1 Torr) before and after the reaction in (a), referenced to the respective sample before exposure to CO. (d) Difference spectrum from (c) showing site changes due to anaerobic CO oxidation.

The specific source of oxygen under anaerobic conditions was further investigated by performing the CO oxidation reaction over a reduced Cu/TiO₂ sample. As described above in Figure 4.3, the reduced catalyst appears to be devoid of Cu²⁺ sites along with

substantially fewer $\text{Cu}^{(2-x)+}$ sites relative to an oxidized catalyst. Figure 4.5 indicates that Cu^{1+} sites do not directly participate in the anaerobic oxidation of CO as they are not depleted during oxidation. Despite the absence of available copper(I) oxides, the reduced catalyst produced appreciable concentrations of gas-phase CO_2 (Figure 4.4b). Importantly, measurements performed over both the oxidized and reduced catalysts followed the same trend as a function of CO pressure. Taken together, this information suggests that lattice oxygen atoms on titania regions of the material serve as the active sites for catalysis under flow conditions. The source of surface oxygen for CO_2 production was further probed by tracking changes to the material. Infrared spectra of the catalyst before and after anaerobic CO exposure (Figure 4.4c, d) reveal that the features assigned to CO adsorbed to Ti^{4+} , Cu^{2+} , and $\text{Cu}^{(2-x)+}$ decrease during oxidation, while charge redistribution results in a slight blueshift to the vibrational frequency for CO bound to Cu^{1+} . The oxidized sites are replaced by reduced species in the form of Ti^{3+} , Cu^{1+} , and Cu^0 , as indicated by the increase in absorbance for features assigned to CO bound these reduced surface sites. Therefore, upon initial exposure of the particles to CO, oxygen is removed from a variety of surface sites as the sample is reduced to produce CO_2 .

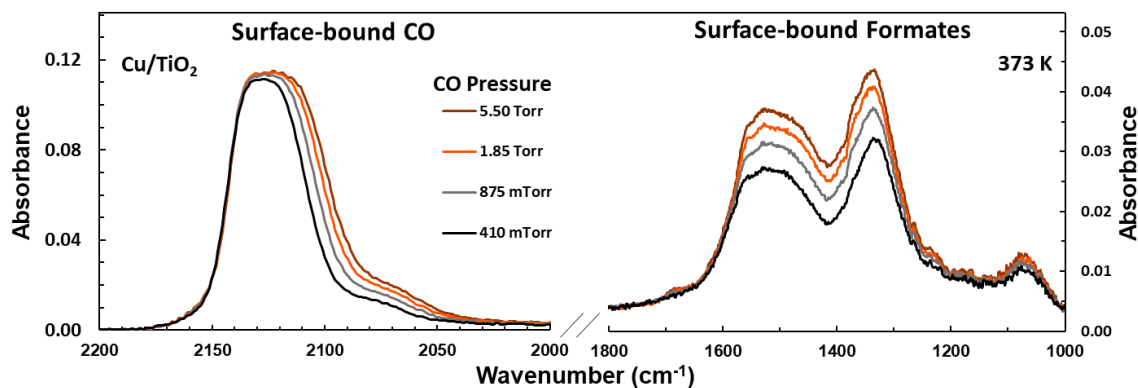


Figure 4.5 Infrared spectra of the Cu/TiO₂ surface during the reaction of CO on Cu/TiO₂ at different dosing pressures. Results correspond to the same experiment displayed in Figure 4.4a, where gas-phase spectra are shown. The left side displays the CO triple bond region, and the right side displays the lower frequency region of the IR spectra.

While initial exposure of the sample to CO rapidly reduces the available surface sites, sustained CO₂ production (as demonstrated in Figure 4.1) through a catalytic cycle requires the regeneration of active surface oxygen. Previous work demonstrates that the metallic copper sites are stable below 423 K and do not re-oxidize until much higher temperatures.¹¹⁵ In contrast, Ti³⁺ sites are easily re-oxidized (i.e., the bridging oxygen atoms are regenerated) under the flow conditions employed above (Figure 4.1). This information, together with the control study that demonstrated a pure TiO₂ aerogel is not active for CO oxidation, highlights the important role of copper particles. The presented results are consistent with other supported metal particles that have been shown to activate oxygen near the metal NPs for reaction with CO.^{17,57,63,159} The particles, though not the source of oxygen, play the role of activating TiO₂ lattice oxygen atoms for extraction to establish a Cu-assisted MvK reaction mechanism. The data does not disprove an Eley-Rideal mechanism, but if it were the primary mechanism, Ti³⁺ sites would not be generated and CO₂ would not be formed under anaerobic conditions.

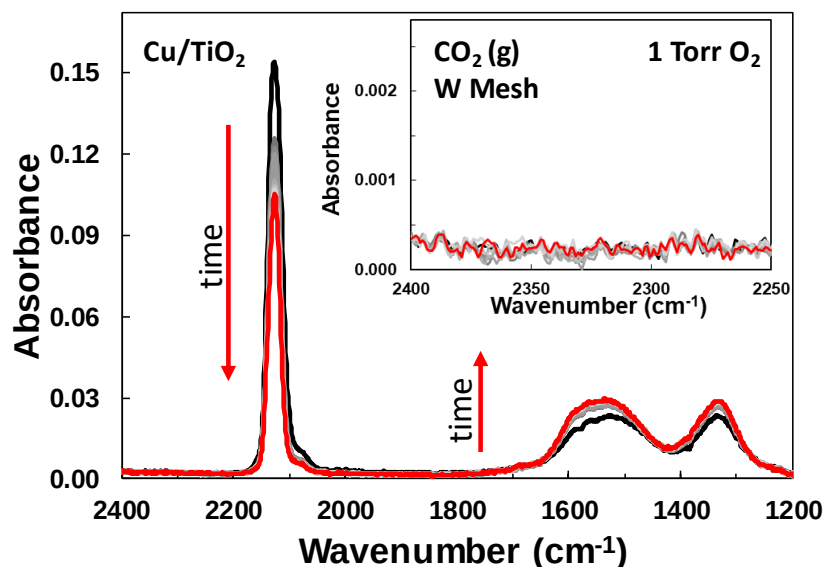


Figure 4.6 FTIR spectra taken on the Cu/TiO₂ aerogel surface (main) and monitoring evolution of gas-phase CO₂ (inset) in 1 Torr O₂ after CO was adsorbed onto the aerogel sample at 323 K. 5 Torr CO was introduced to the chamber for 15 minutes before evacuation and subsequent exposure to O₂.

Additional evidence in support of the MvK reaction pathway comes from an experiment in which the Cu/TiO₂ catalyst was initially saturated with CO via exposure for 15 min at 300 K. At such an elevated sample temperature, the short lifetime of CO at coordinatively unsaturated Ti sites precludes significant occupation of these sites;¹³⁸ rather, the CO is located primarily at sites associated with the Cu nanoparticles. Following the evacuation of gaseous CO, 1 Torr of O₂ was introduced to the sample while infrared spectra were recorded to search for the emergence of gas-phase CO₂ and changes to the surface CO coverage. The results (Figure 4.6) show no production of CO₂(g) above the limits of detection (about 47 mTorr). Furthermore, the amount of CO bound to copper depleted by less than 30% during the O₂(g) exposure. Thus, even when CO resides directly on the

copper NPs (bound to Cu^{1+} sites) and $\text{O}_2(\text{g})$ impinges on the surface, oxidation does not appear to occur because the bound CO cannot readily access lattice TiO_2 oxygen. Under reaction conditions, interactions of CO from the gas phase with lattice oxygen appear to be the dominant reaction pathway for CO_2 production.

Previous mechanistic studies on other Cu/TiO_2 and Au/TiO_2 materials spotlight the unique surface chemistry of the Cu/TiO_2 aerogels. Typical (non-aerogel) decorated Cu/TiO_2 particles that are active for CO oxidation have been shown to follow a Langmuir-Hinshelwood type mechanism, with CO activated on Cu^0 or Cu^{1+} while O_2 is activated on the oxide.²³ In contrast, Au/TiO_2 catalysts exhibit temperature-dependent CO oxidation mechanisms. Specifically, Yates et al. reported that a Langmuir-Hinshelwood pathway proceeds at low temperatures (120 K), where CO adsorbs at Ti^{4+} sites and reacts with activated oxygen at dual-perimeter sites.¹⁷⁸ At elevated temperatures (> 353 K), others have shown, through temporal analysis of products, that CO oxidation over a Au/TiO_2 catalyst follows a MvK reactive pathway, consistent with observations for the Cu/TiO_2 catalyst.^{17,57,63}

4.3.4 CO_2 on Cu/TiO_2 and Proposed Reaction Mechanism

Despite the active nature of the Cu/TiO_2 aerogel catalyst to cycle oxidation state during CO exposure and CO_2 production, sustained oxidation of CO in oxygen over the catalyst does not appear to be appreciable below temperatures of 450 K. Other catalysts, such as Au/TiO_2 and Pt/FeO_x are active for CO oxidation at much lower temperatures.^{2,3,179} To achieve sustained CO_2 production over the Cu/TiO_2 aerogel catalyst, elevated temperatures may be required to remove surface adsorbates. The IR spectra reveal that two

broad features appear at 1330 and 1500 cm^{-1} during the reaction (Figure 4.5). Similar features were found by researchers studying the CO oxidation on Au/TiO₂, and were attributed to surface-bound carboxylates.^{158,180} No C-H stretches were observed in the high wavenumber region to indicate that formates were generated. The surface-bound carboxylates are likely due to CO or CO₂ interactions with the TiO₂ support that block the ability of O₂(g) to replenish the active sites, thereby stifling the catalytic cycle.

The hypothesis that surface sites become blocked at low temperatures by adsorbates was tested by analyzing the low-wavenumber region of the infrared spectra. Key bands at 1330 and 1500-1550 cm^{-1} that emerged after CO oxidation on the Cu/TiO₂ sample are consistent with respective symmetric and asymmetric stretches of an O-C-O species on TiO₂, as previously assigned.^{181,182} Importantly, the same bands developed when 1 Torr of CO₂ was exposed to Cu/TiO₂ (Figure 4.7). The same CO₂ exposure on both an oxidized (Figure 4.7, black trace) and reduced (Figure 4.7, red trace) catalyst shows that more CO₂ adsorbs to the reduced sample, as seen from the asymmetric and symmetric O-C-O stretches, suggesting that bridging oxygen vacancies, or Ti³⁺ sites, are preferential adsorption sites for CO₂.¹⁸²

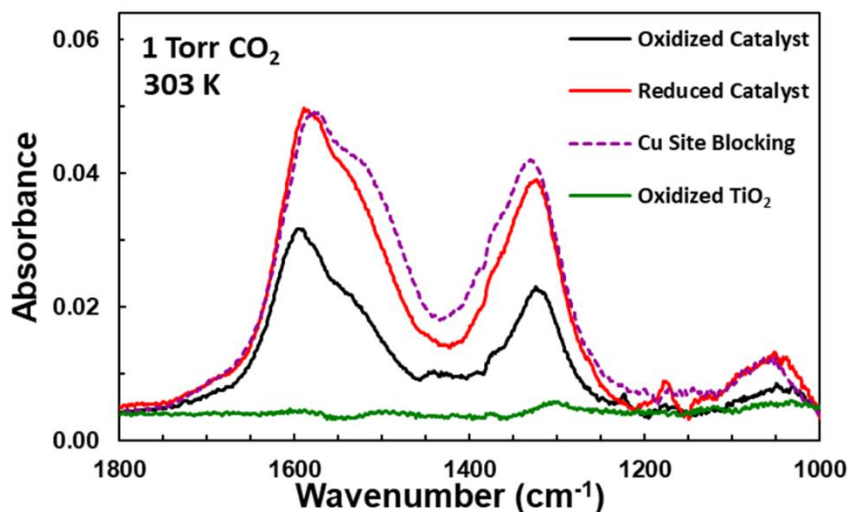


Figure 4.7 Infrared difference spectra of CO₂ on Cu/TiO₂ that underwent an oxidative pretreatment (black), a reductive pretreatment (red), a reductive pretreatment followed by 183 K CO adsorption (dashed purple), and TiO₂ that underwent a reducing pretreatment (green). Spectra referenced to clean corresponding materials (Cu/TiO₂ aerogel and TiO₂ aerogel) at 303 K.

To understand the role of Cu in CO₂ adsorption, CO was employed to selectively block Cu surface sites from CO₂ adsorption. Carbon monoxide was first exposed to the clean but reduced Cu/TiO₂ sample at cryogenic temperatures (183 K), followed by evacuation to remove weakly-bound CO from the titania regions. This initial deposition treatment leaves CO bound to the Cu sites. Exposure of the CO-covered particles to CO₂ resulted in an IR spectrum that was nearly identical to that recorded for the same experiment in the absence of the carbon monoxide adsorbate (Figure 4.7, dashed purple trace). Therefore, Cu does not appear to directly bind CO₂. Rather, CO₂ adsorption likely occurs through interactions with V_O on TiO₂. Interestingly, no CO₂ adsorbs to the pure TiO₂ aerogel, further demonstrating that the copper NPs affect the support in significant ways. As the presence of copper is needed for adsorption but does not directly interact with CO₂, it is hypothesized that EMSIs like those described in Chapter 2 are responsible for the binding of CO₂ in the Cu/TiO₂ aerogels.

This surface-bound O-C-O species is likely an intermediate along the pathway to full CO oxidation. Thus, catalysis is truncated when the intermediate remains bound to the surface at lower temperatures. Together with the results described above, it is proposed

that the overall mechanism follows one similar to a Cu-assisted MvK mechanism shown in Figure 4.8. In this scheme, charge transfer from the Cu NPs to TiO_2 observed in Chapter 3 partially reduces the regions around the periphery of the metal NPs. The charge transfer activates lattice oxygen for extraction by gas-phase CO. In this proposed mechanism, CO first interacts with the active site, bridging oxygen atoms on the periphery of Cu NPs. CO may then extract oxygen to form CO_2 either from the copper particles or from the titania lattice; however, V_O formation within the lattice appears to be required for sustained catalysis. Once $\text{CO}_2(\text{g})$ desorbs and a V_O is generated, another molecule of CO coordinates to a neighboring bridging O to generate the O-C-O intermediate. $\text{CO}_2(\text{g})$ can alternatively adsorb at reduced Ti sites at temperatures below that for which CO_2 evolves from the surface. The interaction forms a strong bidentate interaction that blocks re-oxidation by gas-phase O_2 to poison the catalyst. At high temperatures ($> 433 \text{ K}$), CO_2 desorbs from the TiO_2 support, and oxygen regenerates the catalyst to close the cycle.

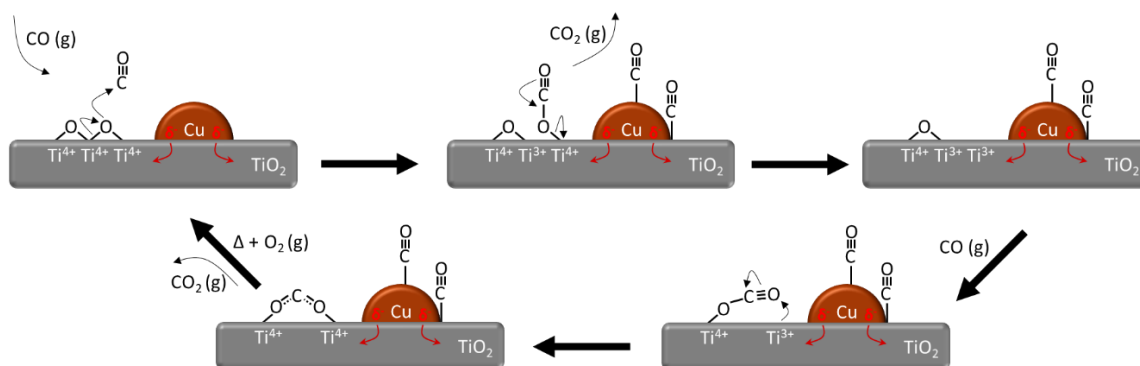


Figure 4.8 Proposed CO oxidation mechanism on Cu/ TiO_2 .

The origin of the active oxygen species within the TiO_2 lattice is not fully understood. The observed charge transfer described above may help account for the oxygen activation if additional electron density on TiO_2 weakens the Ti-O bond, but more

experimental and computational studies are needed to support this hypothesis. Recent review articles and other investigations into the interfacial charge transfer often arrive at conflicting explanations for the physics behind the role of charge transfer in the activation of MvK-type catalytic reactions.^{24,26,102,104,105,183} Clearly, the energy of the metal material work function relative to the Fermi-energy of the support plays a major role in the charge transfer dynamics, but bulk-metal work function values are not applicable to the nanoscale.^{12,108} Thus, the heterogeneous catalysis field will benefit from future computational and experimental studies that investigate the effect of charge transfer on oxygen extraction efficiency.

4.4 Summary

In this work, an infrared probe molecule (CO) was used to characterize various surface sites within Cu/TiO₂ aerogels. Spectroscopic and spectrometric evidence was provided that catalytic CO oxidation over the Cu/TiO₂ aerogel proceeds primarily by a Cu-assisted Mars-van-Krevelen type mechanism. Interfacial charge transfer from low-valent Cu NPs to the TiO₂ support displayed in Chapter 3 may play an important role in the activation of lattice oxygen. Carboxylate intermediates generated upon oxidation appear to coordinate to Ti³⁺ sites, and prevent the active form of the catalyst from being regenerated. The active sites are replenished at elevated temperatures that remove CO₂ from the surface to open a channel for O₂ to fill the oxygen vacancies within the support. This understanding of the CO oxidation mechanism and the role of interfacial charge transfer on aerogel-supported Cu NPs lay the foundation for future studies into more complex oxidation reactions.

Chapter 5

Mechanistic Insights into the Catalytic Oxidation of Methanol on Cu/TiO₂ Aerogels

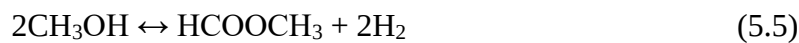
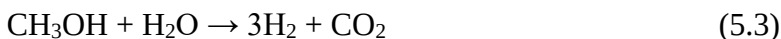
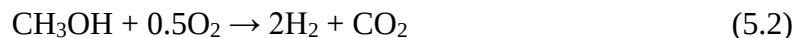
5.1 Introduction

Since the discovery of catalytic gold,^{2,3} metal nanoparticles (NPs) supported on metal oxides have been of particular interest to the catalysis community.¹²⁴ The most studied metal NPs are precious metals with low abundance (Au, Pd, Pt, Ir) due to their high catalytic activity and desired product selectivity for reactions such as CO oxidation,^{50,58,159,184} methanol oxidation,^{73,160} and the decomposition of organophosphorus chemical warfare agents/simulants.^{48,78,80,83} Economic and abundance concerns have driven researchers to investigate and design metal catalysts using more Earth-abundant metals. Copper nanoparticles have been shown to be an attractive alternative to precious metal NPs, showing oxidation activity in various applications.^{24,26,48–50,108,115,164,185,186} Stability of the active forms of copper has been a concern, due to instability during operational conditions.¹⁶¹ Stability of low valent Cu through the use of a networked oxide support, a TiO₂ aerogel, has been shown by recent efforts.^{50,115,187}

The uncovering of reaction dynamics and mechanisms for model reactions on new catalyst designs can yield insights into how the material will operate under more complex reactions. To this end, Cu/TiO₂ aerogels were previously studied to determine the mechanism for CO oxidation.⁵⁰ It was found that an interfacial charge transfer from lower work function copper NPs to the TiO₂ support accompanied the lattice oxygen extraction of the TiO₂ support in a Cu-assisted Mars van-Krevelen type mechanism. The surface reaction is similar to that of CO oxidation on Au/TiO₂ at elevated temperatures, as

discovered by Widmann and Behm, with Au assisting in the extraction of lattice oxygen in TiO₂ at the periphery of the metal NP.^{17,57} Critically, the Langmuir-Hinshelwood type mechanism for CO oxidation on Au/TiO₂ that occurs on the metal NP at low temperatures as found by Green et al. does not occur on Cu/TiO₂ aerogels.^{50,165} Chemical and electronic interactions, particularly at the NP/oxide interface, play a critical role in catalytic dynamics and mechanisms.^{17,58,94} These results also highlight the importance of the support oxide, and the effect it has on the stability of the supported NP as well as the direct influence on catalysis. The combination of understanding electronic interactions with elucidating reaction mechanisms opens the novel Cu/TiO₂ aerogel materials for further studies into more complex oxidation reactions.

Methanol oxidation, like CO, is an important surface probe reaction.^{188,189} Methanol oxidation can be sensitive to the surface structure of the catalyst, where selectivity depends on the arrangement of surface atoms.¹⁸⁸ Depending on the catalyst structure, reaction temperature, reactants, and reactant partial pressures, several products can be formed. The reaction of methanol can proceed through many pathways, most commonly including methanol combustion (Eq. 5.1), partial oxidation of methanol (Eq. 5.2), methanol steam reforming (Eq. 5.3), methanol decomposition (Eq. 5.4), and the dehydrogenation of methanol (Eq. 5.5).



Methanol is also extremely important for fuel cells in the production of H_2 ,¹⁹⁰ and as an intermediate in the chemical industry, used to synthesize hydrocarbons and mild oxidation products (including formaldehyde, dimethyl ether, methyl formate, formic acid, and dimethoxymethane). Panayotov et al. investigated methanol photooxidation on TiO_2 and elucidated the electronic interactions between dissociatively adsorbed methanol and both the conduction band and shallow trap states of TiO_2 .¹⁶⁰ Additionally, they found the main role of oxygen was to remove the photogenerated electrons through superoxide formation. On Au/TiO_2 , Nuhu and coworkers found potential methoxy and formate intermediates before reacting to CO_2 , CO , CH_4 , H_2O , and H_2 , but were unable to elucidate a reaction mechanism or determine how the catalyst formed the varying products.¹⁹¹ Camellone et al. were able to elucidate the importance of O_2 activation at dual perimeter sites on Au/TiO_2 in methanol oxidation, where co-adsorbed methanol reacts directly on top of activated molecular oxygen to form a Au-stabilized CH_3OH-O_2 intermediate via an Eley-Rideal mechanism before subsequent oxidation to formaldehyde.⁷² These studies vary in their findings and focus, but all stress the importance of elucidating the reaction dynamics on catalyst surfaces.

In this study, vibrational spectroscopic studies were applied to study the catalytic methanol oxidation mechanism on Cu/TiO_2 aerogels. Through comparisons to metal NP-free TiO_2 aerogels, the promotional effect of Cu is shown to be vitally important to the reaction. Supported by packed-bed reactor studies, *in situ* infrared spectroscopic evidence is provided of lattice oxygen extraction from TiO_2 regions of the catalyst as the main mechanism for oxidation to gaseous CO_2 . These studies provide insight into the adsorption

profile and reaction dynamics of the adsorbed alcohol on an aerogel-supported Cu NP catalyst.

5.2 Procedural Methods

5.2.1 Cu/TiO₂ Synthesis

Cu/TiO₂ aerogels were prepared by photodepositing Cu nanoparticles onto TiO₂ aerogels in a manner described previously.^{36,81,115} First, TiO₂ aerogels were prepared using a sol-gel method.³⁷ A wet gel is formed by adding a solution of Ti(ⁱOPr)₄ (Alfa Aesar, 97+%) in 3.9 g of ethanol (absolute ethanol, Warner-Graham) to a mixture of H₂O (0.39 g), ethanol (4.0 g), and nitric acid (78 mg of 70% HNO₃, Fisher). After aging for 24 h, the wet gel was rinsed 10 times with acetone over multiple days. The wet gels were loaded under acetone into a supercritical dryer and rinsed with liquid CO₂ at 283 K before heating the dryer to 314 K and then venting to atmospheric pressure. The TiO₂ aerogels were calcined in air at 698 K (2 K min⁻¹ heating and cooling ramp, 4 h dwell) to produce nanocrystalline anatase aerogels. Following an established method,²⁸ Cu nanoparticles were photodeposited onto the TiO₂ aerogels by illuminating slurries containing ~150 mg TiO₂ aerogel suspended in a solution of 110 mL of 2 mM Cu(NO₃)₂ (Sigma-Aldrich, 98%) in 9:1 (vol:vol) H₂O:CH₃CH₂OH (adjusted to pH 9.5 ± 0.5) for a period of 24 h with a 500 W Xe arc lamp (Newport Oriel). The Cu/TiO₂ aerogels were collected by centrifugation followed by re-suspension in Ultrapure 18 MΩ cm water (Barnstead Micropure) for 10 cycles. The Cu/TiO₂ aerogels were then dried in air at 373 K overnight.

5.2.2 Vacuum Studies with Infrared Spectroscopy

Infrared spectroscopic studies were performed in a stainless-steel high-vacuum reactor cell with a base pressure of 1×10^{-8} Torr (see Chapter 2). Cu/TiO₂ and TiO₂ aerogel samples were pressed (at 5000 psi) as 7 mm disks into the void space of a 50- μ m thick tungsten mesh (Tech-Etch), secured onto a stainless-steel sample holder. The tungsten mesh sample holder allows for both samples to be exposed to the same gaseous and thermal environments, enabling direct comparisons between the materials.⁸⁹ A K-type thermocouple was attached directly to the tungsten mesh, within 3 mm of the samples, to monitor sample temperature. The tungsten mesh was resistively heated using copper rods attached to an external power supply. Details of the high-vacuum cell can be found in previous work.⁸⁵ An FTIR spectrometer with an external MCT-A detector (Thermo, Nicolet Nexus 470 FTIR, resolution 2 cm⁻¹, optical velocity 1.8988 cm/s) couples to the vacuum chamber to provide the *in situ* infrared spectroscopic measurements.

Samples were pretreated in the vacuum chamber by exposure for 1 hour at 673 K in 10 Torr of O₂ followed by 30 minutes at 673 K in vacuum. This pretreatment procedure effectively removes weakly-bound organic species on the surface, as confirmed by infrared spectroscopy of the samples. For exposures of O₂ (99.994% purity, Airgas Ultra High Purity), methanol (Fisher Chemical, HPLC Grade), formic acid (98.0-100%, Sigma-Aldrich), and H₂O (Fisher Chemical, HPLC Grade), a gas manifold affixed to the vacuum chamber allowed for quantifiable amounts of each gas to be introduced into the chamber and exposed onto each material. About 2 mL of the liquids were added to vapor dosing bulbs and subjected to at least 3 freeze-pump-thaw cycles before vapor introduction into the vacuum chamber.

5.2.3 Ambient Pressure Packed-Bed Flow Reactor

Catalyst activity was screened with a packed-bed reactor (Altamira Instruments, μ BenchCAT) coupled to multiple detection methods, including a differentially-pumped quadrupole mass spectrometer (ABB Extrel MEXM) and an FTIR spectrometer (Thermo, Nicolet Nexus 870 FTIR, resolution 4 cm^{-1} , optical velocity 0.6329 cm/s). The apparatus is described in Chapter 2. 3 mg of Cu/TiO₂ aerogel catalyst was packed into a 0.25-inch diameter quartz tube and secured by quartz wool on both sides of the tube. Gaseous reactant flow into the cell was controlled with mass flow controllers. Methanol was stored in a glass bubbler and carried by an inert Ar flow (99.999% Praxair Ultra High Purity) separate from an O₂ stream, before combining to mix before introduction to the catalyst. The temperature of the catalyst bed was monitored with a K-type thermocouple. Prior to each experiment, the Cu/TiO₂ sample was activated at 573 K under 10 SCCM flow of O₂ for 30 minutes.

5.3 Results and Discussion

Methanol reaction pathways on the surface of Cu/TiO₂ aerogels have been investigated by infrared spectroscopy in a high-vacuum cell and a packed-bed reactor. Specifically, in situ infrared spectroscopic measurements tracked surface-bound adsorbates while simultaneously identifying the gaseous reaction products. The packed-bed reactor, coupled to a mass spectrometer and an IR detector, was utilized to both characterize IR-inactive gas-phase molecules and to analyze the catalysis under operational conditions.

5.3.1 Catalytic Activity of Cu/TiO₂ for Methanol Oxidation

The oxidation of methanol, as facilitated by the Cu/TiO₂ aerogel catalyst described above, was characterized within a packed-bed reactor. In these studies, pure methanol vapor and gaseous O₂, with a balance of inert Ar, comprised the reactor feed. The feed passed through a packed bed of 5 mg of Cu/TiO₂ aerogel held at a temperature of 623 K while a downstream quadrupole mass spectrometer identified species within the effluent gas stream. Key results of this study are shown in Figure 5.1.

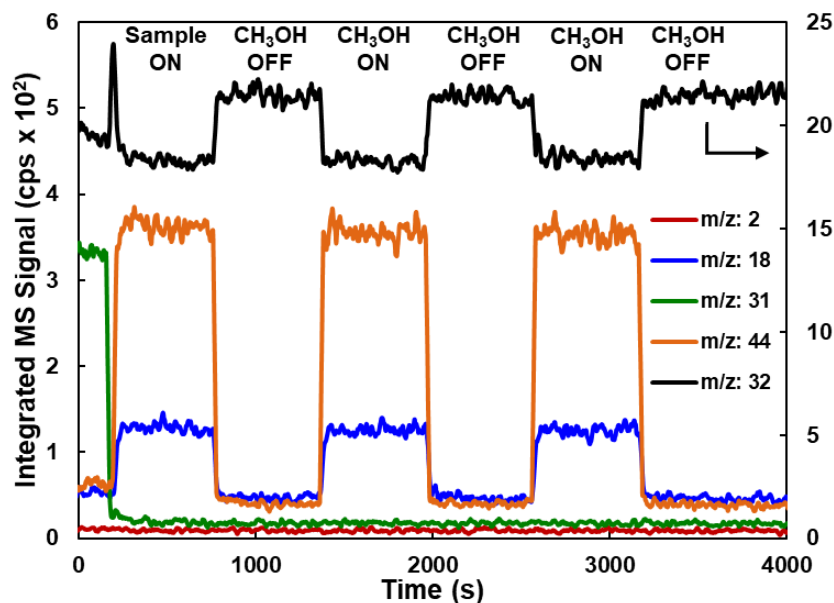


Figure 5.1 Mass spectral signal versus time in the packed-bed reactor studies where O₂ and methanol were passed through a Cu/TiO₂ aerogel catalyst at 573 K. Gas stream consisted of 0.5% methanol vapor, 40% O₂, and 59.5% Ar (inert carrier gas for methanol vapor) at a total flow rate of 50 mL/min. The gas stream was pulsed through the methanol bubbler (ON) and bypassed the bubbler (OFF).

Immediately upon methanol/O₂ introduction to the Cu/TiO₂ sample ($t = 175$ s), methanol signal (the 31 m/z trace in green) decreased while CO₂ signal (the 44 m/z trace in orange), and H₂O signal (the 18 m/z trace in blue) rose to steady-state values (Figure 5.1). The clear conversion of methanol vapor to combustion products (CO₂ and H₂O) indicates the Cu/TiO₂ aerogel is active for complete methanol oxidation at 623 K. The methanol within the gas feed was modulated to both record a baseline signal in the absence of the methanol reactant, and to examine the catalyst stability and recyclability. During each methanol pulse, the CO₂ and H₂O signals reached the same steady-state value as found for the initial pulse, which suggests that active sites within the Cu/TiO₂ aerogel remained available throughout the experiment. In addition, the amount of methanol exiting the reactor remained below the limit of detection for the duration of the experiment (even during each methanol pulse). That is, the catalyst reproducibly oxidized $98 \pm 2\%$ of the methanol in the initial feedstock. As a control, a metal NP-free TiO₂ aerogel material was subjected to the same flow reactor conditions, and no products were observed, highlighting the importance of Cu NPs in the active catalyst. Notably, no gaseous H₂ at 2 m/z was observed. The data in Figure 5.1 suggests that the methanolic hydrogen contributes exclusively to the formation of H₂O. Other possible gaseous by-products such as formaldehyde (30 m/z) from incomplete combustion were not observed, but formic acid (m/z 45, 46) was present in trace amounts in the effluent gas stream. While the characterization of the vaporous effluent shows complete methanol combustion, characterization of the surface-bound species is required for a more comprehensive understanding of the overall reaction.

5.3.2 Initial Methanol Adsorption on Cu/TiO₂

Infrared spectroscopic studies of adsorbed methanol on the Cu/TiO₂ aerogel revealed significant similarities to methanol adsorbed on the pure TiO₂ aerogel (in the absence of Cu particles). The IR spectral features within the C-H stretching region (Figure 5.2a) for methanol adsorbed at both Cu/TiO₂ and TiO₂ are in close agreement. The band assignments and wavenumbers of the bands in the C-H stretching region are consistent with other studies involving TiO₂ nanoparticles. That is, evidence is found for both dissociative uptake ($\nu_{\text{sym}}(\text{CH}_3)$ at 2818 cm⁻¹, $\nu_{\text{as}}(\text{CH}_3)$ at 2923 cm⁻¹) and molecular uptake ($\nu_{\text{sym}}(\text{CH}_3)$ at 2844 cm⁻¹, $\nu_{\text{as}}(\text{CH}_3)$ at 2948 cm⁻¹).^{160,192–195}

The presence of both dissociative and molecular adsorption is consistent with prior investigations that describe methanol dissociation into adsorbed CH₃O and H.^{193–197} Although dissociation likely generates surface hydroxyl groups,^{160,192,197} our infrared spectra appear to be insensitive to the anticipated $\nu(\text{OH})$ band formation. The spectral features associated with surface O-H stretches are hypothesized to be obscured by low transmissivity in this region. Molecular adsorption is evidenced by an overtone of the $\delta(\text{CH}_3)$ deformation mode of methanol in Fermi resonance with $\nu_{\text{as}}(\text{CH}_3)$ vibrations that give rise to the feature observed at 2889 cm⁻¹.^{192,198}

As found for the C-H stretching region, vibrational modes in the lower-frequency region of the infrared spectra are similar for methanol adsorbed on TiO₂ with and without the Cu NPs. The feature at 1142 cm⁻¹ corresponds to an adsorbed methyl $\rho(\text{CH}_3)$ and bands at 1439 cm⁻¹ and 1429 cm⁻¹ correspond to $\delta(\text{CH}_3)$ vibrational motions.^{160,194,198,199} Features assigned to $\nu(\text{OC})$ bridge and mono-bonded methanol appear between 1050–1070 cm⁻¹ and 1110–1125 cm⁻¹, respectively. These $\nu(\text{OC})$ bands are the only IR features that are both

shifted and change in relative intensity between the Cu/TiO₂ and TiO₂ materials. Close agreement in band positions between the materials and the lack of distinguishing IR features present on the Cu/TiO₂ aerogel indicates that methanol almost exclusively binds to TiO₂ regions of the Cu/TiO₂ sample (at room temperature).^{200–202}

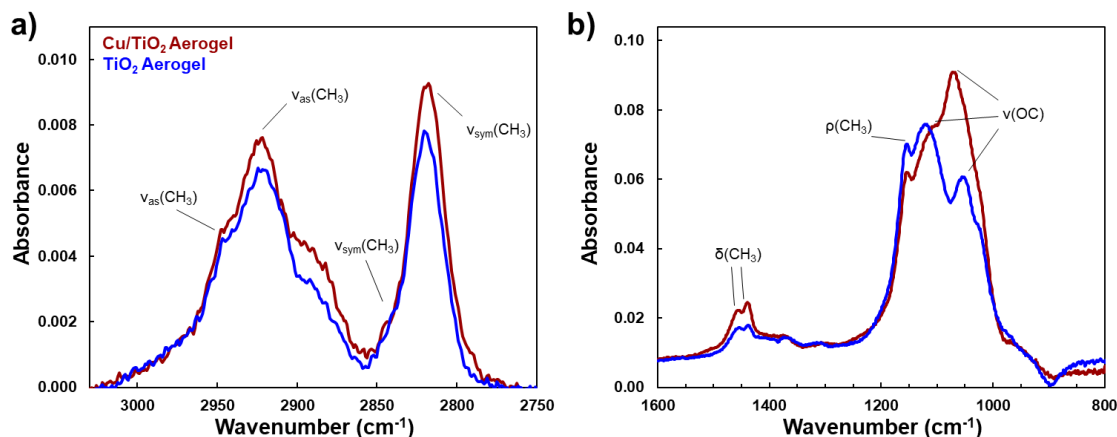


Figure 5.2 Infrared spectra of methanol adsorbed to a Cu/TiO₂ aerogel (brown) and a TiO₂ aerogel (blue). Spectra were taken with samples held at 303 K under vacuum (1.0×10^{-6} Torr) after a 15-minute exposure to 4.5 Torr methanol. (a) shows the C-H stretching region and (b) shows the lower frequency region.

Although containing many similarities, as noted above, the relative intensity and frequency for v(OC) bands associated with methanol adsorbed in the mono-bonded (1110–1125 cm⁻¹) and bridge-bonded (1050–1070 cm⁻¹) configurations are significantly different for the pure TiO₂ aerogel versus the Cu/TiO₂ aerogel. The spectra clearly show a higher proportion of the v(OC) feature in the bridge-bonded form for the Cu/TiO₂ aerogel. Based on insights from a previous study⁵⁰ and the observed frequency shift for both v(OC) features, the differences in methanol binding are hypothesized to originate from electronic

structure effects caused by charge transfer between Cu NPs and the TiO₂ aerogel support. Alternatively, the Cu particles may promote bridging coordination at the periphery of the Cu NPs, where Cu-O-Ti sites participate in binding the adsorbed methanol/methoxy species. Further computational support is needed to elucidate the specific origins of the differing $\nu(\text{OC})$ characteristics in the TiO₂ aerogel compared to the Cu/TiO₂ aerogel, however.

5.3.3. Infrared Studies of Methanol Oxidation

The oxidation of methanol on the surface of the Cu/TiO₂ aerogel catalyst was probed with IR spectroscopy. After methanol was adsorbed onto the Cu/TiO₂ surface, gaseous O₂ was introduced to the sample while the sample surface and the gases present in the closed cell were simultaneously tracked. Figure 5.3 shows the surface and gaseous species in the closed cell as temperature increased from 303 to 623 K. Between 303 and 473 K, IR features at 1375 and 1575 cm⁻¹ emerged on the Cu/TiO₂ surface (Figure 5.3a, spectra ii, iii, and iv). These frequencies are consistent with the symmetric and asymmetric O-C-O stretches of a bound formate species, respectively, adsorbed on TiO₂.^{197,203,204} The assignment of these IR features to O-C-O formate was confirmed by exposure of both the Cu/TiO₂ and TiO₂ aerogel surface to formic acid (Appendix). Formic acid is well-known to dissociatively adsorb on the surface of titania to form surface-bound formates.^{205–208} The infrared spectra for the C-H stretching region over this temperature range indicates that the adsorbed methanol slowly reacts to form a surface formate species as shown by the IR feature at 2877 cm⁻¹ (Figure 5.4). No intermediate species were observed before the formation of surface formate.

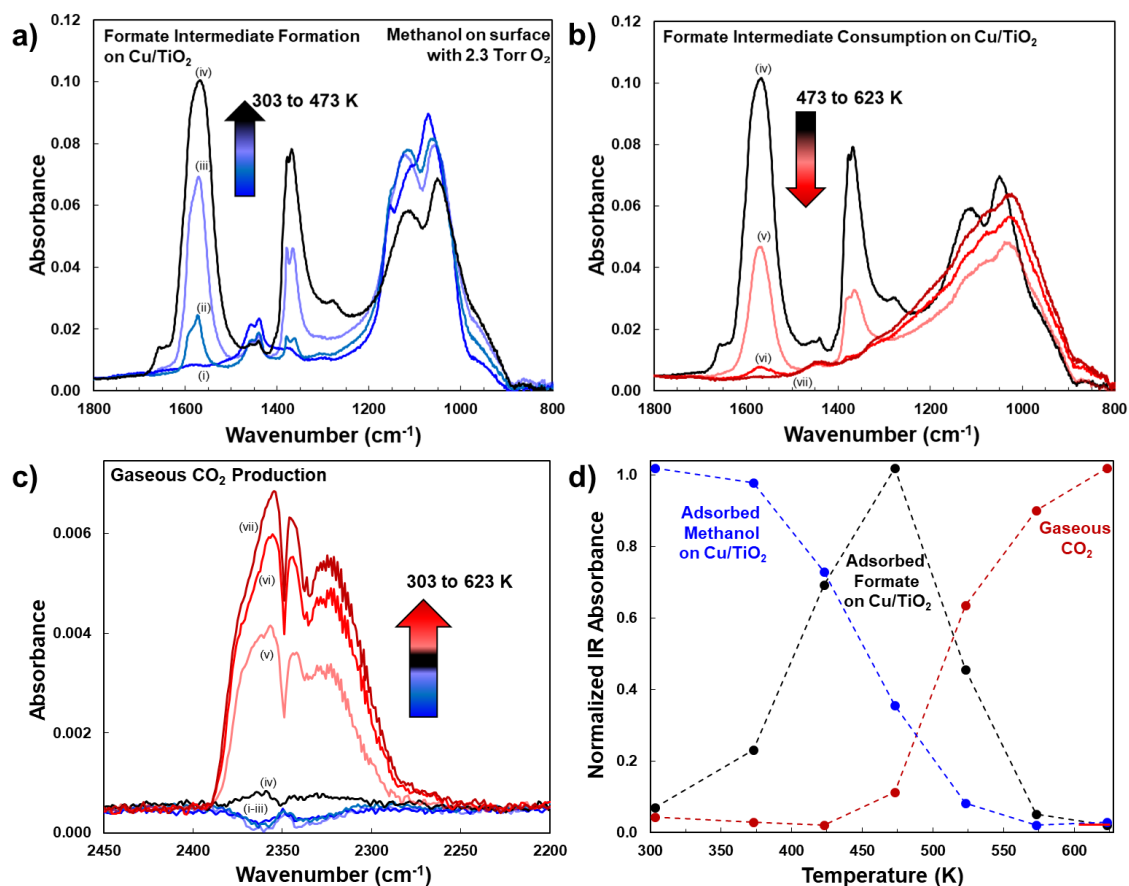


Figure 5.3 IR temperature-programmed oxidation of adsorbed methanol on Cu/TiO₂ aerogels. All spectra are baseline subtracted. Surface Cu/TiO₂ scans are shown for the lower frequency range during intermediate formation between 303 and 473 K (a) and during intermediate consumption between 473 and 623 K (b). Gaseous spectra following CO₂ production over the entire temperature range are also shown (c). Data is summarized in (d) to show the reaction process for adsorbed reactants and intermediates as well as gaseous product formation.

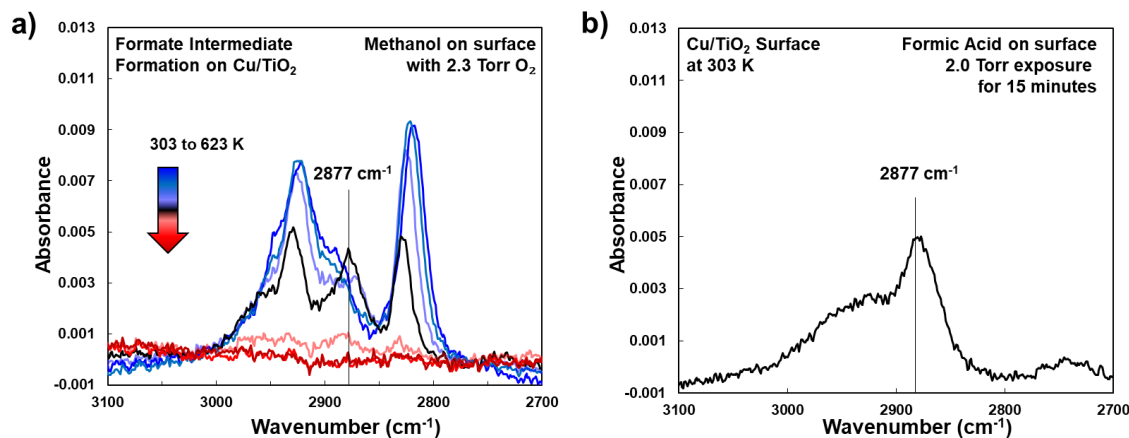


Figure 5.4 (a) IR temperature-programmed oxidation of adsorbed methanol on Cu/TiO₂ aerogels in the same experiment as represented in Figure 5.3, showing the high-frequency C-H stretching region between 303 K and 623 K. (b) IR spectra in the same range for pure formic acid on the Cu/TiO₂ aerogel.

Above 473 K, where the intensity of the bands associated with adsorbed formate is most intense and reaches a plateau, the formate begins to react with the gaseous O₂ to evolve CO₂ from the surface (Figures 5.3b, c). The surface formate was confirmed to be the intermediate by performing the same temperature-programmed oxidation as shown in Figure 5.3 but with formic acid instead of methanol (Figure 5.5). Conversion of formic acid, through initial formate production, to CO₂ was observed at the same temperature that the formate intermediates convert to CO₂ during the methanol reaction. The correlation not only confirms the assignment of key bands that develop during methanol oxidation, but also validates the promotional effect that Cu has on decomposing organics. To this point, our results show that the pure TiO₂ aerogel is ineffective in generating CO₂ even when starting with the formate intermediate species created by formic acid adsorption (Appendix). Therefore, the TiO₂-supported Cu particles are necessary for both the

oxidation of methanol to formates and the subsequent full oxidation of the intermediates to CO_2 .

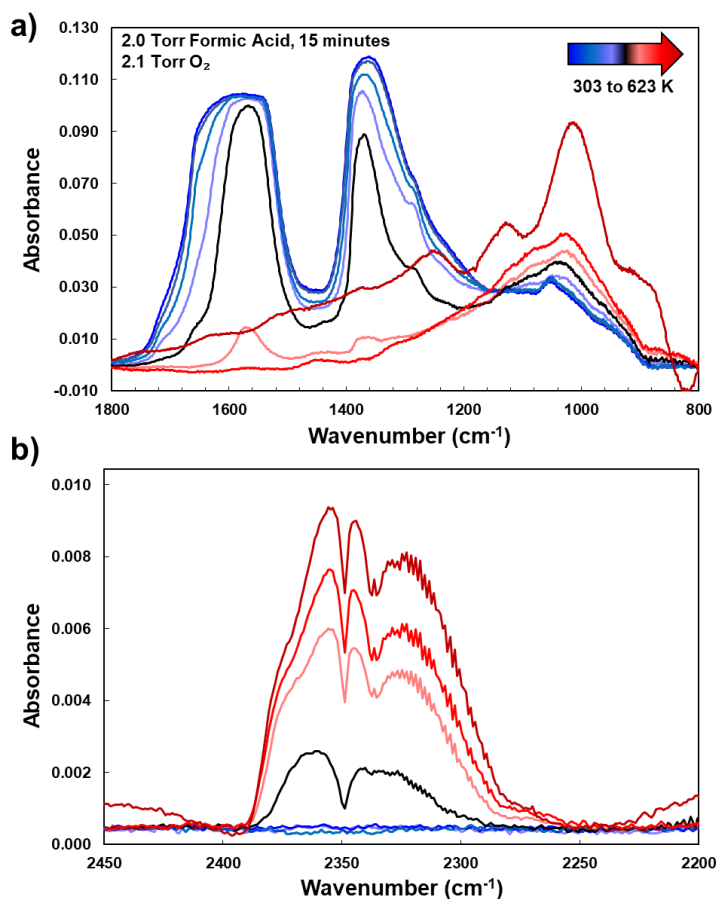


Figure 5.5 IR temperature-programmed oxidation of adsorbed formic acid on Cu/TiO₂ aerogels. All spectra are baseline subtracted. Surface Cu/TiO₂ scans are shown for the lower frequency range (a) and gaseous spectra following CO₂ production (b) are also shown. Temperature was increased from 303 K to 623 K.

The reaction sequence involving the conversion of methanol to the formate intermediate followed by formate consumption to generate CO₂ is exemplified by the data presented in Figure 5.3d. Gaseous and surface IR data are compiled over the 303 K – 623 K temperature range with the normalized absorbance for adsorbed methanol (sum of 2817

and 2921 cm^{-1} bands shown in Figure 5.4), adsorbed formic acid (sum of 1367, 1377, and 1575 cm^{-1} bands) and gaseous CO_2 (2357 cm^{-1}) displayed versus the temperature of the catalyst. The blue trace in Figure 5.3d clearly shows that the surface-adsorbed formate has intermediate-like behavior. Adsorbed formates are produced as methanol is consumed on the Cu/TiO₂ surface, followed by the consumption of the surface-bound formate to evolve gaseous CO_2 .

The oxygen supply for methanol oxidation and CO_2 production may originate from either the gas phase or from the oxide surface. Evidence of a lattice extraction process for methanol oxidation was observed by exploring the reaction under anaerobic conditions within the plug-flow reactor. The results of the anaerobic reaction are shown in Figure 5.6. For the first 5 minutes of methanol flow, CO_2 is produced as active surface oxygen atoms are plentiful, and oxidation clearly progresses in the absence of gaseous O_2 . As the activated and available O atoms on TiO₂ are consumed, titania is reduced and the complete oxidation slows. The concentration of the product, CO_2 diminishes until it is no longer produced at 30 minutes. As the CO_2 signal approaches zero, the methanol signal rises to steady-state concentration. Water is produced slightly after CO_2 in the anaerobic exposure, likely indicating stronger binding to the Cu/TiO₂ surface. No other partial oxidation products were observed. The anaerobic production of CO_2 and H_2O suggests that oxygen atoms from TiO₂ regions of the catalyst are the active form of O in the catalytic oxidation of methanol on Cu/TiO₂ aerogels. Electronic metal-support interactions for Cu/TiO₂ aerogels have previously been shown to promote TiO₂ reducibility for CO oxidation.⁵⁰ The specific source of active O atoms could however originate from bridging O atoms in the TiO₂ lattice or from active adsorbed molecular oxygen remaining from the

pretreatment.^{17,57} Therefore, further studies of the TiO₂ regions of the catalyst were conducted.

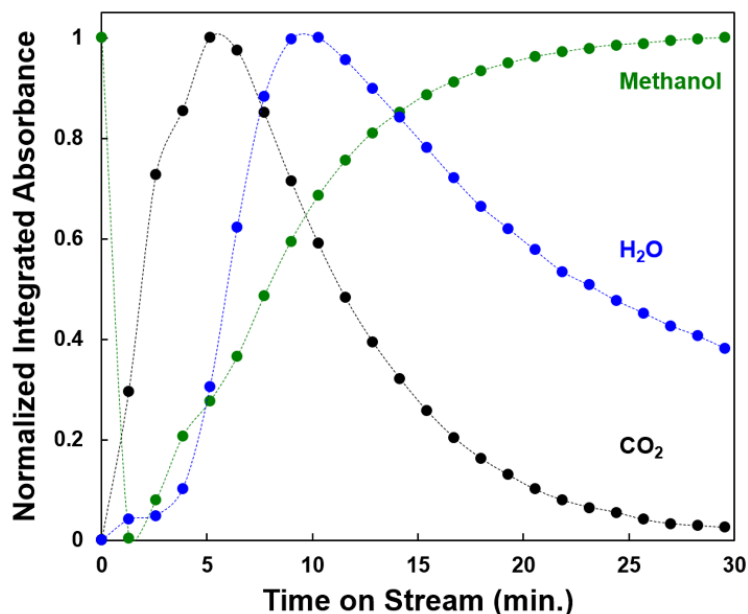


Figure 5.6 Flow cell IR data of anaerobic methanol oxidation over Cu/TiO₂ aerogels at 623 K. Data points are integrated for CO₂ (between 2280 and 2410 cm⁻¹), H₂O (between 3790 and 3960 cm⁻¹), and methanol (between 2600 and 3200 cm⁻¹). The gas stream consisted of 0.5% methanol vapor and 99.5% Ar (inert carrier gas for methanol vapor) at a total flow rate of 50 mL/min.

5.3.4 IR Probe of TiO₂ Reduction and the Role of Water

Evidence for lattice extraction of oxygen from the TiO₂ support can be provided through infrared spectroscopy. Researchers have shown that the observation of a broad featureless absorbance in the IR spectrum is attributed to the removal of lattice oxygen from TiO₂.^{196,209,210} The removal of lattice oxygen generates shallow-trap states (Ti³⁺) in TiO₂ that results in a baseline rise through the acoustic phonon-coupled scattering of

electrons.^{196,209–214} Similar phenomena have been observed upon H spillover onto TiO₂, where electrons trapped in conduction band edge states contribute towards the spectral changes.^{210,215} Thermal energy can also excite the trapped electrons into the conduction band.²⁰⁹ The observation of shallow-trap or conduction band electrons indicates the reduction of TiO₂, an important process to characterize during catalysis. Here, a fixed amount of pure methanol vapor was exposed to the Cu/TiO₂ aerogel at 303 K with an applied temperature ramp during the interaction with the surface. Surface IR spectra were recorded during the interaction between methanol and Cu/TiO₂ to monitor changes to the surface, as shown in Figure 5.7.

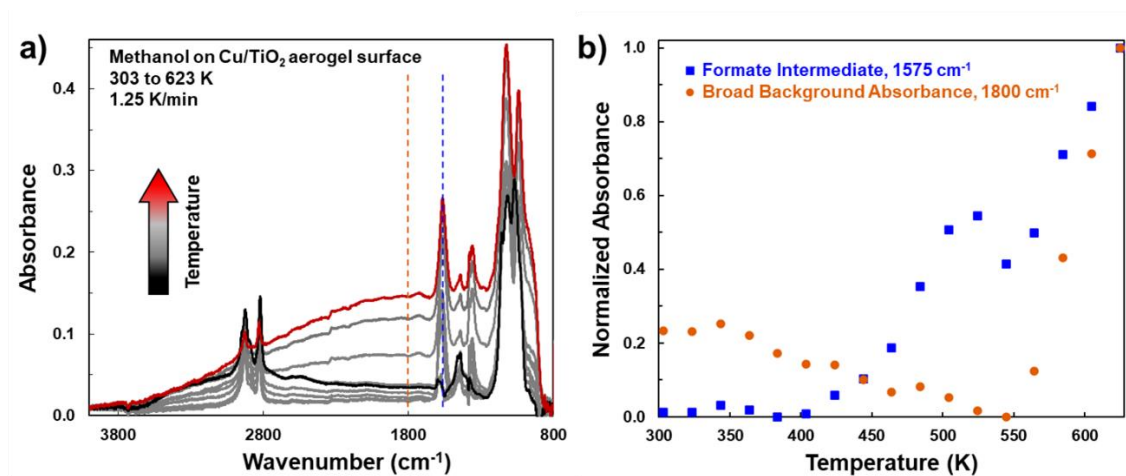


Figure 5.7 Surface IR spectra of Cu/TiO₂ during exposure to methanol vapor during a 1.25 K/min temperature ramp from 303 to 623 K. (a) Baseline subtracted spectra over the entire spectral window shows the broad baseline rise indicative of TiO₂ reduction. (b) Normalized absorbances taken from the spectra show how the surface-bound formates (blue) and broad background IR absorbance (orange) change over the temperature ramp.

The recorded spectra in Figure 5.7 show the background increasing in absorbance throughout the reaction. From other works,²¹⁶ the signal at 1800 cm⁻¹ was selected to

characterize the baseline rise due to the frequency of the maximum increase and the lack of overlap with IR active species on the surface.^{187,196} Notably, the broad background absorbance (BBA) in the IR spectra is observed to decrease between 300 and 550 K. This decreasing behavior at 1800 cm^{-1} is not attributed to the shallow trap state electrons (Ti^{3+}), as there is clearly a significant amount of water on the surface from methanol adsorption/dissociation leading to the initial absorbance above zero at 303 K. Water on TiO_2 has been shown to influence the broad IR baseline signal due to hydrogen bonding interactions to frequencies as low as 1200 cm^{-1} and is in agreement with additional studies of water on TiO_2 conducted in this work (Appendix) and in the literature.²¹⁷ Prerequisite to the reduction of TiO_2 by methanol is the formation of the formate intermediate. If the baseline rise were from H atoms (from the formate production) reducing TiO_2 regions of the catalyst, the baseline rise would likely accompany the formate production. Instead, the baseline rise occurs after a significant amount of the formates are already produced. In fact, the baseline rise occurs simultaneously with the drop in the formate signal. This behavior could be attributed to formate oxidation to CO_2 that desorbs from the catalyst surface and leaves a bridging oxygen vacancy on titania. The dehydrogenated formates continue to form at available adjacent bridging O sites or fill in new O vacancies in TiO_2 , while the formed H_2O desorbs above 550 K leaving abundant vacancies behind. Alternatively, close agreement between the temperature of water desorption from a methanol oxidation light-off curve (Figure 5.8) and the BBA increasing could suggest that the removal of bound water from the surface TiO_2 lattice is necessary for the oxide reduction. Either route indicates the central role that TiO_2 regions of the catalyst, bridging O atoms in particular, have an active role in the direct oxidation of the alcohol.

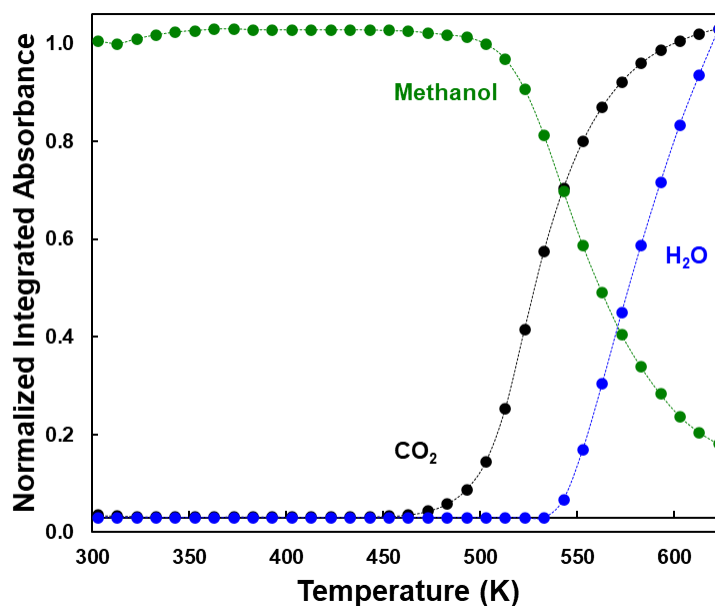


Figure 5.8 Methanol oxidation light-off curves showing normalized integrated infrared absorbance of the methanol reactant (green trace) along with CO₂ (black trace) and H₂O products (blue trace) vs temperature. A packed bed of about 5 mg of Cu/TiO₂ was exposed to a reaction stream consisting of 0.5% methanol vapor, 40% O₂, and 59.5% Ar (inert carrier gas for methanol vapor) at a total flow rate of 50 mL/min. The packed catalyst bed was exposed to a thermal ramp of 10 K/min.

Further evidence of TiO₂ reduction after interacting with methanol anaerobically is shown by a post-reaction surface characterization with CO at cryogenic temperatures in Figure 5.9. It is important to note the significant difference in overall absorbance between the pre- and post-reaction data. The significant loss of surface sites in the post-reaction characterization is due to the remaining coverage of surface methanol and formates, preventing CO from reaching adsorption sites. Additionally, some peaks changed position due to changes in the electronic structure of the Cu particles due to the presence of

adsorbates. More detail into the significance of the frequency shifts will be provided in Chapter 6.3.3. In short, the assignments of the post-reaction CO-Cu features as shown in Figure 5.9b are based on the frequencies observed in CO displacement studies by gaseous alcohols. However, if the Cu^{1+} and Ti^{3+} peaks did not change positions due to changes in the electronic structure, the qualitative conclusions would remain the same. The integrated areas of the Ti^{3+} and Ti^{4+} component peaks appear to increase after the reactive anaerobic exposure to methanol. Using a ratio of the integrated area of these peaks would effectively normalize the number of available sites between the two surfaces. Upon evaluation, the $\text{Ti}^{3+}/\text{Ti}^{4+}$ ratio indeed increases from 0.85 pre-reaction to 4.62 post-reaction, indicating a significant reduction of TiO_2 -regions of the Cu/TiO_2 aerogel catalyst after interaction with methanol.

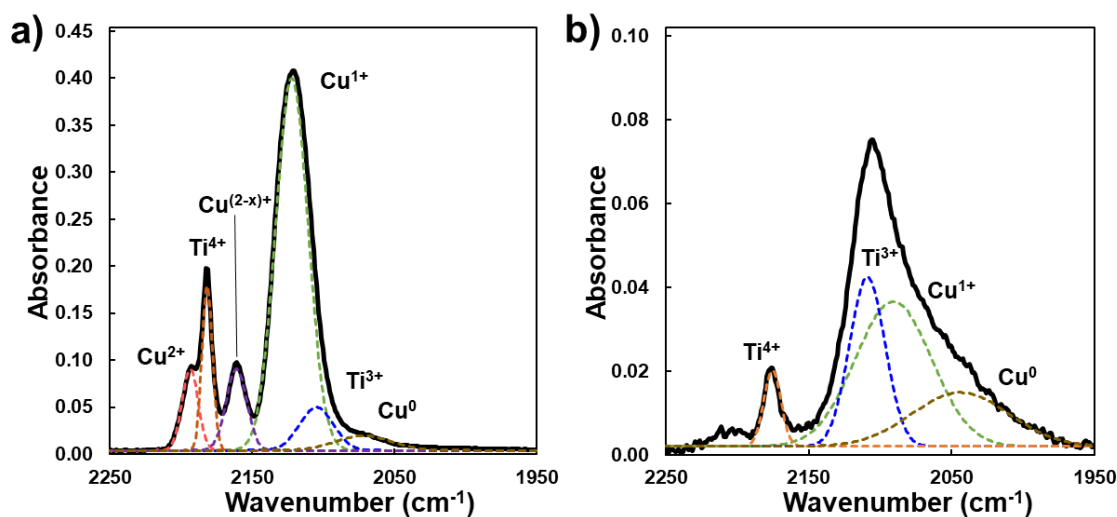


Figure 5.9 IR CO characterization of Cu/TiO_2 aerogels before (a) and after (b) anaerobic methanol oxidation. 1 Torr of CO was exposed to the sample at 193 K in both studies, with spectra taken at the same temperature.

The evidence suggests that both formate oxidation and water desorption contribute toward the BBA and titania reduction during the methanol oxidation reaction. This specific active site is consistent with the mechanism for CO oxidation on the same Cu/TiO₂ aerogel.⁵⁰ Weakened Ti-O bonds due to the additional charge density on Ti atoms (charge transfer from the Cu NPs) are hypothesized to be activated for oxidation and are the active sites in this catalytic system, consistent with metal-assisted Mars-van Krevelen mechanisms.^{17,57,63} Helali et al. reported vacancy formation energies (E_{vac}) of TiO₂ to be between 2.9 and 4.2 eV, depending on the crystal form of TiO₂.²¹⁸ The E_{vac} of metal oxides has also been shown to decrease in the presence of a low-work function metal, like Cu or Au, by up to 2.2 eV.⁹⁴ The removal of lattice oxygen as the dominant reaction pathway and form of active O is supported by the energetics, as the only other possibility under anaerobic conditions is the cleavage of nearby methanol C-O bonds (not observed spectroscopically) that has a higher bond dissociation energy of 3.94 eV.^{219,220}

Water has been implicated in other works as playing an influential role in O₂ activation.^{21,65–70} However, the consistent results between vacuum and plug-flow reactor systems show that water desorbs from the surface as a reaction product at temperatures where reaction occurs. The role of water was investigated by adding water to the methanol/O₂ reaction mixture and was found to be inhibitive towards complete oxidation at the surface concentration studied (Figure 5.10). Inhibited product formation is likely due to competitive adsorption at active sites with methanol molecules and prevents the dissociative adsorption of the alcohol. The reaction inhibition is also consistent with other works on Pt/Al₂O₃ and iron/molybdenum oxide catalysts.^{71,221}

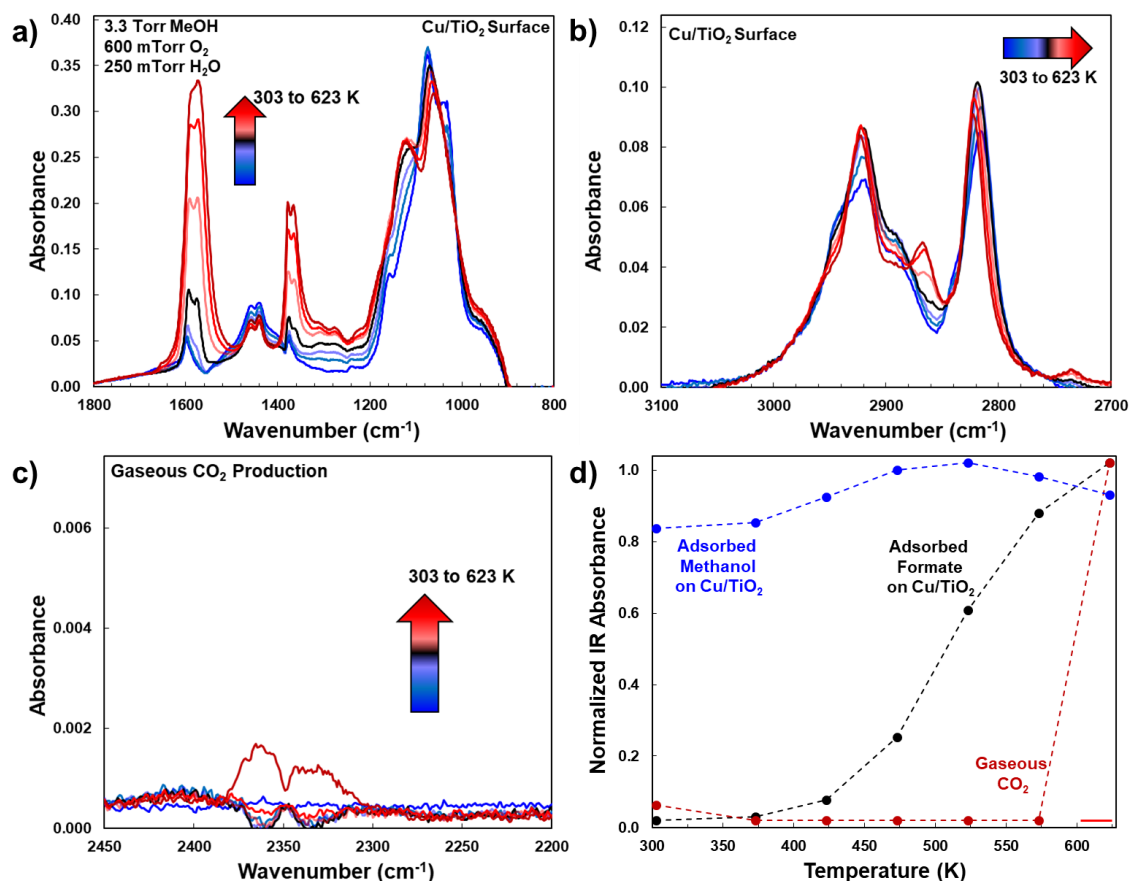


Figure 5.10 IR temperature-programmed oxidation of adsorbed methanol on Cu/TiO₂ aerogels with co-adsorbed H₂O. All spectra are baseline subtracted. Surface Cu/TiO₂ scans are shown for the lower frequency range (a) and for the higher frequency C-H stretching range (b) between 473 and 623 K. Gaseous spectra following CO₂ production over the same temperature range is also shown (c). Data is summarized in (d) to show the reaction process for adsorbed reactants and intermediates as well as gaseous product formation.

5.3.5 Proposed Methanol Oxidation Mechanism

The findings from the above studies can be compiled to propose the mechanism in Figure 5.11. Methanol first dissociatively adsorbs onto TiO₂ regions of the catalyst, forming a bound methoxy and a titania hydroxyl. Dehydrogenation occurs to form surface

H₂O and an additional hydroxyl on titania alongside the bound formate. The final dehydrogenation can occur to leave bidentate CO₂ on TiO₂ regions of the catalyst and another water molecule. With the methanol molecule completely oxidized to desorbed CO₂ and H₂O at elevated temperatures, the catalyst surface is left with bridging oxygen vacancies from the lattice extraction pathways. The vacancies are then filled by gaseous oxygen to replenish the catalyst. The chemistry that occurs on the Cu/TiO₂ surface is unique relative to most metal NP-supported catalysts in that the reaction appears to be localized on the support. However, the Cu NP is necessary to induce activity on the TiO₂ surface.

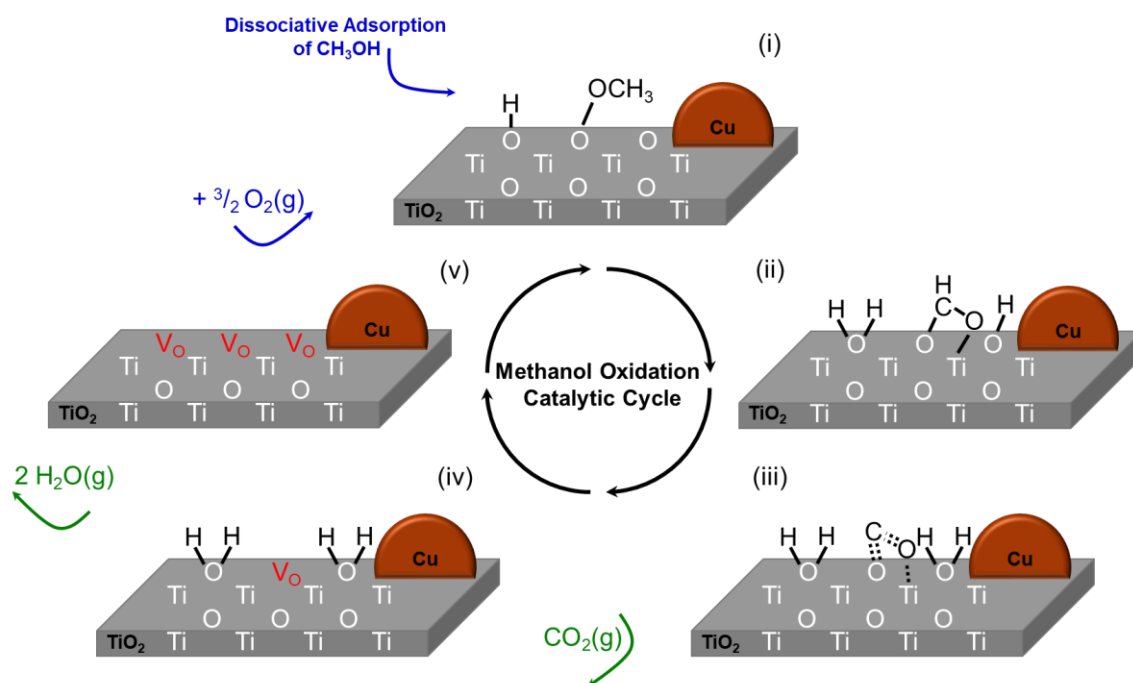


Figure 5.11 Proposed methanol oxidation reaction mechanism on a Cu/TiO₂ aerogel catalyst.

5.4 Conclusions

Methanol oxidation is an important reaction for industrial chemicals and H_2 production in fuel cells, and has therefore been at the focus of numerous studies involving both investigations into reaction mechanisms and understanding the alcohol's impact on a material surface. In this work, methanol adsorption and oxidation activity were analyzed on Cu/TiO₂ aerogels. Spectroscopic and spectrometric evidence was provided, indicating the methanol oxidation mechanism occurs catalytically on titania sites likely on the periphery of Cu NPs where the reduction of titania is distinctly observed. The dissociative adsorption of methanol occurs first on titania sites, before decomposing to surface-bound formates and water on the catalyst surface. The surface formate intermediate then loses its H atom to a nearby bridging O in the support oxide. Lattice oxygen extraction of TiO₂ regions of the catalyst accompanies the complete selective oxidation to CO₂ and H₂O, as observed both by the broad baseline absorbance rise in the IR spectrum and by anaerobic exposure of Cu/TiO₂ to methanol at reactive temperatures. The data supports the identification of bridging O atoms on TiO₂ as the active oxygen in the reaction, resulting in the reduction of TiO₂. Oxygen vacancies generated from the surface reaction are replenished by gaseous O₂. The understanding this work provides on the methanol oxidation mechanism on Cu/TiO₂ aerogels lays the foundation for future studies into more complex oxidation reactions and smarter catalyst design.

Chapter 6

2-Propanol Partial and Complete Oxidation on Cu/TiO₂ Aerogels and the Effects of Binding Sites

6.1 Introduction

The oxidation of 2-propanol is a seldom-studied reaction in the literature. It is, however, an important reaction for commodity chemical and material production. 2-propanol is utilized in the production of isopropyl acetate (a solvent), sodium isopropylxanthate (a herbicide and an ore flotation reagent), titanium isopropoxide (a catalyst), and aluminum isopropoxide (a reagent).²²² In addition to its importance as an intermediate, 2-propanol is widely used in the semiconductor and precision machinery industries as a washing agent but it generates tens of thousands of tons of waste a year.^{223,224} The waste generated by the solvent emits volatile organic compounds (VOCs) which are potent air pollutants. The catalytic decomposition of VOCs has been an important research topic for many years.^{225–227} Typically, 2-propanol vapor is thermally incinerated in a very energy-intensive process and the catalytic decomposition of 2-propanol would lead to drastic improvements in energy usage.²²³ Partial oxidation of the alcohol could also yield other useful reagents for the chemical industry.

Researchers have found catalysts for 2-propanol oxidation that require varying energy sources for catalysis, resulting in different products.^{228–231} For example, Chang et al. showed complete photooxidation of 2-propanol to CO₂ on commercial P25 TiO₂, apart from initial short-lived conversion to acetone.²³² Long irradiation times confirmed the selectivity to complete combustion products. In addition, a potential H-bonded species was

discussed as an intermediate for acetone formation. Brinkley et al. then detected 2-propanol converting to small amounts of acetone during UV illumination of TiO_2 .²³³ Another study found propene formation at 570 K through one reactive pathway, but a lower temperature propene formation at 410 K upon the increased density of surface oxygen vacancies on rutile (110) TiO_2 .²³⁰ Each of these products formed is important for either cleanup of VOCs or production of important chemical intermediates. The works discussed are also primarily assisted by exposure to UV light, which provides practical challenges when trying to implement novel catalysts into industrial usage. There is a clear need for catalysts that can efficiently oxidize 2-propanol without the necessity of UV light for reaction.

Catalytic decomposition of chemical warfare agents (CWAs) is also closely related to the oxidation of 2-propanol. Specifically, the deadly nerve agent, sarin, contains an isopropoxy group within the molecule, which can dissociate from the parent nerve agent and mimic dissociatively adsorbed 2-propanol on catalyst surfaces.^{83,234,235} Researchers who have investigated sarin decomposition on metal oxide-supported metal nanoparticles often ignore the fate of the dissociative isopropoxy group. However, the fate of this species can lead to either catalyst poisoning (if not further reacted) or to other undesirable side products.^{76,77}

Desario et al. probed the decomposition of the CWA sarin on the same Cu/TiO_2 aerogels that are the focus of this dissertation.⁴⁹ They showed that with diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), Cu/TiO_2 aerogels can degrade sarin GB to isopropyl methylphosphonic acid (IMPA) and methylphosphonic acid (MPA) products with oxygenated air without broadband (BB) illumination inducing photochemistry. The formation of MPA indicates isopropoxy loss from the parent CWA.

Under BB illumination, the catalyst exhibited enhanced degradation of sarin to IMPA, MPA, phosphonic acid (PA), formates/carbonates, CO, and CO₂. Unfortunately, no mechanistic insights were determined in the study. Methanol oxidation on Cu/TiO₂ as shown in Chapter 5 formed surface formates and gaseous CO₂. Since the carbonaceous products from sarin must come from the dissociation of either the methyl or isopropoxy groups of the CWA, further studies for a mechanistic understanding of the oxidation of 2-propanol are needed to understand the fate of the sarin degradation products. The studies presented here complement these results by providing mechanistic insights into 2-propanol oxidation on Cu/TiO₂ aerogels and further elucidation of the specific binding of alcohols onto Cu NPs.

6.2 Procedural Methods

6.2.1 Cu/TiO₂ Aerogel Synthesis

Synthetic procedures were performed by the Debra Rolison group at the Naval Research Laboratory. Further information about the synthetic procedure is provided in a previous work of theirs.³⁶ Cu/TiO₂ aerogels were prepared by photodepositing Cu nanoparticles onto TiO₂ aerogels in a manner described previously.^{36,81,115} First, TiO₂ aerogels were prepared using a sol-gel method.³⁷ A wet gel is formed by adding a solution of Ti(ⁱOPr)₄ (Alfa Aesar, 97+%) in 3.9 g of ethanol (absolute ethanol, Warner-Graham) to a mixture of H₂O (0.39 g), ethanol (4.0 g), and nitric acid (78 mg of 70% HNO₃, Fisher). After aging for 24 h, the wet gel was rinsed 10× with acetone over multiple days. The wet gels were loaded under acetone into a supercritical dryer and rinsed with liquid CO₂ at 283 K before heating the dryer to 314 K and then venting to atmospheric pressure. The TiO₂

aerogels were calcined in air at 698 K (2 K min⁻¹ heating and cooling ramp, 4 h dwell) to produce nanocrystalline anatase aerogels. Following an established method,²⁸ Cu nanoparticles were photodeposited onto the TiO₂ aerogels by illuminating slurries containing ~150 mg TiO₂ aerogel suspended in a solution of 110 mL of 2 mM Cu(NO₃)₂ (Sigma-Aldrich, 98%) in 9:1 (vol:vol) H₂O:CH₃CH₂OH (adjusted to pH 9.5 ± 0.5) for a period of 24 h with a 500 W Xe arc lamp (Newport Oriel). The Cu/TiO₂ aerogels were collected by centrifugation followed by re-suspension in Ultrapure 18 MΩ cm water (Barnstead Micropure) for 10× cycles. The Cu/TiO₂ aerogels were then dried in air at 373 K overnight.

6.2.2 Vacuum Studies with Infrared Spectroscopy

Infrared spectroscopic studies were performed in a stainless-steel high-vacuum reactor cell with a base pressure of 1×10^{-8} Torr (see Chapter 2). Cu/TiO₂ and TiO₂ aerogel samples were pressed (at 5000 psi) as 7 mm disks into the void space of a 50-μm thick tungsten mesh (Tech-Etch), secured onto a stainless-steel sample holder. The tungsten mesh sample holder allows for both samples to be exposed to the same gaseous and thermal environments, enabling direct comparisons between Cu/TiO₂ and TiO₂ aerogel materials.⁸⁹ A K-type thermocouple was attached directly to the tungsten mesh, within 3 mm of the samples, to monitor sample temperature. The tungsten mesh was resistively heated using copper rods attached to an external power supply. Details of the high-vacuum cell can be found in previous work.⁸⁵ An FTIR spectrometer with an external MCT-A detector (Thermo, Nicolet Nexus 470 FTIR, resolution 2 cm⁻¹, optical velocity 1.8988 cm/s) coupled to the vacuum chamber to provide the *in situ* infrared spectroscopic measurements.

Samples were pretreated oxidatively in the vacuum chamber by exposure for 1 hour at 673 K in 10 Torr of O₂ followed by 30 minutes at 673 K in vacuum. Reducing pretreatments in the vacuum chamber were performed by heating the samples to 673 K in vacuum for 2.5 hours to remove the weakest bridging O in the TiO₂ lattice. These pretreatment procedures effectively remove weakly-bound organic species on the surface, as confirmed by infrared spectroscopy of the samples. For exposures of O₂ (99.994% purity, Airgas Ultra High Purity) and CO (99.3% purity, Airgas CP300), a gas manifold affixed to the vacuum chamber allowed for quantifiable amounts of the gas to be introduced into the chamber and exposed onto each material. For vapor dosing, about 2 mL of the liquids were added to vapor dosing bulbs and subjected to at least 3 freeze-pump-thaw cycles before vapor introduction into the vacuum chamber. Liquids for vapor dosing include methanol (Sigma-Aldrich, HPLC Grade), ethanol (Sigma-Aldrich, HPLC Grade), 1-propanol (Sigma-Aldrich, HPLC Grade, ≥99.9%), 2-propanol (Fisher Chemical, HPLC Grade), 1-butanol (Sigma-Aldrich, HPLC Grade, ≥99.7%), and isobutanol (2-methyl-1-propanol, Sigma-Aldrich, anhydrous, 99.5%)

6.2.3 Ambient Pressure Packed-Bed Flow Reactor

Catalyst activity was characterized with a packed-bed reactor (Altamira Instruments, μ BenchCAT) coupled to an FTIR spectrometer (Thermo, Nicolet Nexus 870 FTIR, resolution 4 cm⁻¹, optical velocity 0.6329 cm/s). The apparatus is described in Chapter 2. 3 mg of Cu/TiO₂ aerogel catalyst was packed into a 0.25-inch diameter quartz tube and secured with quartz wool present on both sides of the tube. Gaseous reactants that flowed into the cell were controlled with mass flow controllers. Alcohols were stored in a

glass bubbler and carried by an inert Ar flow (99.999% Praxair Ultra High Purity) separate from the O₂ stream before combining to mix before introduction to the catalyst bed. The temperature of the catalyst bed was monitored with a K-type thermocouple. Prior to each experiment, the Cu/TiO₂ sample was activated at 573 K under 10 SCCM flow of O₂ for 30 minutes.

6.3 Results and Discussion

6.3.1 2-Propanol Surface Adsorption and Oxidation

Infrared spectra of adsorbed 2-propanol on a Cu/TiO₂ aerogel (Figure 6.1) show features similar to those for absorption on the TiO₂ aerogel. 1.8 Torr of 2-propanol was exposed to Cu/TiO₂ and TiO₂ aerogels at 303 K for 15 minutes before evacuation and the acquiring of IR spectra *in vacuo*. The C-H stretching region between the two samples is in close agreement, and slight differences only appear in the band intensities. As band intensities throughout both samples are consistently larger on the one containing copper, most likely from a larger amount of the material pressed into the W mesh, differences between absolute intensities are not evaluated. All wavenumbers and band assignments, including 2970 cm⁻¹ $\nu_{as}(\text{CH}_3)$, 2934 cm⁻¹ $\nu_s(\text{CH}_3)$, and 2869 cm⁻¹ $\nu(\text{C-H})$ are consistent between both samples and agree with other works on TiO₂ materials.^{236,237} The lower frequency region shows a similar alignment of IR features. A $\delta_{as}(\text{CH}_3)$ mode appears at 1465 cm⁻¹ and its symmetric counterpart $\delta_s(\text{CH}_3)$ appears at 1384 cm⁻¹.^{237,238} The 1384 cm⁻¹ symmetric bend is unique to dissociatively adsorbed 2-propanol, leaving a surface-bound isopropoxy species on the titania surface.^{228,237,239} The feature assigned to $\nu_{as}(\text{C-C})$ modes can be found at 1366 cm⁻¹ with nearby 1332 cm⁻¹ relating to C-H deformation modes.^{236,238}

The feature at 1295 cm^{-1} is attributed to $\delta(\text{OH})$ strongly bound to Ti(IV) Lewis acid sites, an exclusively non-dissociative mode.^{237–239} A dissociative isopropoxy $\nu_s(\text{C-C})$ feature is observed at 1165 cm^{-1} and $\nu(\text{C-O})$ is observed at 1128 cm^{-1} .^{238,240} O-H stretching modes are not observed in the IR spectrum as they are scattered or suppressed as described previously in Chapter 5.3.2. However, the presence of dissociative features indicates the likely presence of TiOH groups on the surface as dissociative adsorption of 2-propanol proceeds as follows: $(\text{CH}_3)_2\text{CHOH} + 2^* \leftrightarrow (\text{CH}_3)_2\text{CHO}^* + \text{H}^*$, where ‘*’ represents an adsorption site.^{238,240} In the case of H^* , dissociated H atoms on TiO_2 are commonly observed to generate TiOH groups on bridging O atoms on the surface of the oxide. While the close agreement between the two materials and lack of unique features present on the Cu/ TiO_2 aerogel might suggest a selective binding of 2-propanol to TiO_2 regions of the catalyst, such a conclusion cannot be confirmed with the data from Figure 6.1. An absorption study with CO coordinated to copper sites revealed the displacement of CO on copper by 2-propanol (more details in Chapter 6.3.3) and indicate the likely coordination to the metal nanoparticles.

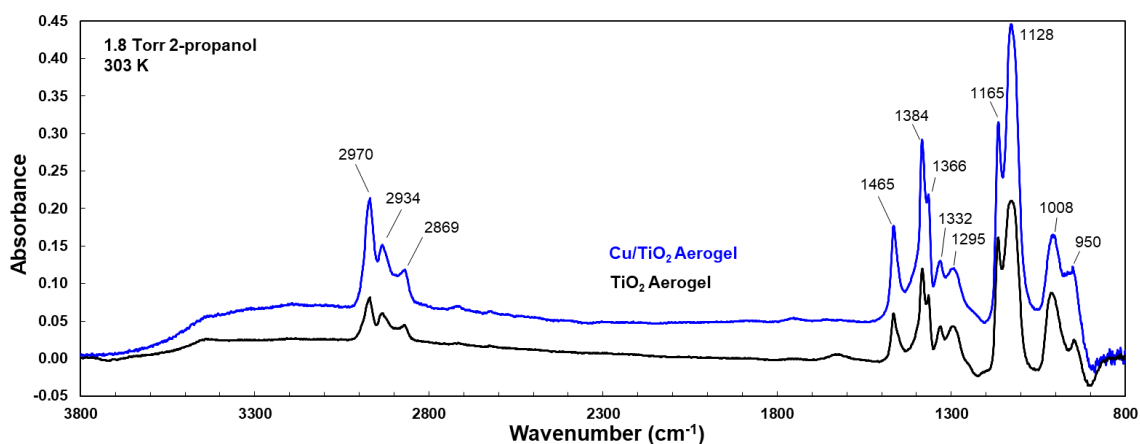


Figure 6.1 Infrared spectra of 2-propanol adsorbed to a Cu/ TiO_2 aerogel (blue) and a TiO_2

aerogel (black). Spectra were taken with samples held at 303 K under vacuum (1.0×10^{-7} Torr) after a 15-minute exposure to 1.8 Torr 2-propanol.

Wu et al. used the IR features at 1384 cm^{-1} and 1165 cm^{-1} as evidence for the dissociative adsorption of 2-propanol on titania in previous work.²³⁷ The same bands observed here indicate that on aerogel materials, 2-propanol also dissociatively absorbs. This dissociative adsorption does not describe 100% of all adsorbed 2-propanol, however, with the presence of the 1295 cm^{-1} feature indicating some degree of molecular or non-dissociative adsorption. There is not a drastic difference in the degree of dissociation of 2-propanol on the Cu/TiO₂ and TiO₂ aerogel surfaces, as the relative ratio of the intensities of the 1129 cm^{-1} dissociative feature (I_D) and the 1295 cm^{-1} non-dissociative feature (I_{ND}) are consistent between the aerogel materials. The ratio I_D/I_{ND} was calculated to be 6.40 for the Cu/TiO₂ aerogel and 4.35 for the TiO₂ aerogel, indicating a slight promotional effect for dissociation due to the presence of copper. As dissociative absorption is the first elementary step in the catalytic oxidation of methanol on Cu/TiO₂ aerogels, as described in Chapter 5, surface oxidation of 2-propanol on the copper-based catalyst will now be evaluated.

After 2-propanol was adsorbed onto the Cu/TiO₂ surface, the sample was introduced to gaseous O₂ while monitoring both the sample surface and the gases present in the closed cell. As the surface temperature was increased from 303 to 623 K, reaction intermediates and products were observed by IR spectroscopy (Figure 6.2). Between 303 and 473 K, IR features at 1375 cm^{-1} and 1575 cm^{-1} began to form on the Cu/TiO₂ surface, similar to methanol oxidation (Figure 6.2a). These frequencies are consistent with the

symmetric and asymmetric O-C-O stretches of a bound formate species, respectively, adsorbed on TiO₂.^{197,203,204} The O-C-O formate assignment of these IR features was confirmed by direct exposure of both the Cu/TiO₂ and TiO₂ aerogel surface to formic acid (as shown in Chapter 5.3.3). The unique C-H stretch attributed to formic acid/surface formates that occurs at 2877 cm⁻¹ is not obviously apparent in the 2-propanol oxidation study due to the significant overlap with the central C-H stretch on the molecularly adsorbed alcohol/isopropoxide. A careful examination of the spectra however does show a shift from 2870 cm⁻¹ to 2877 cm⁻¹ to indicate that the $\nu(\text{C-H})$ mode is converting from a 2-propanol CH to one associated with formate (Figure 6.2c). One important note in the oxidation of surface-bound 2-propanol and isopropoxides is that at the same temperatures that the surface formates are generated, there is a simultaneous loss of the $\nu_s(\text{C-C})$ mode and rise of a new IR feature at 1439 cm⁻¹. These changes are indicative of C-C bond cleavage and surface methoxy formation, as recognized from the assignments above and in Chapter 5. The non-dissociative molecular 2-propanol OH bend at 1295 cm⁻¹ is also rapidly removed before formate production, indicating the continued dissociation (or desorption) of the adsorbed 2-propanol. As dehydroxylation continues, the CH deformation mode at 1332 cm⁻¹ is also decreasing in intensity, suggesting continued reaction. Above 473 K, where the formate species is at its maximum intensity, the reaction appears to proceed the same as methanol oxidation: the formate intermediate loses its H atom to form evolved H₂O (not observed) and CO₂ from the surface (Figures 6.2b, d). A sample of pure TiO₂ aerogel was subjected to the same reaction conditions as Cu/TiO₂ and did not exhibit any behavior indicating a reaction occurred. In addition, the generated formates and methoxy groups on the TiO₂ aerogel standard were not removed by further reaction. This

suggests that the presence of the Cu NPs significantly decreases the activation energy barriers for reaction on TiO₂.

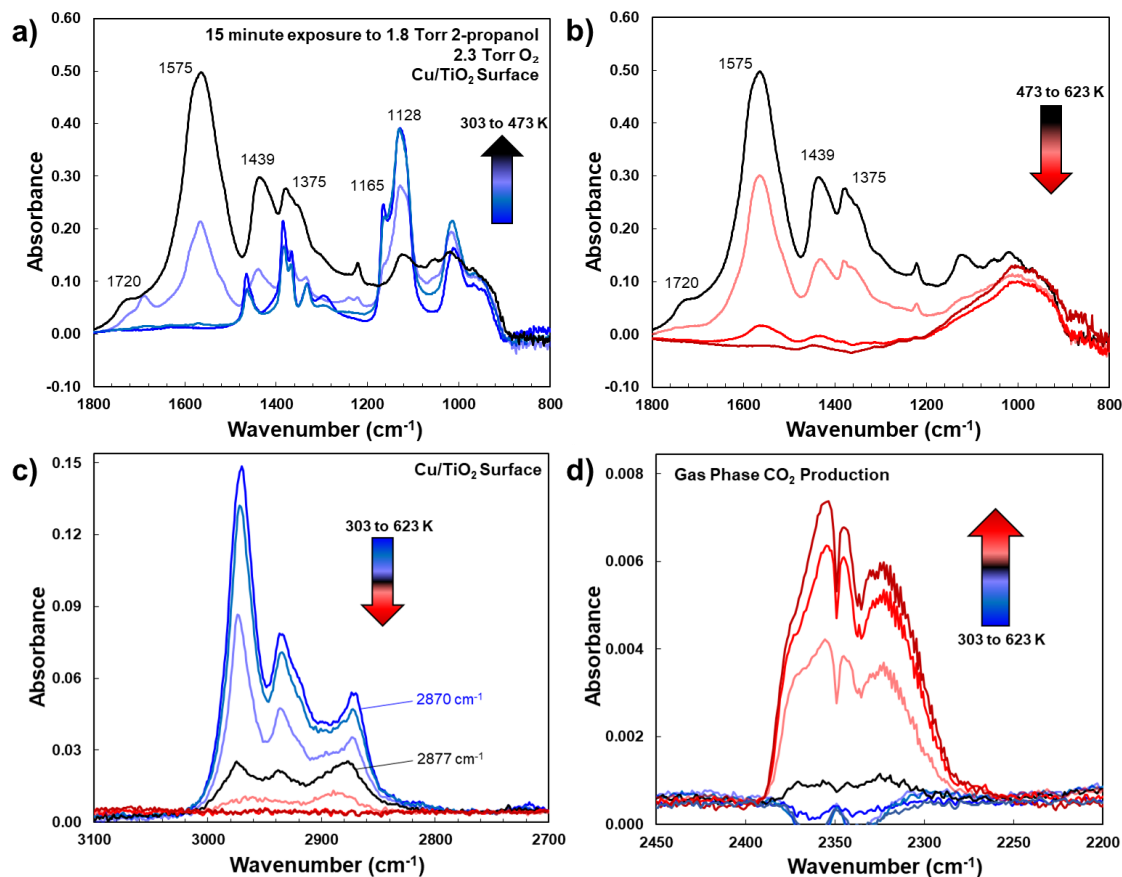


Figure 6.2 IR temperature-programmed oxidation of adsorbed 2-propanol on Cu/TiO₂ aerogels. All spectra are baseline subtracted. Surface Cu/TiO₂ scans are shown for the lower frequency range during intermediate formation between 303 and 473 K (a) and during intermediate consumption between 473 and 623 K (b). The C-H stretching region throughout the entire temperature range is shown in (c). Gaseous spectra following CO₂ production over the entire temperature range are shown in (d).

The initial surface reactivity of 2-propanol on Cu/TiO₂ aerogels initially appears to undergo a similar pathway to that of methanol shown in Chapter 5 (pictorially in Figure

5.11). After 2-propanol dissociation, C-C bond cleavage forms surface methoxys that results in a similar surface to dissociative methanol adsorption. The formation of the formate intermediates even peaks at the same temperature as that of methanol, 473 K, before they undergo consumption. As there are more carbonaceous species (formates and methoxys/methyls) on the surface per molecule of adsorbate upon 2-propanol decomposition relative to methanol, the influence of surface oxygen compared to gaseous oxygen is important to distinguish and will be the focus of studies in section 6.3.2. In the literature, Xu et al. monitored similar reactivity of 2-propanol through an acetone or propene intermediate on TiO₂, though the usage of high energy UV light was necessary for photocatalysis to occur.²²⁸ Other researchers have observed wither low selectivity to products like acetone and propene,^{229,230} or form harmful methyl radicals that corrode metals.²³¹ The complete selective oxidation of 2-propanol to CO₂ without high energy light sources is novel and warrants further surface studies.

6.3.2 Effects of Reduced TiO₂ on Reaction with 2-Propanol

As discussed in depth in Chapter 5.3.4, lattice extraction of the TiO₂ support can be studied by monitoring the surface of the catalyst with IR spectroscopy in the vacuum chamber. The observation of a broad featureless absorbance in the IR spectrum is attributed to the removal of lattice oxygen from TiO₂.¹⁹⁶ The removal of lattice oxygen generates shallow-trap states (Ti³⁺) in TiO₂ that results in a baseline rise through acoustic phonon-coupled scattering or the absorption of conduction band electrons.^{196,209–214} To confirm if lattice extraction during 2-propanol oxidation occurs, as it does in methanol oxidation, a

Cu/TiO₂ aerogel sample was exposed to 1.3 Torr 2-propanol at 623 K for one hour. The results are shown in Figure 6.3.

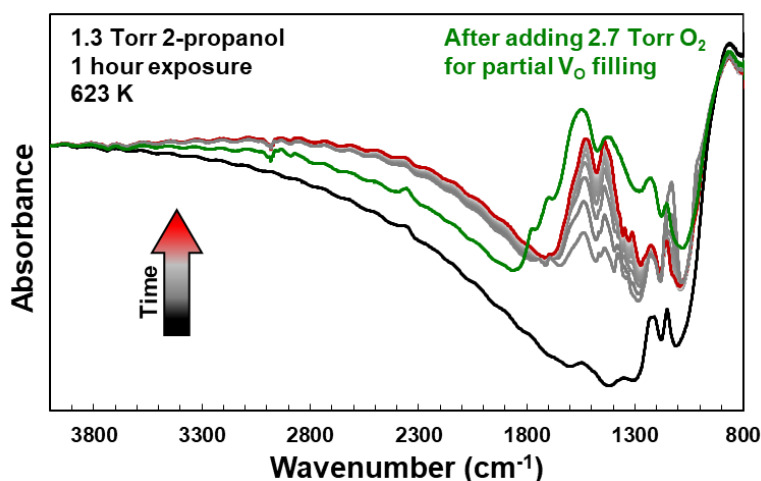


Figure 6.3 Surface IR spectra of Cu/TiO₂ during exposure to 2-propanol vapor for one hour at 623 K. Spectra highlight the broad baseline rise indicative of TiO₂ reduction (from black to red traces), followed by partial quenching of that reduction through the introduction of gaseous O₂ (green trace).

The black trace in Figure 6.3 shows the Cu/TiO₂ aerogel before exposure to 2-propanol. Immediately upon alcohol exposure, the baseline of Cu/TiO₂ significantly rises. The baseline rise over the mid IR range is indicative of titania reduction.^{196,209–214} As the exposure time proceeds, both surface-bound formate and methoxy species are shown to form (with increasing bands at 1540 cm⁻¹, 1430 cm⁻¹, and 1370 cm⁻¹) indicating that even as the TiO₂ surface cannot be further reduced, partial decomposition of 2-propanol can still proceed. After one hour of exposure to 2-propanol where no further changes were detected in the IR spectra, 2.7 Torr O₂ was added to the cell. Introduction of O₂ to a reduced TiO₂ surface should result in the filling of oxygen vacancies and subsequent lowering of the

broadband IR absorbance closer to that of the baseline (clean Cu/TiO₂, black trace).¹⁶⁰ The spectrum of Cu/TiO₂ after oxygen introduction is shown (Figure 6.3, green trace). The baseline does significantly decrease, but only by about 50%. The incomplete filling of the TiO₂ bridging O vacancies is hypothesized to result from surface formates and methoxy species situated in those vacancies after initial lattice O removal. The most accessible vacancies are filled while the inaccessible vacancies likely contain bound species with strong adsorption energy. In addition to the decreased broadband IR signal, the addition of O₂ to the cell led to the further reaction of 2-propanol. The features associated with the surface formate and methoxy intermediates clearly increase. New IR features at about 1700 and 1750 cm⁻¹ are also observed. Features in this regime of the IR spectrum are usually attributed to carbonyls and could indicate that partial oxidation of 2-propanol can occur, a topic covered in more depth in Chapter 6.3.3.

A closer look at interactions between 2-propanol and a reduced Cu/TiO₂ surface would provide further insight into the role that the support and its bridging O atoms have on the oxidation of the alcohol. To study these interactions, the Cu/TiO₂ aerogel underwent a reducing pretreatment (623 K, 2.5 hours, vacuum) to thermally remove some lattice O from TiO₂ regions of the catalyst. After that reducing pretreatment, a small amount of 2-propanol was added to the Cu/TiO₂ surface by only exposing it to 5 x 10⁻⁵ Torr for 30 minutes. O₂ (2.3 Torr) was added to the reaction cell after the reduced Cu/TiO₂ was partially saturated with 2-propanol. Evidence for reaction with the reduced catalyst can be observed in Figure 6.4

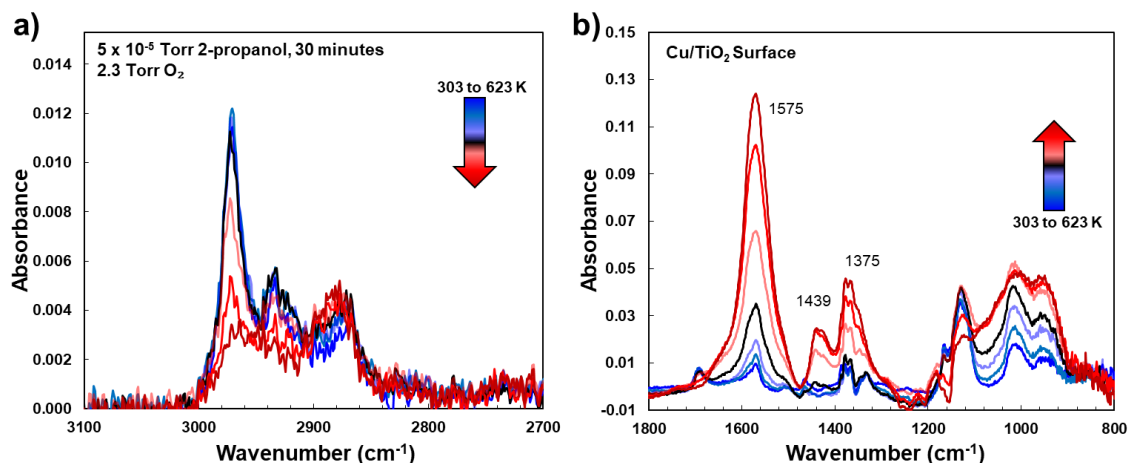


Figure 6.4 IR spectra monitoring 2-propanol oxidation on a reduced Cu/TiO₂ aerogel material. The 2-propanol-dosed surface was exposed to 2.3 Torr oxygen before increasing temperature from 303 to 623 K while monitoring the surface with IR. The C-H stretching region is shown in (a) and the lower frequency region is shown in (b).

The reaction between 2-propanol and reduced Cu/TiO₂ aerogel does not proceed the same as on the oxidized catalyst. The C-H stretching region of the IR spectra shows incomplete removal of adsorbed 2-propanol over the same temperature range as performed in Figure 6.2. The same blue-shift from 2870 to 2877 of the C-H stretching mode of 2-propanol converting to surface formate is observed, however. The lower frequency region of the IR spectra displays only the formation of surface species including formates (1575 cm⁻¹, 1375 cm⁻¹) and methoxys (1435 cm⁻¹). These surface species on the reduced catalyst do not have the intermediate-like characteristics that they do on the oxidized catalyst, as they are not further reacted to CO₂ and H₂O (as confirmed by IR spectra taken of the gaseous species during this experiment). Instead, the surface species build up throughout

the temperature range and block active sites from being regenerated. It is hypothesized that the active site for 2-propanol oxidation is the same as methanol oxidation due to the similar oxidative pathways on a clean surface (see Chapter 5.3.2 and 6.3.1). Following this hypothesis, bound surface formates and methoxys are likely to be situated within bridging O vacancies (generated from the reducing pretreatment) and therefore block those sites from oxidation. The catalyst is considered poisoned at the temperatures studied due to the surface species still present on the surface at the highest temperatures reached. The inability to thermally remove surface adsorbates situated at O vacancies is important in the understanding of potential catalyst poisoning mechanisms. Likely, the lack of neighboring bridging O atoms to accept H atoms to dehydrogenate formates and methoxys into surface O-C-O prevents the complete oxidation product CO₂. The reaction of 2-propanol on reduced Cu/TiO₂ also appears to have a higher activation barrier associated with it. The $\nu_s(\text{CC})$ mode at 1165 cm⁻¹ does not start to decrease significantly until about 523 K, where subsequent methoxy formation at 1435 cm⁻¹ is first observed. On the oxidized Cu/TiO₂ catalyst, this process occurred between 373 and 423 K. The reduced Cu/TiO₂ aerogel has a limited activity for 2-propanol oxidation, highlighting the importance of lattice O atoms within the TiO₂ aerogel support.

Interactions between reduced Cu/TiO₂ and 2-propanol were further studied by removing gaseous O₂ from the reaction cell. 2-propanol (1.8 Torr) was introduced to Cu/TiO₂ after a reducing pretreatment, and in a closed system underwent the same temperature increase as the studies shown in Figures 6.2 and 6.4. The results for the thermal effects of the alcohol on reduced Cu/TiO₂ are shown in Figure 6.5. Similar to the previous investigation on reduced Cu/TiO₂, adsorbed 2-propanol does not undergo complete

conversion, with C-H stretches still present (Figure 6.5a). The lack of a $\nu(\text{CH})$ band shift from 2870 to 2877 cm^{-1} or IR features at 1575 and 1375 cm^{-1} (Figure 6.5b) on Cu/TiO₂ informs that without gaseous O₂, the dehydrogenation of 2-propanol cannot occur on the reduced surface. Surface-bound methoxys are also absent from the spectra at 1435 cm^{-1} . However, a new IR feature appears on Cu/TiO₂ at 1686 cm^{-1} between 573 and 673 K, consistent with acetone on TiO₂.²⁴¹ To support this assignment, gas-phase spectra were recorded to show gaseous acetone formed at the same temperatures as surface acetone. The gaseous assignment was confirmed with IR spectra reported by NIST. Conversion of 2-propanol is also observed, with decreasing gas-phase signals between 2800 and 3000 cm^{-1} and between 3600 and 3700 cm^{-1} . Lower frequency 2-propanol features (gaseous) also decrease in intensity as well as a shift to known acetone frequencies (1365 and 1217 cm^{-1}). This is the first observation of any desorbed product from alcohol oxidation on Cu/TiO₂ aerogels outside of CO₂ and H₂O. Partial oxidation in the absence of O₂ is a fascinating result as it raises many questions regarding new active sites, alternate mechanisms, and the fate of H atoms that can be studied in further depth.

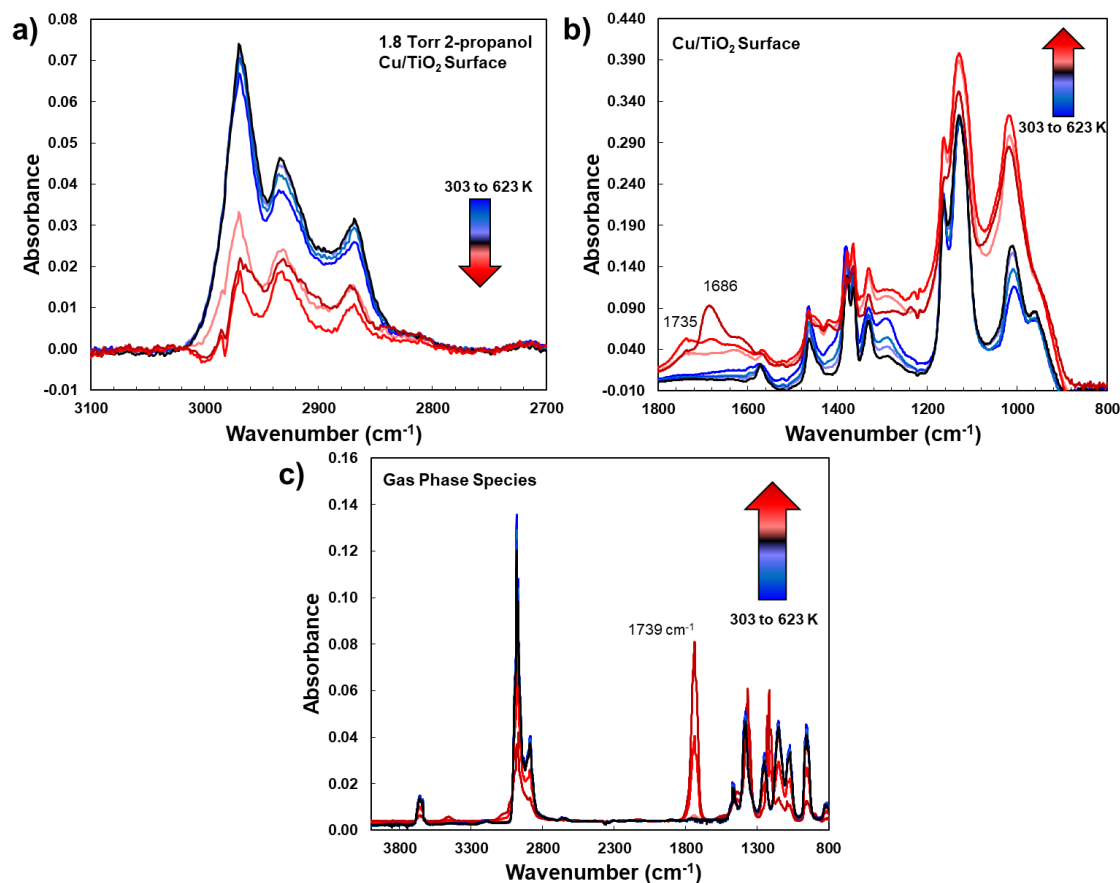


Figure 6.5 IR spectra monitoring the thermal effects of 2-propanol interacting with reduced Cu/TiO₂ aerogels. 1.8 Torr of 2-propanol was introduced at 303 K to Cu/TiO₂ and was allowed to increase in temperature up to 623 K. The Cu/TiO₂ surface was monitored in (a) for the CH stretching region and (b) for the lower frequency region. Gas-phase spectra are shown in (c).

Packed-bed flow cell studies of the Cu/TiO₂ aerogels confirm the oxidative activity and show conversion of 2-propanol to gaseous CO₂ (Figure 6.6a). When oxygen is removed from the system, however, the reactivity appears to change (Figure 6.6b). In an anaerobic 2-propanol exposure (with inert He gas) at 623 K where oxidation is known to occur, initial exposure to the alcohol shows conversion to CO₂. Both exposure conditions form low

signals of water. The complete surface-based oxidation of 2-propanol in the absence of gaseous O₂, similar to CO and methanol (see Chapters 4 and 5) underscores the versatile oxidative ability of the Cu/TiO₂ aerogels. In addition, the oxidation of 2-propanol appears to occur with the same mechanism as the CO and methanol oxidation reactions. Similar active sites and reactivity to methanol are observed through the surface reaction (Figures 5.3 and 6.2) and the broad baseline absorbance rise on TiO₂ (Figures 5.7 and 6.3). The reactivity with methanol differs once active oxygen species on the surface are depleted, where acetone is instead formed in the reactor as CO₂ production rapidly falls to zero. Acetone production in the absence of gaseous O₂ suggests that complete oxidation and partial oxidation pathways are available for 2-propanol reactivity, dependent on reaction conditions. Interestingly, partial oxidation of 2-propanol to acetone is active for significantly longer than complete oxidation to CO₂, and even appears to continue beyond the 30-minute duration of the experiment. The formation of acetone is unique to Cu/TiO₂ aerogels, and no products are observed with the anaerobic exposure of 2-propanol to Cu-free TiO₂ aerogels. The loss of 2 hydrogen atoms in the conversion from 2-propanol to acetone can be explained by one of two phenomena: hydrogen spillover or hydrogen gas evolution.^{214,217,242} Formation and subsequent removal of water via the bridging O in titania isn't considered as a process in the partial oxidation mechanism, as the anaerobic reaction would be limited by the amount of activated lattice O in TiO₂ regions of the catalyst. Both potential pathways are not detectable with the IR flow cell methods deployed or with the vacuum chamber. Further studies with mass spectrometric methods are needed to pinpoint the exact mechanism of the partial oxidation of 2-propanol to acetone.

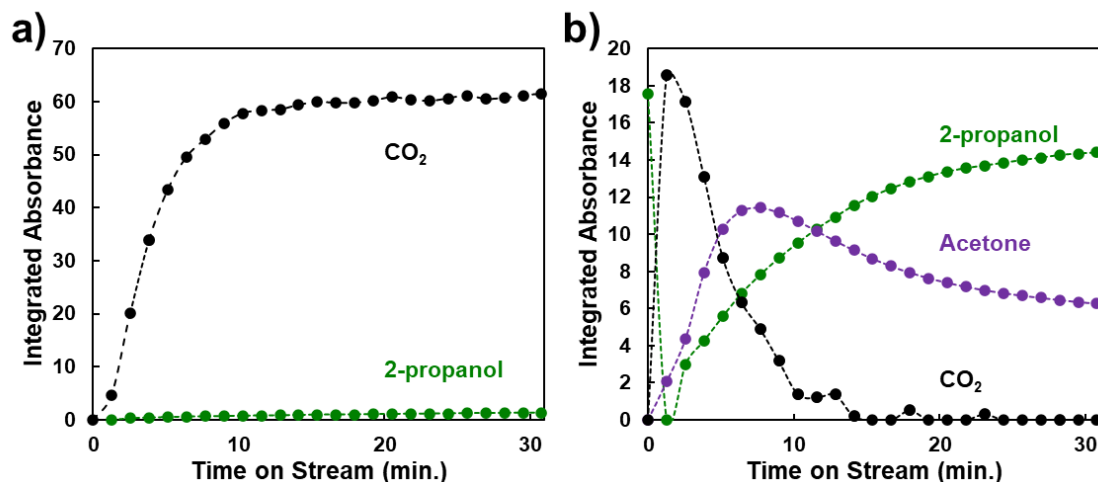


Figure 6.6 Integrated IR data 2-propanol oxidation on Cu/TiO₂ aerogels in the packed-bed reactor at 623 K. Aerobic oxidation (a) was performed with a reactant mixture of 0.5% 2-propanol, 40% O₂, and 59.5% Ar. Anaerobic oxidation (b) was performed with a reactant mixture of 0.5% 2-propanol and 99.5% Ar. CO₂ signal was integrated between 2280 and 2410 cm⁻¹, 2-propanol signal was integrated between 2850 and 3030 cm⁻¹, and acetone signal was integrated between 1600 and 1820 cm⁻¹. Each data point is the average of 50 scans

6.3.3 Alcohol Binding to Cu Nanoparticles and Relationship to Partial Oxidation

The active site for the partial oxidation pathway is not trivial to discern. As binding is the first major step in heterogeneous catalysis, a closer look at binding sites can yield insights into the partial oxidation active site. The 2-propanol IR adsorption spectra discussed previously did not uncover any differences between the Cu/TiO₂ and TiO₂ aerogels which might suggest that the alcohol does not bind effectively to Cu sites. But if the surface residence time or molar absorptivity of this potential alcohol-Cu binding mode is too small, the IR mode would not be observed. Therefore, CO was employed as a Cu-

selective site-blocking molecule in a competitive adsorption study with 2-propanol. CO was cryogenically (at 193 K) adsorbed onto Cu/TiO₂ aerogels before adjusting the sample temperature to 303 K. Cryogenic exposure ensures the nonreactive adsorption of CO onto the Cu/TiO₂ surface, while increasing the sample temperature in vacuum removes weakly bound adsorbates and leaves CO adsorbed exclusively to Cu¹⁺ and Cu⁰ sites. Subsequent exposure of the CO-saturated Cu/TiO₂ material to alcohols will allow for any changes to the Cu-CO features to be evaluated, yielding valuable information on relative binding strengths.

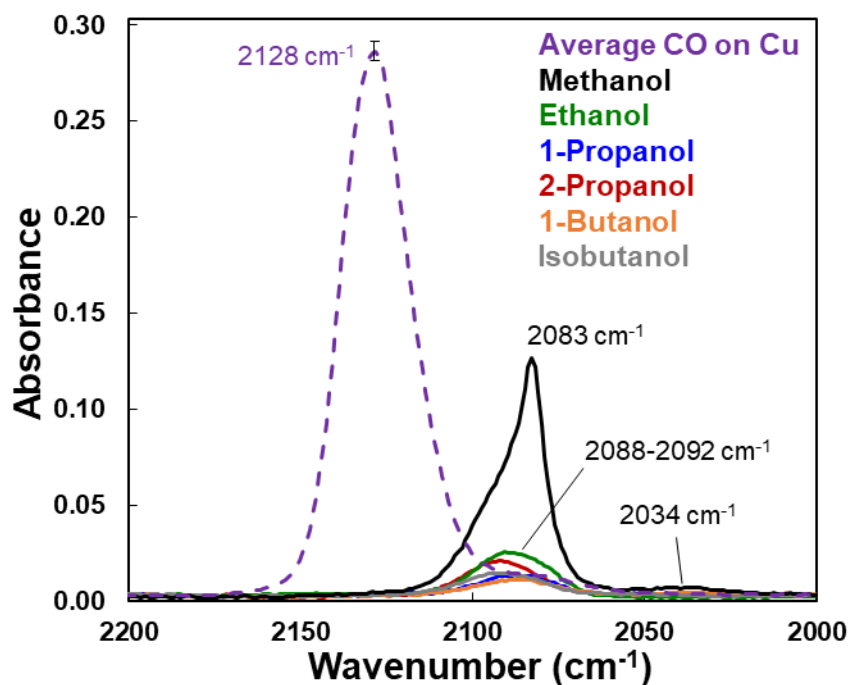


Figure 6.7 IR spectra of CO displacement by adsorbed alcohols on Cu/TiO₂ aerogels at 303 K. CO on Cu after a 193 K exposure to 1 Torr CO for 15 minutes (purple dashed trace) averaged between 6 experiments/exposures where the error bar represents the standard deviation from the exposures. 350 mTorr of an alcohol was then exposed to the CO-saturated Cu/TiO₂ aerogel before remaining spectra were taken.

The results of the CO/alcohol adsorption on Cu study are shown in Figure 6.7. The dashed purple trace indicates CO on Cu at 303 K prior to alcohol exposure. There is a clear signal at 2128 cm^{-1} indicating Cu^{1+} sites binding with CO, with a lower intensity broad shoulder at about 2080 cm^{-1} showing some Cu^0 present in the material. After 350 mTorr of 2-propanol is introduced to the CO-saturated material (red trace), the IR signature dramatically changes. The integrated area of the CO-Cu signal decreases by about 94%, while red-shifting to 2088 cm^{-1} . The drop of CO signal intensity in the presence of an adsorbate suggests that the 2-propanol is competing for Cu sites and displacing the CO on Cu. Adsorption of 2-propanol onto Cu sites is therefore supported, despite the absence of IR features indicating alcohol-Cu NP binding in prior studies (Figure 6.1).

While 2-propanol adsorption energetics on Cu surfaces has not been specifically studied, the adsorption energetics of CO, methanol, and ethanol have been investigated. CO adsorption energies on metallic Cu surfaces vary significantly in the literature, and range from -27.0 kJ/mol to -193.5 kJ/mol ,^{243–245} with most experimental results averaging near -48.1 kJ/mol .^{246–248} On oxidized surfaces, CO adsorbs to Cu^{1+} sites between -65 and -85 kJ/mol and displays weaker binding to Cu^{2+} sites at -45 kJ/mol according to investigations of Cu ions within a zeolite.²⁴⁹ In comparison to alcohols, methanol binds to Cu between -25.1 kJ/mol and -53.1 kJ/mol , with dramatically increased strength if dissociation to methoxy groups were to occur (up to -315 kJ/mol).^{250,251} Ethanol was also calculated to adsorb on Cu with an adsorption energy of -32.8 kJ/mol .²⁵² The high degree of variance in the literature stresses the need for relative binding studies to clarify results in different systems. The high degree of displacement of CO in Figure 6.7 likely indicates that the alcohols adsorb more strongly to the CuNPs.

The presence of an adsorbate with high electron density changes the electronic structure of the surface to which it is bound, as shown by other researchers, and can lead to a significant change in the vibrational frequency of CO at that surface site.²⁵³ McEntee et al. showed a frequency shift of $< 3 \text{ cm}^{-1}$ for CO on Au NPs supported on TiO_2 when electron donor (CH_4 , C_2H_6 , C_3H_8) or acceptor (SF_6) molecules were adsorbed selectively onto TiO_2 regions of the material. Compared to the results in Figure 6.7, the clear displacement of CO on Cu and the large observed frequency shift of 36 cm^{-1} suggests that 2-propanol binds to Cu sites in addition to TiO_2 regions of the catalyst. Influence of electron structure changes is likely to be somewhat delocalized when adsorption is limited to the support oxide, which leads to the smaller CO-NP frequency shift in the presence of a donor or acceptor molecule.²⁵³ One explanation is that as adsorption of the donor (2-propanol) also occurs on the Cu NP to which CO is bound, the proximity and localization of the adsorbate charge transfer has a more dramatic impact on the change in CO vibrational frequency. Further work involving detailed electronic structure calculations is needed to support this hypothesis.

The same competitive adsorption study was repeated with methanol as the donor molecule (Figure 6.7, black trace). A similar phenomenon was observed, with the apparent displacement of CO occurring on Cu sites by the alcohol adsorbate, and a 45 cm^{-1} red-shift of CO on Cu^{1+} . With methanol, Cu^0 sites are still present and similarly shifted to 2034 cm^{-1} . The CO- Cu^0 features with and without methanol (2034 and 2088 cm^{-1} , respectively) also have similar relative intensities to that of CO- Cu^{1+} . The main difference appears in the remaining intensity of the CO- Cu^{1+} feature. Here, the integrated intensity of the shifted CO- Cu^{1+} IR feature only decreased by 72% upon introduction of the alcohol adsorbate.

The lesser amount of displaced CO on Cu for methanol in comparison to 2-propanol is a challenging result to contextualize. It can be anticipated that a change in the electronic structure of the Cu NP upon alcohol adsorption would affect the molar absorptivity of the CO-Cu¹⁺ IR band. The consistent CO-Cu¹⁺ frequency shifts between the different alcohols suggests similar electronic structure changes to the Cu NP across all alcohols. Therefore, the assumption can be made that changes in the relative CO-Cu¹⁺ signal loss between alcohols, and not purely absolute signal loss, would indicate the binding differences between alcohols. The data is analyzed with this assumption that a significant portion of the CO-Cu¹⁺ signal loss from methanol co-adsorption is due to a molar absorptivity change, while the difference between methanol and 2-propanol induced CO-Cu¹⁺ signal loss is due to differences in adsorption/coverage. Most simply, 2-propanol adsorbs onto Cu NPs strongly, displacing CO at high coverages, significantly higher than methanol. The same binding study was repeated for several other alcohols to observe trends between alcohol structure and binding to Cu NPs. The results in Figure 6.7 show that ethanol, 1-propanol, and 1-butanol all behave very similarly to 2-propanol binding. The binding of the alcohols to Cu is not limited by steric interactions, or 2-propanol would display decreased binding affinity due to the two methyl groups compared to methanol's one. This leaves the likely difference in binding to different charge distributions.

Table 6.1 Calculated atom-centered charge for alcohols from the Entos Envision online program. The terminal C on each alcohol is highlighted.

Atom-Centered Charge							
	Methanol	Ethanol	1-Propanol	2-Propanol	1-Butanol	Isobutanol	
O	-0.420	-0.423	-0.422	-0.425	-0.422	O	-0.426
C ₁	0.197	0.221	0.213	0.243	0.215	C ₁	0.209
C ₂	-	-0.051	-0.010	2 x -0.056	-0.019	C _{2,C}	0.040
C ₃	-	-	-0.025	-	0.015	C ₃	-0.029
C ₄	-	-	-	-	-0.023	C ₃	-0.037

Table 6.2 Calculated electrostatic potential at nuclei for alcohols from the Entos Envision online program. The terminal C on each alcohol is highlighted.

Electrostatic Potential at Nuclei							
	Methanol	Ethanol	1-Propanol	2-Propanol	1-Butanol	Isobutanol	
O	0.201	0.204	.203	0.206	0.203	O	0.205
C ₁	-0.101	-0.113	-0.108	-0.122	-0.109	C ₁	-0.106
C ₂	-	0.045	0.024	2 x 0.046	0.029	C _{2,C}	-0.005
C ₃	-	-	0.022	-	0.001	C ₃	0.013
C ₄	-	-	-	-	0.017	C ₃	0.026

Utilizing the Entos Envision program²⁵⁴ for information on the electronic structure of the alcohols in question, the atom-centered charge and nucleic electrostatic potential (ESP) were found for every atom (H's withheld) within various alcohols including methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and isobutanol. The results are summarized in Tables 6.1 and 6.2. The O atom in every alcohol has a similar electronic structure, with a highly negative atom-centered charge and ESP. The main difference between the two categories of alcohols (weaker binding to Cu like methanol vs stronger binding to Cu like the remaining alcohols) lies in the electronics of the terminal C atom. Methanol has a positive value for terminal C centered charge (0.197), while the other

alcohols have negative values ranging from -0.023 to -0.133. The trend follows for the ESP of the terminal C where methanol's negative terminal C ESP indicates the atom's affinity for negative point charges and other alcohols' positive terminal C ESPs indicate the atom's affinity for positive point charges. These values can be related to the results from the CO displacement study shown above. A similar electronic structure for the O atom in these alcohols indicates that any differences in binding to Cu are likely to come from binding through a different atom/adsorption mode. As the terminal C on methanol possesses a positive charge and the Cu particles also possess a largely positive charge (with sites of Cu^0 , Cu^{1+} , and Cu^{2+}), decreased binding affinity can be expected. 2-propanol and the other remaining alcohols have a terminal C that possesses a negative charge and is experimentally observed to bind stronger than both CO and methanol to Cu NPs. Other explanations for the difference in binding of the larger alcohol molecules, like larger dispersion interactions and lower vapor pressures that could lead to larger coverage on Cu, are hypothesized to not be a factor. If dispersion interactions/vapor pressure affected the alcohol coverage on Cu, a difference in the CO displacement between a molecule of ethanol's size and volatility (0.45 nm and 44.6 Torr at 293 K, respectively)^{255,256} and 1-butanol's (2.0 nm, 4.35 Torr at 293 K)^{255,257} would likely be observed.

Combining the alcohol-CO displacement results along with the computational electronic parameters together show a clear difference between methanol and the other alcohols, displayed in Figure 6.8. While there isn't a direct linear relationship, there is a clear clustering of molecules with a negative terminal C atom-centered charge (or positive electrostatic potential of the terminal C) and a high amount of displaced CO on Cu by the adsorbed alcohol. Inversely, methanol with a relatively large positive charge on its terminal

C and negative electrostatic potential has the least amount of displaced CO on Cu by the adsorbed alcohol. Methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and isobutanol all have similar electronics to methanol on the O-adjacent C atom. Consistent with the argument for the oxygen atom, the similar electronics of the O-adjacent C are ignored from the relationship to binding, as the large differences between methanol and the higher-order alcohols cannot be discerned. Steric hindrance also prevents the O-adjacent C from playing a large role in binding.

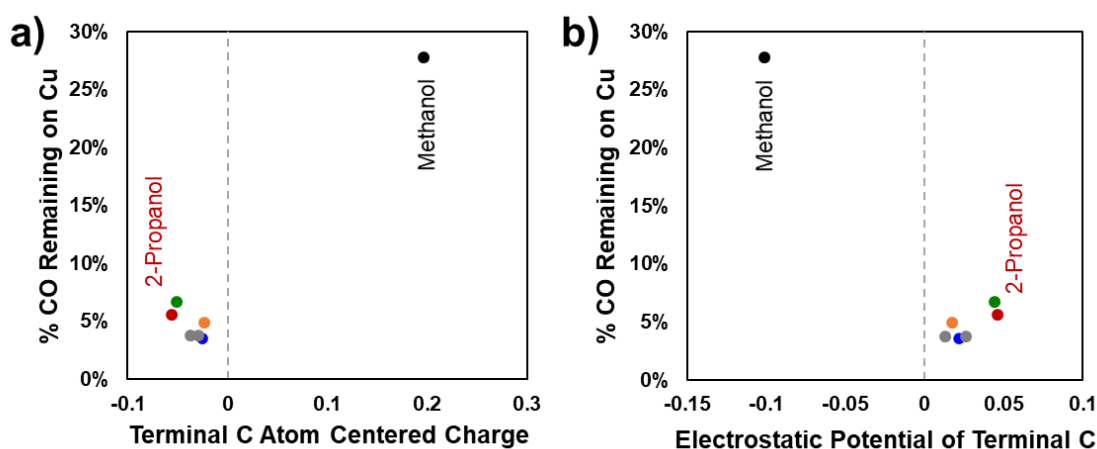
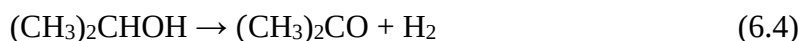
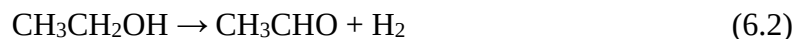
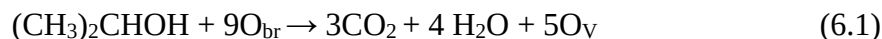


Figure 6.8 Percent of CO remaining on Cu sites after exposure to 350 mTorr of an alcohol (methanol as black, ethanol as green, 1-propanol as blue, 2-propanol as red, 1-butanol as orange, isobutanol as gray) vs the atom-centered charge of the terminal C (a) and vs the electrostatic potential of the terminal C (b). Data compiled from the study in Figure 6.7 and Tables 6.1 and 6.2.

Methanol and the higher-order alcohols are significantly different in terms of their terminal C electronics and their binding to Cu NPs, and this difference is additionally highlighted when investigating partial oxidation pathways in anaerobic conditions. Higher-

order alcohols not investigated in-depth thus far in this dissertation (ethanol, 1-propanol, 1-butanol) were studied for both complete oxidation and partial oxidation using similar packed-bed reactor methods. The results appear in the Appendix. Briefly, when Cu/TiO₂ was exposed to a reaction stream containing both oxygen and one of the alcohols (in studies replicating the one shown in Figure 6.6), complete oxidation to CO₂ was observed. Removal of O₂ from the reaction stream led to the same behavior as observed in Figure 6.6 with 2-propanol. Initial oxidation to CO₂ occurs before the active lattice O from the TiO₂ support is removed (Eq. 6.1), followed by the initiation and extended lifetime of partial oxidation to the aldehyde/ketone associated with the parent alcohol (Eqs. 6.2-6.5). Ethanol was partially oxidized to acetaldehyde (Eq. 6.2), 1-propanol to propionaldehyde (Eq. 6.3), 2-propanol to acetone (Eq. 6.4), and 1-butanol to butyraldehyde (Eq. 6.5) as confirmed by recorded IR spectra in comparison to NIST standards.



Again, methanol (shown in Chapter 5) was unable to undergo a partial oxidation pathway under anaerobic conditions, suggesting the importance of binding to Cu sites. There is still future work (both in terms of computational support and further experimentation) needed to confirm the working hypothesis that increased binding of an alcohol onto Cu NPs within the Cu/TiO₂ aerogel facilitates a partial oxidation pathway of the alcohol to the associated aldehyde/ketone. Specifically, investigating the bond strength of the alpha H atoms in

relation to both the amount of CO remaining on Cu during the displacement studies shown previously as well as the overall conversion of alcohol to aldehyde/ketone would provide valuable information. A product analysis with mass spectrometry would also assist in determining the fate of H atoms in the partial oxidation pathway. Differentiating between H₂O formation, H₂ generation, or H spillover on the catalyst would provide valuable insights into the feasibility for Cu/TiO₂ aerogels as fuel cell catalysts.

6.4 Summary

In summary, *in situ* spectroscopic techniques were applied to analyze the adsorption and oxidation activity of 2-propanol on Cu/TiO₂ aerogels. Evidence has been provided to describe the complete oxidation of 2-propanol proceeds similarly to that of methanol, occurring catalytically on titania sites on the periphery of Cu NPs. The dissociative adsorption of 2-propanol occurs first on titania sites before C-C cleavage can occur to leave surface methoxy species. Surface methoxy groups decompose to surface-bound formates before further reaction to CO₂ and likely water that is evolved from the catalyst surface. The reduction of titania is distinctly observed and effects of a reduced surface before alcohol exposure are shown to dramatically inhibit product formation. Cu-localized alcohol binding was then analyzed in-depth to further understand the partial oxidation pathway that is observed for 2-propanol. A relationship was found between the electronics of the terminal C of an alcohol and its binding affinity for Cu NPs, which was hypothesized to be vital for unlocking the partial oxidation of the alcohol to its associated aldehyde/ketone.

Chapter 7

Detoxification of the Chemical Warfare Agent Simulant Dimethyl Chlorophosphate on Cu/TiO₂ Aerogel Surfaces

7.1 Introduction

Since their discovery in the 1930s, organophosphorus (OP) compounds have been used as chemical warfare agents (CWAs) due to their effectiveness as toxic nerve agents. In recent times, the nerve agent sarin (GB) has been at the center of headlines due to its identification in military warzones and lethal usage on non-military civilians.^{258,259} Researchers have been looking for and attempting to design catalytic materials that have enhanced activity and avoid the main limitation of the current class of materials: nondestructive adsorption.²⁶⁰ Reactive decontamination has been utilized in bulk settings with Zr(OH)₄, but has not been utilized in the field and is primarily implemented in lab settings for bulk destruction because of the necessity of liquid reagents.^{261,262} The usage of this lethal class of chemicals in current events stresses the need for new materials that can go beyond sorption to detoxify the agent and desorb benign compounds.

Oxide surfaces have been a commonly studied material for decomposition reactions of GB and its CWA simulants due to promising initial activity.^{76,77,268–271,78,79,235,263–267} TiO₂ was shown to be one of the more reactive surfaces towards the degradation of dimethyl methylphosphonate (DMMP, structure in Figure 1.6), the most commonly used chemical simulant of GB.^{76,77,79,264–268} Most of the investigations concluded that GB or its simulants decompose on TiO₂ surfaces upon either adsorption or further reactive pathways. The TiO₂ surfaces, however, are poisoned by the buildup of surface PO_x species. The nonvolatile

phosphorus compounds are strongly bound to the TiO_2 surface and even thermal reactivation of a PO_x -saturated surface cannot restore the reactive pathway.⁷⁶

Researchers have used different methods to alter the reactivity and try to design effective catalysts toward CWA decontamination while addressing the problem of catalyst poisoning. More reducible oxides like CeO_2 or the addition of metal nanoparticles to TiO_2 have been shown to increase the lifetime of the catalyst and react for more cycles than pure TiO_2 before deactivation.^{272,273} The addition of Au NPs on TiO_2 resulted in the further oxidation of DMMP, with a surface-bound methoxy group formed from initial decomposition continuing to react, forming CO and CO_2 .⁷⁸ Here, similar to the studies in Chapters 4 and 5, lattice oxygen around the periphery of Au NPs was determined to be active for reaction under anaerobic conditions. In addition, hydrolysis occurred along the perimeter of Au to form methanol on the catalyst surface. A charge transfer was observed under aerobic conditions from Au to adsorbed O_2 to generate an active O species that was able to oxidize the carbonaceous species from DMMP to CO_2 .⁷⁸

Nanostructured TiO_2 materials like an aerogel would significantly increase the surface area and stability of nanoparticles through the 3-D support structure (see Chapter 1.2.3). High energies (either thermal, photonic, or chemical) are likely needed to remove strongly bound phosphorus-containing species, so the increased stability of the aerogel can help solve some of the catalytic challenges, like sintering during high temperature treatment for the removal of strongly bound products. Investigations of GB and DMMP decomposition on Cu/TiO_2 aerogels suggested enhanced reactivity for hydrolysis and oxidation pathways, forming products such as surface methoxy groups, formates, acetone, CO(g) , and $\text{CO}_2\text{(g)}$.^{48,83} The enhanced hydrolytic activity of DMMP on Cu/TiO_2 aerogels

relative to Au/TiO₂ was attributed to both the stability of OH groups and the redox ability.⁴⁸ Broad-band UV illumination of the Cu/TiO₂ aerogel was able to decompose GB to IMPA, MPA, PA, formates, CO, and CO₂ as observed by DRIFTS (see Figure 7.1 for OP-based products).⁸³ Mechanistic details to these reactions, however, have not yet been investigated.

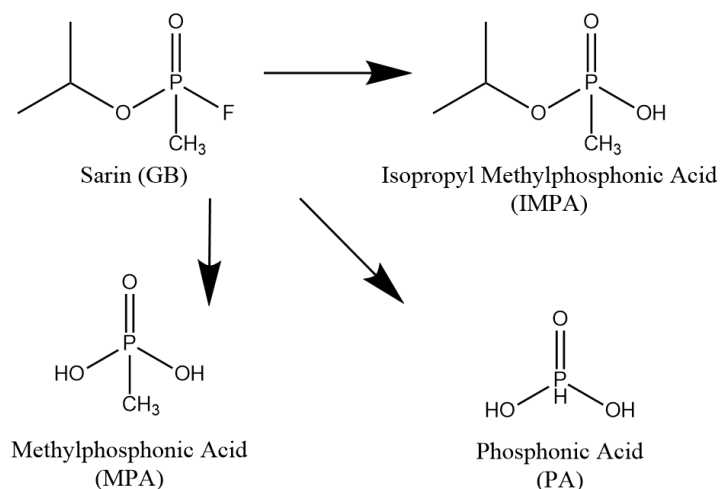


Figure 7.1 Common decomposition products for the CWA sarin.

In this study, Cu/TiO₂ aerogels are analyzed during the decomposition of the GB chemical simulant dimethyl chlorophosphate (DMCP) with *in situ* surface spectroscopy and flow cell reactor studies as motivated by the importance of CWA destruction. Adsorption and oxidation on the TiO₂ support are shown to be promoted by the presence of Cu nanoparticles. CH₃Cl is identified as the major decomposition product from a multi-step decomposition pathway that has not been observed by researchers before on a TiO₂-based material. The analogous products from a similar projected decomposition of GB, either CH₃F or (CH₃)₂CHF, are significantly less toxic compounds than either HF (single-step product) or the GB molecule itself, indicating a promising detoxification pathway.

7.2. Procedural Methods

7.2.1 Cu/TiO₂ Synthesis

Cu/TiO₂ aerogels were prepared by photodepositing Cu nanoparticles onto TiO₂ aerogels in a manner described previously.^{36,81,115} First, TiO₂ aerogels were prepared using the sol-gel method.³⁷ A wet gel is formed by adding a solution of Ti(ⁱOPr)₄ (Alfa Aesar, 97+%) in 3.9 g of ethanol (absolute ethanol, Warner-Graham) to a mixture of H₂O (0.39 g), ethanol (4.0 g), and nitric acid (78 mg of 70% HNO₃, Fisher). After aging for 24 h, the wet gel was rinsed 10 times with acetone over multiple days. The wet gels were loaded under acetone into a supercritical dryer and rinsed with liquid CO₂ at 283 K before heating the dryer to 314 K and then venting to atmospheric pressure. The TiO₂ aerogels were calcined in air at 698 K (2 K min⁻¹ heating and cooling ramp, 4 h dwell) to produce nanocrystalline anatase aerogels. Following an established method,²⁸ Cu nanoparticles were photodeposited onto the TiO₂ aerogels by illuminating slurries containing ~150 mg TiO₂ aerogel suspended in a solution of 110 mL of 2 mM Cu(NO₃)₂ (Sigma-Aldrich, 98%) in 9:1 (vol:vol) H₂O:CH₃CH₂OH (adjusted to pH 9.5 ± 0.5) for a period of 24 h with a 500 W Xe arc lamp (Newport Oriel). The Cu/TiO₂ aerogels were collected by centrifugation followed by re-suspension in Ultrapure 18 MΩ cm water (Barnstead Micropure) for 10 cycles. The Cu/TiO₂ aerogels were then dried in air at 373 K overnight.

7.2.2 Ambient Pressure Packed-Bed Flow Reactor

Catalyst activity was screened with a packed-bed reactor (Altamira Instruments, μBenchCAT) coupled to a differentially-pumped quadrupole mass spectrometer (QMS) (ABB Extrel MEXM). The apparatus is described in Chapter 2. About 3 mg of Cu/TiO₂

aerogel catalyst was packed into a 0.25-inch diameter quartz tube and secured by quartz wool on both sides of the tube. Gaseous reactant flow into the cell was controlled with mass flow controllers. DMCP was stored in a glass saturator cell, maintained at 288 K by a circulating water chiller, and carried by an inert He flow (99.999% Praxair Ultra High Purity). O₂ and He/DMCP flow were initially separated and combined in a mixing cell for thorough incorporation before introduction to the catalyst. The temperature of the catalyst bed was monitored with a K-type thermocouple. Prior to each experiment, the Cu/TiO₂ sample was activated at 573 K under 10 SCCM flow of O₂ for 30 minutes.

7.2.3 Vacuum Studies with Infrared Spectroscopy

Infrared spectroscopic studies were performed in a stainless-steel high-vacuum reactor cell with a base pressure of 1×10^{-8} Torr (see Chapter 2). Cu/TiO₂ and TiO₂ aerogel samples were pressed (at 5000 psi) as 7 mm disks into the void space of a 50- μ m thick tungsten mesh (Tech-Etch), secured onto a stainless-steel sample holder. The tungsten mesh sample holder allows for both samples to be exposed to the same gaseous and thermal environments, enabling direct comparisons between the materials.⁸⁹ A K-type thermocouple was attached directly to the tungsten mesh, within 3 mm of the samples, to monitor sample temperature. The tungsten mesh was resistively heated using copper rods attached to an external power supply. Details of the high-vacuum cell can be found in previous work.⁸⁵ An FTIR spectrometer with an external MCT-A detector (Thermo, Nicolet Nexus 470 FTIR, resolution 2 cm⁻¹, optical velocity 1.8988 cm/s) couples to the vacuum chamber to provide the *in situ* infrared spectroscopic measurements.

Samples were pretreated oxidatively in the vacuum chamber by exposure for 1 hour at 673 K in 10 Torr of O₂ followed by 30 minutes at 673 K in vacuum. Reducing pretreatment in the vacuum chamber was performed by increasing the Cu/TiO₂ surface to 673 K in vacuum for 2 hours. These pretreatment procedures effectively remove weakly-bound organic species on the surface, as confirmed by infrared spectroscopy of the samples. For exposures of O₂ (99.994% purity, Airgas Ultra High Purity) and DMCP (97%, Sigma-Aldrich), a gas/vapor manifold affixed to the vacuum chamber allowed for quantifiable amounts of each gas/vapor to be introduced into the chamber and exposed onto each material. About 2 mL of DMCP liquid was added to a vapor dosing bulb and subjected to at least 3 freeze-pump-thaw cycles before vapor introduction into the vacuum chamber.

7.3. Results and Discussion

DMCP interactions with Cu/TiO₂ aerogels have been investigated using a similar combination of methods as discussed in previous chapters; packed-bed flow reactor studies monitored by mass spectrometry and surface infrared spectroscopy. The use of the vacuum IR cell allows for the tracking of surface species during the adsorption and reaction processes, while also allowing for the analysis of the TiO₂ support and desorbed gaseous products. The packed-bed reactor with the mass spectrometer measures gaseous reactants and products with a finer time resolution (0-10 seconds compared to minutes with the surface IR) to track short-lived products and monitor *in situ* reactivity under operational conditions.

7.3.1 Determination of DMCP Decomposition Cu/TiO₂ Aerogels

The packed-bed reactor was first used to test the ability of Cu/TiO₂ aerogels to decompose the CWA. Experiments were performed by flowing DMCP over a packed bed of thermally treated Cu/TiO₂ aerogel material in the presence of O₂. The reactant gas stream was made up of 50% O₂ and 50% He saturated with DMCP (held at 288 K) vapor. Significant equilibration time of the reactant gas stream monitored by the QMS through a reference cell was allowed for the dissipation of any impurities or DMCP degradation products, like CH₃Cl (Appendix). Once the reactant stream reached a steady-state concentration, the flow was directed over the packed catalyst bed to monitor reactivity. The full mass spectra and integrated selected peaks over time are shown in Figure 7.2. The DMCP signal displayed in Figure 7.2 inset is the 109 m/z signal (not shown, representing the DMCP molecule with a lost Cl atom) throughout the reaction. The fragments of DMCP with detectable signal (m/z of 47, 79, 93, and 144) all had the same behavior as the 109 m/z signal, which was chosen for display for clarity.

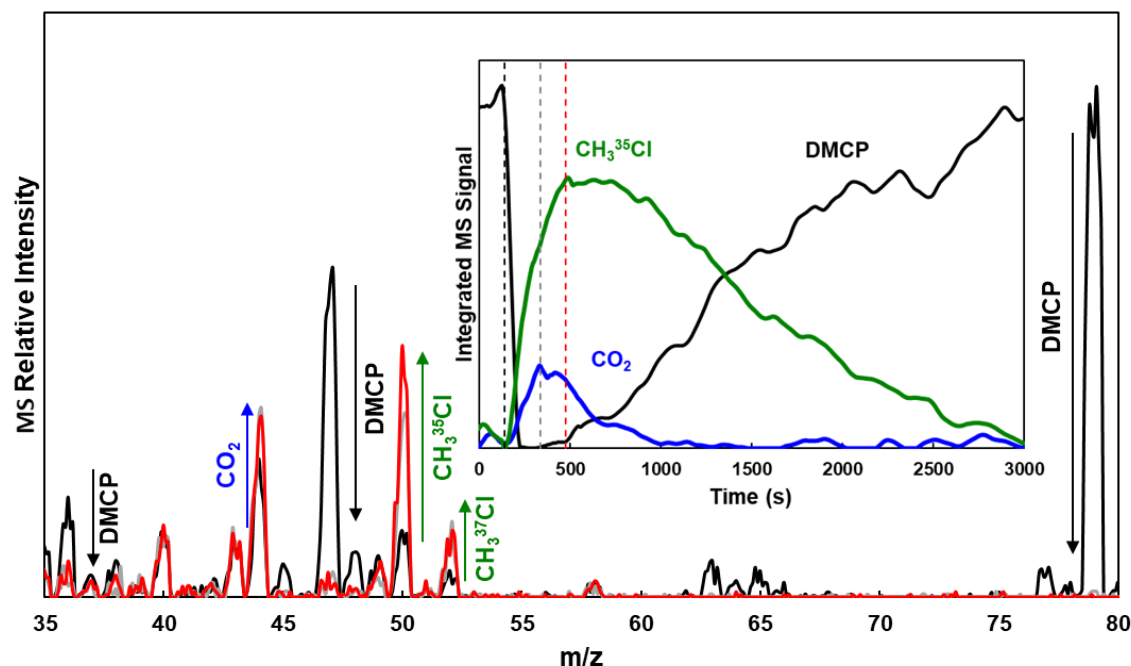
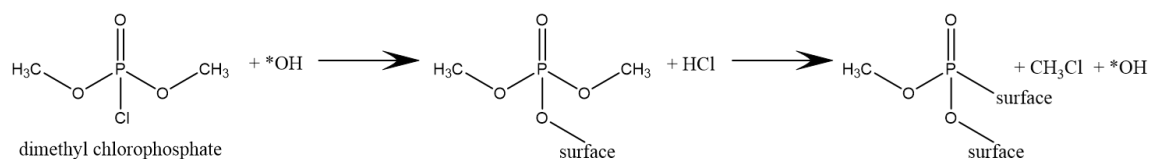


Figure 7.2 Quadrupole mass spectrometry data tracking the degradation of DMCP over a packed bed of Cu/TiO₂ aerogel at 523 K at three key points in the reaction: the saturated reactant stream before exposure to the catalyst bed (black trace), the maximum of CO₂ formation over Cu/TiO₂ (gray trace), and the maximum of CH₃³⁵Cl over Cu/TiO₂ (red trace). The inset shows integrated data over time of exposure to the packed catalyst bed, smoothed with a 5-point moving average, and normalized. The reactant mixture was made of 50% O₂ and 50% DMCP-saturated He at 10 mL/min.

The data in Figure 7.2 indicates that DMCP decomposes when passed through Cu/TiO₂ aerogels, evidenced by the appearance of m/z features at 44 associated with gaseous CO₂ and features at 50 and 52 associated with CH₃³⁵Cl and CH₃³⁷Cl respectively. The CO₂ signal decreases after about 300 seconds while the CH₃Cl decreases after about 660 seconds. Once the product formation stops, and reactivity tails off, DMCP increases back to its baseline level in the reactant stream. No other products were observed over the

entirety of the m/z range evaluated (13-160). It is important to note that the DMCP signal has been normalized to account for the pressure drop through the packed catalyst bed. The results are consistent with a multi-step decomposition mechanism previously suggested by Florent et al., as shown in Scheme 7.1.²⁷⁴ Surface hydroxyl groups react with the P-Cl bond to produce HCl, which subsequently reacts with methoxy groups to form CH₃Cl and restore the surface TiOH (see Scheme 7.1). Importantly, H₂O is not observed in the mass spectrum as there is insufficient thermal energy to desorb H₂O from the surface at the experimental conditions (523 K). Chapter 5.3.4 showed that H₂O is removed from the Cu/TiO₂ surface at temperatures above 530 K. While water on the surface can contribute towards the observed deactivation, surface-bound phosphoryl species are likely to contribute to deactivation in a more significant way due to the strong binding affinity for TiO₂ surfaces.^{76,77,79,264–268} CO (that is observed upon adsorption of DMCP onto Cu/TiO₂ aerogels) was also not observed at 28 m/z . This signal does overlap with N₂ (which is present in the mass spectrum), but closer analysis of the m/z 12:28 ratio monitoring the fragmentation to atomic C vs molecular CO, indicated no molecular CO was fragmenting and the signal was due to ambient N₂. The decomposition to CH₃Cl is important from a toxicity standpoint, as the analogous reaction for the decomposition of the GB agent itself (Figure 7.1) would produce CH₃F, which is dramatically less toxic than HF. But, the fate of any phosphorus-containing compounds is still unknown from the flow reactor results, and more surface-based studies are needed to characterize the DMCP decomposition reaction on Cu/TiO₂ aerogels.



Scheme 7.1 Possible reaction pathway for DMCP decomposition to CH_3Cl on the surface of Cu/TiO_2 aerogels, following similar chemistry to Florent et al.²⁷⁴

7.3.2 IR Spectroscopy of DMCP Adsorption on Cu/TiO_2 and TiO_2 Aerogels

To monitor surface interactions between DMCP and Cu/TiO_2 , DMCP was adsorbed onto the surface and probed with IR spectroscopy. 400 mTorr of DMCP was exposed to both Cu/TiO_2 and TiO_2 aerogels for 15 minutes at 303 K before evacuation and spectra were recorded. Infrared spectra of adsorbed DMCP on the TiO_2 aerogel in comparison to the Cu/TiO_2 aerogel are shown in Figure 7.3. Significant spectral features including bands at 2962 cm^{-1} and 2855 cm^{-1} in the C-H stretching region are indicative of molecularly bound DMCP, $\nu_a(\text{CH}_3)$ and $\nu_s(\text{CH}_3)$ respectively, on TiO_2 regions of the materials (see Figure 7.2 inset). Similar features are observed in other works with the analogous CWA simulant DMMP (structure in Chapter 1.7).^{76–78,264} Hydrogen bonding interactions are observed in both Cu/TiO_2 and TiO_2 aerogel materials through the characteristic loss of free Ti-OH stretches ($3600\text{--}3800\text{ cm}^{-1}$) and the rise of a broad ($2800\text{--}3600\text{ cm}^{-1}$) bound OH feature, where the red-shift due to coordination is observed in similar oxide systems.^{275–277} The loss of the 3732 cm^{-1} feature on Cu/TiO_2 that is not consistent with TiO_2 is attributed to H-bonding interactions with surface OH groups stabilized near interfaces between Cu and TiO_2 .^{48,49} Surface OH groups native to the surface even after pretreatment could be important towards the CH_3Cl formation observed in Figure 7.2. Molecular adsorption is not the only process that occurs during the interactions of DMCP and the Cu/TiO_2 aerogel,

however. The feature at 2923 cm^{-1} is consistent with the dissociative adsorption of DMCP to form a bound methoxy ($-\text{OCH}_3$).^{155,160,193–195} This dissociation is not detected on the pure TiO_2 aerogel, highlighting the promotional effects of Cu. Other signature bands of DMCP on the TiO_2 surface include the 1451 cm^{-1} band corresponding to $\delta(\text{CH}_3\text{O})$, $1250\text{--}1242\text{ cm}^{-1}$ corresponding to $\nu(\text{P}=\text{O})$, 1186 cm^{-1} representing $\rho(\text{CH}_3\text{O})$, and 1052 cm^{-1} relating to $\nu_s(\text{C}-\text{O})$.^{76–78,264}

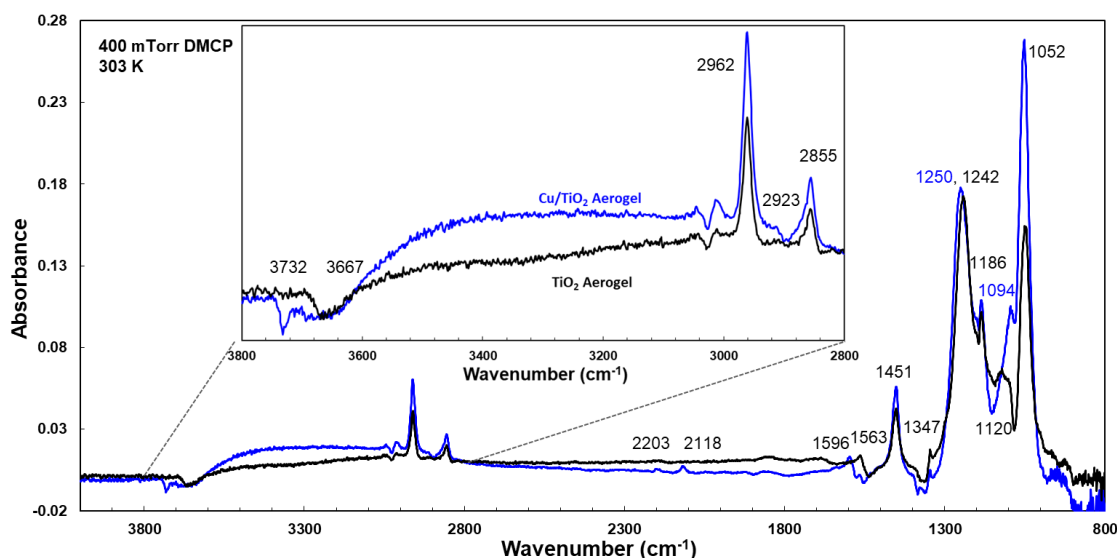


Figure 7.3 Infrared spectra of DMCP adsorbed to a Cu/TiO_2 aerogel (blue) and a TiO_2 aerogel (black). Spectra were taken with samples held at 303 K under vacuum after a 15-minute exposure to 400 mTorr of DMCP.

Some of the spectral features from Figure 7.3 are indicative of reactive adsorption. Dissociation to CO is observed upon DMCP adsorption to two different Cu sites; CO on Cu^{1+} is detected at 2118 cm^{-1} and CO on Cu^{2+} is detected at 2203 cm^{-1} (see Chapter 4.3.2).¹⁷⁰ The CO on Cu^{2+} is blue-shifted 8 cm^{-1} compared to the clean, oxidatively pretreated CuTiO_2 sample described in Chapter 4.3.2 where the surface sites were

identified. This significant shift is indicative of a change in the electronic structure, likely from the adsorption of DMCP, that may allow the CO to remain stable on Cu^{2+} sites at 303 K (with pure CO adsorption, CO on Cu^{2+} is removed under vacuum at 193 K). Features at 1347 cm^{-1} on both samples, 1563 cm^{-1} on TiO_2 , and 1596 cm^{-1} on Cu/TiO_2 are most likely the $\nu_a(\text{O-C-O})$ and $\nu_s(\text{O-C-O})$ vibrational modes of surface formates.

The remaining IR features that appear in the spectra are not consistent with molecularly adsorbed DMCP and can indicate reactive or dissociative adsorption. The 1120 cm^{-1} and 1094 cm^{-1} features are of particular ambiguity, and differ between the two samples: the 1094 cm^{-1} feature is exclusive to the Cu/TiO_2 aerogel while the 1120 cm^{-1} feature is present on both the Cu and metal-free TiO_2 aerogel. Some researchers suggest similar features are representative of dissociated methoxys on Cu^{1+} .²⁷⁰ The results from Chapters 5 and 6 however aren't fully in agreement with this assignment. Methoxy groups were shown to not have favorable binding to Cu sites in comparison with other alcohols and adsorbates, and the band locations were not consistent ($1050\text{-}1060\text{ cm}^{-1}$ for a $\nu_m(\text{C-O})$ vs the observed 1094 cm^{-1}). Others have observed similar features representative of surface-bound $\nu(\text{O-P-O})$.⁸³ The frequency of the $\nu(\text{O-P-O})$ feature has been shown to vary significantly by several researchers, and depends on the degradation of the organophosphorus molecule with different frequencies observed for IMPA and MPA (Figure 7.1).^{83,277-279} A similar interpretation of the phenomenon would suggest that the $\nu(\text{O-P-O})$ features would be sensitive to the surface sites to which it is bound. As shown in Chapter 3, the electronic structure of the TiO_2 aerogel is significantly altered by the presence of CuNPs. The 1120 cm^{-1} and 1094 cm^{-1} features are consistent with $\nu(\text{O-P-O})$ assignments in the literature^{83,277-279} and are hypothesized to bind as follows: the 1120 cm^{-1}

¹ feature on TiO₂ is a Ti-O-P-O-Ti moiety while the 1094 cm⁻¹ on Cu/TiO₂ is either a similar Ti-O-P-O-Ti shifted due to the electronic structure changes or involving Cu in a Cu-O-P-O-Ti or Cu-O-P-O-Cu moiety. A study that selectively adsorbed CO onto Cu sites (via low-temperature adsorption and evacuation) aided in the evaluation of DMCP binding onto Cu sites is shown in Figure 7.4. The spectra in Figure 7.4 show that CO molecules on Cu sites are displaced by the adsorption of DMCP, indicating some degree of binding onto Cu. Note that the shift in CO-Cu¹⁺ wavenumber is likely due to bound PO_x species that are not completely removed from thermal treatment of the material between experiments. This study suggests that the Cu-O-P-O-Ti binding mode is a possibility and one that could contribute toward the 1094 cm⁻¹ infrared feature on Cu/TiO₂. Differences also appear in the 1242-1250 cm⁻¹ region of Figure 7.3, as the ν(P=O) band is shifted between the two materials. Gas-phase DMCP has a ν(P=O) at 1309 cm⁻¹.^{277,280} Adsorption of DMCP onto surfaces can shift the ν(P=O) vibrational mode as it interacts with Lewis acid sites to lower frequencies. The decreased red-shifting of the ν(P=O) on CuTiO₂ compared to TiO₂ (Δν = 59 cm⁻¹ and 67 cm⁻¹, respectively) aligns with the studies in Chapter 3 indicating a weakening of the Lewis acidity of Ti⁴⁺ centers in the presence of CuNPs.

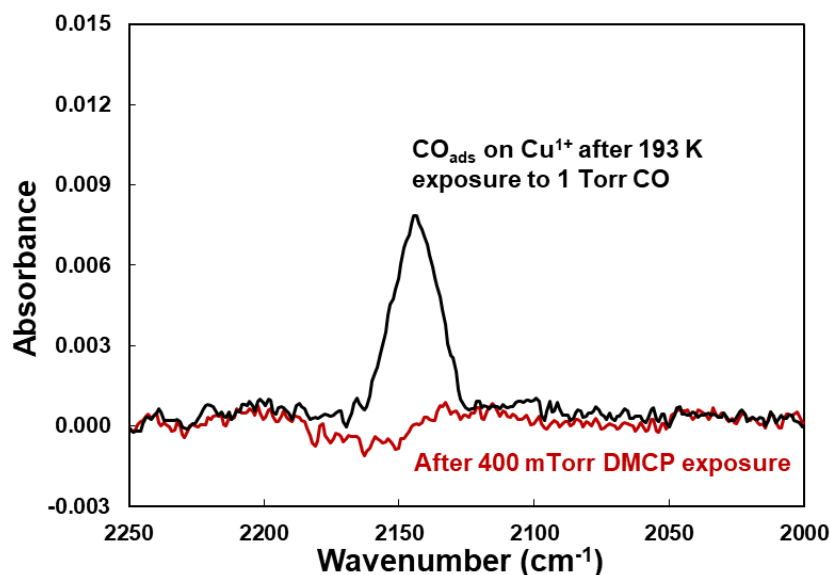


Figure 7.4 CO on Cu/TiO₂ (black trace) after 1 Torr exposure at 193K prior to DMCP introduction (400 mTorr, red trace). Both spectra acquisition and DMCP exposure occurred at 303 K.

7.3.3 DMCP Temperature Programmed Reaction on Cu/TiO₂

DMCP decomposition with O₂(g) on the surface of Cu/TiO₂ aerogels was also probed by IR spectroscopy. After DMCP was adsorbed onto the surface, as in Figure 7.3, the sample was introduced to gaseous O₂ while the sample surface and gases present in the closed cell were simultaneously tracked with increasing reaction temperature. Figure 7.5 shows the Cu/TiO₂ aerogel and TiO₂ aerogel surface species between 303 K and 623 K. All spectra are difference spectra related to the DMCP-saturated surface at 303 K prior to the addition of gaseous O₂. The low-frequency region of the IR spectra (Figure 7.5a) indicates that a reaction occurred on the Cu/TiO₂ surface.

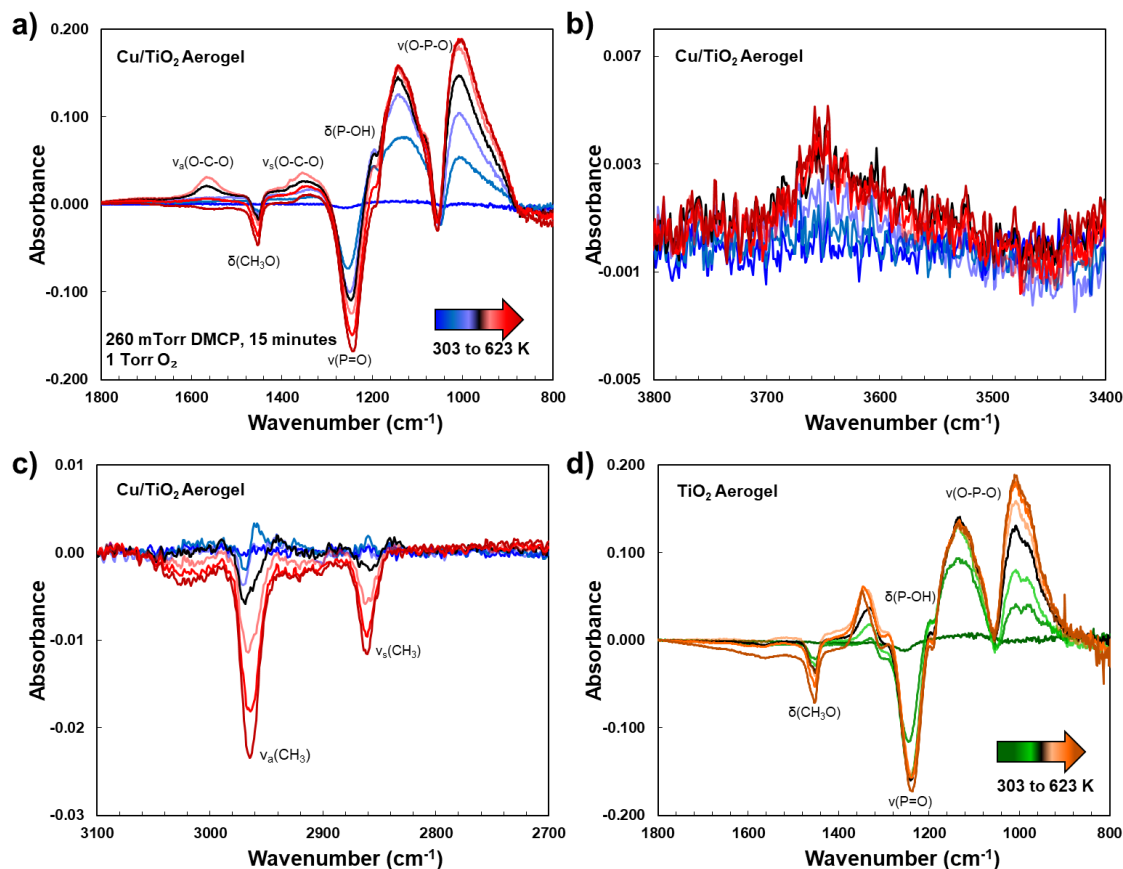
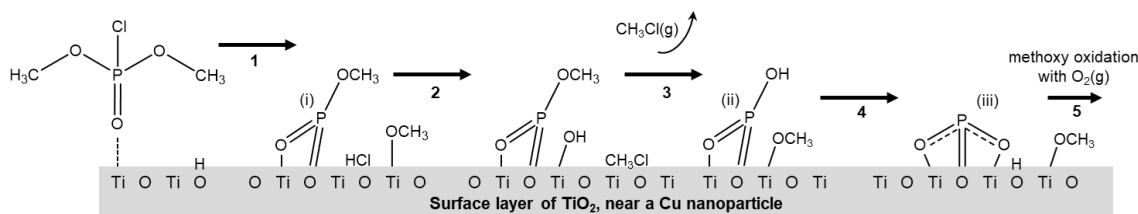


Figure 7.5 IR temperature-programmed reaction of adsorbed DMCP on oxidatively pretreated Cu/TiO₂ and TiO₂ aerogels. 260 mTorr of DMCP was exposed to the samples for 15 minutes before removal and the addition of 1 Torr O₂ that remained for the duration of the reaction. All spectra are baseline subtracted. Surface Cu/TiO₂ scans are shown for the lower frequency region (a), the OH stretching region (b), and the C-H stretching region (c) while the lower frequency region of the pure TiO₂ aerogel is shown in (d), all between 303 and 623 K.

The surface reaction of DMCP on Cu/TiO₂ is shown by significant changes in the low-frequency region, shown in Figure 7.5a. The proposed DMCP decomposition pathway based on the surface studies is shown in Scheme 7.2. Depletion of $\nu(\text{P}=\text{O})$ and the $\delta(\text{CH}_3\text{O})$

features at 1250 cm^{-1} and 1451 cm^{-1} , respectively, are observed while new IR features appear at 1003 cm^{-1} and 1136 cm^{-1} . The 1003 cm^{-1} and 1136 cm^{-1} features can be identified as surface-bound PO_x species, or O-P-O features, consistent with previous works (species i through iii in Scheme 7.2).^{76,83} Surface-bound intermediates are observed in the form of formates, with broad $\nu_a(\text{O-C-O})$ and $\nu_s(\text{O-C-O})$ features at 1570 cm^{-1} and 1375 cm^{-1} , respectively, increasing in intensity until 523 K. Above 523 K, these formate intermediates are shown to decrease in intensity until almost depleted. It is hypothesized that adsorbed DMCP underwent P-O bond cleavage to form surface-bound methoxy groups that proceed to react similarly to methanol (see Chapter 5 and Scheme 7.2). The 1375 cm^{-1} feature does appear to have a neighboring peak at about 1350 cm^{-1} that can be attributed to adsorbed CH_3Cl .²⁸¹ Wong et al. observed vibrational features associated with CH_3Cl at 2958 cm^{-1} , 1439 cm^{-1} , and 1351 cm^{-1} relating to $\nu(\text{C-H})$ and $\delta(\text{C-H})$ modes, respectively.²⁸¹ The CH_3Cl assignments all appear in the DMCP reaction spectra presented in Figures 7.5a and 7.5c, with some overlap in the 2958 cm^{-1} and 1439 cm^{-1} features. An additional intermediate is observed at about 1200 cm^{-1} that forms more rapidly than the formates and reaches its maximum at 423 K before being depleted. Other studies have suggested the feature at about 1200 cm^{-1} relates to either a $\delta(\text{P-OH})$ mode on degradation products like phosphonic acid or a P=O stretch bound to surface OH groups.^{83,277,278} The presence of OH stretches that appear throughout the reaction at 3652 cm^{-1} , see Figure 7.5b, does not follow the response to O_2 /temperature of the 1200 cm^{-1} feature (initial formation followed by decreasing signal) could suggest that the feature is not a $\nu(\text{P=O})$ mode bound to surface hydroxyls. The response to O_2 /increasing temperature of the two hydroxyl-related peaks should coincide with one another if they were to be directly related as surface-bound hydroxyls. Therefore,

the 1200 cm^{-1} intermediate feature is tentatively assigned to $\delta(\text{P-OH})$ modes that further degrade through dehydroxylation to form more of the surface PO_x species represented by the 1003 cm^{-1} and 1136 cm^{-1} features (Scheme 7.2, species iii).



Scheme 7.2 Proposed decomposition pathway of DMCP on the oxide regions of Cu/TiO₂ aerogels. The reaction after methoxy formation proceeds similarly to that of methanol oxidation (Chapter 5) following the dissociative adsorption of methanol. Surface-bound OP degradation was modeled after work by Panayotov et al.⁷⁸ and Florent et al.²⁷⁴

The C-H stretching region of the Cu/TiO₂ catalyst reaction with DMCP is shown in Figure 7.5c. This region shows clear depletion of both $\nu_a(\text{CH}_3)$ and $\nu_s(\text{CH}_3)$ vibrational modes throughout the reaction, and a depletion of the broad 3016 cm^{-1} shoulder. The only other changes are observed as a slight red-shift in the 2962 cm^{-1} $\nu_a(\text{CH}_3)$ feature between 373 and 473 K and similar behavior to a lessened degree with the analogous $\nu_s(\text{CH}_3)$ feature. The slight red-shift could indicate dissociation from a P-OCH_3 to a surface-bound Ti-OCH_3 group, as the frequency shifts closer to that of a bound methoxy group. Otherwise, the alteration of the feature could be attributed to surface CH_3Cl as described previously as the feature shifts to 2958 cm^{-1} which coincides with the chlorinated product. Importantly, the C-H stretch relating to the formate intermediate species does not appear at all when the feature should form at 2877 cm^{-1} (see Chapter 5.3.2). The spectra in the C-H region indicate

that no other carbonaceous species are formed, and the loss of methoxy groups is the only observable change.

Figure 7.6 shows gas-phase spectra during the DMCP oxidation on Cu/TiO₂. In the gas phase, only CO₂ (2350 cm⁻¹) is detected by IR spectroscopy at 623 K. The temperature of gaseous CO₂ formation coincides with the depletion of formates on Cu/TiO₂, suggesting that the reaction after P-OCH₃ cleavage follows a similar pathway to methanol oxidation as described in Chapter 5, but with a higher population of surface OH groups that require high temperatures to remove and free an active site on TiO₂ regions of the catalyst. CH₃Cl is not observed in the gas phase, where features would appear at 2951-2966 cm⁻¹, 1437-1454 cm⁻¹, and 1335-1354 cm⁻¹.²⁸¹ As CH₃Cl is observed as a product in the flow cell studies previously described (Figure 7.2), it is hypothesized that the molar absorptivity of CH₃Cl is sufficiently small to avoid spectroscopic detection at the concentrations in which it was produced. The fact that no gaseous H₂O is formed alongside the increase of surface hydroxyls may suggest increased stability of Ti-OH groups in the presence of DMCP and its decomposition products. The surface hydroxyls also play a role in the decomposition of DMCP to form the CH₃Cl product (Scheme 7.2).²⁷⁴

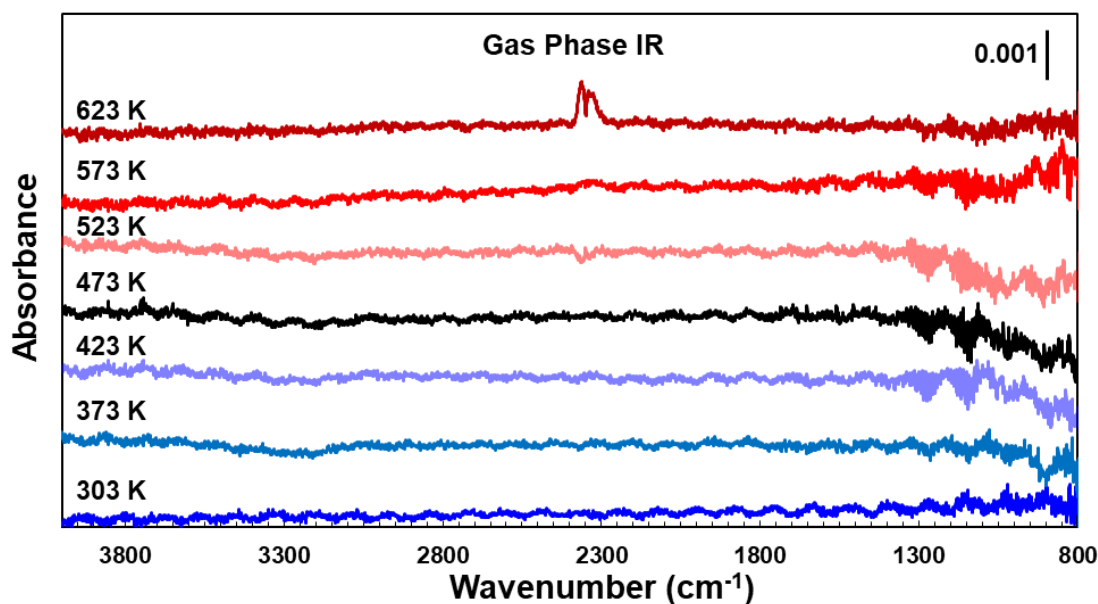


Figure 7.6 Gas-phase IR spectra of any reaction products or desorbed species during the temperature-programmed reaction shown in Figure 7.5 between 303 K and 623 K. All are difference spectra relative to the corresponding temperature of the blank W mesh under vacuum ($< 1 \times 10^{-6}$ Torr) and offset for clarity.

The same DMCP interactions with the Cu-free TiO_2 aerogel show that the metal oxide can react in a similar pathway (Figure 7.5d). Depletion of 1242 cm^{-1} $\nu(\text{P}=\text{O})$ and 1451 cm^{-1} $\delta(\text{CH}_3\text{O})$ in favor of broad PO_x or O-P-O stretches at 1003 cm^{-1} and 1136 cm^{-1} . Similar depletion of $\nu_a(\text{CH}_3)$ and $\nu_s(\text{CH}_3)$ in the C-H region and formation of surface OH groups at 3655 cm^{-1} are also observed (not shown). The main difference in the chemistry on the pure TiO_2 aerogel is the lack of intermediate formation. The characteristic broad $\nu_a(\text{O}-\text{C}-\text{O})$ and $\nu_s(\text{O}-\text{C}-\text{O})$ features of surface formates at 1570 and 1350 cm^{-1} do not form on the TiO_2 aerogel throughout the reaction with DMCP. There is a significant growth of an IR band at 1325 cm^{-1} that blue-shifts during its growth with increasing temperature to

1347 cm^{-1} . This 1347 cm^{-1} is significantly narrower in shape (with a lower FWHM) than the 1350-1370 cm^{-1} feature on Cu/TiO₂ and does not have an accompanying broad $\nu_a(\text{O-C-O})$ signal at 1570 cm^{-1} , which suggests that it could be CH₃Cl instead of formates. The differences on the pure aerogel are also seen in the character of the 1200 cm^{-1} intermediate attributed to degradative $\delta(\text{P-OH})$ modes. On the TiO₂ aerogel, there is a significantly diminished production of the $\delta(\text{P-OH})$ modes for similar PO_x species formed at lower frequencies compared to the Cu/TiO₂ aerogel. The minimal production of $\delta(\text{P-OH})$ and lack of formate intermediate production on the Cu-free TiO₂ aerogel showcases the promotional effects that Cu has on the decomposition of DMCP.

7.3.4 Effects of Surface O_{br} on the Decomposition of DMCP

To analyze the impact of bridging oxygen atoms on TiO₂, similar oxidation of DMCP on Cu/TiO₂ aerogels was performed after a reductive pretreatment. IR spectra recorded throughout the reaction are shown in Figure 7.7. Data from the pure TiO₂ aerogel interacting with DMCP is omitted because no differences are observed in comparison to the reaction following oxidative pretreatment. The data from Figures 7.7a-c all show very similar behavior to the oxidatively pretreated Cu/TiO₂ catalyst from Figure 7.5. In short, depletion of the features at 1250 cm^{-1} ($\nu(\text{P=O})$) and 1451 cm^{-1} ($\delta(\text{CH}_3\text{O})$) is observed while new IR features appear at 1003 cm^{-1} and 1136 cm^{-1} ($\nu(\text{O-P-O})$ or PO_x). Intermediate formate species are formed and then consumed during the reaction with features at 1570 cm^{-1} and 1370 cm^{-1} , similar to the methanol oxidation mechanism in Chapter 5. Small amounts of new O-H stretches are detected (Figure 7.7b), while C-H stretches from adsorbed DMCP are depleted (Figure 7.7c). Small shifts are observed in the C-H stretching

region between 2800 cm^{-1} and 3000 cm^{-1} which could indicate CH_3Cl formation. The only spectral differences on the Cu/TiO_2 surface appear in the depletion of the 1200 cm^{-1} feature. With the oxidatively pretreated Cu/TiO_2 , the degradative $\delta(\text{P-OH})$ feature at 1200 cm^{-1} related to DMCP decomposition to MPA or PA was completely depleted after forming during the reaction. After the reducing pretreatment, some of the $\delta(\text{P-OH})$ modes remain. The baseline also appears to decrease at higher temperatures. The $1300\text{-}1800\text{ cm}^{-1}$ range decreasing in overall absorbance possibly suggests the oxidation of TiO_2 .^{196,209–214} The re-oxidation of TiO_2 regions of the catalyst coincides with the evolution of $\text{CO}_2(\text{g})$ allowing the subsequent O_V site to be re-oxidized by $\text{O}_2(\text{g})$.

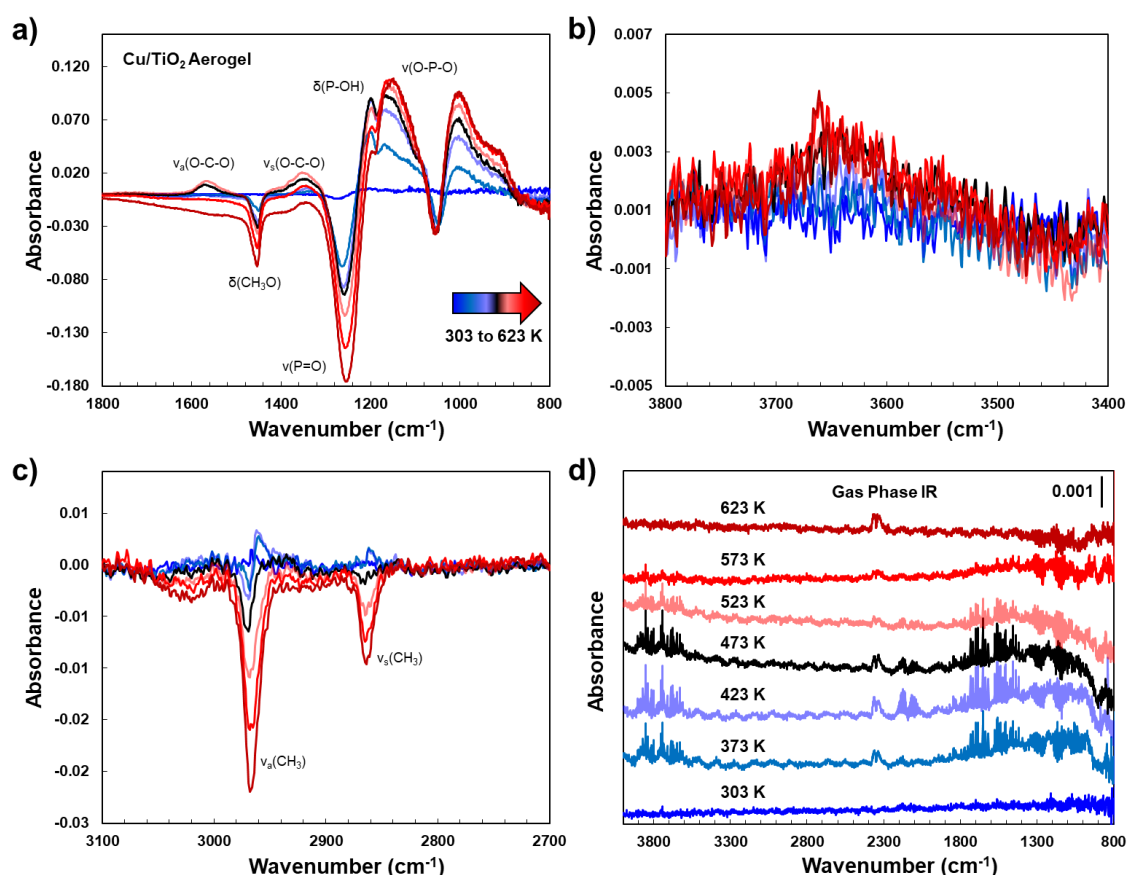


Figure 7.7 IR temperature-programmed reaction of adsorbed DMCP on Cu/TiO_2 and TiO_2 aerogels after a reducing pretreatment between 303 K and 623 K. 260 mTorr of DMCP

was exposed to the samples for 15 minutes before removal and the addition of 1 Torr O₂. Surface Cu/TiO₂ scans for the lower frequency region (a), the OH stretching region (b), and the C-H stretching region (c) are all displayed as baseline subtracted difference spectra relative to the DMCP-saturated surface before O₂ introduction. Gas-phase spectra of any reaction products or desorbed species during the reaction (d) are difference spectra relative to the corresponding temperature under vacuum ($< 1 \times 10^{-6}$ Torr) and offset for clarity.

More significant changes in the DMCP reaction dynamics on a reduced Cu/TiO₂ aerogel sample are in the gas-phase spectra (Figure 7.7d). It is important to note that CO₂ and H₂O observed should largely not be considered relevant in this experiment, due to fluctuations in the purge gas generator that didn't remove CO₂ and H₂O from the air used to purge the spectrometer and optics enclosures. These fluctuations are observed between 373 K and 523 K in this study, as CO₂ and H₂O appear in the spectra only to disappear at 573 K. At 623 K, CO₂ appears without H₂O and can likely be attributed to true product formation. Outside of the CO₂ and H₂O, gaseous CO at 2143 cm⁻¹ is formed between 423 and 473 K. CO production that does not consistently coincide with the H₂O and CO₂ fluctuations attributed to the purge gas generator is considered unique. Indeed, CO production was observed from DMCP adsorption (Figure 7.3) and during reaction with Cu/TiO₂ aerogels has been reported previously.⁸³ CO production unique to a reducing pretreatment shows that bridging O atoms in the support have an impact on the reactivity of DMCP on Cu/TiO₂ aerogels. After formation, the CO(g) is reacted to form CO₂ as described in Chapter 4.⁵⁰

The buildup of PO_x species on the surface that are not thermally removed at temperatures up to 623 K poses a problem for sustained catalysis. As observed in Figure 7.2, the decomposition of DMCP over Cu/TiO_2 aerogels is deactivated over time. The link between nonvolatile PO_x surface species and catalyst poisoning has been made before by other researchers.^{76–78,234,265,266,277} While Cu/TiO_2 aerogels do show promising oxidation activity for the destruction of the CWA, a material that is more resistant towards PO_x poisoning will be needed for the next generation of CWA decomposition catalysts. Previous investigations of DMMP on TiO_2 indicated that thermal activation at very similar conditions (675 K, 20 Torr O_2 , 1 hour) was not able to restore the reactive adsorption pathway observed on a clean surface.⁷⁶ The working hypothesis behind the difference in reactivation ability between Cu/TiO_2 and TiO_2 is the enhanced ability for Cu/TiO_2 to lose bridging O atoms in the TiO_2 lattice, where the PO_x species are known to adsorb.^{76,77} A TiO_2 -based material with lower oxygen vacancy formation energies should then be able to have enhanced resistance to PO_x poisoning.

DMCP oxidation has been shown to proceed on Cu/TiO_2 aerogels to form CO , CO_2 , CH_3Cl , and surface-bound PO_x and formates. The decomposition to CH_3Cl proceeds beyond the formation of CO_2 before catalyst poisoning is a novel discovery not reported in publications about the chemical destruction of DMCP. While the data presented shows clear evidence that the methyl chloride product formation occurred over Cu/TiO_2 and shows promise towards fine-tuning the selectivity in the next generation of aerogel materials, CH_3Cl is also a naturally forming decomposition product of DMCP when stored at near-ambient temperatures. QMS data was collected for DMCP flowing through a blank quartz reference cell to monitor the fragmentation pattern of the CWA simulant

(Appendix). It was found that before the main spectral signatures of DMCP appeared in the mass spectrum (at m/z of 47, 79, 93, and 109), CH_3Cl is detected immediately upon the addition of DMCP to the gas stream. While the methyl chloride signal does decay as the DMCP fragmentation signals increase to reach a steady-state concentration, the initial detection, along with fragmented Cl^- ions at 35 m/z indicates that the DMCP molecule is degrading in storage to form CH_3Cl . Ambient decomposition of a molecule over time limits its usefulness as a CWA simulant, as ambient decomposition vs chemical decomposition from a catalyst can be nontrivial to discern. While the CWA simulant does decay in storage, the results presented still suggest catalytic decomposition to CH_3Cl due to the experimental design and allowing the simulant to equilibrate before its introduction to the catalyst.

7.4 Conclusions

DMCP has been shown to dissociatively adsorb onto Cu/TiO_2 aerogels and react with $\text{O}_2(\text{g})$. *In situ* measurements from the packed-bed flow reactor show conversion of DMCP to form gaseous CO_2 and CH_3Cl . Additional *in situ* spectroscopic measurements identified a reaction pathway that involves the breakdown of adsorbed DMCP through the cleavage of $\text{P}-\text{OCH}_3$ and $\text{P}-\text{Cl}$ bonds to form surface-bound formates, PO_x species, CH_3Cl , and $\text{Ti}-\text{OH}$ groups. Surface-bound formates are hypothesized to follow the previously described methanol oxidation mechanism toward CO_2 production. Gaseous CO is also detected as an alternate reaction product exclusively following a reducing pretreatment of the Cu/TiO_2 aerogel and contributes toward the formation of CO_2 high temperatures. The catalyst is deactivated, however, through surface-bound oxidized phosphorus species that are not removed from the surface at temperatures up to 623 K. The multi-step

decomposition to CH_3Cl on DMCP would relate to CH_3F on the CWA analog sarin, which is dramatically less toxic than HF.

Chapter 8

Conclusions and Future Work

8.1 Conclusions

The primary goal of this work was to develop a fundamental understanding of the reaction mechanisms that occur between small gas/vapor molecules and the surface of a Cu/TiO₂ aerogel catalyst. The creation of successful next-generation catalytic materials is based around such fundamental understandings that are leveraged to improve material performance in various industrial and environmental processes/applications. *In situ* vibrational spectroscopy and mass spectrometry methods were employed to elucidate the dynamics of important reactions such as CO oxidation, methanol/alcohol oxidation, and decomposition of chemical warfare agent simulants.

Charge transfer was probed to understand the electronic interactions between metal nanoparticles and their oxide support. Utilizing the variable-temperature infrared spectroscopy method, differences between evaluated adsorption enthalpies of a TiO₂ material and NP/TiO₂ (where NP = Au, Cu, or Pt nanoparticles) are related to differences in the work functions of the NPs and TiO₂. Differences in work function between the metal nanoparticles and the TiO₂ support result in an interfacial charge transfer upon metal deposition that alters the electronic structure of the support oxide. Alteration of the electronic structure of TiO₂ was hypothesized to play a major role in catalysis, specifically the reported “Au-assisted Mars-van Krevelen” mechanism for CO oxidation on a Au/TiO₂ material. Cu/TiO₂ aerogel materials were identified as a candidate for further catalytic investigations of oxidation reactions.

The surface sites of the Cu/TiO₂ aerogel were then characterized with CO as an infrared probe molecule, identifying multiple stable oxidation states of Cu within the material, especially the seldom stabilized Cu⁰. Oxidation of CO was investigated and proposed to occur through a Cu-assisted Mars-van Krevelen type mechanism, as reaction in the absence of gaseous O₂ occurs. Spectroscopic identification of Ti³⁺ sites after anaerobic reaction aided in the identification of surface oxygen atoms of the TiO₂ support as the active site for CO oxidation, activated for extraction by the presence of and proximity to Cu nanoparticles.

The oxidation of alcohols on Cu/TiO₂ exemplified similar activity and highlighted the promotional effects that Cu NPs have on the TiO₂ support. Methanol oxidation was spectroscopically determined to react and form a surface-bound formate intermediate, that reacts further to produce gaseous CO₂ and H₂O at elevated temperatures. Lattice oxygen extraction of TiO₂ regions of the catalyst accompanies the complete selective oxidation to CO₂ and H₂O, as observed both by the broad baseline absorbance rise in the IR spectrum and by anaerobic exposure of Cu/TiO₂ to methanol at reactive temperatures. 2-propanol oxidation was then studied to understand decomposition with larger molecules, and found that once C-C bond cleavage occurs, the oxidation of the resulting surface methoxy groups proceeds similarly to that of methanol. Further investigations into anaerobic reactions with alcohols indicated that a partial oxidation pathway is available for alcohols larger than methanol, forming an aldehyde/ketone product for each alcohol. Focused adsorption studies revealed that the enhanced binding of larger alcohols, relative to methanol, onto Cu sites could be the origin of the anaerobic partial oxidation pathway on Cu/TiO₂ aerogels.

Decomposition of an organophosphorus-based chemical warfare agent simulant on the Cu/TiO₂ aerogel was investigated with similar methods. *In situ* spectroscopic measurements identified a reaction pathway that involves the breakdown of adsorbed DMCP through the cleavage of P-OCH₃ and P-Cl bonds to form surface-bound formates, PO_x species, CH₃Cl, and Ti-OH groups. Gaseous CO₂ and CH₃Cl are also detected as reaction products and are notably less toxic than the full DMCP molecule. Gaseous carbon monoxide is also detected through an alternate reactive pathway exclusively following a reducing pretreatment of the Cu/TiO₂ aerogel, and contributes toward the formation of CO₂ at high temperatures. Deactivation is observed, however, through strongly bound oxidized phosphorus species.

8.2 Future Work

The presented work in this thesis highlights the importance of understanding the promotional effects of metal nanoparticles supported on an oxide surface. While the results describe a novel discovery and method of probing interfacial charge transfer between the NP and the oxide, there is still a lot more that needs to be understood about how the charge transfer is affected. Specifically, more systematic studies of altering the particle size, weight loading, and oxidation state of a metal nanoparticle and measuring the corresponding change to CO adsorption enthalpy can yield further insights into the relevant synthetic parameters towards optimizing catalyst materials. To assist in the systematic measurements, evaluation of the corresponding apparent activation energies towards relevant catalytic reactions like CO oxidation (specific to Mars-van Krevelen extraction mechanisms of consistent sites) would expand the holistic understanding of how the charge

transfer is impacting the reactivity of lattice oxygen bonds on the oxide support. Computational support would be a major addition to the description of interfacial charge transfer, not only in the change to Ti-CO adsorption enthalpy but also in the investigation of Ti-O bond strength near metal nanoparticles in relation to particle size, metal identity, and work function. Finally, expanded surface-based studies of low Ti-O bond energy materials for CWA decomposition may provide insights toward solving the problem of strong binding of organophosphorus-based compounds to the metal/metal oxide systems.

Appendix A

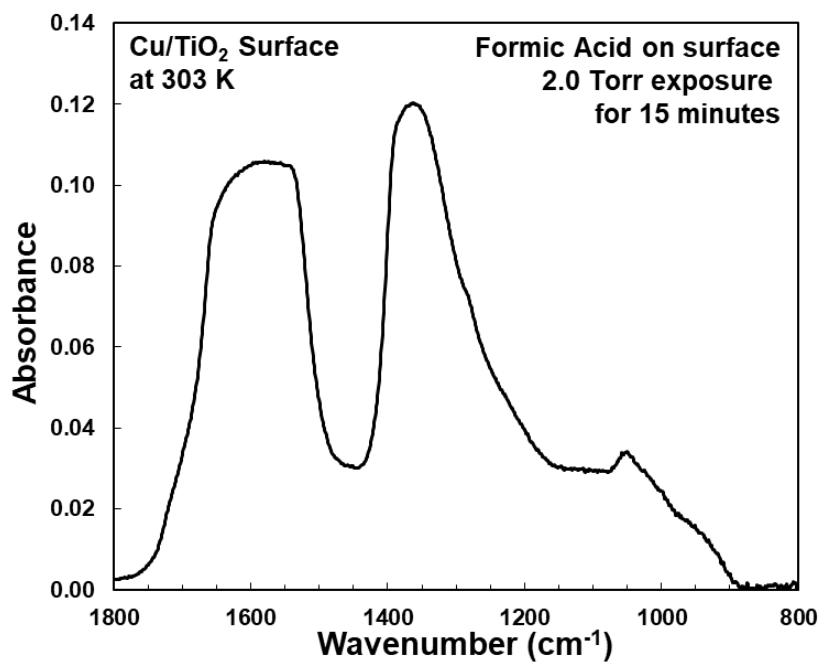


Figure I. Infrared spectrum of the low-frequency region of formic acid adsorbed onto a Cu/TiO₂ aerogel at 303 K. The sample was exposed to 2.0 Torr of formic acid vapor for 15 minutes before evacuation from the chamber, where the spectrum was taken at 1×10^{-6} Torr.

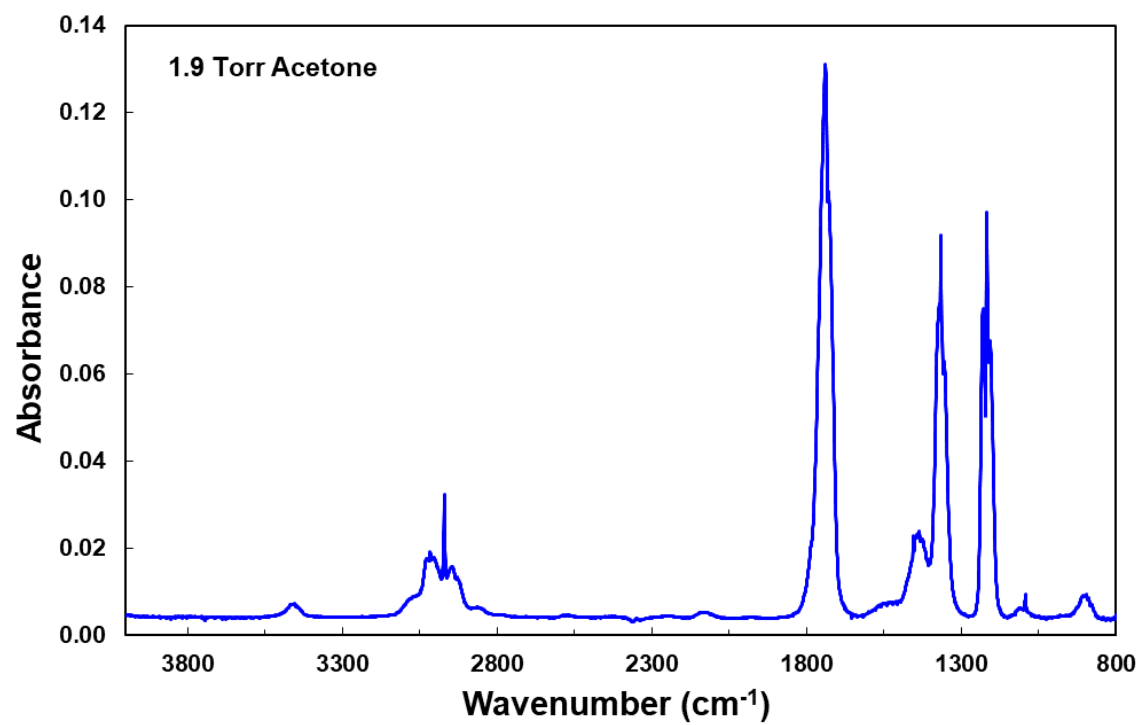


Figure II. Infrared spectrum of gaseous acetone at 303 K.

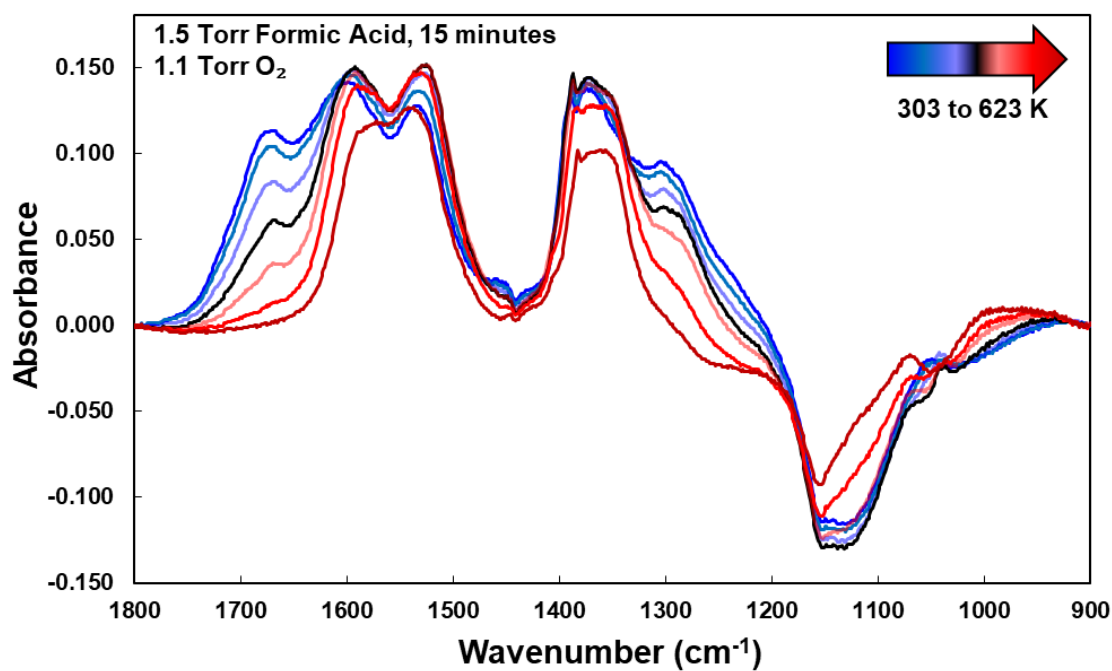


Figure III. IR temperature-programmed oxidation of adsorbed formic acid on a metal-free TiO₂ aerogel sample. The TiO₂ aerogel sample was exposed to 1.5 Torr of formic acid for 15 minutes before removal via vacuum and followed by exposure to 1.1 Torr O₂. Spectra were recorded with increasing temperature from 303 to 623 K. All spectra are baseline subtracted. Surface TiO₂ scans are shown for the lower frequency range.

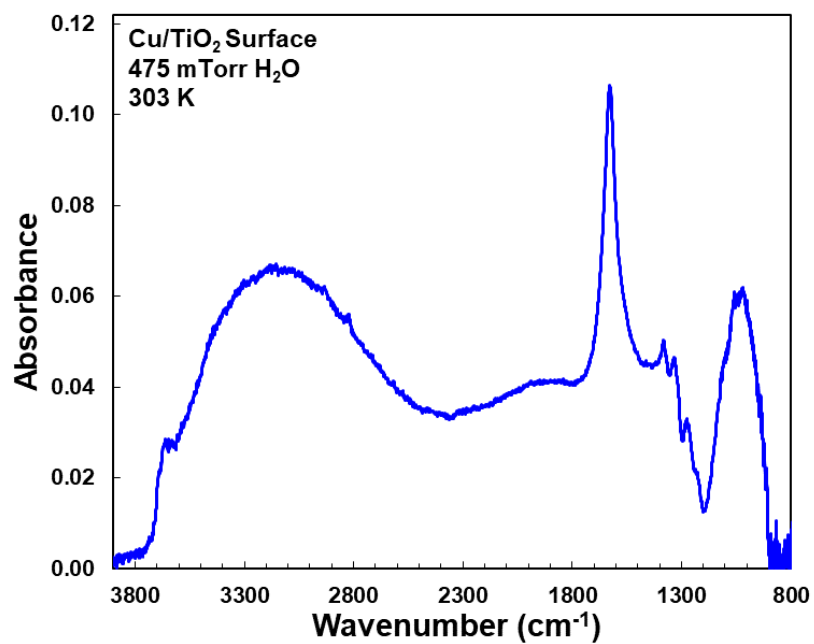


Figure IV. Infrared spectrum of H₂O adsorbed onto a Cu/TiO₂ aerogel at 303 K. The sample was exposed to 475 mTorr of H₂O vapor for 15 minutes before evacuation from the chamber, where the spectrum was taken at 1×10^{-6} Torr.

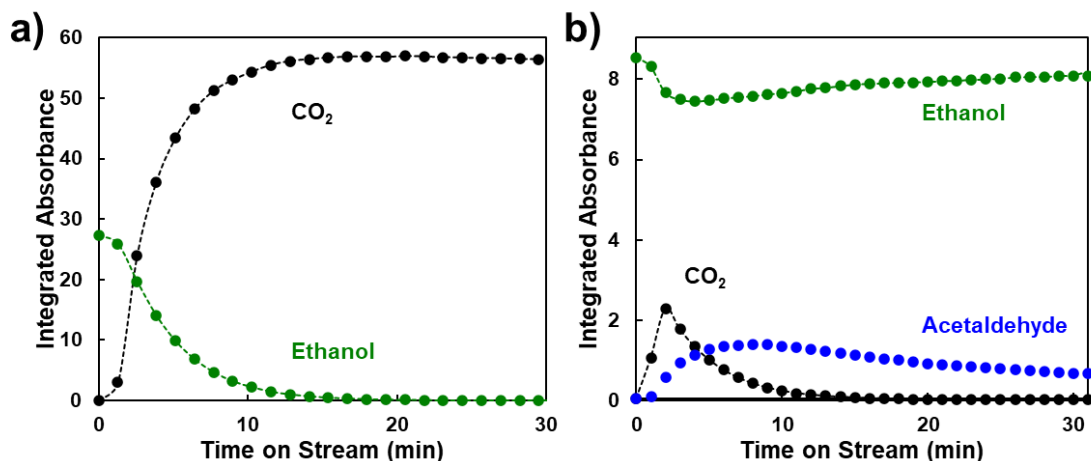


Figure V. Integrated IR data ethanol oxidation on Cu/TiO₂ aerogels in the packed-bed reactor at 623 K. Aerobic oxidation (a) was performed with a reactant mixture of 0.5% ethanol, 40% O₂, and 59.5% Ar. Anaerobic oxidation (b) was performed with a reactant mixture of 0.5% ethanol and 99.5% Ar. CO₂ signal was integrated between 2280 and 2410 cm⁻¹, ethanol signal was integrated between 2600 and 3200 cm⁻¹, and acetaldehyde signal was integrated between 1660 and 1830 cm⁻¹. Each data point is the average of 50 scans

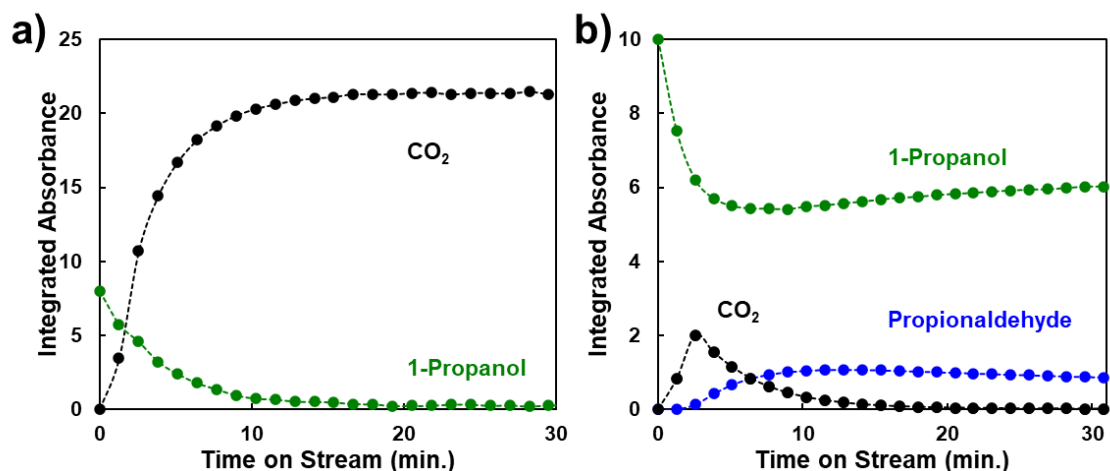


Figure VI. Integrated IR data 1-propanol oxidation on Cu/TiO₂ aerogels in the packed-bed reactor at 623 K. Aerobic oxidation (a) was performed with a reactant mixture of 0.5% 1-propanol, 40% O₂, and 59.5% Ar. Anaerobic oxidation (b) was performed with a reactant mixture of 0.5% 1-propanol and 99.5% Ar. CO₂ signal was integrated between 2280 and 2410 cm⁻¹, 1-propanol signal was integrated between 2600 and 3200 cm⁻¹, and propionaldehyde signal was integrated between 1600 and 1820 cm⁻¹. Each data point is the average of 50 scans

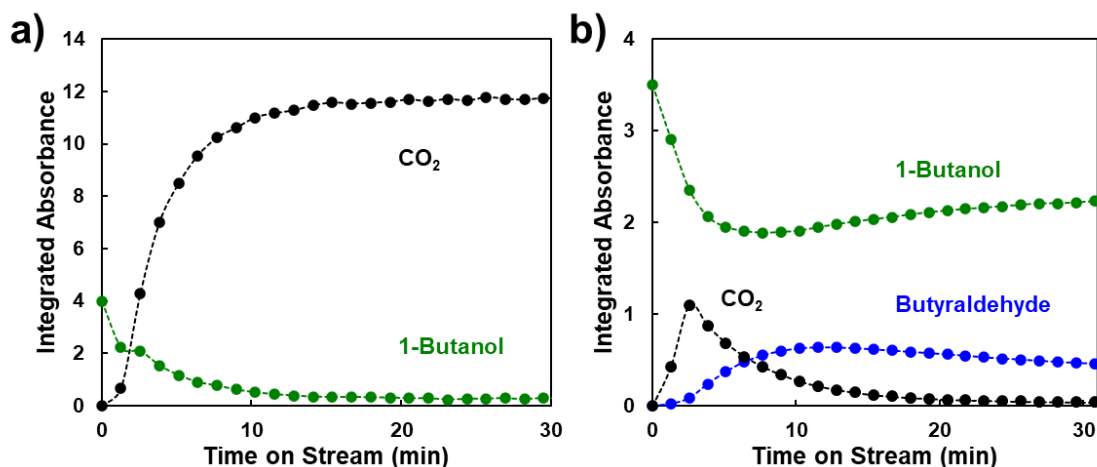


Figure VII. Integrated IR data 1-butanol oxidation on Cu/TiO₂ aerogels in the packed-bed reactor at 623 K. Aerobic oxidation (a) was performed with a reactant mixture of 0.5% 1-butanol, 40% O₂, and 59.5% Ar. Anaerobic oxidation (b) was performed with a reactant mixture of 0.5% 1-butanol and 99.5% Ar. CO₂ signal was integrated between 2280 and 2410 cm⁻¹, 1-butanol signal was integrated between 2750 and 3050 cm⁻¹, and butyraldehyde signal was integrated between 1600 and 1820 cm⁻¹. Each data point is the average of 50 scans

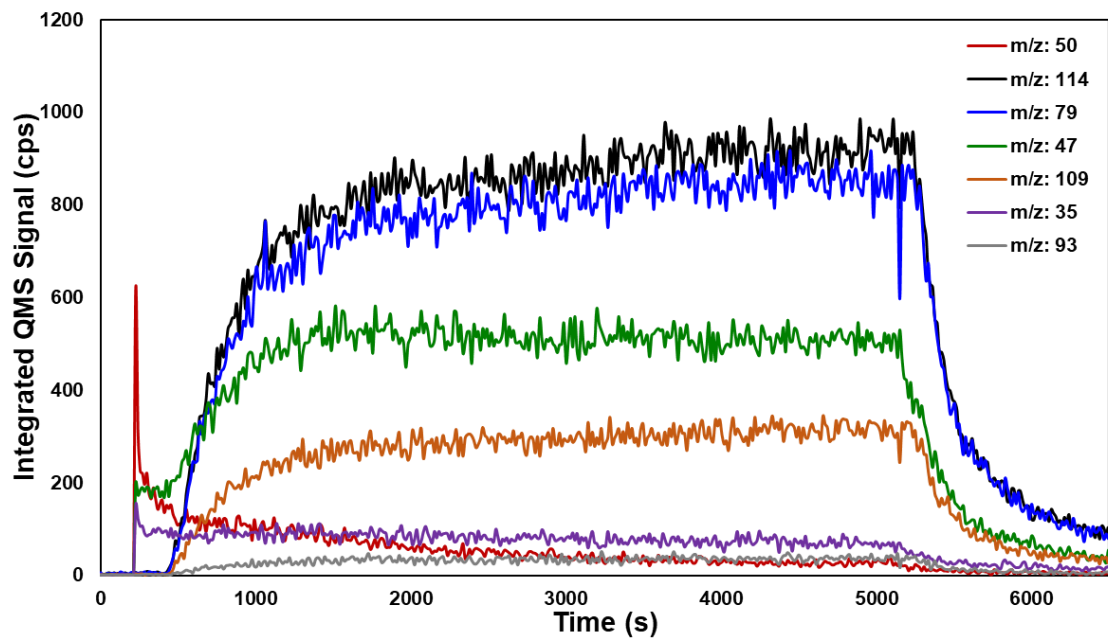


Figure VIII. Integrated quadrupole mass spectrometry signal for key DMCP fragments while flowing through an empty glass reference tube in the flow reactor system. CH_3Cl signal (50 m/z) observed at early times is indicative of decomposition of the DMCP molecule during storage at 288 K in the saturator cell.

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