Doped Titanium Dioxide Aerogels for Various Catalytic and Photocatalytic Applications

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Doped Titanium Dioxide Aerogels for Various Catalytic and Photocatalytic Applications

Steven Murphy, Ph.D.
University of Connecticut, 2018

Abstract

A reasonable, repeatable synthesis for titania sol gels and the production of titania aerogel was developed and optimized via a statistical design of experiments approach. Optimal conditions were determined by gel quality obtained. The TiO₂ aerogel produced was characterized at various calcination temperatures and shown to be active for visible light photocatalysis of a model dye system, methylene blue.

Improvement of the TiO₂ for dye degradation reactions was successfully achieved via the incorporation of a zirconium metal dopant, which showed an increase in overall activity and a reduction in reaction time by 30 minutes over the conventional titania catalyst. Zirconium doped into the material was shown to impact the band gap of the material by shifting the band gap to lower energies, making a more photoactive catalyst, along with the promotion of the development of anatase titania at lower calcination temperatures.

The TiO₂ aerogel was used as a support to disperse Cu and Fe through the material for use in the selective, partial oxidation reaction of cyclohexane to cyclohexanol. Preliminary work showed the Cu-TiO₂ to be the most active, with optimized conditions leading to >99% conversion of cyclohexane, and >99% selectivity for cyclohexanol.
A hybridization of a mesoporous TiO$_2$ synthesis with the aerogel procedure presented here led to a high surface area, high pore volume material with an ordered mesoporous structure. Various metal dopants (Fe, Cu, Mn, Zr) were incorporated into the material, with all resulting catalysts showing activity for both methylene blue degradation and cyclohexane oxidation. All samples maintained their ordered mesoporous structures and high surface area/pore volumes at elevated temperatures. Unoptimized Cu-UCT-TiO$_2$ aerogels showed higher activity than the unoptimized Cu-TiO$_2$ aerogels, opening the door for development of a more efficient catalyst upon optimization.
Doped Titanium Dioxide Aerogels for Various Catalytic and Photocatalytic Applications

Steven Murphy
B.S., Binghamton University, 2012

A Dissertation
Submitted in Partial Fulfillment of the
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at the
University of Connecticut

2018
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Steven C. Murphy
Doctor of Philosophy Dissertation
Doped Titanium Dioxide Aerogels for Various Catalytic and Photocatalytic Applications
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University of Connecticut
2018
Dedicated to Samantha,
Without Whom None of This Would be Possible.
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Chapter 1. Synthesis and Optimization of Titania Aerogels for Heterogeneous Photocatalytic Applications.

1.1 Introduction

Titanium dioxide has long been considered a versatile and active material for a variety of industrial applications.\textsuperscript{1–9} These range from catalytic organic oxidation reactions, to photocatalytic degradations of both gaseous\textsuperscript{1,10–13} and liquid pollutants\textsuperscript{14}, to catalyst supports\textsuperscript{15,16}, to electrochemical applications such as solar cells\textsuperscript{17,18} and batteries\textsuperscript{19,20}. The most prevalent of these and the thrust of this work focuses on heterogeneous catalysis applications.

A catalyst is a material that lowers the activation energy, or energy barrier, required for a reaction or process to proceed. Heterogeneous catalysis is a catalytic system whereby the catalyst and the reactant are not in the same phase, typically in the form of a solid catalyst and either gaseous or liquid reactants.\textsuperscript{21–24} The primary advantage of this type of catalysis over its homogenous counterpart has to do with the ease of separation post-reaction, something that is rather difficult in a homogeneous setting. This, in turn, allows for higher sample throughput and saves the time, money, and energy that would go into separation. A variety of factors affect heterogeneous catalytic processes, chief among them the physical and chemical properties of the catalyst such as structure, surface area, pore size, pore volume, oxidation states, oxidative/reductive capabilities, etc. The general rule of thumb is that higher surface areas lend themselves to more active sites and thus more activity. Pore size is more flexible as pore size is more dependent on what particular catalytic reaction is occurring and the sizes of the molecule involved.\textsuperscript{21} Multiple oxidation states, or the ability to effectively change oxidation states in a material has been shown in the literature, especially in the case of transition metals such as
nicked, copper, iron and manganese, to have beneficial effects on catalytic processes dependent on those pathways.

Photocatalysis has long been a popular method of catalysis in the heterogeneous regime. The main goal of research is to find materials that effectively utilized visible light as its primary light source. This is due to the fact that over 40% of the energy received via the sun is in the visible spectrum while only approximately 5% comes in the form of UV. Numerous materials show activity when exposed to UV but this number drops precipitously when the light source is converted to visible wavelengths. This is partially due to the fact that many of the cheaper, state-of-the-art catalyst in this area are inorganic transition metal oxides, many of which are intrinsic semi-conductors with photo band gaps firmly in the UV range. As such, there is ever a drive towards creating a visibly active material that utilizes the energy provided by the sun more efficiently and effectively.

Titania is well-studied due to the ability to tune its properties to the application that is being used. All varieties of nano (rods, fibers, particles), porous (mesoporous, microporous) and high surface area (aerogels, meso and microporous) can be synthesized in the lab in high yields, and in scalable processes. Structure can be tuned via calcination, with crystallization onset occurring typically at 200 °C with the first appearing of the 101 reflection of anatase titania appearing, with rutile appearing first at approximately 600 °C and brookite, the third and final form at 1000 °C. Titania itself is cheap and therefore considered economically viable, resistant to corrosion from light, and nontoxic.

While titania has many advantages, titania suffers from a significant disadvantage present in most metal oxides: wide bandgap. The band gap (Eg) of titania lies firmly in the UV portion of the electromagnetic spectrum (Anatase = 3.2-3.4 eV, Rutile = 3.0 eV). Because of this Eg, TiO2
can only inefficiently utilize energy from the sun. Numerous methods exist to try to change this $E_g$, such as doping, incorporation of mediators of charge transfers, moieties that absorb visible light, doping with metals or nonmetals to reposition either the valence or conduction bands and lower the absolute $E_g$ value.\textsuperscript{13}

The anatase phase of titanium dioxide has been determined in literature to be the most photocatalytically active phase of titanium dioxide. While the rutile phase has a lower $E_g$, anatase has the higher potential activity primarily due to the way in which charge carriers travel in the material. Deposited films of anatase and rutile compared via photocatalytic degradation of a model organic dye (methyl orange) have shown that anatase is more active at the same film thickness values. Moreover, increases in film thickness for the anatase phase have shown increasing catalytic activity, whereas the rutile film has no significant change. This speaks to how mobile charge carriers are in the anatase material versus their rutile counterparts. Mobilization of charge carriers from the bulk of anatase appear to be responsible for the majority of its catalytic activity.\textsuperscript{4}

It is often the case that activity of a catalyst can be increased directly as a function of the catalyst surface area. Of all classes of materials, aerogels are the ones that have the highest observable surface area, and increasing the surface area of the synthesized titania is one possible solution to increase the activity.\textsuperscript{33} An aerogel is a material typically achieved when a gel produced via a sol-gel procedure is dried via a method that induces no capillary pressure on the pore network as the solvent leaves (\textbf{Figure 1.1}).
Figure 1.1- Depiction of type of dryings effects on the resultant gel.\textsuperscript{34}

The sol-gel method utilized in this work takes advantage of the facile sol-gel preparation of titania from a titanium alkoxide precursor dissolved in an alcohol solvent. The reaction is initiated by water to begin hydrolyzing the titanium alkoxide precursor, yielding a titanium (IV) hydroxide intermediate. This intermediate, in the presence of catalytic amounts of strong acid and water, begins to form an interconnected Ti-O-Ti network that eventually leads to condensation into the gel.

\begin{align*}
\text{Ti(OR)}_4 (\text{l}) + 4 \text{H}_2\text{O} (\text{l}) & \rightarrow \text{Ti(OH)}_4 (\text{l}) + 4 \text{ROH} (\text{l}) \\
\text{Ti(OH)}_4 (\text{s}) + \text{Ti(OH)}_4 (\text{s}) & \rightarrow (\text{HO})_3\text{Ti-O-Ti(OH)}_3 (\text{s}) + \text{H}_2\text{O} (\text{l}) \\
\text{Ti(OH)}_4 (\text{s}) + \text{Ti(OR)}_4 (\text{l}) & \rightarrow (\text{HO})_3\text{Ti-O-Ti(OR)}_3 (\text{s}) + \text{ROH} (\text{l})
\end{align*}

The rate of hydrolysis and subsequent condensation/alchololysis can be modulated via pH and water amounts used in the reaction. Eventually, the vast majority of titanium precursor will be converted into a Ti-O-Ti network that forms the gel network.
This differs from ambigels, which dry under low capillary pressure conditions, and xerogels, which dry from high capillary pressure conditions. High capillary pressure is the most destructive to the solid network, leading to the largest particles and the lowest surface areas. To accomplish this zero-capillary pressure drying, a supercritical fluid is often employed as the solvent; the most common of which is super critical carbon dioxide (SCCD). SCCD was chosen due to its low and easily attainable supercritical point (31 °C, 1100 psi), along with the ease in which numerous solvents can be substituted with liquid CO₂.

The goal of this work is to develop a reliable synthetic method for high surface area, highly crystalline TiO₂ aerogel materials. This is the first step in a process of developing a highly effective, visibly-active catalyst.

1.2 Experimental

1.2.1 Chemicals

Titanium (IV) tetraisopropoxide (TTIP, 97+% purity), nitric acid (70%), 1-butanol (>99.4%) and acetone were obtained from Sigma Aldrich and used as received. Industrial grade carbon dioxide in a tank equipped with a siphon tube was obtained from Airgas and used as received.

1.2.1 Sol Preparation and Optimization

The creation of a titanium dioxide aerogel started with the formation of a titanium dioxide sol-gel. The main variables that were varied in this procedure were the ratio of metal precursor to catalyst to solvent. Titanium precursor in the form of titanium tetraisopropoxide was used in this procedure, with the solvent system being 1-butanol and the catalyst being a mixture.
of water and concentrated nitric acid. Previous research has determined that TTIP, 1-BuOH, and HNO$_3$ are the best precursors, solvent, and catalyst, respectively. In a typical synthesis, two beakers were prepared. Beaker A housed the titanium precursor and 1-BuOH. Beaker B housed 1-BuOH, concentrated nitric acid, and water. Beaker B was added drop-wise into beaker A, which is under magnetic stirring, until all of the solution from beaker B was used up. After allowing the solution to stir for 5-10 minutes, the magnetic stir bar was retrieved and the sample was covered and set aside to allow for aging.

A modified design of experiment approach was employed where values for the mole ratios of 1-BuOH, HNO$_3$ and water were varied with respect to the TTIP amount employed, which was kept constant. The quality of sols created were graded on a variety of factors, including gelation time, and clarity of the gel. From these experiments, a statistical analysis was done to both minimize the gelation time and maximize the clarity of the gel. From this, an optimum mole ratio for reactants was established as 1:0.128:3:15, TTIP:HNO$_3$:H$_2$O:1-BuOH; this ratio was carried forward for the duration of these syntheses.

**1.2.2 Supercritical Drying Apparatus and Procedure**

Modifications were made to an existing supercritical drying manifold (Figure 1.2). A cavity capable of holding a 20 mL beaker (the size all gel syntheses were performed in) sits in the center of a stainless steel 4-way cross. The top of the cross allows liquid CO$_2$ to come in from the tank when all valves are open to the tank, where temperature and pressure are both monitored via an in-line thermocouple and pressure gauge with an equipped emergency pressure release valve. The bottom of the cross allows for the removal of excess CO$_2$ with dissolved gel solvent. Solid CO$_2$ removed out of the bottom is allowed to sublime and leftover solvent in the container
is used to monitor the progress of the solvent exchange to determine if additional purges are necessary. The left and right crosses are NPT male plugs, with the right plug containing a window built into the hex to allow viewing of the chamber.

Figure 1.2- a) Supercritical drying manifold, b) freezer and c) purge line

In a typical procedure, the completed gel is loaded into the cavity of the 4-way cross with excess solvent placed on top of the gel surface to prevent drying. This cavity is then sealed and the entire apparatus is placed in a freezer at -30 °C. Liquid CO$_2$ is leaked into the cavity and the system is allowed to equilibrate for 24 hours. Following this equilibration, every six hours solid CO$_2$ containing acetone solvent is removed from the system until the temperature reaches 0 °C. This is repeated 3-6 times, depending on the results of purge. Presence of solvent indicates that
more purges are necessary. Variations in the amount of solvent placed on top of the gel result in slight fluctuations in the number of purges, but on average 3-4 purges have proven sufficient.

After purging is complete, the apparatus is closed off from the tank, removed from the freezer, and carefully heated to a point past the supercritical point of CO$_2$ (1100 psi, 31 °C) following a strict schedule (Table 1.1). The pressure is not allowed to vary more than +/- 100 psi from a steadily increasing pressure. Heat is applied via a handheld heat gun to the main cavity, with pressure being regulated through a leak valve. Once the goal temperature and pressure (42 °C, 1300 psi) is reached, the system is allowed to sit for 30 minutes.

<table>
<thead>
<tr>
<th>Temperature Range (°C)</th>
<th>Base Pressure (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-30 to -20</td>
<td>800</td>
</tr>
<tr>
<td>-20 to -10</td>
<td>900</td>
</tr>
<tr>
<td>-10 to 0</td>
<td>1000</td>
</tr>
<tr>
<td>0 - 10</td>
<td>1050</td>
</tr>
<tr>
<td>10 - 20</td>
<td>1100</td>
</tr>
<tr>
<td>20 - 30</td>
<td>1200</td>
</tr>
<tr>
<td>30 - 42</td>
<td>1300</td>
</tr>
</tbody>
</table>

Table 1.1- Heating and pressure schedule for supercritical drying procedure.

The next step was to apply heat and raise the internal temperature and pressure to 60 °C and 1400 psi. The sample is allowed to sit for 20 minutes before heat is again applied to raise the pressure back to approximately 1300 psi and a temperature of near 60 °C. From here, the system leak valve is opened and the apparatus is allowed to cool down and depressurize to atmospheric conditions over 2-3 hours. Once ambient conditions have been reached, the sample is collected, ground with a mortar and pestle, and heated to various calcination temperatures (50-500 °C) using a ramp rate of 5 °C/min and a dwell time of six hours.
1.2.3 Characterization

Powder XRD patterns were recorded on a Rigaku Ultima IV X-ray diffractometer operated at 40 kV and 44 mA using Cu Kα radiation (1.5418 Å). All patterns were taken as continuous scans at 2.00° min⁻¹. SEM was carried out on all samples using a FEI Nova NanoSEM 450 with a beam voltage of 2 kV. Little to no charging was present on the samples so no coatings were necessary. Each sample was mounted on aluminum stubs with carbon tape.

BET (Brunauer-Emmett-Teller) surface area measurements were performed using NOVA-e Series Model 25/26 NovaWin/NovaWin-CFR Gas Sorption System. Samples were either dried in a vacuum oven at 120 °C or degassed on the instrument itself for 3 hours prior to analysis, with the exception being the sample calcined to 50 °C which were dried at 50 °C. Surface area was determined via multi-point BET method using the first five data points of the adsorption curve. Energy-dispersive spectroscopy (EDS) was carried out using an Oxford AZtecEnergy Microanalysis System with X-Max 80 Silicon Drift Detector and an accelerating voltage of 15 kV. Samples were probed for relative zirconium amount. Each sample was mounted on aluminum stubs with carbon tape. Raman spectroscopy was carried out using a Renishaw System 2000 with a laser wavelength of 514 nm and microscope objective set to 50X. Two accumulations were collected for each sample at 50% laser power to avoid burning. UV-Vis spectroscopy measurements were made using a Shimadzu UV-2450 ultraviolet-visible spectrophotometer with a scanning range of 200-800 nm. Diffuse-reflectance UV-Vis (DRUV-VIS) was measured using 50 mg of catalyst diluted in barium sulfate using an attachment for the Shimadzu instrument. X-ray photoelectron spectroscopy was run using a PHI model 590 spectrometer with multiprobes (Physical Electronics Industries Inc.), using Al Kα radiation (λ = 1486.6 eV) operated at 250 W.
1.3 Results

1.3.1 Design of Experiments – Factorial Approach

A design of experiment approach was carried out to optimize parameters for the creation of the sol-gel. (Figure 1.3) shows an example of a good gel and a bad gel. A “good” gel is one that gels quickly and has little to no precipitation, whereas a “bad” gel is one in which there is precipitation or no gelation. In the first level of screening, trial 5 and 6 showed less precipitation than the others and gelled in about a day.

Figure 1.3- An example of a) poor gelation and b) good gelation.

The second level of screening was carried out using the full factorial to move closer to the optimum values where trial 5 showed little precipitation and also gelled in about a day. The third level of screening used a path of steepest ascent calculation to determine where the true optimum existed, where trial 3 yielded a gel with no precipitation and gelled in less than 12 hours.
### Table 1.2- First level of three-factor factorial for sol-gel optimization.

<table>
<thead>
<tr>
<th>Trial</th>
<th>Catalyst (mL)</th>
<th>Water (mL)</th>
<th>Solvent (mL)</th>
<th>Grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.017</td>
<td>0.121</td>
<td>12.298</td>
<td>0.5</td>
</tr>
<tr>
<td>2</td>
<td>0.051</td>
<td>0.121</td>
<td>6.149</td>
<td>0.5</td>
</tr>
<tr>
<td>3</td>
<td>0.017</td>
<td>0.605</td>
<td>6.149</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>0.051</td>
<td>0.605</td>
<td>12.298</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>0.034</td>
<td>0.363</td>
<td>9.2235</td>
<td>4</td>
</tr>
<tr>
<td>6</td>
<td>0.034</td>
<td>0.363</td>
<td>9.2235</td>
<td>4</td>
</tr>
</tbody>
</table>

### Table 1.3- Second level of full, three-factor factorial.

<table>
<thead>
<tr>
<th>Trial</th>
<th>HNO$_3$ (mL)</th>
<th>Water (mL)</th>
<th>1-BuOH (mL)</th>
<th>Final Grade</th>
<th>Calculated Final Grade</th>
<th>Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0365</td>
<td>0.360</td>
<td>7.663</td>
<td>1</td>
<td>4.28</td>
<td>10.7</td>
</tr>
<tr>
<td>2</td>
<td>0.0365</td>
<td>0.360</td>
<td>10.737</td>
<td>6</td>
<td>4.53</td>
<td>2.2</td>
</tr>
<tr>
<td>3</td>
<td>0.0365</td>
<td>0.481</td>
<td>7.663</td>
<td>1</td>
<td>1.02</td>
<td>0.0</td>
</tr>
<tr>
<td>4</td>
<td>0.0365</td>
<td>0.481</td>
<td>10.737</td>
<td>1</td>
<td>1.27</td>
<td>0.1</td>
</tr>
<tr>
<td>5</td>
<td>0.0535</td>
<td>0.360</td>
<td>7.663</td>
<td>9</td>
<td>8.53</td>
<td>0.2</td>
</tr>
<tr>
<td>6</td>
<td>0.0535</td>
<td>0.360</td>
<td>10.737</td>
<td>8</td>
<td>8.77</td>
<td>0.6</td>
</tr>
<tr>
<td>7</td>
<td>0.0535</td>
<td>0.481</td>
<td>7.663</td>
<td>6</td>
<td>5.27</td>
<td>0.5</td>
</tr>
<tr>
<td>8</td>
<td>0.0535</td>
<td>0.481</td>
<td>10.737</td>
<td>3</td>
<td>5.52</td>
<td>6.4</td>
</tr>
<tr>
<td>9</td>
<td>0.0450</td>
<td>0.420</td>
<td>9.200</td>
<td>6</td>
<td>4.9</td>
<td>1.2</td>
</tr>
<tr>
<td>10</td>
<td>0.0450</td>
<td>0.420</td>
<td>9.200</td>
<td>8</td>
<td>4.9</td>
<td>9.6</td>
</tr>
</tbody>
</table>

### Table 1.4- Path of steepest ascent trials.

<table>
<thead>
<tr>
<th>Trial</th>
<th>HNO$_3$ (mL)</th>
<th>Water (mL)</th>
<th>1-BuOH (mL)</th>
<th>Final Grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.048</td>
<td>0.402</td>
<td>9.236</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>0.052</td>
<td>0.383</td>
<td>9.272</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>0.055</td>
<td>0.365</td>
<td>9.308</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>0.065</td>
<td>0.31</td>
<td>9.415</td>
<td>3</td>
</tr>
</tbody>
</table>
1.3.2. Phase Characterization

Powder XRD was done on all samples from calcined from 50-500 °C to ascertain crystallinity. As the calcination temperature increases, there is a distinct increase in the height of the (101) peak, which indexes to the anatase phase of titania (Figure 1.4). Crystallinity overall increases as well, along with the crystallite size calculated using the Debye-Scherrer equation (Table 1.5). At 400 °C and 500 °C, reflections and crystal planes can be observed at 25.3° (101), 38° (112, 103, 004), 48.1° (200), 54.1° (211), 55.1° (105), 62.9° (204), 69.2° (116), and 70.0° (220). All of these reflections index to anatase titanium dioxide.

Figure 1.4- X-Ray diffraction pattern for 50-500 °C TiO$_2$ aerogels.
<table>
<thead>
<tr>
<th>TiO₂ Calcination Temperature (°C)</th>
<th>Crystallite Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>2.3</td>
</tr>
<tr>
<td>200</td>
<td>3.8</td>
</tr>
<tr>
<td>300</td>
<td>5.4</td>
</tr>
<tr>
<td>400</td>
<td>7.4</td>
</tr>
<tr>
<td>500</td>
<td>10.0</td>
</tr>
</tbody>
</table>

Table 1.5- Crystallite sizes for 50-500 °C TiO₂ aerogels.

Raman spectroscopy was performed on all samples. As calcination temperature increases, an initial increase in the baseline at high wavenumbers can be seen at 200 °C, with slow decreases of this baseline at 300 °C and 400 °C (Figure 1.5)(Figure 1.6). The first evolution of peaks for the anatase phase can be observed at 400 °C. At 500 °C, the baseline at high wavenumbers flattens completely out and we observe the most intense peaks of all samples. Peaks are observed for the $E_g(1)$, $E_g(2)$, $B_{1g}(1)$, $B_{1g}(2)$, $A_{1g}$ and $E_g(3)$. This profile matches observed literature values for anatase titanium dioxide peak intensities and relative locations (Table 1.6). There is no evidence of contaminant phases or materials.
Figure 1.5- Raman spectra for 50-300 °C calcined TiO$_2$ samples.
Figure 1.6- Raman Spectra for 400 and 500 °C calcined TiO₂ samples.

TGA were obtained for the 50 °C calcined TiO₂ aerogel sample, with a temperature ramp rate of 10 °C/min up to check point temperatures of 100, 200, 300, 400, and 500 °C and holds of 30 minutes at each of those check point temperatures (Figure 1.7). A mass loss can be observed throughout the heating scheme, with a leveling off occurring after 400 °C.
Figure 1.7- TGA data showing mass loss versus temperature and time for 50 °C TiO$_2$ aerogel.

SIMS was done on all TiO$_2$ aerogel samples calcined from 50-500 °C (Figure 1.8). The total intensity of carbon signal decreases overall as calcination temperature increases up to 500 °C. Each frame is equivalent to one monolayer in the powder sample, with the gap in time between each frame being equal to approximately one minute. At 500 °C, there is only one monolayer of carbon left.
Figure 1.8- SIMS of 50-500 °C calcined TiO₂ aerogels.
<table>
<thead>
<tr>
<th>Major Peak Locations (cm(^{-1}))</th>
<th>Observed</th>
<th>Literature*</th>
</tr>
</thead>
<tbody>
<tr>
<td>144</td>
<td>144</td>
<td></td>
</tr>
<tr>
<td>199</td>
<td>196</td>
<td></td>
</tr>
<tr>
<td>398</td>
<td>394</td>
<td></td>
</tr>
<tr>
<td>519</td>
<td>516</td>
<td></td>
</tr>
<tr>
<td>638</td>
<td>638</td>
<td></td>
</tr>
</tbody>
</table>

Table 1.6- Peak position comparisons between synthesizes TiO\(_2\) and literature values for TiO\(_2\)

\(\text{N}_2\) adsorption/desorption isotherms were obtained for all titania aerogels samples calcined from 50-500 °C (Figure 1.9). A reduction of the total volume at STP can be observed as calcination temperature is increased. Surface area, pore volume, and average pore size measurements can be observed and calculated from these data (Figure 1.10, Table 1.7). There is an overall downward trend in both surface area and pore volume, with the highest value being 701 m\(^2\)/g for the 50 °C and a value of 118 m\(^2\)/g for the 500 °C. The pore volume drops precipitously from a value of 3.6 cc/g to 0.76 cc/g from 50 °C to 500 °C.
Figure 1.9- N\textsubscript{2} adsorption/desorption isotherms for TiO\textsubscript{2} aerogels calcined from 50-500 °C.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Surface Area (m\textsuperscript{2}/g)</th>
<th>Pore Volume (cc/g)</th>
<th>Average Pore Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>701</td>
<td>3.6</td>
<td>20.3</td>
</tr>
<tr>
<td>200</td>
<td>380</td>
<td>1.6</td>
<td>16.4</td>
</tr>
<tr>
<td>300</td>
<td>334</td>
<td>1.3</td>
<td>13.2</td>
</tr>
<tr>
<td>400</td>
<td>166</td>
<td>0.96</td>
<td>23.2</td>
</tr>
<tr>
<td>500</td>
<td>118</td>
<td>0.76</td>
<td>12.9</td>
</tr>
</tbody>
</table>

Table 1.7- Summary of N\textsubscript{2} sorption data for TiO\textsubscript{2} aerogels calcined from 50-500 °C.
Figure 1.10- Surface area, pore volume, and pore size data for TiO$_2$ aerogels calcined from 50-500 °C.

SEM images of the surface of the titania aerogel show nano features as part of the overall morphology of the material (Figure 1.11). There are little to no observable differences between the samples at different calcination temperatures in the SEM images. TEM images show the general size of the titania crystallites, confirming data obtained via XRD crystallite size calculations (Figure 1.12).
Figure 1.11- SEM images for 50-500 °C calcined titanium dioxide aerogel.
Figure 1.12- TEM images of a) 50, b) 200, c) 300, d) 400, and e) 500 °C calcined TiO$_2$ aerogels.
1.4 Discussion

1.4.1 Design of Experiment Approach

The design of experiments approach was employed to reduce the overall processing time for the gels that have been made. A typical synthesis would take between 7-10 days via the method pre-optimization. Due to a number of logistical issues (freezer size, manuclave size, etc.), the scale of the product synthesized is such that slowdowns in the synthesis had dramatic impacts on the ability to effectively do research on these materials. The limitation of the size of the manuclave particularly hinders us here, due to limiting our reaction vessel size to roughly the size of a 20 mL beaker. The design of experiments approach serves to optimize the gelation time step, bringing gelation time down from 2-3 days to less than one day and in some cases only a few hours. Also, the reduction in the overall amount of solvent that is being employed serves to reduce the number of solvent washes and purges that need to be done once the material is in the drier. The combination of these effects serves to increase the throughput capability of the drier.

Controlling the rate of gelation is also critical towards producing a higher quality gel for this synthesis. Too slow gelation makes use of the method impractical, while too fast gelation has tended to come with accompanying precipitation of titanium dioxide rather than the formation of a disperse network suspended in solvent. Via the design of experiment approach, the gelation quality was maintained with that of the conventional titania sol-gel synthetic method that had been previously employed.

The three-factor factorial that was done served to isolate the importance of each individual factor in terms of its impact on the material produced. Arbitrary number grades were given to the material produced based on two primary criteria: gelation time and gelation quality.
A good grade was given to materials that formed a gel quickly (< 1 day considered ideal) and that had little to no precipitation evident. From the initial data \(\text{(Table 1.2)}\), trials 5 and 6 showed the most promise. In the factorial itself, these served as center trials, with trials both above and below them that differed via standard amounts. In this process, the catalyst for gelation \(\text{(HNO}_3\text{)}\), solvent \(\text{(1-BuOH)}\), and titanium precursor \(\text{(TTIP)}\) did not change. In an effort to reduce the variability and the necessary experiments involved in this process, these parameters were kept constant.

Data gathered from trials 5 and 6 were used to next factorial in an effort to move closer to the optimum values. The trial that gave the best combination of observed (best) and calculated (based on the previous factorial, second best) results was trial 5 \(\text{(Table 1.3)}\). It is from this trial that a path of steepest ascent calculation was done. Trial 3 showed the best results, with a 50% reduction in gelation time over previous screening trials and no precipitation present \(\text{(Table 1.4)}\). The mole ratio of reactants in all materials was then changed from the original \(1:20:0.08:3, \text{Ti:1-BuOH:HNO}_3:H_2O\) to the new ratio \(1:15:0.128:3\).

The reduction in volume of the solvent from previous methods necessitated an increase in the overall amount of nitric acid used. These experiments show that the ratio between nitric acid and water in these systems is critical to the quality of the gel obtained. As a result of this, the reduction of solvent had a drastic impact on the relative pH of the resulting sols. Discussed previously was the importance of pH in the hydrolysis and condensation reactions that control the formation of the gel.

These trials enabled the reductions of various other parameters with regards to the gelation and supercritical drying process. Less solvent used reduced the number of acetone washes needed for each sample, along with reducing the amount of time needed for solvent
exchanges in the supercritical drier. This reduced the amount of time necessary for the creation of the aerogel, from start of synthesis to removal from the supercritical drier.

1.4.2 Material Characterization

XRD data confirming the presence of anatase titania were expected upon heating of these gels, and was observed for both the 400 °C and 500 °C samples (Figure 1.4). A slight increase over the baseline can be observed where the (101) peak should be from 50-300 °C, with an extremely sharp peak visible from 400 °C on. Crystallite size, in general, increases as temperature increases and crystallite begin growing larger with increasing amounts of energy given to the crystallite system (Table 1.5). TEM data appear to confirm the crystallite size (Figure 1.12) and show there is an increase in crystallinity as calcination temperature increases, which is evident via the formation of clear crystallites as calcination temperature increases to 500 °C.

The high surface area of the material is partially confirmed with the presence of nanofeatures that appear on the surface of the particles imaged in SEM (Figure 1.11). Often these larger particles seem to be agglomerations of smaller particles coalescing into a much larger, several micron-sized particles, as is observed here. N₂ sorption measurements show the true surface area values, confirming the initial hypotheses from SEM (Figure 1.9, Figure 1.10). The high surface area of the as-synthesized titania samples is commensurate with that of an aerogel at 701 m²/g, along with its high pore volume of 3.6 cc/g. As calcination temperature increased, both of these numbers came down, settling at 118 m²/g and 0.76 cc/g for surface area and pore volume, respectively (Table 1.7). This is expected as increases in temperatures causes
particles to sinter together, resulting in smaller surface areas exposed, smaller pores and smaller pore volumes.

The Raman spectroscopy that was gathered for each sample showed the presence of carbon on the surface for the 50-300 °C samples, with little remaining at 400 °C and higher (Figure 1.5, Figure 1.6). Incomplete removal of trapped solvent and precursor materials at the lower calcination temperatures lead to the formation of a deposited amorphous carbon layer of variable thickness on the surface of all of these particles. This carbon layer leads to a fluorescent background that decreases as we scan from high to low wavenumbers. The 500 °C sample matches literature almost exactly, with no background fluorescence (Table 1.6).

These data are also confirmed via TGA (Figure 1.7) and SIMS (Figure 1.8), which shows the presence of only a surface monolayer of carbon from the environment at 500 °C and, after a hold at 400 °C, there is no mass loss visible. For future catalytic activity, it is important to completely remove as much of this carbon as possible to allow facile access to the surface of the titania aerogel.
1.5 Conclusion

An optimized method was developed for the production of titania sol-gel using a modified design of experiments approach. These sol-gel materials then underwent solvent exchanges with acetone and supercritical drying via a custom-built supercritical drying apparatus. Materials produces were characterized via typical materials techniques, with XRD and Raman spectroscopy confirming the presence of the anatase phase of titania. XRD shows increasing crystallite size as a result of calcination temperature and TEM appears to confirm this for the 500 °C sample. SEM showed nano features on the surface of the material, indicative of a material with a high surface area. BET results confirm the high surface area but show no ordered pore structure is present.
Chapter 2. Zr-Doped Titania Aerogels for Photocatalytic Degradation of Methylene Blue Dye

2.1 Introduction

Industrial pollution continues to be an unfortunate byproduct of industrialization in most modern countries. In the textile industry, this pollution takes the form of dyes which pollute the natural waterways around many of these industrial sites.\cite{35,36} We are concerned particularly with organic dye pollution, which has numerous environmental implications. One such dye is methylene blue, which is an anionic, organic dye used for staining in the textile industry, along with uses as a treatment in the case of some diseases. Excesses of methylene blue, however, have a variety of negative impacts on both humans and the environment. The dye is carcinogenic and in many people effects such as breathing difficulties, fever, chest pain, nausea and hemolysis have been observed, along with significant effects such as hemolytic anemia and skin desquamation being observed at very low doses (< 4 mg/kg of bodyweight) in infants and toddlers.\cite{35} The light absorbing ability of this material makes its impact especially negative in waterways via the blocking of light, which effectively starves out living organisms that depend on light to survive.\cite{37}

Because these dyes have such a negative impact on the environment around them, it becomes prudent and necessary to properly remove or sequester these materials. Popular methods include using membranes to separate the dye from the source water, adsorption of the dye on highly porous, sorbent materials such as activated carbon, coagulation/coagulation-flocculation methods that trap the dye in a gel-like system, or chemical oxidations. Of all of these methods, the only one that has the potential to fully degrade and permanently destroy the dye in
one self-contained method is chemical oxidation.\textsuperscript{36} In this work, chemical oxidation in the form of photocatalytic oxidation will be employed, with the end goal being the complete removal of the dye and its degradation to its most simple components, primarily water and carbon dioxide. To accomplish this, we will use our synthesized titanium dioxide aerogels.

Titanium dioxide, while an excellent photocatalytic material in its own right, has its limitations. The primary drawback has to do with its bandgap, which, as discussed previously, is firmly in the UV region with average band gaps between 3.2 and 3.4 eV.\textsuperscript{38} The ultimate goal of most photocatalytic systems is a material that is active and efficient in the visible region and below, which is the result of a reduced optical band gap. Our aerogel material that has been produced has ample surface area and a high pore volume that ensures that there is plenty of space on the catalyst surface for reactions with the dye molecules to take place but, due to the vast majority of the material being in the anatase phase, its wide band gap will serve to limit the ability of the catalyst to perform without a UV light source present to adequately separate electron-hole pairs in the material. Also, inherent to semiconductor materials such as these is the recombination effect, which occurs when electron-hole pairs recombine rather than travel separately doing chemistry, which effectively kills the materials activity.\textsuperscript{6,30,31,39,40} As such, the band gap needs to be modified in such a way to promote visible activity. To accomplish this, we will dope a metal ion into the titanium dioxide structure.

Doping in a semiconductor system is the act of putting metal or non-metal species into a semiconductor to either lower the conduction band or raise the valence band. Which effect a dopant has on the semiconductor is highly dependent on the number of valence electrons that are being brought in the material. These dopant ions would be either substituting directly for Ti\textsuperscript{4+} ions or filling in vacancies in the titanium dioxide structure. If the dopant material has more
valence electrons than the titanium, the dopant will serve to raise the valence band (n-type doping); if the dopant has less, the dopant will serve to lower the conduction band (p-type doping). The raising and lower of these bands has to do with the introduction of additional electronic states to them. The bands are a continuum of electronic states in a semiconducting material that result from the bunching of these electronic states together which creates effectively a spectrum of energies around that particular energy. The addition of more states to either the conduction or valence band results in the billowing out of the band in both directions with the creation of either a higher “effective” valence band, or a lower “effective” conduction band. Regardless of which band is moving, the overall effect should be a reduction in the band gap itself which leads to shift in the absorption spectrum of the material. The absolute value is impossible to predict at the outset but similar systems made with titania have shown that dramatic red shifts are possible, including moving completely into the visible spectrum in the case of some ion dopants, mainly noble metals. Estimates of this shift are possible using calculations such as density functional theory (DFT) calculations prior to experimental methods.

While these are primary examples, movement of the bandgap can be accomplished with doping that fits into neither of these categories, such as doping of a transition metal species with other transition metals. In this case, the exact mechanism of the band gap change becomes situation specific as to what will happen to the valence and conduction bands, often with both moving. Doping with multiple elements and combinations of elements has been observed across the breadth of the periodic table, from alkaline metals, alkaline earth metals, transition metals, and non-metals. We have chosen to use zirconium as our dopant metal because literature has shown that zirconium has the band gap lowering effect that we desire. Zr⁴⁺, being a
transition metal in the same group as titanium, has been shown to have a p-type effect in that zirconium introduces states to the conduction band, which in turn reduces the band gap (Figure 2.1).[^39]

![Figure 2.1](image.png)

**Figure 2.1- Schematic diagram for the expected band gap of a) anatase titanium dioxide and b) p-doped anatase titanium dioxide.**

One factor for this has to do with Zr existing in the 4+ oxidation state exclusively. Ti in TiO\(_2\) is mostly Ti\(^{4+}\), but there also are small amounts of Ti\(^{3+}\) defects as well. The lowering of the band gap via this zirconium ion doping should lower the band gap enough that we can observe improved visible light activity from our catalyst.

[^39]: Reference or citation for Figure 2.1.
2.2 Experimental Section

2.2.1 Chemicals

Titanium (IV) tetraisopropoxide (TTIP, 97+% purity), zirconium propoxide (70% in propanol, nitric acid (70%), 1-butanol (>99.4%), methylene blue hydrate, and acetone were obtained from Sigma Aldrich and used as received.

2.2.2. Catalyst Preparation

The base titania gel was synthesized via a sol-gel method employing a mole ratio of TTIP:1-BuOH:H₂O:HNO₃ of 1:15:3:0.128, respectively. For example, 8.990 mL of 1-BuOH was split into two beakers, A and B, where A is 20 mL in size. Beaker A contained 5.104 mL of 1-BuOH and 2.00 mL of TTIP was added to beaker A. For doped samples, a calculated mole percentage amount of zirconium precursor was added to this solution. To beaker B, 3.886 mL of 1-BuOH was added along with 55 microliters of HNO₃ and 0.369 mL of H₂O. Under magnetic stirring, the solution was beaker B was pipetted slowly into beaker A. Following this addition, the sample was covered with parafilm and aged under ambient conditions for approximately 48 hours. Subsequently, a clear gel that maintains its form when inverted was obtained, though this process took significantly longer for the doped cases (in excess of 1-2 weeks).

Due to the sensitivity of the zirconium precursors to the H₂O/HNO₃ ratios, numerous trials were required in order to synthesize a successful gel. A successful gel was designated was one that was clear, with no signs of precipitation, that maintained form when the containing beaker was inverted. This ratio required adjustment each time an increase was made in dopant percentage past 1%.
Following successful gelation, the 1-BuOH solvent was exchanged with acetone several times to remove gelation byproducts and to replace the butanol with acetone. The sample is then loaded into a custom-built supercritical CO$_2$ drier with excess acetone to prevent premature drying. CO$_2$ is then exchanged into the system, and the acetone is purged via a check valve along with solid carbon dioxide. This is repeated until no acetone is observed in collected carbon dioxide.

In the first step of the drying process, the manuclave body is heated incrementally from -20 °C to 42 °C, with pressure being increased to 1300 psi. CO$_2$ was released manually via a ball valve to keep the pressure change from fluctuating greater than ±100 psi from a steady value. Once at the desired values for temperature and pressure, the system is closed and held isobarically and isothermally for thirty minutes, then heated to a temperature of 60 °C and pressure of 1400 psi. This system is again held isobarically and isothermally for twenty minutes, then reheated to 60 °C and a pressure of 1300 psi. These steps are taken to ensure that the system stays above or at the supercritical point of carbon dioxide (1071 psi at 31 °C), which is critical to this drying process and the obtaining of the aerogel material. Once the last step is completed, the drier is allowed to depressurize slowly over the course of approximately three hours.

### 2.2.3 Characterization

Powder XRD patterns were recorded on a Rigaku Ultima IV X-ray diffractometer operated at 40 kV and 44 mA using Cu K$_\alpha$ radiation (1.5418 Å). All patterns were taken as continuous scans at 2.00° min$^{-1}$. SEM was carried out on all samples using a FEI Nova NanoSEM 450 with a beam voltage of 2 kV. Little to no charging was present on the samples so no coatings were necessary. Each sample was mounted on aluminum stubs with carbon tape.
BET (Brunauer-Emmett-Teller) surface area measurements were performed using NOVA-e Series Model 25/26 NovaWin/NovaWin-CFR Gas Sorption System. Samples were dried in a vacuum oven at 100 °C for 3 hours prior to analysis. Surface area was determined via multi-point BET methods using the first five data points of the adsorption curve. Energy-dispersive spectroscopy (EDS) was carried out using an Oxford AZtecEnergy Microanalysis System with X-Max 80 Silicon Drift Detector and an accelerating voltage of 15 kV. Samples were probed for relative zirconium amount. Each sample was mounted on aluminum stubs with carbon tape. Raman spectroscopy was carried out using a Renishaw System 2000 with a laser wavelength of 514 nm and microscope objective set to 50X. Two accumulations were collected for each sample at 50% laser power to avoid burning. UV-Vis spectroscopy measurements were made using a Shimadzu UV-2450 ultraviolet-visible spectrophotometer with a scanning range of 200-800 nm. Diffuse-reflectance UV-Vis (DRUV-VIS) was measured using 50 mg of catalyst diluted in barium sulfate using an attachment for the Shimadzu instrument. X-ray photoelectron spectra (XPS) characterization of the synthesized materials were done on a PHI model Quantum 2000 spectrometer with scanning ESCA multiprobe (Φ Physical Electronics Industries Inc.), using Al K$_\alpha$ radiation ($\lambda$=1486.6 eV) as the radiation source. The spectra were recorded in the fixed analyzer transmission mode with pass energies of 187.85 eV and 29.35 eV for recording survey and high resolution spectra, respectively. The powder samples were pressed on a double sided carbon tape mounted on an Al coupon pinned to a sample stage with a wash and screw then placed in the analysis chamber. The XPS spectra obtained were analyzed and fitted using CasaXPS software (version 2.3.16). Sample charging effects were eliminated by correcting the observed spectra with the C 1s BE value of 284.8 eV.
Aqueous samples (1.6 mL, 0.1 mgmL\(^{-1}\)) with known pH were analyzed using the Brookhaven Zeta Plus zeta potential analyzer (Holtsville, NY). The samples were measured in a plastic cuvette, and 3 runs were performed for each sample. Samples were analyzed for electrophoretic mobility using laser Doppler velocimetry and, Smoluchowski fit (software provided by manufacturer) was used to calculate the zeta potential.

### 2.2.4. Adsorption Testing

The adsorption ability of all catalysts produced was tested by mixing 25 mg of prepared catalyst with a 100-mL solution of 1 \(\times\) 10\(^{-4}\) M methylene blue. At 30 minute intervals over the course of 2 hours 3 mL aliquots were taken, centrifuged and UV-Vis spectroscopy was performed, tracking the 665 nm absorption peak to monitor dye loss from solution.

### 2.2.5. Photocatalytic Activity Testing

Cool white (\(\lambda = >350\)–700 nm, centered at 8 W) lamps were used as sources of visible light. Sixteen lamps were installed and equally spaced in a Rayonet Model RPR-100 photochemical chamber reactor. The activity of the catalyst was measured specifically in terms of degradation of methylene blue (MB) dye with a starting concentration of 1 \(\times\) 10\(^{-4}\) M. To this solution, 25 mg of catalyst was added along with a magnetic stir bar. Aliquots (3 mL) were taken every 30 minutes for 180 minutes. Samples were centrifuged to separate catalyst from the solution and UV-Vis spectroscopy was then run, with tracking of the 665 nm absorption peak being used to monitor degradation. Degradation efficiency was calculated percent concentration remaining in solution at the given time (\(C/C_0 \times 100\%\)).
2.2.6. Recycle Testing

Following degradation, the catalyst-dye mixture was separated and centrifuged, with excess solution being removed. The remaining catalyst was then washed multiple times with ethanol and centrifuged. The resulting wet catalyst was then calcined at 500 °C. PXRD, Raman spectroscopy, SEM and N₂ sorption techniques were then repeated to check for changes.

2.3. Results

2.3.1 Phase Characterization

Determining the phase of the material produced is paramount and as such PXRD was run to track the expected transformation. Fresh X% Zr-TiO₂ was heat treated to 50, 200, 300, 400 and 500 °C and as calcination temperature increases, crystallinity increases across for all samples (X = 0%, 1%, 5% and 10% Zr) (Figure 2.2, Figure 2.3, Figure 2.4, Figure 2.5). Reflections and peaks can be observed at 25.3° (101), 37.5° (101, 103, 004), 47.9° (200), 54.6° (211, 105), 62.7° (204), and 69.8° (116, 220) for the 5% Zr-doped titania aerogels calcined to 500 °C. As doping concentration increases, we observe a decrease in the crystallinity onset temperature, with 0% Zr-TiO₂ having a crystallinity onset at 400 °C and both 5% and 10% Zr-TiO₂ showing crystallinity at 50 °C. There was no noticeable change in the 1% Zr-TiO₂ sample relative to the undoped samples. There is a significant increase in the degree of crystallinity between the 5% and 10% samples as well, with the anatase peaks (101) being more intense. No evidence of rutile or other phase peaks can be observed in this diffraction pattern up to the highest calcination temperature of 500 °C. All peaks present index to anatase titanium dioxide. There is also no evidence of zirconium dioxide in any diffraction patterns. Peak shifts are observable in the (004) (103) (112) combined peak as dopant concentration increases from 0 to 10% Zr.
Figure 2.2 - 0% Zr-TiO$_2$ X-Ray diffraction pattern for 50-500 °C.
Figure 2.3- 1% Zr-TiO2 X-Ray diffraction pattern for 50-500 °C.
Figure 2.4- 5% Zr-TiO₂ X-Ray diffraction pattern for 50-500 °C.
Crystallite size was calculated using the Scherrer equation and utilizing the (200) peak present in the material (Table 2.1). In general, there is an increase in crystallite size in a dopant series as the temperature increases. There is a trend initially for the 50 °C calcined samples where the crystallite size is increasing as doping percentage increases, but this trend inverts as we move to higher calcination temperatures, with 10% Zr-TiO₂ having the smallest crystallite size of all samples at 500 °C and undoped TiO₂ having the largest (Figure 2.6).
<table>
<thead>
<tr>
<th></th>
<th>Crystallite Size (nm)</th>
<th></th>
<th>Crystallite Size (nm)</th>
<th></th>
<th>Crystallite Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10% Zr-TiO₂</td>
<td>50</td>
<td>4.8</td>
<td>50</td>
<td>50</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>4.5</td>
<td>200</td>
<td>200</td>
<td>2.7</td>
</tr>
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<td></td>
<td>300</td>
<td>5.4</td>
<td>300</td>
<td>300</td>
<td>4.2</td>
</tr>
<tr>
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<td>400</td>
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<td>400</td>
<td>400</td>
<td>6.0</td>
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<td>500</td>
<td>6.9</td>
<td>500</td>
<td>500</td>
<td>7.7</td>
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<tr>
<td>5% Zr-TiO₂</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>2.7</td>
<td>50</td>
<td>50</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>3.6</td>
<td>200</td>
<td>200</td>
<td>3.8</td>
</tr>
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<td></td>
<td>500</td>
<td>9.0</td>
<td>500</td>
<td>500</td>
<td>10.0</td>
</tr>
</tbody>
</table>

Table 2.1- Crystallite size calculations for Zr-doped TiO₂ samples.

![Graph showing crystallite size calculations for Zr-doped TiO₂ samples.](image)

**Figure 2.6-** Crystallite size calculations for Zr-doped TiO₂ samples.

SEM images were collected for the untreated and 500 °C heated samples for all doping levels. In all cases, nanotexture can be observed on the surface of all particles surveyed. Particle
size varied across the surveyed areas for each sample, with no clear preferred size being observed, with sizes ranging from 5-50 microns.

Figure 2.7- SEM image of uncalcined TiO$_2$ aerogel.

Figure 2.8- SEM image of uncalcined 1% Zr-TiO$_2$ sample.
Figure 2.9- SEM image of uncalcined 5% Zr-TiO₂ sample.

Figure 2.10- SEM image of uncalcined 10% Zr-TiO₂ sample.
EDX showed the presence of zirconium, visible down to the 1% doped sample. Zirconium concentration increased accordingly from the 0% to 10% sample (Figure 2.11). Observed concentrations correlated with the nominal calculated values, but were slightly lower comparatively (Table 2.2). EDX mapping shows Zr location through the material, with Zr being regularly dispersed across the surface of the material (Figure 2.12).

Figure 2.11: EDX of uncalcined a) TiO₂, b) 1% Zr-TiO₂, c) 5% Zr-TiO₂ and d) 10% Zr-TiO₂ samples.
<table>
<thead>
<tr>
<th>Calculated Zr %*</th>
<th>Observed Zr %*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1%</td>
<td>0.8%</td>
</tr>
<tr>
<td>5%</td>
<td>4.0%</td>
</tr>
<tr>
<td>10%</td>
<td>8.9%</td>
</tr>
</tbody>
</table>

Table 2.2- Calculated and observed zirconium molar percentages from EDX.
Figure 2.12 - EDX elemental mapping of the surface of uncalcined a) TiO$_2$, b) 1% Zr-TiO$_2$, c) 5% Zr-TiO$_2$, and d) 10% Zr-TiO$_2$ samples.
BET surface area measurements were carried out for all samples. Representative data from the 5% Zr-TiO$_2$ series are shown below (Figure 2.13). A type H3 isotherm can be observed in all samples. A shift to overall lower volumes can be seen as calcination temperatures increase, with a local maximum at 300 °C and then decreasing again as the temperature is increased to 500 °C from there. The 50 °C has the highest surface area at 323 m$^2$/g whereas the lowest is the 500 °C sample which is at 120 m$^2$/g. Pore volumes decrease initially at the 200 °C calcination temperature to 1.1 cc/g but then increase past the original pore volume of 1.4 cc/g to 1.6 cc/g for both the 400 °C and 500 °C samples.

![N$_2$ adsorption/desorption isotherms for 50-500 °C calcined samples of 5% Zr-TiO$_2$.](image)

Figure 2.13- N$_2$ adsorption/desorption isotherms for 50-500 °C calcined samples of 5% Zr-TiO$_2$.  

47
<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Surface Area (m²/g)</th>
<th>Pore Volume (cc/g)</th>
<th>Avg. Pore Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>323</td>
<td>1.4</td>
<td>17.8</td>
</tr>
<tr>
<td>200</td>
<td>198</td>
<td>1.1</td>
<td>21.4</td>
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<tr>
<td>300</td>
<td>203</td>
<td>1.2</td>
<td>23.8</td>
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<tr>
<td>400</td>
<td>184</td>
<td>1.6</td>
<td>34.0</td>
</tr>
<tr>
<td>500</td>
<td>120</td>
<td>1.6</td>
<td>44.2</td>
</tr>
</tbody>
</table>

Table 2.3- Summary of surface area and pore analysis data for 5% Zr-TiO₂ from 50-500 °C.

XPS results showed the presence of Zr⁴⁺ via the Zr 3p³/₂ peak (1090 CPS, 333.5 eV), and the Zr 3d doublet (1%- 290 CPS, 185.2 eV; 314 CPS, 182.4 eV, 5%- 545 CPS, 185.1 eV; 660 CPS, 182.7 eV, 10% - 1120 C/s, 185.2 eV; 1480 C/s, 182.8 eV). For all samples, the Ti 2p doublet was visible as well, which confirms the presence of Ti⁴⁺ (1%- 210 CPS, 465.0 eV; 465 CPS, 459.3 eV, 5%- 230 CPS, 465.0 eV; 525 CPS, 459.3 eV, 10% - 3000 CPS, 464.9 eV; 6700 CPS, 459.2 eV). With increasing dopant concentration, we observe corresponding increases in the Zr 3d peaks (Figure 2.14, Figure 2.15, Figure 2.16).
Figure 2.14- High-resolution XPS spectrum for 1% Zr-TiO$_2$ calcined to 500 °C.
Figure 2.15- High-resolution XPS spectra for 5% Zr-TiO₂ calcined to 500 °C.
Figure 2.16- High-resolution XPS spectra for 10% Zr-TiO₂ calcined to 500 °C.
TEM images were gathered for all 500 °C calcined samples (Figure 2.17). General particle size observed agrees with crystallite size calculated using gathered X-ray data on average. A variety of sizes is observed ranging from 5-15 nm. All samples show discrete crystallite have formed.

![TEM images](image1)

**Figure 2.17-** TEM images for a) TiO$_2$, b) 1% Zr-TiO$_2$, c) 5% Zr-TiO$_2$, and d) 10% Zr-TiO$_2$ 500 °C calcined samples.

Solid state DRUV-Vis was done for all samples (Figure 2.18) and Tauc plots were constructed for the purpose of determine the band gap (Figure 2.19). Calculation of the band gap
from these shows a decrease in the band gap for all samples relative to the undoped sample (Table 2.4).

Figure 2.18- DRUV-Vis spectroscopy for all 0-10% Zr-doped TiO$_2$ aerogel samples.
Figure 2.19- Tauc plots for 0-10% Zr-doped TiO$_2$ aerogels.

<table>
<thead>
<tr>
<th>% Zr</th>
<th>Band Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.13</td>
</tr>
<tr>
<td>1</td>
<td>3.13</td>
</tr>
<tr>
<td>5</td>
<td>3.06</td>
</tr>
<tr>
<td>10</td>
<td>3.13</td>
</tr>
</tbody>
</table>

Table 2.4- Band gap calculations from Tauc plots for 0-10% Zr-TiO$_2$ samples.
Raman spectroscopy was run on the 500 °C heat treated samples for all dopant levels. Peaks for the $E_g(1,2,3)$, $B_{1g}(1,2)$, and $A_{1g}$ can all be observed in all samples with the exception of the $E_g(2)$, which disappeared as we move from TiO$_2$ to doped TiO$_2$ samples. There also is a parabolic nature to the peak intensities as a function of the doping percentage, with TiO$_2$ having the most intense peak profile, followed by 1% Zr-TiO$_2$, 10% Zr-TiO$_2$ and 5% Zr-TiO$_2$.

![Raman spectroscopy for 0-10% Zr-TiO$_2$ aerogel samples.](image)

Zeta potential measurements were made to ascertain the surface charge for each Zr-TiO$_2$ sample (Table 2.5). An overall increase in the negativity of the catalyst surface can be observed up to a doping percentage of 5% Zr, after which the effect levels off.
<table>
<thead>
<tr>
<th>Zr %</th>
<th>Zeta-Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>-9.05</td>
</tr>
<tr>
<td>1%</td>
<td>-14.32</td>
</tr>
<tr>
<td>5%</td>
<td>-22.40</td>
</tr>
<tr>
<td>10%</td>
<td>-21.18</td>
</tr>
</tbody>
</table>

Table 2.5- Zeta-potential values for 0-10% Zr-TiO$_2$ aerogels calcined to 500 °C.

Dye degradation experiments were carried out on all undoped titanium dioxide samples at all calcination temperatures. The 50 °C sample performed the worst, with 90.9% dye remaining after 3 hours. The 500 °C sample performed the best, with 0% dye detected in solution at the 150 minute mark. The 500 °C calcination temperature was carried through to future trials (Figure 2.21).
Figure 2.21- Concentration of dye remaining versus time for titania aerogel samples calcined from 50-500 °C.

Additional degradation experiments were carried out on the Zr-doped titania aerogels calcined at 500 °C (Figure 2.22). The 5% Zr-doped titania achieved 0% dye detected at the 120 min mark along with the 1% Zr-doped. The 5% Zr doped sample reached < 1% dye remaining at the 90 minute mark whereas the 1% Zr doped sample had 3.3% dye remaining at the 90 minute mark.
Adsorption studies were done to ascertain the adsorptive capabilities of all catalysts and to determine whether equilibration times would be needed. Catalyst was left to soak in the dye solution and kept in the dark under magnetic stirring. We observed no change in the absorbance measured at 665 nm for any of the samples or solutions at any time (Figure 2.23).
Figure 2.23- Dye adsorption experiment for 0-10% Zr-TiO$_2$ aerogels calcined to 500 °C, conducted with no light.

Post-catalysis characterization was carried out on all samples. A representative sample is shown from the 5% Zr-TiO$_2$ aerogels. N$_2$ sorption (Figure 2.24), XRD (Figure 2.26), SEM (Figure 2.25), and Raman spectroscopy (Figure 2.27) were run for all samples. There was a slight increase in the surface area, pore volume, and pore size pre-catalysis to post-catalysis. The surface area increased from 147 m$^2$/g to 152 m$^2$/g, the pore volume increased from 1.07 cc/g to 1.50 cc/g and the pore size increased from 14.5 nm to 15 nm. The general shape of the hysteresis loop did not change. SEM images obtained for both samples shows no change in the surface morphology. The XRD patterns remain unchanged with the same characteristic anatase titania peaks visible between the pre and post catalysis. Raman data for both also indicate anatase titania
with little change. The only difference being a slight difference in intensity, with the post-catalysis being more intense.

Figure 2.24- N₂ sorption data for 5% Zr-TiO₂ photocatalyst pre and post reaction.

Figure 2.25- SEM images for 5% Zr-TiO₂ photocatalyst pre and post reaction.
Figure 2.26- XRD data for 5% Zr-TiO₂ photocatalyst pre and post reaction.

Figure 2.27- Raman spectroscopy for 5% Zr-TiO₂ photocatalyst pre and post reaction.
2.4. Discussion

2.4.1 Material Characterization

A shift in the XRD peak as a result of dopant incorporation into the framework of the host material is common. While this shift may be indicative of such an incorporation, the convolution of the three peaks, all of which have similar relative intensities, makes ascertaining the meaning of the shift difficult. There’s no evidence of such a shift in the most prominent peak, the (101) peak (Figure 2.2, Figure 2.3, Figure 2.4, Figure 2.5). Zirconium is observed to play the role of a promoter in that higher concentrations of Zr used result in an early onset of crystallization, and effect that is maximized as we proceed from 0% Zr-TiO$_2$ to 10% Zr-TiO$_2$. The 101 peak begins to become visible above the baseline noise at 50°C for both the 5% and 10% Zr samples, with the 10% also beginning to show the same general peak outlines as the higher calcined samples.

Calcination temperature plays a significant role in determining the crystallite size. When using the Scherrer equation for this calculation, the absolute value is dependent on the full-width half-maximum (FWHM) of the peak in question, typically one that lies between the range of 30-50 $\theta$. As calcination temperature increases, the FWHM tends to get smaller as the sample becomes transformed from amorphous to crystalline. As such, via the Scherrer equation the crystallite size will get larger. Physically speaking, this is because higher temperatures stabilize larger crystallites, which in turn will yield sharper and more intense peaks. These larger crystallite sizes are also observable in the TEM data (Figure 2.17).

The zirconium impacts crystallite size in a different way. Zirconium enters the framework of the TiO$_2$ lattice via defect sites which, due to its larger size, broaden the peak
obtained. This broadening gives rise to a larger FWHM, and thusly, a smaller crystallite size. This is confirmed by our highest calcination temperature of 500 °C, as the presence of more Zr in the 10% sample leads to its smaller crystallite size compared to that of the undoped TiO$_2$ samples (Figure 2.6, Table 2.1).

The incorporation of zirconium directly impacts the surface properties of the titania samples obtained, including the surface area, pore volume, and pore size (Figure 2.13, Table 2.3). Relative to the undoped titania, Zr-doped TiO$_2$ shows a decreased surface area (323 m$^2$/g compared to 701 m$^2$/g), pore volume (1.4 cc/g compared to 3.6 cc/g) and average pore size (17.8 nm compared to 20.3 nm) at 50 °C (Figure 1.9, Table 1.7). The doped samples calcined to 500 °C maintained similar surface areas and high pore volumes relative to that of the undoped samples (120 m$^2$/g vs. 118 m$^2$/g, 1.6 cc/g vs. 0.76 cc/g). The pore size was significantly higher for that of the Zr-doped TiO$_2$ relative to that of the undoped (44.2 nm vs. 12.9 nm). Evidence of this high surface area can be seen across the board in SEM images obtained for all doped samples (Figure 2.8, Figure 2.9, Figure 2.10). Nanoscale features can be observed for all samples, similar to what was seen for the undoped material (Figure 2.7).

Observed EDX values differed from the calculated values in all instances, with a difference of -0.24%, -1.0%, and -1.1% for 1% Zr, 5% Zr, and 10% Zr, respectively (Figure 2.11, Table 2.2). Because EDX as a technique does penetrate deep into the surface of the material, a distance of 1-2 μm into the material, it is impossible to comment from this technique on the relative distribution of the zirconium ion in the particular titania aggregate at which we are looking. Mapping shows that the zirconium is dispersed in the titania sample and not aggregating in one particular place (Figure 2.12).
XPS confirms the increase in doping percentage as we see the $3d_{3/2}$ and $3d_{5/2}$ peaks for Zr$^{4+}$ increase in size as a function of zirconium doping percentage from 0-10%. Deconvolution shows little to no change in the values for the 3d doublet for zirconium’s binding energy, with the peak area increasing over time as the percentage of zirconium increases from 1% to 10% (Figure 2.14, Figure 2.15, Figure 2.16).

### 2.4.2 Photocatalytic Activity

The band gap of the material is one of the most important aspects of a photocatalyst. DRUV-Vis (Figure 2.18, Figure 2.19) results confirmed a decrease in the band gap of the 5% Zr-TiO$_2$ sample, whereas the calculated band gap remained the same in all other samples (Table 2.4). Lack of incorporation of the zirconium in these other samples is what leads to the unchanged values for these samples.

To quantify the photoactivity of these catalysts and choose the best one, we carried out dye degradation experiments on a model dye system, methylene blue. The zeta potential analysis revealed to us that the surface of our titania was negative in nature, which is why we chose a cationic dye such as methylene blue (Table 2.5). As doping percentage increased from 0% to 10%, we noticed an increase in the overall negativity of the surface charge, leveling off after 5% Zr-doping was reached. The ideal catalyst for this system would be one with a high surface area, high pore volume, and high degree of crystallinity, specifically in this case showcasing the anatase titanium dioxide phase, which is where the material truly becomes photoactive.

Dye degradation experiments were carried out on all undoped titanium dioxide samples first, with the purpose of deciding on the proper calcination temperature for this material (Figure 2.21). With the 500 °C sample performing the best, this was carried forward as the optimal
calcination temperature. The main reason for this increase in activity relative to that of the other samples is the larger degree of crystallinity and presence of the anatase titanium dioxide. Interestingly, the 300 °C calcined sample also showed good activity relative to that of the other materials, with < 1% dye remaining after 3 hours. At present, we are unsure of why this is the case.

Additional degradation experiments were carried out on the Zr-doped titania aerogels calcined at 500 °C to determine the optimal doping percentage for these reactions (Figure 2.22). All samples had no detectable levels of methylene blue after 150 minutes. At the 2 hour mark, the 5% Zr and 1% Zr both show no detectable levels of dye, with the undoped showing < 1% dye remaining in solution. The 5% Zr-TiO₂ sample accomplished decolorization quicker, with an almost 75% drop in the concentration of the dye after 30 minutes and < 5% remaining after 60 minutes, making 5% Zr-TiO₂ the best catalyst in this series. To ensure all concentration decreases were the result of degradation and no other pathways such as adsorption, dark experiments were run under all the same conditions as the degradation with the exception of the light, which was kept off for the duration (Figure 2.23). No difference was observed between initial concentrations and final concentrations for any samples in this study.

Post-catalysis information was gathered for these materials to determine if the reaction had any effect on the properties of the catalyst itself. XRD (Figure 2.26), N₂ sorption experiments (Figure 2.24), Raman spectroscopy (Figure 2.27), and SEM (Figure 2.25) were carried out. Prior to analysis, catalyst was collected, separated from degradation solution, washed with ethanol and calcined to 500 °C. Little to no change was observed in the XRD, confirming anatase titania is still present after the reaction. This is further confirmed via the Raman spectroscopy measurements that were obtained. Surface areas for these materials changed
minimally, but the pore volume increased following the reaction. This is the result of the change in pore size post reaction, which may be the result of subjecting the material to additional heating.
2.5 Conclusions

A zirconium-doped titanium dioxide aerogel was successfully synthesized using methods previously optimized in previous work. XRD showed no effect of the zirconium incorporation on the overall structure of the titania, but lowered the onset temperature of crystallization. Characteristic peaks in the Raman data matched anatase titania, with no change observed despite intensity changes as doping percentage increases. SEM data shows the same surface data for doped samples as well as the undoped, and EDX shows a well dispersed dopant throughout the material with observed doping percentages that correspond well with the calculated values. Zeta potential measurements show an increase in the overall negativity of the surface, and the band gap was shown to decrease for the 5% Zr-TiO$_2$ sample, remaining the same in all other cases. Measured activity, kept track of using UV-Vis spectroscopy, shows definitively that the 500 °C TiO$_2$ aerogel is the most active, due to the generation of the anatase crystal phase. When applied to the zirconium systems, 5% Zr-TiO$_2$ calcined at 500 °C was shown to have the highest overall activity, and going forward 5% was chosen as the initial doping percentage for these various systems.
Chapter 3. M-doped Titania Aerogels for Organic Oxidation Reactions (M = Cu, Fe)

3.1 Introduction

Organic transformations and reactions have long been the study and of interest to both organic and non-organic chemists alike. Both groups recognize the importance of being able to readily manipulate organic materials and change their forms to meet the needs of various applications. Chemical oxidations, specifically selective oxidations, are important among these. The ability to control the rate and degree of oxidation among organic molecules is important for the production of molecules with various degrees of functionalities.

Transition metals have unique properties that have lent them to being useful catalysts and catalyst components for many of the reactions discussed before. Both copper and iron have been shown to be active in various organic redox reactions.\textsuperscript{21,54–59} The ability to easily transition from oxidation states (between +1 and +2 for Cu, +2 and +3 for Fe) readily enables redox chemistry to occur, with the ability to regenerate the material with heating in air for further catalysis.\textsuperscript{60,61} The more suitable Cu and Fe sites that are available for these reactions to occur, the more effective the catalyst material that is produced.

Often in catalysis the presence of a high surface area material leads to an increase in the overall catalytic activity because this generally correlates with an increase in available active sites in the material.\textsuperscript{62,63} Previous work in this dissertation has focused on the creation of a high surface area, high pore volume titanium dioxide aerogel. The incorporation of these active metal
ions into the titania material, either on the surface or in the bulk of the titanium dioxide, should serve to increase the overall activity.

Titania has frequently been used as a catalyst support due to how stable titania is chemically and thermally. The ability to tune its surface area, pore sizes, pore structures, and pore volumes serves to further enhance its viability. For numerous reactions titania has been dubbed an “active” support due to how titania contributes to material activity for whatever is supported upon the titania. This is theorized to be due to adsorption of superoxide (O$_2^-$) species.

Cyclohexane oxidation is an important reaction in industry. The production of numerous important materials, such as Nylon, fibers, and food additives, depend on the primary products of this oxidation, cyclohexanone and cyclohexanol. Selectivity remains a primary concern, however, as over-oxidation of these carbonyl groups happens with relative ease. Conventional catalysts today utilize dangerous and harsh reagent mixtures that often are unselective. This lack of selectivity is countered by efforts that often make the reaction conversions low.

Both iron and copper have been shown in the literature to be active in terms of their ability to catalyze cyclohexane conversion. The combination of a high surface area support, such as the titania aerogels we have previously been able to synthesize materials with the inherent activity of the metals may be promising, and is the goal of this work.
3.2 Experimental

3.2.1 Chemicals

Titanium (IV) tetraisopropoxide (TTIP, 97+\% purity), iron (III) nitrate nonahydrate, copper (II) nitrate trihydrate, nitric acid (70\%), 1-butanol (>99.4\%), tert-butylhydroperoxide, cumene-hydroperoxide, phthalic acid, benzoyl peroxide, 3-chloroperoxybenzoic acid, cyclohexane and acetone were obtained from Sigma Aldrich and used as received.

3.2.2 Catalyst Preparation

The base titania gel was synthesized via a sol-gel method employing a mole ratio of TTIP:1-BuOH:H\(_2\)O:HNO\(_3\) of 1:15:3:0.128, respectively. For example, 9.23 mL of 1-BuOH was split into two beakers, A and B, where A is 20 mL in size. Beaker A contained 5.02 mL of 1-BuOH and 2.00 mL of TTIP was added to beaker A. For doped samples, a calculated mole percentage amount of solid copper or iron precursor was added to beaker B and allowed to dissolve prior to the addition of the TTIP. To beaker B, 4.21 mL of 1-BuOH was added along with 55 \(\mu\)L of HNO\(_3\) and 0.369 mL of H\(_2\)O. Under magnetic stirring, the solution was beaker B was pipetted slowly into beaker A. Following this addition, the sample was covered with parafilm and aged under ambient conditions for approximately 24 hours. Subsequently, a clear gel that maintains its form when inverted was obtained.

Addition of the copper precursor had little to no impact on the gelation procedure in terms of gelation time and gel quality. The iron precursor had a similar effect to that of additional acid, and as such, the water amount was increased slightly to encourage gelation (by 10 \(\mu\)L). This was the only adjustment that had to be made as only a 5 \text{mol\%} was used in each case.
Following successful gelation, the 1-BuOH solvent was exchanged with acetone several times to remove gelation byproducts and to replace the butanol with acetone. The sample is then loaded into a custom-built supercritical CO$_2$ drier with excess acetone to prevent premature drying. CO$_2$ is then exchanged into the system, and the acetone is purged via a check valve along with solid carbon dioxide. This is repeated until no acetone is observed in collected carbon dioxide.

In the first step of the drying process, the manuclave body is heated incrementally from -20 °C to 42 °C, with pressure being increased to 1300 psi. CO$_2$ was released manually via a ball valve to keep the pressure change from fluctuating greater than ±100 psi from a steady value. Once at the desired values for temperature and pressure, the system is closed and held isobarically and isothermally for thirty minutes, then heated to a temperature of 60 °C and pressure of 1400 psi. This system is again held isobarically and isothermally for twenty minutes, then reheated to 60 °C and a pressure of 1300 psi. These steps are taken to ensure that the system stays above or at the supercritical point of carbon dioxide (1071 psi at 31 °C), which is critical to this drying process and obtaining the aerogel material. Once the last step is completed, the drier is allowed to depressurize slowly over the course of approximately three hours.

3.2.3. Characterization

Powder XRD patterns were recorded on a Rigaku Ultima IV X-ray diffractometer operated at 40 kV and 44 mA using Cu K$_\alpha$ radiation (1.5418 Å). All patterns were taken as continuous scans at 2.00° min$^{-1}$. SEM was carried out on all samples using a FEI Nova NanoSEM 450 with a beam voltage of 2 kV. Little to no charging was present on the samples so no coatings were necessary. Each sample was mounted on aluminum stubs with carbon tape.
BET (Brunauer-Emmett-Teller) surface area measurements were performed using NOVA-e Series Model 25/26 NovaWin/NovaWin-CFR Gas Sorption System. Samples were dried in a vacuum oven at 100 °C for 3 hours prior to analysis. Surface area was determined via a multi-point BET method using the first five data points of the adsorption curve. Energy-dispersive spectroscopy (EDS) was carried out using an Oxford AZtecEnergy Microanalysis System with X-Max 80 Silicon Drift Detector and an accelerating voltage of 15 kV. Samples were probed for relative zirconium amount. Each sample was mounted on aluminum stubs with carbon tape. UV-Vis spectroscopy measurements were made using a Shimadzu UV-2450 ultraviolet-visible spectrophotometer with a scanning range of 200-800 nm. Diffuse-reflectance UV-Vis (DRUV-VIS) was measured using 50 mg of catalyst diluted in barium sulfate using an attachment for the Shimadzu instrument.

X-ray photoelectron spectra (XPS) characterization of the synthesized materials were done on a PHI model Quantum 2000 spectrometer with scanning ESCA multiprobe (Φ Physical Electronics Industries Inc.), using Al Kα radiation (λ=1486.6 eV) as the radiation source. The spectra were recorded in the fixed analyzer transmission mode with pass energies of 187.85 eV and 29.35 eV for recording survey and high resolution spectra, respectively. The powder samples were pressed on a double sided carbon tape mounted on an Al coupon pinned to a sample stage with a wash and screw, then placed in the analysis chamber. The XPS spectra obtained were analyzed and fitted using CasaXPS software (version 2.3.16). Sample charging effects were eliminated by correcting the observed spectra with the C 1s BE value of 284.8 eV. Secondary Ion Mass Spectrometry (SIMS) analysis of samples was made using the Hiden SIMS Workstation. The instrument is fitted with cesium and oxygen primary ion guns and the MAXIM quadrupole mass spectrometer for the detection of positive and negative secondary ions. The powder
samples were imprinted into indium chips and excess was blown off with nitrogen to create a thin layer on the surface of the indium. All data were collected using oxygen as the primary ion at 5 keV. Where a reference is not available, direct comparison between samples can provide valuable information about the relative concentrations in the material.

### 3.2.4 Catalytic Oxidation of Cyclohexane

A general procedure for the oxidation of cyclohexane is given below. 1 mL of cyclohexane (13mmol) was mixed with 10 mg of catalyst and 0.1 mL of tert-Butylhydroperoxide. The reaction was allowed to stir at room temperature for 20 minutes and then was loaded in a high pressure reactor under 50 psi He and 100 psi oxygen. The reaction was raised to 120 °C for 12 hours. The mixture was cooled post the reaction, the catalyst was removed by filtration and the solution was analyzed under an Agilent 5975 Gas Chromatograph equipped with an Electron Impact-Quadrupole Mass Spectrometer. The conversion was measured by comparing the peak areas of the reactant and products. The selectivity was calculated as follows: (peak area of particular product/peak area of all products) x 100%.

### 3.3 Results

#### 3.3.1 Material Characterization

XRD was done on the Cu and Fe-doped TiO$_2$ samples as-synthesized and at 500 °C to determine the phase of the titanium dioxide that was produced and to qualitatively assess whether contaminant phases (namely CuO$_x$ or Fe$_x$O$_y$) existed in the material. Data obtained from the instrument show an amorphous material with little evidence of crystallization outside of the initial evolution of the (101) planes in both the Cu and Fe-doped TiO$_2$ (Figure 3.1, Figure 3.2).
Calcination to 500 °C results in the evolution of a complete anatase phase, with the (101) peak clearly shown. No evidence can be found for any contaminant phases (e.g. Cu$_x$O$_y$, Fe$_x$O$_y$) present in this material. Reflections and crystal planes can be observed at 25.3° (101), 37.8° (103, 004, 112), 48.0° (200), 54.9° (105, 211), 62.7° (213, 214), 70.5° (116, 220), and 74.9° (215, 301) for Fe-TiO$_2$ calcined to 500 °C and 25.3° (101), 37.8° (103, 004, 112), 48.0° (200), 54.1° (105), 55.1° (211), 62.8° (213, 204), 69.0° (116), 70.4° (220), and 75.2° (215, 301) for Cu-TiO$_2$ calcined to 500 °C.

![Figure 3.1- 5% Fe-TiO$_2$ X-Ray diffraction pattern for 50 °C and 500 °C.](image)

*Figure 3.1- 5% Fe-TiO$_2$ X-Ray diffraction pattern for 50 °C and 500 °C.*
Fig. 3.2 - 5% Cu-TiO₂ X-Ray diffraction pattern for 50 °C and 500 °C.

N₂ sorption isotherms for these materials were gathered (Fig. 3.3, Fig. 3.4). The surface area of the material was significantly higher for the Cu-TiO₂ aerogel heated to 50 °C versus the 500 °C (412 m²/g vs. 81 m²/g). Pore volume decreased and pore size increased as temperature increased (2.5 to 1.1 cc/g, 24.5 to 54 nm). Little to no change was observed for any of these properties as a result of the heat treatment for the Fe-TiO₂ aerogels (Table 3.1).
Figure 3.3- N₂ sorption isotherms for 5% Cu-TiO₂ aerogels calcined to 50 °C and 500 °C.
Figure 3.4- N₂ sorption isotherms for 5% Fe-TiO₂ calcined to 50 °C and 500 °C.

Table 3.1- Summary of N₂ sorption data for calcined and uncalcined Fe-TiO₂ and Cu-TiO₂ aerogels.

<table>
<thead>
<tr>
<th>Sample Identity</th>
<th>Surface Area (m²/g)</th>
<th>Pore Volume (cc/g)</th>
<th>Pore Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuTiO₂ – 50 °C</td>
<td>412</td>
<td>2.5</td>
<td>24.5</td>
</tr>
<tr>
<td>CuTiO₂ – 500 °C</td>
<td>81</td>
<td>1.1</td>
<td>54.0</td>
</tr>
<tr>
<td>FeTiO₂ – 50 °C</td>
<td>112</td>
<td>1.1</td>
<td>36.0</td>
</tr>
<tr>
<td>FeTiO₂ – 500 °C</td>
<td>118</td>
<td>1.1</td>
<td>37.9</td>
</tr>
</tbody>
</table>
SEM images were obtained for the uncalcined and calcined Fe and Cu-TiO\textsubscript{2} samples (Figure 3.5). Some charging effects are observed but do not hinder analysis of the image proper at a distance, but did limit the magnification ability during analysis (WD < 10 µm for uncalcined, WD < 5µm for calcined). Nanotextures can be observed on all samples regardless of dopant and calcination temperature. EDS measurements show that both Cu and Fe are present in the doped samples (Figure 3.6). Elemental mapping shows the Cu and Fe dispersed throughout the surface of the sample (Figure 3.7).
Figure 3.5- SEM images for a) 5% Fe-TiO$_2$ as synthesized, b) 5% Cu-TiO$_2$ as synthesized, c) 5% Fe-TiO$_2$ calcined to 500 °C, and d) 5% Cu-TiO$_2$ calcined to 500 °C.
Figure 3.6- EDS graphs for a) 5% Fe-TiO\(_2\) and b) 5% Cu-TiO\(_2\).
Figure 3.7- EDS mapping for a) Cu-TiO$_2$ and b) Fe-TiO$_2$ aerogels.

High resolution XPS data were obtained for the 500°C calcined Cu and Fe-TiO$_2$ samples (Figure 3.8, Figure 3.9). For Cu-TiO$_2$, the Cu 2p 3/2 peak can be observed at 933.41 eV, and Ti 2p 3/2 and 2p ½ at 459.36 and 465.05 eV, respectively. Deconvolution of the O 1s shows two distinct areas, one attributable to the Ti-O bond at 530.66 eV and one a Ti-OH bond at 532.39 eV. The Fe-TiO$_2$ shows a 2p ½ and 2p 3/2 at 723.85 eV and 710.43 eV, respectively, with evidence of a satellite peak for the 2p 3/2 at 714.32 eV. The Ti region shows the 2p 3/2 and 2p ½ at 459.73 and 465.42 eV, respectively, with the O 1s deconvoluting into the Ti-O and Ti-OH regions as with the Cu, with peak positions at 530.60 eV and 532.54 eV, respectively.
Figure 3.8- High-resolution XPS spectra for 5% Cu-TiO$_2$ calcined to 500 °C.
Figure 3.9- High-resolution XPS spectra for 5% Fe-TiO$_2$ calcined to 500 °C.
SIMS data were gathered for both the Cu and Fe-doped TiO$_2$ aerogels calcined to 500 °C (Figure 3.10, Figure 3.11). Each frame corresponds to roughly 1 nm of depth in the material. After 70+ nm for the Cu-TiO$_2$ sample we observe a constant ratio of Cu to Ti total intensities as depth increases. A similar observation can be made for the Fe-TiO$_2$ after approximately 60 nm.

Figure 3.10- SIMS of 5% Cu-TiO$_2$ aerogel heated to 500 °C.
3.3.2 Cyclohexane Oxidation

Oxidation of cyclohexane was carried out using the 5% Fe and 5% Cu-TiO$_2$ aerogels (Table 3.2). Initial experiments focused on determining which catalyst performed the best with respect to conversion and selectivity. Commercial anatase titania was tested and shown to have a conversion percentage of 16%, giving a mixture of the ketone and alcohol products. TiO$_2$ aerogel calcined to 500 °C shows a conversion of 18% with selectivity of 53% alcohol, 47% ketone. The Cu-TiO$_2$ and Fe-TiO$_2$ samples calcined to 500 °C were shown to have conversions of 60% and 50%, respectively, with the Cu-TiO$_2$ exhibiting selectivity of 60% to 40%, alcohol to ketone. No activity was seen under catalyst free conditions.
Cu-TiO₂ was chosen as the ideal catalyst due to the high conversion observed and the next step focused on determining the optimum calcination temperature of the catalyst (Table 3.3). As synthesized, 300 °C, 400 °C and 500 °C samples were tested, with the 500 °C material giving the highest conversion of 60%, with selectivities of 60% and 40%, alcohol to ketone.
Catalyst calcination scheme for oxidation of cyclohexane. \(^a\)Reaction conditions: Cyclohexane (9 mmol, 1.0 mL), 5% Cu-TiO\(_2\) Catalyst (10 mg), 100°C, TBHP (1 mmol, 0.1 mL), 8 h, 100 psi He, 200 psi O\(_2\). \(^b\)Conversions and selectivities were determined by GC-MS.

Catalyst amount was varied to determine its effect on conversion (Table 3.4). 15 mg was shown to give the highest conversion at 75%, with selectivity of 80% to 20%, alcohol to ketone. 20 mg gave the same values as 15 mg.
Table 3.4- Catalyst amount for oxidatin of cyclohexane\textsuperscript{a}. \textsuperscript{a}Reaction conditions: Cyclohexane (9 mmol, 1.0 mL), 5\% Cu-TiO\textsubscript{2} Catalyst, 100°C, TBHP (1 mmol, 0.1 mL), 8 h, 100 psi He, 200 psi O\textsubscript{2}. \textsuperscript{b}Conversions and selectivities were determined by GC-MS.

Oxidant used was varied to determine what impact it would have on conversion (Table 3.5). Oxidants tried were \textit{tert}-butylhydroperoxide (TBHP), cumene-hydroperoxide, phthalic acid, benzoyl peroxide and 3-chloroperoxybenzoic acid. TBHP gave the highest conversions and selectivities, and no activity was observed for the sample with no oxidant.
Table 3.5- Oxidant scope for the oxidation of cyclohexane\textsuperscript{a}. \textsuperscript{a}Reaction conditions: Cyclohexane (9 mmol, 1.0 mL), 5\% Cu-TiO\textsubscript{2} Catalyst (15 mg), 100\textdegree{}C, TBHP (1 mmol, 0.1 mL), 8 h, 100 psi He, 200 psi O\textsubscript{2}. \textsuperscript{b}Conversions and selectivities were determined by GC-MS.

Amount of oxidant was optimized to ensure that correct amount is used to give the highest conversions and selectivities possible (Table 3.6). The highest activity was observed for the 0.2 mL oxidant trial, which gave conversion of 85\% with 85\% selectivity towards the alcohol.
<table>
<thead>
<tr>
<th>Entry</th>
<th>Oxidant Amount (mL)</th>
<th>Conv. (%) (^b)</th>
<th>Selectivity (%) (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.05 mL</td>
<td>50</td>
<td>60</td>
</tr>
<tr>
<td>2</td>
<td>0.10 mL</td>
<td>75</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>0.15 mL</td>
<td>80</td>
<td>85</td>
</tr>
<tr>
<td>4</td>
<td>0.2 mL</td>
<td>85</td>
<td>85</td>
</tr>
<tr>
<td>5</td>
<td>0.22 mL</td>
<td>85</td>
<td>85</td>
</tr>
<tr>
<td>6</td>
<td>None</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 3.6- Oxidant amount scope for the oxidation of cyclohexane\(^a\). \(^a\)Reaction conditions: Cyclohexane (9 mmol, 1.0 mL), 5% Cu-TiO\(_2\) Catalyst (10 mg), 100°C, TBHP, 8 h, 100 psi He, 200 psi O\(_2\). \(^b\)Conversions and selectivities were determined by GC-MS.

Substrate amount was varied to observe the impact it would have on conversion and selectivity (Table 3.7). 0.5 mL of cyclohexane was determine to be the best via the >99% conversion and selectivity that was observed. Below 1.5 mL of substrate, conversions and selectivities remained high (>85%).
Table 3.7 Substrate amount scope for oxidation of cyclohexane.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate Amount (mL)</th>
<th>Conv. (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Selectivity (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1a</td>
<td>2a</td>
</tr>
<tr>
<td>1</td>
<td>0.5</td>
<td>&gt;99</td>
<td>&gt;99</td>
</tr>
<tr>
<td>2</td>
<td>0.75</td>
<td>95</td>
<td>90</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
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<td>85</td>
</tr>
<tr>
<td>4</td>
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<td>65</td>
<td>60</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

Table 3.7- Substrate amount scope for oxidation of cyclohexane.<sup>a</sup> Reaction conditions: Cyclohexane 5% Cu-TiO<sub>2</sub> Catalyst (10 mg), 100°C, TBHP (0.2 mL, 2 mmol), 8 h, 100 psi He, 200 psi O<sub>2</sub>.<sup>b</sup> Conversions and selectivities were determined by GC-MS.

3.4 Discussion

3.4.1 Material Characterization

XRD patterns show little to no difference between the doped materials and the undoped titania aerogels produced previously (<strong>Figure 3.1, Figure 3.2</strong>). SEM images of both uncalcined and calcined Fe and Cu-TiO<sub>2</sub> samples show little difference between the morphologies as function of dopant (<strong>Figure 3.5</strong>). The surface of the uncalcined samples is rough and there are multiple aggregates of smaller particles throughout. This effect becomes more pronounced in the calcined samples. EDS shows a good dispersion of the copper and iron dopants throughout the
material (Figure 3.6, Figure 3.7), which is corroborated by the SIMS data that show the titanium and each dopant track well with each other via the ratio of their relative intensities (Figure 3.10, Figure 3.11). XPS confirms the presence of both Fe and Cu in their respective materials, with peaks in the Fe suggestive of the 2+ oxidation state (Figure 3.8, Figure 3.9). Lack of a satellite peak for Cu$^{2+}$ suggested a +1 oxidation state but is not conclusive.

N$_2$ sorption data show a significant uptake in nitrogen at relative pressures below 0.2 for the 50 °C calcined Cu-TiO$_2$, which is indicative of the presence of micropores in the material (Figure 3.3). The high surface area observed is similar to that which was observed for the 5% Zr-TiO$_2$ synthesized previously (Table 3.1). As expected, the surface area came down for the Cu-TiO$_2$ as calcination temperature increased, along with the pore volume. Pore size increased, which is typical as the material starts to agglomerate and form larger particles which lead to larger pore sizes. Fe-TiO$_2$ showed little to no change in any surface properties with increases in calcination temperature (Figure 3.4). This was unusual as typically these parameters will change drastically with such dramatic temperature changes. It is unclear at present why this has occurred.

### 3.4.2 Oxidation of Cyclohexane

The oxidation reaction of cyclohexane was initially carried out using commercial titania, synthesized titania aerogel, and the Cu/Fe doped TiO$_2$ aerogels produced (Table 3.2). The goal was to determine the best candidate system for optimization. This proved to be the 5% Cu-TiO$_2$, which gave the highest conversions and selectivities relative to the other catalysts chosen. As such, optimization began with this material. With no catalyst present, no reaction took place. This confirms that the activity is the result of the addition of the catalyst.
The Cu-TiO$_2$ catalyst calcination temperature was varied to determine the impact that crystallinity and surface area would play on the overall activity of the material (Table 3.3). Even the 50 °C sample showed some activity for the reaction, with no selectivity (50:50 mixture of alcohol:ketone products with 20% conversion). The 500 °C calcined sample, which was what was used in the initial catalyst scope, proved to give the best conversion (60%). The crystallinity of the titania is playing a role in reaction.

Initial catalyst amounts were 10 mg but this parameter needed to be optimized to see when the effect of the catalyst would be maximized (Table 3.4). This mass was discovered to be 15 mg as above this, conversions and selectivities did not change. This mass was carried through to future reactions.

Oxidation of cyclohexane requires oxidant in order for the reaction to proceed, as proven in the oxidant scope trials (Table 3.5). As such, the oxidant type was varied to determine the impact on both conversion and selectivity toward the alcohol. Peroxide effects were studied using different peroxides compared to the TBHP which had been used for every prior reaction. Acid oxidants were also tried to see the effect they had on the reaction. TBHP gave the highest conversion and selectivities.

With TBHP determined to be the best oxidant, the amount was then optimized (Table 3.6). After 0.2 mL of oxidant, a leveling off in both conversion and selectivity and conversion can be observed, allowing us to conclude that the 0.2 mL is optimal for these conditions.

The last parameter varied was the amount of substrate (Table 3.7). As more substrate is added, the conversions and selectivities decrease above 0.5 mL of substrate. This may be due to not giving the catalyst enough time to work with the additional substrates that we have added.


3.5 Conclusion

Cu-TiO₂ and Fe-TiO₂ catalysts were successfully synthesized and characterized. XRD showed to formation of the anatase phase of titania, while EDS, XPS, and SIMS showed clearly the uniform presence of both Cu and Fe in their respective materials. Both were shown to have relatively high surface areas even after calcination to over 500 °C. Pore volumes were also high, in line with what is expected of an aerogel material. The oxidation of cyclohexane was carried out with both catalysts, with Cu-TiO₂ being determined to be the better of the two. Calcination temperature, catalyst amount, oxidant identity, oxidant amount, and substrate amount were all optimized to yield a set of conditions with the Cu-TiO₂ catalyst that yielded >99% conversion and >99% selectivity for cyclohexanol.
Chapter 4. Mesoporous Metal Oxide Aerogels for Various Applications

4.1 Introduction

Mesoporous materials have been a research focal point for the greater part of the last three decades. They are defined as materials with pore sizes in the 2-50 micron region. In general, these porous materials also have correspondingly high pore volumes and surface areas. The development of these materials took off after the discovery of MCM-41 and MCM-41S by researchers at Mobil, with thousands upon thousands of projects being centered around these types of materials.70

Previously in our research group, we have focused on a particular synthetic method utilizing an inverse micelle approach, whereby metal oxide nanoclusters are formed, stabilized via nitric acid addition and isolated as hydrates in the center of the inverse micelle that is formed using a suitable surfactant material, in these cases being Pluronic P-123 (PEG-PPG-PEG) surfactant. Upon application of heat at controlled rates, the removal of solvent and surfactant would leave behind a porous microstructure, with varied pore size tunable via the final calcination temperature employed during the synthesis.5,29,65

The role of a regular pore structure and the ability to tune the pore structure’s effect on activity have been documented before and shown to be important parameters in overall activity of a given material.71,72 The ability of molecules to readily access active surface area of a catalyst is crucial to the catalytic activity of the material in question. Regular pore sizes, especially when tunable, allow for the facile adaptation of a catalyst to different possible reactions and molecules of varied sizes and shapes.
While this method has yielded interesting results that have been dutifully researched and published, one limitation is that in certain systems the surface area of these materials tends to be on the lower end of the spectrum (< 100 m$^2$/g), at least when compared to the aerogel materials that have been produced in these labs before, especially when calcined to temperatures in excess of 200 °C. As such, incorporation of the mesoporous synthetic scheme into the supercritical drying aerogel procedure could yield a “best of both worlds” material that exhibits extremely high surface area, monomodal mesopores, and high pore volumes.

To take it one step further, previous work has also indicated that the incorporation of metal dopants into the titania network have a vast impact on the overall activity of the material, and has been shown to do so for various reactions including hydrogen production, total oxidations, and solvent-free syntheses. With this knowledge in hand, the combination of all three factors may yield a material with even higher levels of catalytic activity that the previous materials did.

### 4.2 Experimental

#### 4.2.1 Chemicals

Titanium (IV) tetraisopropoxide (TTIP, 97+% purity), iron (III) nitrate nonahydrate, copper (II) nitrate trihydrate, nitric acid (70%), 1-butanol (>99.4%), manganese (II) nitrate tetrahydrate, zirconium (IV) propoxide solution (70 wt%), Poly (ethylene glycol)-block-Poly(propylene glycol)-block-Poly(ethylene glycol) PEO$_{20}$-PPO$_{70}$-PEO$_{20}$ (Pluronic P-123), tert-butylhydroperoxide, cumene-hydroperoxide, phthalic acid, benzoyl peroxide, 3-
chloroperoxybenzoic acid, cyclohexane and acetone were obtained from Sigma Aldrich and used as received.

4.2.2 Catalyst Preparation

A sol-gel method was employed to obtain a clear titanium dioxide gel. In a typical synthesis, 3 mL of TTIP was dissolved in a solution containing 3 mL of 1-butanol, 1 g of P-123, 1 g of nitric acid. The solution is then allowed to gel. The sample is loaded into a custom-built supercritical CO$_2$ drier. CO$_2$ is then exchanged into the system, and the butanol is purged via a check valve along with solid carbon dioxide. This is repeated until no 1-butanol is observed in collected carbon dioxide.

In the first step of the drying process, the manuclave body is heated incrementally from -20 $^\circ$C to 42 $^\circ$C, with pressure being increased to 1300 psi. CO$_2$ was released manually via a ball valve to keep the pressure change from fluctuating greater than ±100 psi from a steady value. Once at the desired values for temperature and pressure, the system is closed and held isobarically and isothermally for thirty minutes, then heated to a temperature of 60 $^\circ$C and pressure of 1400 psi. This system is again held isobarically and isothermally for twenty minutes, then reheated to 60 $^\circ$C and a pressure of 1300 psi. These steps are taken to ensure that the system stays above or at the supercritical point of carbon dioxide (1071 psi at 31 $^\circ$C), which is critical to this drying process and the obtaining of the aerogel material. Once the last step is completed, the drier is allowed to depressurize slowly over the course of approximately three hours.

The resulting sample is removed from the drier and heat treated to 120 $^\circ$C for 3 hours to start the removal process of the P-123 surfactant. The sample is then washed with pure ethanol to
help remove the P-123 surfactant. The sample is then calcined to 150°C, 250 °C, 300 °C, 400 °C, and 500 °C.

4.2.3. Characterization

Powder XRD patterns were recorded on a Rigaku Ultima IV X-ray diffractometer operated at 40 kV and 44 mA using Cu Kα radiation (1.5418 Å). All patterns were taken as continuous scans at 2.00° min⁻¹. SEM was carried out on all samples using a FEI Nova NanoSEM 450 with a beam voltage of 2 kV. Little to no charging was present on the samples so no coatings were necessary. Each sample was mounted on aluminum stubs with carbon tape.

BET (Brunauer-Emmett-Teller) surface area measurements were performed using NOVA-e Series Model 25/26 NovaWin/NovaWin-CFR Gas Sorption System. Samples were dried in a vacuum oven at 100 °C for 3 hours prior to analysis. Surface area was determined via multi-point BET method using the first five data points of the adsorption curve. Energy-dispersive spectroscopy (EDS) was carried out using an Oxford AZtecEnergy Microanalysis System with X-Max 80 Silicon Drift Detector and an accelerating voltage of 15 kV. Samples were probed for relative zirconium amount. Each sample was mounted on aluminum stubs with carbon tape. Raman spectroscopy was carried out using a Renishaw System 2000 with a laser wavelength of 514 nm and microscope objective set to 50X. Two accumulations were collected for each sample at 50% laser power to avoid burning.

UV-Vis spectroscopy measurements were made using a Shimadzu UV-2450 ultraviolet-visible spectrophotometer with a scanning range of 200-800 nm. Diffuse-reflectance UV-Vis (DRUV-VIS) was measured using 50 mg of catalyst diluted in barium sulfate using an attachment for the Shimadzu instrument. X-ray photoelectron spectra (XPS) characterization of
the synthesized materials were done on a PHI model Quantum 2000 spectrometer with scanning ESCA multiprobe (Φ Physical Electronics Industries Inc.), using Al Kα radiation (λ=1486.6 eV) as the radiation source. The spectra were recorded in the fixed analyzer transmission mode with pass energies of 187.85 eV and 29.35 eV for recording survey and high resolution spectra, respectively. The powder samples were pressed on a double sided carbon tape mounted on an Al coupon pinned to a sample stage with a wash and screw, then placed in the analysis chamber. The XPS spectra obtained were analyzed and fitted using CasaXPS software (version 2.3.16). Sample charging effects were eliminated by correcting the observed spectra with the C 1s BE value of 284.8 eV.

Secondary Ion Mass Spectrometry (SIMS) analysis of samples was made using the Hiden SIMS Workstation. The instrument is fitted with cesium and oxygen primary ion guns and the MAXIM quadrupole mass spectrometer for the detection of positive and negative secondary ions. The powder samples were imprinted into indium chips and excess was blown off with nitrogen to create a thin lay on the surface of the indium. All data were collected using oxygen as the primary ion at 5keV. Where a reference is not available, direct comparison between samples can provide valuable information about the relative concentrations in the material.

4.2.4. Photocatalytic Activity Testing

Cool white (λ = >350-700 nm, centered at 8 W) lamps were used as sources of visible light. Sixteen lamps were installed and equally spaced in a Rayonet Model RPR-100 photochemical chamber reactor. The activity of the catalyst was measured specifically in terms of degradation of methylene blue (MB) dye with a starting concentration of 1 x 10^{-4} M. To this solution, 25 mg of catalyst was added along with a magnetic stir bar. Aliquots (3 mL) were taken
every 30 minutes for 180 minutes. Samples were centrifuged to separate catalyst from the solution and UV-Vis spectroscopy was then run, with tracking of the 665 nm absorption peak being used to monitor degradation. Degradation efficiency was calculated percent concentration remaining in solution at the given time ($C/C_0 \times 100\%$).

### 4.2.5. Cyclohexane Oxidation Reaction

A general procedure for the oxidation of cyclohexane is given below. 1 mL of cyclohexane (13mmol) was mixed with 10 mg of catalyst and 0.1 mL of tert-Butylhydroperoxide. The reaction was allowed to stir under room temperature for 20 minutes and then was loaded in a high pressure reactor under 50 psi He and 100 psi oxygen. The reaction was raised to 120 °C for 12 hours. The mixture was cooled post the reaction, the catalyst was removed by filtration, and the solution was analyzed under an Agilent 5975 Gas Chromatograph equipped with an Electron Impact-Quadrupole Mass Spectrometer. The conversion was measured by comparing the peak areas of the reactant and products. The selectivity was calculated as follows: (peak area of particular product/peak area of all products) $\times 100\%$.

### 4.3 Results

#### 4.3.1 Characterization of UCT-$\text{TiO}_2$ aerogels

XRD was done on these resulting materials post calcination showed the presence of anatase $\text{TiO}_2$ as low as the 150 °C calcination temperature (Figure 4.1). As the calcination temperature increases from 150 to 500 °C, we observe an increase in the relative intensity of the 101 peak of anatase but also at evolution of the (100) peak for the rutile phase of TiO$_2$. No other peaks for rutile are observed in this or any other sample from this series.
Figure 4.1 - XRD pattern for 150-500 °C calcined Aero UCT-TiO2.

N2 sorption data were obtained for samples at all calcination temperatures (Figure 4.2).

A shift in the isotherm to higher relative volumes can be observed as the calcination temperature is increased, with the shift peaking at 300 °C. Type IV isotherms, indicative of mesoporous range (2-50 nm) pore sizes is observed for all samples. The 150 °C sample shows large volume uptake in the low relative pressures region ( > 0.1), which indicates microporous pores (< 2 nm in size). From here, the isotherm shifts to lower volumes up until 500 °C, which is well below the original 150 °C isotherm. A similar trend can be observed in the surface area and pore volumes (Figure 4.3), with both values peaking at 300 °C (359 m²/g, 0.61 cc/g) and decreasing as the temperature increases to 500 °C (145 m²/g, 0.31 cc/g) (Table 4.1). The pore size distribution overall shifts to
larger pore sizes, with an increase in peak height of the distribution and a shift to larger pore sizes as the calcination temperature increases (Figure 4.4). Average pore sizes also increase throughout, from 3.5 nm to 8.6 nm (Figure 4.5)(Table 4.1).

![N2 adsorption/desorption isotherms for 150-500 °C calcined samples of Aero UCT-TiO2.](image)

Figure 4.2- N2 adsorption/desorption isotherms for 150-500 °C calcined samples of Aero UCT-TiO2.
Figure 4.3- Pore volume and BET surface area measurements as a function of calcination temperature from 150-500 °C Aero UCT-TiO2.
Figure 4.4-BJH pore size distribution for 150-500 °C calcined Aero UCT-TiO₂.
Figure 4.5- Average pore size for 150-500 °C calcined aero UCT-TiO₂.
<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Surface Area (m²/g)</th>
<th>Pore Volume (cc/g)</th>
<th>Avg. Pore Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>249</td>
<td>0.43</td>
<td>3.5</td>
</tr>
<tr>
<td>250</td>
<td>355</td>
<td>0.57</td>
<td>6.4</td>
</tr>
<tr>
<td>300</td>
<td>359</td>
<td>0.61</td>
<td>6.8</td>
</tr>
<tr>
<td>400</td>
<td>231</td>
<td>0.47</td>
<td>8.1</td>
</tr>
<tr>
<td>500</td>
<td>145</td>
<td>0.31</td>
<td>8.6</td>
</tr>
</tbody>
</table>

Table 4.1- Summary of N₂ adsorption/desorption data for 150-500 °C calcined aero UCT-TiO₂.

XRD data for the samples calcined directly from 150 °C to 500 °C showed similar crystallographic information relative to that of the stepwise heating method. A broad anatase (110) peak can be observed at 150 °C, developing into a sharp peak at the higher calcination temperature. A small, but sharp, peak can be seen for the (101) of the rutile phase, which occurs in the 500 °C sample (Figure 4.6).
Figure 4.6- XRD of aero UCT-TiO$_2$ calcined directly to 500 °C.

N$_2$ sorption data for these samples show a stark decrease in the volume adsorbed as calcination temperature is increased (Figure 4.7). This can be correlated with an overall decrease in the pore volume and surface areas (227 m$^2$/g, 0.43 cc/g to 77 m$^2$/g, 0.16 cc/g, respectively) (Figure 4.8) (Table 4.2). The pore size distribution shifts to larger values with the increase in calcination temperature (Figure 4.9) and the average pore size increased from 6.2 to 8.4 nm. Type IV isotherms are observed for both calcination temperatures, which is indicative of mesoporous (2-50 nm) pore sizes in the material.
Figure 4.7 - N$_2$ adsorption/desorption isotherms for aero UCT-TiO$_2$ calcined directly to 500 °C.
Figure 4.8- Surface area, pore volume and pore size for aero UCT-TiO$_2$ calcined directly to 500 °C.
Figure 4.9- BJH pore size distribution for aero UCT-TiO$_2$ calcined directly to 500 °C.
Table 4.2- Summary of N<sub>2</sub> adsorption/desorption data for aero UCT-TiO<sub>2</sub> calcined directly to 500 °C.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Surface Area (m&lt;sup&gt;2&lt;/sup&gt;/g)</th>
<th>Pore Volume (cc/g)</th>
<th>Avg. Pore Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>227</td>
<td>0.43</td>
<td>6.2</td>
</tr>
<tr>
<td>500</td>
<td>77</td>
<td>0.16</td>
<td>8.4</td>
</tr>
</tbody>
</table>

SEM images for these samples show little to no change as calcination temperature increases in both the direct and stepwise calcination methods (Figure 4.10, Figure 4.11). All surfaces show a high degree of surface roughness. No apparent particle size preference is observed, with particles ranging from a few hundred nanometers to a few microns. Some larger sections are agglomerations of smaller nanometer size particles.
Figure 4.10- SEM image of aero UCT-TiO$_2$ calcined directly to 500 °C.
Figure 4.11- SEM images of 150-500 °C calcined aero UCT-TiO₂.

High-resolution XPS was done on both the quick and slow heated UCT-TiO₂ aerogels. No difference was observed so a representative sample is shown (Figure 4.12). Observed are peaks for the Ti 2p 3/2 at 459.38 and 2p ½ at 465.09 eV, and upon deconvolution the O 1s shows peaks for a Ti-O region at 530.59 eV and Ti-OH at 531.60 eV.
Figure 4.12- High-resolution XPS spectra for UCT-TiO\textsubscript{2} aerogel calcined to 500 °C.
4.3.2 Characterization of Doped UCT-TiO$_2$ Aerogel Samples.

XRD data were gathered for all doped UCT-TiO$_2$ aerogels. The Mn, Zr, Cu, and Fe-doped UCT-TiO$_2$ samples all displayed similar diffraction patterns with no real deviation in peak location or intensity (Figure 4.13, Figure 4.14, Figure 4.15, Figure 4.16). The anatase phase is present in all samples at 500 °C calcination temperature. At the 150 °C calcination temperature, all samples show the beginning of the evolution of the (110) peak of anatase titania, which gradually becomes sharper as the calcination temperature is increased.

![XRD graph](image)

Figure 4.13- XRD of 150-500 °C calcined 5% Mn-doped aero UCT-TiO$_2$. 
Figure 4.14- XRD of 150-500 °C calcined 5% Zr-doped aero UCT-TiO₂.
Figure 4.15- XRD of 150-500 °C calcined 5% Cu-doped aero UCT-TiO$_2$. 
Figure 4.16 - XRD of 150-500 °C calcined 5% Fe-doped aero UCT-TiO$_2$.

SIMS was carried out on all samples. The ratio of the total intensities for the Cu, Fe, Mn and Zr dopants in all UCT-TiO$_2$ aerogels to titanium remained constant throughout the material as each monolayer was removed and analyzed (Figure 4.17, Figure 4.18, Figure 4.19, Figure 4.20). There was little significant difference between the Cu, Fe, and Mn intensities relative to the Ti intensity. The Zr intensity is significantly less than that of the Ti but the ratio remains constant.
Figure 4.17- SIMS of 5% Cu-UCT-TiO$_2$ aerogel heated to 500 °C.
Figure 4.18- SIMS of 5% Fe-UCT-TiO$_2$ aerogel heated to 500 °C.
Figure 4.19: SIMS of 5% Mn-UCT-TiO$_2$ aerogel heated to 500 °C.
Figure 4.20- SIMS of 5% Zr-UCT-TiO$_2$ aerogel heated to 500 °C.

N$_2$ sorption experiments were done for all doped samples. All doped samples, excluding the copper, show similar isotherms for their 150°C and 500 °C calcination temperatures (Figure 4.21). All samples display a monomodal pore size distribution that shifts to lower pore sizes as calcination temperature increases, except the copper sample which, when calcined to 150 °C displays a bimodal distribution (Figure 4.22). Surface areas for the Fe, Mn, and Zr doped samples were in excess of 180 m$^2$/g. The copper surface area was much lower at 82 m$^2$/g for the 150 °C sample and 90 m$^2$/g for the 500 °C sample. Pore volumes increased as calcination temperature increased for the Fe and Cu doped samples (0.46 to 0.50 cc/g, 0.12 to 0.19 cc/g), stayed the same for the Zr doped sample (0.34 cc/g) and decreased for the Mn doped sample...
(0.38 to 0.27 cc/g). Pore sizes increased as a function of temperature for the Cu, Fe, and Zr doped samples (6.1 to 8.5 nm, 8.0 to 8.9 nm, and 5.9 to 7.3 nm), and stayed the same for the Mn doped sample (6.1 nm) (Table 4.3).

Figure 4.21- N₂ sorption isotherms for doped UCT-TiO₂ aerogels calcined to 150 °C and 500 °C.
Figure 4.22- BJH pore size distribution for doped UCT-TiO$_2$ aerogels calcined to 150°C and 500 °C.

Table 4.3- Summary of N$_2$ sorption data for doped UCT-TiO$_2$ aerogels calcined to 150 °C and 500 °C.
High resolution XPS data were gathered for all doped UCT-TiO$_2$ aerogel samples (Figure 4.23, Figure 4.24, Figure 4.25, Figure 4.26). In general, all samples contained a Ti 2p 3/2 and 2p ½ peak, which appear at 459.32 and 464.94 eV, 459.31 and 464.98 eV, 459.37 and 465.00 eV and 459.39 and 465.11 eV for Cu, Fe, Mn, and Zr-doped UCT-TiO$_2$ aerogels, respectively. The Cu doped sample shows evidence of Ti$^{3+}$ 2p 3/2 based on the shoulder coming off the primary 2p 3/2 peak at 457.81 eV. Deconvolution for the O 1s in the Cu and Fe doped samples show a similar trend for the Cu and Fe doped samples, which show peaks for Ti-O, Ti-OH, and M-O (M= Cu, Fe). The Mn doped sample shows only Ti-O and Ti-OH upon deconvolution, with Zr doped demonstrating only Ti-O. The Cu, Fe and Mn doped samples all show peaks for 2p 3/2 and 2p ½ at 932.30 and 952.13 eV, 710.21 and 723.89 eV, and 641.96 and 653.94 eV, respectively. Evidence of satellite peaks can be seen in the Fe, with a 2p 3/2 satellite at 714.11 eV, and in Mn with satellite for the 2p 3/2 and 2p ½ at 646.27 and 658.70 eV.
Figure 4.23- High-resolution XPS spectra for Cu-UCT-TiO$_2$ aerogel calcined to 500 °C.
Figure 4.24- High-resolution XPS spectra for Fe-UCT-TiO₂ aerogel calcined to 500 °C.
Figure 4.25- High-resolution XPS spectra for Mn-UCT-TiO$_2$ aerogel calcined to 500 °C.
Figure 4.26- High-resolution XPS spectra for Zr-UCT-TiO$_2$ aerogel calcined to 500 °C.
4.3.3 Photocatalytic Reaction with Doped and Undoped UCT-TiO$_2$ Aerogels

Dye degradation experiments were carried out for all samples made. A comparison was made between the UCT-TiO$_2$ aerogel that was heat treated quickly and the UCT-TiO$_2$ aerogel that was heated slowly following the conventional heating scheme that has been used previously (Figure 4.27). Slower heating scheme degraded dye at a faster rate than that of the quick.

![Figure 4.27- Concentration of dye remaining versus time for UCT-TiO$_2$ aerogels heated slowly and quickly to 500 °C.](image)

Dye degradations were then performed for all doped UCT-TiO$_2$ aerogels and comparisons were made between doped UCT-TiO$_2$ aerogels and doped TiO$_2$ aerogels, where
possible (Figure 4.28). Calcination temperature for the Cu-UCT-TiO₂ aerogel was compared to determine the effect temperature had on degradation observed. 5% Zr-TiO₂, which performed the best previously, remained the best catalyst, with 500 °C giving the highest degradation percentage for the Cu-UCT-TiO₂ series and the Zr-UCT-TiO₂ aerogel performing the best among the doped UCT-TiO₂ aerogels produced.

![Figure 4.28](image.png)

**Figure 4.28**- Concentration of dye remaining versus time for doped UCT-TiO₂ aerogels and doped TiO₂ aerogels.
4.3.4 Catalytic Oxidation of Cyclohexane to Cyclohexanol

The oxidation of cyclohexane was carried out using all synthesized UCT-TiO$_2$ aerogels, doped and undoped (Table 4.4). Initial reactions served the purpose of establishing the catalyst scope. All catalysts tested showed some activity for oxidation reaction, with varied selectivities. Cu-UCT-TiO$_2$ aerogel showed increased activity over the rest of the catalysts, including the Cu-TiO$_2$ aerogel (75% conversion vs. 60% conversion). Fe-UCT-TiO$_2$ also showed higher activity than its aerogel counterpart (55% vs. 50%).
<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conv. (%) b</th>
<th>Selectivity (%) b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>UCT-TiO₂</td>
<td>20</td>
<td>53</td>
</tr>
<tr>
<td>2 c</td>
<td>UCT-TiO₂</td>
<td>15</td>
<td>58</td>
</tr>
<tr>
<td>3 c,d</td>
<td>UCT-TiO₂</td>
<td>38</td>
<td>58</td>
</tr>
<tr>
<td>4</td>
<td>5% Cu-TiO₂</td>
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<tr>
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<td>5% Fe-TiO₂</td>
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</tr>
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</tr>
<tr>
<td>10</td>
<td>None</td>
<td>0</td>
<td>nd</td>
</tr>
</tbody>
</table>

Table 4.4- Catalyst scope for oxidation of cyclohexane a. aReaction conditions: Cyclohexane (9 mmol, 1.0 mL), Catalyst (10 mg), 100°C, TBHP (1 mmol, 0.1 mL), 8 h, 100 psi He, 200 psi O₂. bConversions and selectivities were determined by GC-MS based on concentration cyclohexane. c Aerogels. dQuick ramp to 500°C. nd = not determined by GC-MS.

4.4 Discussion

4.4.1 Determination of Ideal Heating Scheme

The goal of incorporating the P-123 surfactant into the aerogel synthesis is to drive the formation of a monomodal, mesoporous pore size distribution. Preliminary research with similar systems using the P-123 surfact that have been published previously have shown a dependence
on the calcination temperatures used along with the specific methodology used to carry out the heating (ramp rates, hold times, etc.). To try to quantify the effects that these parameters had on the actual material produced, two separate calcination schemes were carried out on the produced UCT-TiO$_2$ aerogel materials. The first material was subjected to the conventional heating scheme that had been published previously, with ramp rates of 1 °C/min and holds at 150 °C, 250 °C, 300 °C, 400 °C, and 500 °C for the sample as it’s ramped to the goal calcination temperature of 500 °C. The second was heated to 500 °C directly using the 1 °C/min as the ramp rate. Initial XRD data obtained showed very slight differences between the two materials. Both show evidence of the evolution of the (101) peak for rutile titania, with the quicker heating scheme showing a slightly more intense peak (Figure 4.1, Figure 4.6).

N$_2$ sorption data show the most intense difference between the materials. The slower heating method reveals more information about what is happening to the overall material at each calcination temperature, with increases in overall surface area and pore volume (Figure 4.2, Figure 4.3, Table 4.1). This is likely attributable to the complete removal of surfactant from the material. The pore size distribution is monomodal for all calcination temperatures, moving to higher pore sizes as the temperature increases but remaining firmly in the low mesoporous range (Figure 4.4). As the calcination temperature increased from here, there was an overall collapse of the structure which led to significantly larger pore sizes relative to the initial values and smaller surface areas and pore volumes (Figure 4.5). By comparison, the quicker heating scheme showed worsening effects of this collapse, with significantly lower surface areas and pore volumes and higher pore sizes compared with the slower heating scheme (Figure 4.7, Figure 4.8, Table 4.2). The pore size distribution remains mostly monomodal with a shift to higher pore sizes as calcination temperature increases (Figure 4.9).
SEM images obtained for both materials show a similar story in terms of the features observed (Figure 4.10, Figure 4.11). The material appears to be a collection of small particle agglomerates that result in a surface featuring nanoscale textures. This suggests a high surface area given the level of nanotexture present, which is confirmed in N₂ sorption experiments.

The slight increase in the amount of rutile present in the quicker heating scheme material led us to hypothesize that this material would perform better than its slower counterpart for photocatalytic reactions. Mixtures of anatase and rutile have performed better for numerous photocatalytic reactions, with higher presences of rutile having beneficial effects on the material. Preliminary work explored this using methylene blue dye degradation as a model system for these reactions. The slower calcination scheme has been shown to be the more active species. At present, it is not possible to say what the difference in activity is attributable to, due to the difference in the general surface characteristics of both materials. The slower heating scheme method, due to its larger surface area and pore volume, may have provided more access to active catalyst surface than the quicker heating method, and as such overpowered any beneficial effects that would have been realized from the additional presence of rutile titania.
4.4.2 Dopant Effects on UCT-TiO$_2$ Aerogel

There was no observable difference between the XRD patterns obtained for all of the doped samples (Mn, Cu, Fe, Zr) (Figure 4.13, Figure 4.14, Figure 4.15, Figure 4.16). They did differ, however, from the undoped UCT-TiO$_2$ aerogel samples in that there was no observable peak for the rutile phase of titania, as every peak indexed to anatase. The incorporation of these metal dopants may have a stabilizing effect on the anatase phase and make it energetically unfavorable at these calcination temperatures to transition to rutile.

SIMS data obtained for all samples showed an even distribution of the metal dopant versus titanium throughout the entirety of the material. This suggests that the dopant penetrated the structure rather than remained on the surface of the material. The intensity of the manganese, copper and iron samples relative to the titanium were within an order of magnitude in value, whereas the zirconium concentration was significantly less than that of the titanium for that sample (Figure 4.17, Figure 4.18, Figure 4.19, Figure 4.20). This may indicate that these other ions were more easily able to penetrate the titania lattice.

High-resolution XPS showed little difference between the state of the titanium in all samples, doped and undoped, with the exception being the Cu-UCT-TiO$_2$ aerogel (Figure 4.12, Figure 4.23, Figure 4.24, Figure 4.25, Figure 4.26). While little movement is seen through all in terms of positioning of the 2p 3/2 and 2p ½ of Ti, the Cu-UCT-TiO$_2$ shows evidence via deconvolution of the Ti$^{3+}$ oxidation, as evident by the shoulder centered at 457.81 eV. A small increase in the baseline signal can be observed in the high-resolution scan for copper, centered at 945 eV, which is typically indicative of Cu$^+$. Under ordinary circumstances, ascertaining copper’s oxidation state via XPS is difficult, but the absence of a strong Cu$^{3+}$ satellite between
the 2p 3/2 and 2p ½ peaks suggests no Cu$^{2+}$ is present in the material. Satellite peaks contained in the high resolution scan for Fe suggest the +2 oxidation state. Zirconium’s 3d 5/2 is centered around 182.79 eV, which is where the 4+ oxidation state is. Manganese has two satellites showing, with the feature at 646.27 eV suggesting a 2+ oxidation state. 

Surface area and pore volume changed slightly with respect to calcination temperature for most doped samples, with decreases in surface area seen for most (with the exception of Cu) and increased in pore volume seen for Cu and Fe doped (Zr stayed the same and Mn decreased) (Figure 4.21, Table 4.3). For Cu, Fe, and Zr-UCT-TiO$_2$ aerogels, there was a shift in the pore size distribution to higher values (Figure 4.22). This is sensible given the propensity of the pore walls to collapse under the strain from the calcination to form higher sizes. Little to no change was observed in the Mn doped sample. For all samples pore volumes remained high despite temperature (>0.1 cc/g).

4.4.3 Catalytic and Photocatalytic Reactions Analysis

Initial results for the photocatalytic activity of the UCT-TiO$_2$ aerogels show similar results to the previously analyzed undoped TiO$_2$ aerogel (Figure 4.27, Figure 2.21). The slow heating scheme showed greater activity in that dye concentration reached undetectable levels at the 2 hour mark, whereas for the fast heating scheme it to 2.5 hrs. A comparison was then made between all materials produced, doped and undoped (Figure 4.28). Part of this comparison was also the non-UCT version of dopants that had been used (Zr, Fe, Cu). Observed from this was that the 5% Zr-doped TiO$_2$ aerogel remained the most active material, with the time to reach undetectable levels of dye set at 1.5 hrs. Of the doped materials, the Zr-UCT-TiO$_2$ was the most active, with the reaction time being 2.5 hrs. The effect of calcination temperature on the activity
was also investigated using the Cu-UCT-TiO$_2$ aerogel as an example. Concentration of dye remaining in solution was reduced at the 3 hr mark as calcination temperature increased from 150 to 500 °C.

The oxidation of cyclohexane was carried out using all the doped and undoped UCT-TiO$_2$ aerogels that were synthesized, with activities compared to the Fe and Cu-TiO$_2$ catalysts produced previously (Table 4.4). While no entry compares to optimized Cu-TiO$_2$ (conversion/selectivity > 99%), the Cu-UCT-TiO$_2$ showed conversions higher than that of the unoptimized Cu-TiO$_2$ (75% vs. 60%). With optimization, it is likely that the Cu-UCT-TiO$_2$ activity may transcend that of the Cu-TiO$_2$. All doped samples showed higher activity than the undoped. Interestingly, UCT-TiO$_2$ calcined fast was more active than slow (38% vs. 15%). The presence of a larger percentage of rutile in the material may be leading to higher conversions versus the slow heated material.
4.5 Conclusion

A UCT-TiO$_2$ aerogel was synthesized and characterized. Evaluation of the heating scheme was conducted to determine the optimal material for catalytic reactions. Higher surface areas and pore volumes were observed in the sample heated slowly versus fast. XRD confirms the presence of both anatase and rutile phases of titania in the material for undoped samples, with the disappearance of the rutile phase upon the incorporation of metal dopants. XPS and SIMS confirm the presence of each dopant in their respective materials, with SIMS suggesting a uniform distribution through at least the surface of the material. All materials reside in the mesoporous range with pore sizes between 3.5 and 8.9 nm, and pore volumes between 0.12 and 0.50 cc/g. Preliminary catalytic results show all materials are active for the catalytic oxidation of cyclohexane and the photodegradation of methylene blue. The Zr-UCT-TiO$_2$ aerogel performed the best for the methylene blue degradation, and unoptimized Cu-UCT-TiO$_2$ proved more active than the previous best catalyst for cyclohexane oxidation in this work.
Chapter 5. Future Work

The method developed herein to produce titania aerogels has proven effective, but may be limited in terms of the ability to scale it up. As a result of this, it is imperative that the catalysts used prove to be recyclable, as without this aspect, cost of implementation will be an impermeable barrier. While some work has been done to show that limited changes occur with the Zr-TiO$_2$ as the result of the photocatalytic reactions with methylene blue, it will be interesting to see how the mesoporous structure developed later on reacts to the experimental conditions and if this structure stays intact. Measurements of activity using recycled catalyst should be made as soon as possible.

The Cu-TiO$_2$ system, both UCT and not, have been shown to be active for the cyclohexane oxidation reaction. While the reaction is well-understood in literature, it is imperative to attempt to provide and offer a proof of the mechanism of this transformation. Also, further optimization of the reaction, including variables such as pressure, time, and temperature, could lead to even better conversions. Experimentation with other alkanes outside of cyclohexane would allow us to comment on how versatile the produced catalysts are for the given reactions.

The substrate scope was limited for the dye degradation reactions to methylene blue initially as the primary goal of the research was to first develop a material that was active for photocatalytic reactions. It will be interesting to see how the catalyst performs with anionic or neutral dye substrates to test the theory of surface charge playing a role in the activity of the material.
Chapter 6. References


(39) Li, C.; Zhao, Y. F.; Gong, Y. Y.; Wang, T.; Sun, C. Q. Band Gap Engineering of Early


(54) Crabtree, R. H. The Organometallic Chemistry of the Transition Metals; 2005; Vol. 18.


