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Evaluation of Titanium Dioxide for the Adsorption and Reactivity of the Sulfur Mustard Simulant 2-Chloroethyl Ethyl Sulfide

A Thesis Presented

by

Edward Viveiros

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I’d also like to immortalize some of my very best friends on acid-free paper while I still have the chance: Mom, Dad, Pedro, Tony, Nicole, Jessy, Adam, Jeff, Mike, and Abdul. Tony, I can’t wait until the day we’re both out of school and playing on the same side of the fence once again. I hope it pans out like that summer we played Everquest together, but permanent. Jessy, what on earth are we going to do without our coffee time? Nikki, Adam & Jeff: where are we going to be in five years? One way or another, I hope it’s together. Mike you are the refrigerator that keeps meats fresh; you’re also my much more creative twin. What little time we’ve spent during these past 2 years has been some of the most soothing. Abdul, although you’ve been in California, you’ve always been around in some form or another. You have no idea how many times I’ve asked myself, “WWAH? (What Would Abdul Have Done?)”. You are a man among men and I’ll never forget how great it was while our lives overlapped at NU.

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ABSTRACT

This thesis reports the investigation of the degradation of the sulfur mustard simulant 2-chloroethyl ethyl sulfide (CEES) over the metal oxide TiO₂. The ultimate goal is the development of catalytic adsorbent materials that more effectively decontaminate surfaces at ambient conditions once they have been exposed to chemical warfare agents (CWAs) such as sulfur mustard (HD). TiO₂ is an appealing candidate for this application because of its reported use in photocatalysis and pollution control under ambient conditions. For this reason, the interactions of CEES on commercially available polycrystalline Evonik-Degussa Aeroxide® P25 and amorphous NanoActive™ TiO₂ were investigated. Each commercial sample was analyzed under two thermal pre-activation schemes: oxidized (200 torr O₂ at 400°C for 2 hrs) or reduced (200 torr H₂ at 400°C for 2 hrs).

The thermal pre-activation procedure was found to induce changes in the morphological and crystalline properties of NanoActive (NA) while the P25 remained unchanged. The magnitude of these changes was similar for either oxidation or reduction. Pre-activation of the amorphous NA yielded anatase crystallites with mean diameter of 10 nm. This crystallite formation was accompanied by a decrease in surface area and pore volume by 80 % and 17 %, respectively. Infrared analysis revealed chemical activity at temperatures well above ambient (> 200°C) and is further confirmed by preliminary differential scanning calorimetry data. Long term (40 days) ambient reactivity investigations showed no reactivity for P25 stored at ambient temperature and light conditions. The influence of moisture conditioning was also investigated at two
levels: below 10% RH and at 50% RH. Changes in this variable did not alter the reactivity of P25.

While these samples exhibit very different responses to the thermal pre-activation procedure, these resulting surfaces do not show any improvement in reactivity when compared to the original sample. Since no chemical activity is observed until temperatures exceeding 200°C, it is concluded that neither P25 nor NA are desirable as catalytic adsorbents for CWA decontamination at ambient conditions.
# TABLE OF CONTENTS

LIST OF FIGURES .................................................................................................................. vii

LIST OF TABLES .................................................................................................................... ix

1.0 INTRODUCTION ........................................................................................................ 1

2.0 CRITICAL LITERATURE REVIEW ........................................................................ 3

  2.1 Principle Reaction Mechanisms Employable in HD Decomposition .......... 3
      2.1.1 HD Hydrolysis ................................................................................................. 3
      2.1.2 Nucleophilic Substitution Assisted Reactions .............................................. 4
      2.1.3 HD Oxidation .................................................................................................. 5
  2.2 Substitution of HD with CEES ................................................................................. 6
  2.3 Identification and Assignment of CEES Infrared Vibrational Modes .......... 7
  2.4 Surface Interactions of CEES Adsorbed onto TiO₂ ............................................. 10
  2.5 Reactivity of CEES Adsorbed onto TiO₂ ................................................................. 12

3.0 EXPERIMENTAL ........................................................................................................ 14

  3.1 Materials Used ......................................................................................................... 14
  3.2 Experimental Equipment ....................................................................................... 14
      3.2.1 FT-IR ............................................................................................................... 14
      3.2.2 Thermal Gravimetric Analysis..................................................................... 18
      3.2.3 X-Ray Diffraction ......................................................................................... 18
      3.2.4 Nitrogen Adsorption ..................................................................................... 18
      3.2.5 Differential Scanning Calorimetry ................................................................. 19
  3.3 Experimental Procedures ....................................................................................... 19

4.0 RESULTS AND DISCUSSION ................................................................................ 21

  4.1 Initial Materials Characterization ......................................................................... 21
      4.1.1 NanoActive and Degussa P25 TiO₂ ................................................................. 21
      4.1.2 Infrared Spectrum of Neat Liquid CEES ...................................................... 26
  4.2 Assessment of Thermal Annealing Affects ........................................................... 28
      4.2.1 X-Ray Diffraction ......................................................................................... 28
      4.2.2 Surface Areas after Thermal Annealing ......................................................... 31
  4.3 Reactions of CEES on TiO₂ .................................................................................... 36
      4.3.1 Ambient Condition Interactions .................................................................... 36
      4.3.2 CEES Adsorption Followed by Progressive Heating ................................... 39
      4.3.3 Summary of CEES Interactions Observed on NA and P25 .......................... 46

5.0 CONCLUSIONS .......................................................................................................... 48
LIST OF FIGURES

Figure 1: The mechanism for HD hydrolysis that incorporates sulfonium aggregation as well as reaction reversibility ................................................................. 4

Figure 2: Comparison of the similar spectra of CEES and HD ............................... 7

Figure 3: The comparative method utilized by Mawhinney et al. to assign IR modes .... 8

Figure 4: Effect of oxidation and reduction on the infrared spectra of TiO$_2$ .......... 12

Figure 5: Schematic of the manifold utilized to control testing conditions during IR analysis ................................................................. 16

Figure 6: The mechanical assembly that permits wafer manipulation once it is isolated in vacuum ................................................................. 17

Figure 7: SEM micrographs of NanoActive and Degussa P25 TiO$_2$ ......................... 22

Figure 8: Thermal gravimetric analysis curves for as received NA and P25 .............. 23

Figure 9: XRD spectra of as received NanoActive and Degussa P25 ....................... 24

Figure 10: Nitrogen adsorption isotherms for NA and P25 at 77 K ......................... 25

Figure 11: Pore size distributions of as received NanoActive and Degussa TiO$_2$ in the mesopore range ................................................................. 26

Figure 12: IR absorption spectra of neat, liquid CEES .............................................. 27

Figure 13: XRD spectra comparing oxidized and reduced NanoActive TiO$_2$ to the initial, un-annealed material ................................................................. 29

Figure 14: XRD spectra comparing oxidized and reduced samples of Degussa P25 TiO$_2$ to the initial, as received material ........................................... 30

Figure 15: The adsorption isotherms of the annealed and un-annealed NanoActive ................................. 32

Figure 16: Full N$_2$ adsorption isotherms before and after annealing NanoActive TiO$_2$ .... 33

Figure 17: Pore size distribution for NA before and after annealing .......................... 34

Figure 18: Comparison of the adsorption isotherms for annealed and as received Degussa samples ................................................................. 35
Figure 19: Specific surface areas of NanoActive and Degussa under different pre-activation conditions. ................................................................. 36

Figure 20: IR spectra of CEES adsorbed at room temperature onto oxidized and reduced NanoActive samples. ............................................................... 37

Figure 21: IR spectra of CEES adsorbed at room temperature onto oxidized and reduced Degussa samples. ................................................................. 39

Figure 22: Spectra of wet, oxidized NanoActive samples obtained on heating from ambient temperature to 300°C. ......................................................... 40

Figure 23: Spectra of wet, reduced NanoActive samples obtained on heating from ambient temperature to 300°C. ......................................................... 41

Figure 24: Spectra of dry, oxidized Nanoscale TiO₂ samples obtained on heating from ambient temperature to 300°C. ......................................................... 42

Figure 25: Spectra of dry, reduced Nanoscale TiO₂ samples obtained on heating from ambient temperature to 300°C. ......................................................... 43

Figure 26: Spectra of dry, oxidized Degussa samples obtained on heating from ambient temperature to 400°C. ......................................................... 44

Figure 27: Spectra of dry, reduced Degussa samples obtained on heating from ambient temperature to 400°C. ......................................................... 45

Figure 28: Spectra of as received NanoActive samples obtained on heating from ambient temperature to 500°C. ......................................................... 46

Figure 29: The 2-chloroethyl ethyl sulfide model used by Sosa et al to distinguish individual atomic vibrational contributions. ......................................................... 47
LIST OF TABLES

Table 1: Global figures for stockpiled and destroyed CWAs as declared in 2006 .......... 2

Table 2: Comparison of oxidation and hydrolysis rates for various sulfur mustard derivates .......................................................... 5

Table 3: Comparing the physical properties of HD and CEES ............................................. 6

Table 4: A comparison of the vibrational assignments for 2-CEES ...................................... 10

Table 5: Mean crystallite diameters of variously annealed NanoActive and Degussa P25 samples.................................................................................................................. 31

Table 6: Mean surface areas for NanoActive/Degussa under different annealing conditions ...................................................................................................................... 35
1.0 INTRODUCTION

Despite ongoing international efforts towards chemical demilitarization, the proliferation of chemical warfare agents (CWAs) is still a matter of national security. The global availability of these agents coupled with the Department of Defense’s post-911 attitude towards preparedness against chemical attacks has spurred additional funding to develop decontamination technologies aimed at countering these threats both at home and abroad.

One approach is to utilize high-capacity adsorbents that physically remove and/or catalyze the degradation of CWAs. The addition of catalytic activity would be ideal as such systems simultaneously couple physical removal and chemical deactivation into one process. Of particular interest to this thesis is HD (sulfur mustard) and its subsequent decontamination on TiO$_2$ substrates. The primary CWAs of interest are VX, HD, GB, and GD$^1$ as these are the most toxic and environmentally persistent. [1, 2] Proliferation of these agents is virtually unabated despite global chemical demilitarization efforts initiated by the Chemical Weapons Convention in 1993. Table 1 on the following page provides a detailed list of CWA quantities reported as destroyed or inventoried in 2006 [3]. Of this amount, HD accounts for about 35 percent of the total global CWA stockpile.

---

$^1$ See Table 1 for chemical names and formulae
Table 1: Global figures for stockpiled and destroyed CWAs as declared in 2006. Adapted from [3].

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Common Names</th>
<th>Chemical Formula</th>
<th>Metric Tons Declared</th>
<th>Metric Tons Destroyed</th>
</tr>
</thead>
<tbody>
<tr>
<td>VX</td>
<td>---</td>
<td>C&lt;sub&gt;11&lt;/sub&gt;H&lt;sub&gt;26&lt;/sub&gt;NO&lt;sub&gt;2&lt;/sub&gt;PS</td>
<td>19,590</td>
<td>1,646</td>
</tr>
<tr>
<td>HD</td>
<td>sulfur mustard, mustard gas</td>
<td>(ClCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;S</td>
<td>17,419</td>
<td>3,393</td>
</tr>
<tr>
<td>GB</td>
<td>sarin</td>
<td>C&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;FO&lt;sub&gt;2&lt;/sub&gt;P</td>
<td>15,074</td>
<td>6,967</td>
</tr>
<tr>
<td>GD</td>
<td>soman</td>
<td>C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;16&lt;/sub&gt;FO&lt;sub&gt;2&lt;/sub&gt;P</td>
<td>9,148</td>
<td>0</td>
</tr>
<tr>
<td>HD/L</td>
<td>mixtures of mustard and lewisite</td>
<td>---</td>
<td>6,747</td>
<td>2,528</td>
</tr>
<tr>
<td>L</td>
<td>lewisite</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;AsCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>345</td>
<td>195</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td><strong>48,733</strong></td>
<td><strong>13,083</strong></td>
</tr>
</tbody>
</table>
2.0 CRITICAL LITERATURE REVIEW

2.1 Principle Reaction Mechanisms Employable in HD Decomposition

Sulfur mustard may be destroyed by either hydrolysis and/or nucleophilic substitution of the terminal Cl atoms as well as through the oxidation of the sulfur atom. The following subsections discuss these three possible modes of sulfur mustard decomposition.

2.1.1 HD Hydrolysis

Work done by Bartlett and Swain [4] to verify the original, S_N1-type hydrolysis mechanism for HD resulted in a confirmation of the mechanism illustrated along the top row of Figure 1. The slow complexation of an ethylenesulfonium ion (II) from HD (I) is followed by subsequent reactions with hydronium to yield the mustard chlorohydrin (III) intermediate and, finally, the desired thiodiglycol product (IV). This mechanism was observed to be fast initially, but then slow due to mass transfer limitations occurring as a result of HD polymerization at the HD-H_2O interface.

Later work done by Yang et al. [5] demonstrated that the above mechanism could not sufficiently describe the entire reaction mechanism without the addition of steps leading to the co-formation of three other stable, aggregated sulfonium byproducts (H-TG, CH-TG, and H-2TG) as shown in Figure 1. It was also observed that some of these byproduct yielding steps were reversible and would lead back to the formation of the initial sulfonium ion (II), which contributed to further undesired byproduct formation. This reverse rate was found to increase with increasing concentrations of TG and HCl.
2.1.2 Nucleophilic Substitution Assisted Reactions

Nucleophile assisted destruction of HD is essentially the same mechanism as described in the previous section, however, it also incorporates reaction enhancing effects that occur upon addition of nucleophilic solvents to an HD-H₂O mixture. Such nucleophiles increase the rate determining, sulfonium complexation step (I → II), and eliminate the formation of the sulfonium aggregates that impede HD destruction. [1] Yang et al. [6] established that the increased rate for the determining step is controlled by the nucleophilic solvent’s polarity.
2.1.3 HD Oxidation

Investigations by Yang et al. [7] found that reactions of this type selectively oxidize the sulfur atom of HD to yield non-toxic, crystalline sulfone, \((\text{ClCH}_2\text{CH}_2)_2\text{S} (=\text{O})_2\), and sulfoxide, \((\text{ClCH}_2\text{CH}_2)_2\text{S}=\text{O}\). The main distinction that sets this mechanism apart from the prior nucleophilic substitution reactions mentioned, particularly hydrolysis, is that inhibitory byproducts are not formed through oxidation. Instead, only one product is yielded – the sulfoxide.

While this mechanism offers such an advantage, reaction rates between oxidation and hydrolysis are reportedly the same for HD. [7] Table 2 illustrates how these rates depend on the functional groups attached to the sulfide. It is interesting to note that while the rates of hydrolysis and oxidation are the same for HD (sulfide 1 in Table 2), there is an order of magnitude difference between rates compared for CEPS (sulfide 1e in Table 2). This is because the terminal phenyl group of CEPS changes the nucleophilic properties of CEPS in a manner that substantially slows hydrolysis rates.

Table 2: Comparison of oxidation and hydrolysis rates for various sulfur mustard derivates. Adapted from [7].

<table>
<thead>
<tr>
<th>sulfides</th>
<th>competition oxidation rate</th>
<th>relative hydrolysis rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{ClCH}_2\text{CH}_2)_2\text{S} (1))</td>
<td>1.0</td>
<td>1.0^d</td>
</tr>
<tr>
<td>(\text{C}_2\text{H}_5\text{SCH}_2\text{CH}_2\text{Cl} (1\text{a}))</td>
<td>4.8</td>
<td>5.9</td>
</tr>
<tr>
<td>((\text{C}_2\text{H}_5)_2\text{S} (1\text{b}))</td>
<td>23.0</td>
<td></td>
</tr>
<tr>
<td>(\text{n-C}_2\text{H}_5\text{S} (1\text{c}))</td>
<td>9.6</td>
<td></td>
</tr>
<tr>
<td>((\text{C}_2\text{H}_5)_2\text{S} (1\text{d}))</td>
<td>0.96</td>
<td></td>
</tr>
<tr>
<td>(\text{C}<em>6\text{H}</em>{13}\text{SCH}_2\text{CH}_2\text{Cl} (1\text{e}))</td>
<td>0.92</td>
<td>0.085</td>
</tr>
<tr>
<td>(\text{C}<em>6\text{H}</em>{13}\text{SCH}_2\text{CH}_2\text{Br} (1\text{f}))</td>
<td>1.8</td>
<td>0.76</td>
</tr>
<tr>
<td>(\text{C}<em>6\text{H}</em>{13}\text{SCH}_2\text{CH}_2\text{OH} (1\text{g}))</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>(\text{CH}_3\text{SCH}_2\text{CH}_2\text{Cl} (1\text{h}))</td>
<td>4.2</td>
<td>4.8</td>
</tr>
<tr>
<td>(\text{CH}_3\text{SCH}_2\text{CH}_2\text{OH} (1\text{i}))</td>
<td>10.0</td>
<td></td>
</tr>
<tr>
<td>(\text{i-C}_3\text{H}_7\text{SCH}_2\text{CH}_2\text{Cl} (1\text{j}))</td>
<td>5.0</td>
<td>7.6</td>
</tr>
<tr>
<td>(\text{i-C}_3\text{H}_7\text{SCH}_2\text{CH}_2\text{Cl} (1\text{k}))</td>
<td>5.0</td>
<td>e</td>
</tr>
<tr>
<td>(\text{n-C}_3\text{H}_7\text{SCH}_2\text{CH}_2\text{Cl} (1\text{l}))</td>
<td>5.0</td>
<td>9.0</td>
</tr>
<tr>
<td>(\text{i-C}_3\text{H}_11\text{SCH}_2\text{CH}_2\text{Cl} (1\text{m}))</td>
<td>5.4</td>
<td>e</td>
</tr>
</tbody>
</table>
2.2 Substitution of HD with CEES

Most of the scientific work performed, particularly in academia, must substitute chemically similar compounds for the sulfur mustard agent as it is a heavily regulated compound. These chemical analogues are used in ways that simulate desired properties when studying specific variables. Such simulants react via similar mechanisms as HD and yield simpler reaction products and kinetic rate expressions. [1] However, since these simulants cannot mimic all of the physical properties of HD, one should remain critical of their physical properties when designing experiments or evaluating their subsequent results.

Table 3: Comparing the physical properties of HD and CEES. Sources: (a) Knovel [8], (b) and (d) Wagner et al. [9,10], (c) Bennet et al. [11], (e) Kaiser et al. [12].

<table>
<thead>
<tr>
<th>Agent</th>
<th>Molecular Weight (gm/mol)</th>
<th>Boiling Point °C</th>
<th>Vapor Pressure (torr)</th>
<th>Density gm/cm³</th>
<th>Molecular Diameter Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>HD</td>
<td>159.08</td>
<td>215-217</td>
<td>0.072b</td>
<td>1.2741</td>
<td>5.9d</td>
</tr>
<tr>
<td>CEES</td>
<td>124.59</td>
<td>156-157.1</td>
<td>3.4c</td>
<td>1.07</td>
<td>5.8e</td>
</tr>
</tbody>
</table>

Shown above in Table 3 are selected data illustrating how the physical properties of CEES and HD, particularly those related to mass transfer, are sufficiently different to call into question whether one should expect similar results with HD when performing experimental work with CEES. Compared to sulfur mustard, CEES is also less viscous and possesses a lower surface tension than HD. [13]
The main physical property desired for the experimental work here performed is spectral similarity to HD when analyzed through Fourier transform infrared spectroscopy. In this respect, CEES very closely resembles sulfur mustard (Figure 2) and facilitates straightforward interpretation of spectral results. An added incentive of using CEES is that it possesses essentially the same molecular diameter as HD, which is presumably useful when considering adsorption into the porous materials here studied.

![Comparison of the similar spectra of CEES and HD. Adapted from [14]](image)

**Figure 2:** Comparison of the similar spectra of CEES and HD. Adapted from [14]

### 2.3 Identification and Assignment of CEES Infrared Vibrational Modes

Efforts to classify the vibrational bands (Raman and IR) of sulfur mustard and its simulants were originally conducted by Sosa *et al.* [15] Utilizing *ab initio* molecular
orbital models, predictions were made for the vibrational modes of sulfur mustard, DES (diethyl sulfide), and CEES. These values were compared against values determined using empirical constants derived by Shimanouchi et al. [16, 17] and were found to yield similar values (at the time, no IR data was published for CEES). Subsequent experimental IR and Raman data were soon published by S. D. Christesen for liquid phase DES, CEES, and HD. [14] This experimentally determined IR and Raman spectra correlated well with the theoretical values predicted by Sosa et al. (within 10 %).

An alternative assignment for the IR modes of CEES was made by Mawhinney et al. [18] in which a correlation between functional groups and their resulting IR bands was established by direct comparison of the CEES and CEPS (2-chloroethyl phenyl sulfide) compounds, as shown in Figure 3. This initial work conducted by Sosa, Christesen, and Mawhinney et al. have since been used as primary sources for identifying IR bands belonging to CEES, DES, and HD. [19, 20, 21]

Figure 3: The comparative method utilized by Mawhinney et al. to assign IR vibrational modes. Adapted from [18].
Compared on the following page (Table 4) is the CEES vibrational assignments of Sosa, Christesen, and Mawhinney et al. [15, 14, and 18] This table is not an exhaustive list of their individual assignments. It can be seen from the table that there are some discrepancies in the assignments of the three authors, implying that the matter has not been fully resolved. This is particularly true for the 1264 and 1213 cm⁻¹ bands as both either reflect C-CH₂ vibrations or S-CH₂ and Cl-CH₂ vibrations, respectively. This becomes especially significant when considering that the loss of either of these bands could be equally interpreted to mean the loss/modification of chlorine and sulfur groups or the loss/modification of a carbon belonging to a terminal methyl group. These are clearly different outcomes. For this reason, it is important to note that while an absolutely correct vibrational assignment isn’t necessary to draw conclusions from the interactions of CEES adsorbed onto the surfaces, the reader should be aware that misinterpretation of IR spectra is possible if relying on this method alone.
Table 4: A comparison of the vibrational assignments for 2-CEES as proposed by [15, 14, and 19]. Refer to Section 7.0 for vibrational nomenclature.

<table>
<thead>
<tr>
<th>Wavenumber cm⁻¹</th>
<th>Sosa</th>
<th>Christesen</th>
<th>Mawhinney</th>
</tr>
</thead>
<tbody>
<tr>
<td>2967</td>
<td>ν(CH₂)as</td>
<td>ν(CH₂)as</td>
<td>C-H stretch</td>
</tr>
<tr>
<td>2925</td>
<td>ν(CH₂)s, ν(CH₃)as</td>
<td>ν(CH₂)s, ν(CH₃)as</td>
<td>C-H stretch</td>
</tr>
<tr>
<td>2871</td>
<td>ν(CH₂)s, ν(CH₃)s</td>
<td>ν(CH₃)s</td>
<td>C-H stretch</td>
</tr>
<tr>
<td>1454</td>
<td>γ(CH₂)</td>
<td>δ(CH₃)</td>
<td>CH₃ def</td>
</tr>
<tr>
<td>1425</td>
<td>γ(CH₂), δ(CH₃)as</td>
<td>δ(CH₃)</td>
<td>CH₃ def</td>
</tr>
<tr>
<td>1406</td>
<td>δ(CH₃)s</td>
<td>δ(CH₃)s</td>
<td></td>
</tr>
<tr>
<td>1290</td>
<td>ω(C-CH₂)</td>
<td>ω(C-CH₂)</td>
<td></td>
</tr>
<tr>
<td>1264</td>
<td>ω(C-CH₂)</td>
<td>ω(C-CH₂)</td>
<td>(S-CH₂) sciss</td>
</tr>
<tr>
<td>1213</td>
<td>ω(C-CH₂)</td>
<td>ω(C-CH₂), τ(C-CH₂)</td>
<td>(Cl-CH₂) sciss</td>
</tr>
<tr>
<td>1126</td>
<td>τ (C-CH₂), ω(CH₂)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1054</td>
<td>ρ(CH₃)ip</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1036</td>
<td>τ (C-CH₂), ρ(C-CH₂)</td>
<td>ρ(CH₃)op</td>
<td>τ (C-CH₂), ρ(C-CH₂)</td>
</tr>
<tr>
<td>1015</td>
<td>τ (C-CH₂), ρ(C-CH₂)</td>
<td>ρ(CH₃)op</td>
<td>ν(C-C)</td>
</tr>
<tr>
<td>970</td>
<td>ν(C-C)</td>
<td>τ (C-CH₂), ρ(C-CH₂)</td>
<td></td>
</tr>
<tr>
<td>927</td>
<td>τ (C-CH₂), ρ(C-CH₂)</td>
<td>ν(C-C)</td>
<td></td>
</tr>
<tr>
<td>783</td>
<td>ρ(C-CH₂), ρ(CH₃)op</td>
<td></td>
<td></td>
</tr>
<tr>
<td>769</td>
<td>ρ(C-CH₂)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>758</td>
<td>ρ(C-CH₂)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>731</td>
<td>ρ(C-CH₂)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>697</td>
<td>ν(C-S), δ(CH₂)</td>
<td>ν(C-S), ν(C-Cl)</td>
<td></td>
</tr>
<tr>
<td>653</td>
<td>ν(C-Cl), ν(C-S)</td>
<td>ν(C-Cl), ν(C-S)</td>
<td></td>
</tr>
</tbody>
</table>

2.4 Surface Interactions of CEES Adsorbed onto TiO₂

The nature of CEES interactions with surface hydroxyls was conducted by Panayotov and Yates Jr. on TiO₂-SiO₂ mixed oxides. [22] These oxide samples were
thermally annealed under vacuum at 400 °C in order to reduce the surface density of associated hydroxyl groups in favor of an increased presence of isolated hydroxyls. TiO$_2$ isolated hydroxyl groups were identified as yielding two bands at 3716 and 3674 cm$^{-1}$ [22] (See Figure 4B) and matches assignments made independently by D. J. C. Yates [23] and Tsyganenko and Filimonov [24, 25].

Interactions with CEES was observed to shift these isolated Si and Ti hydroxyl bands towards two lower, distinct vibrational modes that suggested hydrogen bonding corresponding to X–OH···Cl and X–OH···S where X = Si, Ti. [22] While it was found that CEES adsorption yielded characteristic –OH red shifting behavior, little consideration was given to check the implicit assumption of hydroxyl conservation upon exposure to CEES vapor.

Follow-up investigations by Panayotov and Yates Jr. were conducted on Degussa P25 TiO$_2$ the following year. [26] Utilizing infrared spectral background shifts that occur as a result of the semiconducting properties of TiO$_2$, Panayotov and Yates Jr. characterized CEES adsorption as a process that draws electrons from the bottom of the conduction band of TiO$_2$. Their main conclusions were that: 1) the electron transfer to CEES facilitates strong surface adsorption to the surface, and 2) these conduction band electrons selectively transfer through the Cl moiety of CEES.

The electronic effects associated with surface annealing are illustrated in Figure 4A and B. Sample reduction replenishes conduction band electrons and results in a higher background absorbance, particularly in the 2500-1000 cm$^{-1}$ region. Oxidation behaves in the reverse manner - conduction band electrons are depleted and yield a decreased background absorbance. Although not explicitly shown in this thesis, all
spectroscopic work correlated closely with the absorbance shifts observed by Panayotov and Yates Jr. [26, 27]

![Figure 4: Effect of oxidation and reduction on the infrared spectra of TiO$_2$. Adapted from [27].](image)

Since atmospheric moisture affects the extent of H$_2$O surface coverage on TiO$_2$, [28, 29] Panayotov and Yates Jr. further investigated how H$_2$O coverage affects the electron transfer properties of TiO$_2$. [27] This led to the observation that hydroxyl group formation and molecular water adsorption increased electron consumption in a manner that agrees with water adsorption models [30, 31, and 32] that predict –OH group production as the result of H$_2$O dissociation at a bridged O-vacancy.

### 2.5 Reactivity of CEES Adsorbed onto TiO$_2$

Prior work investigating the possible application of TiO$_2$ towards CEES has been conducted by Thompson et al. [19] The adsorption of gas phase CEES onto the surface of
Degussa P25 yielded spectral behavior suggestive of ethoxy species formation at the surface of TiO$_2$ at temperatures ranging from 100-250°C. At temperatures above 250°C, thermal decomposition into hydrocarbon fragments as well as HCl and oxygenated products were reported. [19]

Similar work, conducted by Brevett et al. [33], investigated ambient temperature interactions over a six month span utilizing $^{13}$C MAS NMR to track changes in the molecular structure of CEPS upon adsorption onto Degussa P25. Their main findings were that hydrolysis and ether formation occurred at room temperature though this occurrence required the elapsing of 5 and 6 months, respectively.
3.0 EXPERIMENTAL

3.1 Materials Used

The CEES used was supplied by Sigma-Aldrich (CAS 693-07-2) and was 98% pure. It was used as received. The titanium dioxide samples evaluated were NanoActive\textsuperscript{TM} TiO\textsubscript{2} and Aeroxide\textsuperscript{®} P25 which were supplied by NanoScale Inc (Cat. No. AC112-0100) and Evonik-Degussa (CAS 13463-67-7). All gases used were supplied by Med-Tech Gases, Medford, MA.

3.2 Experimental Equipment

The following section describes the equipment used to study the physical and chemical differences between the NanoActive and Degussa TiO\textsubscript{2} as well as to observe their resulting interactions with CEES.

3.2.1 FT-IR

Infrared spectra were obtained using a Perkin-Elmer Model 1600 fourier transform infrared spectrometer. The optical system consists of a 633 nm helium-neon laser (intensity $< .3$ mW) and a lithium tantalate (LITA) detector. Spectra were recorded as an accumulation of 64 scans taken in ratio mode to permit subtraction of existing background spectra. Resulting spectra were measured in the 400-4,000 cm\textsuperscript{-1} range at a 4 cm\textsuperscript{-1} resolution. Spectral acquisition time was 4.2 minutes. The unit was purged with prepurified nitrogen gas at a rate of 20 cc/min in order to displace residual carbon dioxide and water vapor build-up inside the optical system. The IR spectrometer was calibrated against polystyrene films supplied by Perkin-Elmer.
3.2.1.1 Sample Chamber

The sample chamber is the main compartment where sample wafers are housed during IR scanning. The outer diameter of the sample chamber is 2.5 cm and has a path length of roughly 12 cm. On either end of the sample chamber are NaCl windows of dimensions 32x3 mm that are permanently bonded to the sample chamber with Loctite quick set epoxy sealed-over by Apiezon W wax.

3.2.1.2 Vacuum Manifold

The vacuum manifold through which the IR work was conducted is shown in Figure 5. Operating pressures varied from ambient to 2 torr vacuum. The pump is a Welch 0.5 L/sec vacuum pump (Model 1400). Pressures were measured with an Edwards-Datametrics pressure transducer (Barocel, Type 600A-1000T-R12-H22X-4 capacitance manometer, 0-1000 torr range). This particular transducer is located between stopcocks V-7 and V-8 in Figure 5.

The manifold itself is constructed primarily of Pyrex tubing except at the furnace (quartz instead). The system is equipped with two optional liquid nitrogen traps and a feed inlet for recharging reservoir gases as well. Desired gases are stored in any of five spherical reservoirs that range from 1-3 L in volume.
The furnace is the principal means of heating wafer samples to desired temperatures. It consists of a 3 cm thick, high temperature fiberglass insulation that runs down a 20 cm quartz section of the sample column. The furnace itself is positioned roughly 20 cm above the IR sample chamber. Furnace temperatures are monitored and controlled using a K-type thermocouple in conjunction with a Staco Energy Products variable transformer (Type 3PN1010) and an Omega temperature controller (Model 4002-KC, range 0-1000 °C). Operating temperatures typically range from ambient to 500 °C. The thermocouple itself is not inside the sample column. It resides inside a small, hollow quartz tube blown into the inner core of the furnace tubing.
Sample wafers are introduced into the sample chamber through the use of the removable assembly shown in Figure 6. The horizontal closed tube is a removable rotating arm attached to a ground joint sealed with Apiezon N high vacuum grease. The arm rotates freely and facilitates positioning of the wafer in order to make it perpendicular to the IR beam’s path. The quartz wafer holder measures 14 cm in length and 2 cm in width and is suspended on a wire assembly weighed down by a Pyrex enclosed magnet.
3.2.2 Thermal Gravimetric Analysis

Thermal gravimetric analysis (TGA) was conducted using a CAHN 2000 microbalance. All TGA plots presented herein were obtained by calcining samples from ambient to 500°C at a rate of 2°C/min. During heating, a venting valve was left open to atmosphere for pressure relief purposes.

3.2.3 X-Ray Diffraction

X-ray powder diffraction (XRD) analyses were conducted using a Bruker D5005 0:2θ Bragg-Brentano diffractometer (CuKα radiation, 40 kV, 30 mA) equipped with a curved graphite crystal diffracted beam monochromator and a NaI scintillation detector. The XRD data were collected between 20 and 80 °2θ with a step increment of 0.02 °2θ and a count time of 16 or 2.5 s/step.

Samples were loaded into aluminum or plastic specimen holders. Diffraction patterns were identified using the Joint Committee on Powder Diffraction Society (JCPDS) database. [34] Crystalline particle sizes were determined by applying the Scherrer equation to the diffraction peaks at 2θ ≈ 25.3° and 48.0° for anatase and 2θ ≈ 27.4° for rutile. The full-width-at-half-maximum of these peaks was determined using the EVA software supplied from Bruker. Instrumental broadening was corrected by using the SRM660a reference specimen (LaB₆).

3.2.4 Nitrogen Adsorption

Nitrogen adsorption analysis was conducted using a Beckman Coulter Omnisorp 100CX instrument calibrated against a silica-alumina standard. The standard was supplied by Micrometrics and has an average BET surface area of 188 ± 6 m²/gm, a total
pore volume of 0.82 ± 0.08 cc/gm, and an average pore diameter of 17.3 ± 15 nm. The nitrogen adsorbate was a prepurified supply used as received. The helium adsorbate used in determining sample dead volumes was a high purity helium, also used as received. Both were supplied by MED-TECH gases. The analyzed samples were typically 200 mg in mass and were dried \textit{in vacuo}.

Specific surface areas were calculated using the BET method. The BET linear slope was determined by taking the slope through the mesoporous region (0.05-0.25 \(\text{P/\text{P}_0}\)). Micropore volumes were calculated using the t-plot method with a film thickness range of 3.5-10 Å and were compared against volumes computed via the MP method, a similar procedure that instead treats film thickness as a function of \(\text{P/\text{P}_0}\) and not as a function of the adsorbate itself. These agreed by as much as 5-20%.

\textbf{3.2.5 Differential Scanning Calorimetry}

Differential scanning calorimetry (DSC) was carried out using a Mettler-Toledo DSC822\textsuperscript{e} module. Samples ranging in mass from 2-8 mg were loaded into 40 \(\mu\text{l}\) aluminum crucibles each with a pinhole pierced through the top lid for pressure relief purposes. Experiments were conducted in dry air supplied by MED-Tech gases (USP grade, hydrocarbon content < 25 ppm, water content < 50 ppm, CO content < 10 ppm) and flowing at 50 ml/min. Samples were heated from 25 to 500 °C at a rate of 5 °C/min.

\textbf{3.3 Experimental Procedures}

Titania wafers were produced by briefly milling the powders with a mortar and pestle. This powder was then poured into a stainless steel die assembly and hydraulically
pressed at 3,000-6,000 psi for 30-45 seconds on a standard bench top Carver press. This produced self supporting wafers typically measuring about 30 mg/cm² for NanoActive and about 50 mg/cm² for Degussa samples. These samples were thermally annealed at 400 °C for two hours under 200 torr hydrogen and oxygen, depending on the desired oxidation state. Samples prepared in this manner were 5-10 % transparent for the NanoActive and 10-15 % transparent for the Degussa samples. Thinner wafers were possible by this method but were too brittle to endure subsequent CEES exposures and analyses.

Prior to CEES exposure, samples were dessicated overnight at a relative humidity of 54 % by using magnesium nitrate hexahydrate and are referred to as “Wet” humidification conditions when dessicated in this manner. “Dry” samples were instead dessicated at an RH below 10 % by using DRIERITE. Storage under dessication in DRIERITE was used to control the influence of water in order to characterize oxidized and reduced samples without this added variable as surface water may play a role in the reaction of CEES with titania.

CEES exposure was accomplished by pipetting 12 % by mass across the surface of the sample wafers. This weight percent was chosen in order to more closely correspond with prior investigations performed by Brevett et al. [33] in which 10 % by mass was added to the TiO₂ samples prior to ¹³C MAS NMR analysis. Samples were either analyzed at ambient conditions for 4 consecutive hours or analyzed in between 5 minute heating steps from room temperature to 500°C at 100°C increments. Little spectral changes were observed above 300°C and, for that reason, are usually omitted.
4.0 RESULTS AND DISCUSSION

4.1 Initial Materials Characterization

Various analytic methods were employed to characterize the initial titania and CEES supplies used in these experiments. This was done in order to make initial comparisons for the as received materials as well as for establishing a reference point for determining whether any unintended changes occurred upon titania pre-activation or CEES thermal decomposition.

4.1.1 NanoActive and Degussa P25 TiO₂

Although both NanoActive (NA) and Degussa P25 (P25) are two commercially available titania products, the two materials share little else in common. As received NA and P25 samples were very dissimilar in terms of crystallinity, surface area, and water content. The following subsections elaborate upon these characterizations.

4.1.1.1 Scanning Electron Microscopy Imaging

SEM micrographs of NA and P25 indicate they are morphologically quite different. Figure 7 provides SEM images of hydraulically pressed NA and P25 samples (left and right columns) at low and high magnification. At low magnification, particle features are virtually indistinguishable for P25 whereas NA possesses features clearly visible as agglomerates measuring about 5 µm in mean diameter. At high magnification, the P25 features are discernable as particles measuring 20 nm in mean diameter. NanoActive under high magnification reveals much finer particles that exist between the agglomerates.
4.1.1.2 Thermal Gravimetric Analysis

Thermal gravimetric analysis was employed to compare the water contents of these samples. Gravimetric losses (Figure 8) are smoothed with a polynomial smoothing function and normalized for mass. The temperature profile increases from ambient to 500 °C at a rate of 2 °C/min.

Little desorption was observed above 150 °C, confirming that water accounts for the majority of the weight lost. Changes in mass occurring above 300 °C are the result of buoyancy changes between the quartz sample holder and the surrounding air. Supplier estimates suggest the moisture content of NanoActive is larger than P25 by a factor of 2.5.
The TGA results below indicate an approximate weight loss ratio of $9/3.5 \approx 2.6$ which closely matches the expected factor of 2.5.

![Thermal gravimetric analysis curves for as received NA and P25.](image)

**Figure 8:** Thermal gravimetric analysis curves for as received NA and P25.

4.1.1.3 X-Ray Diffraction

XRD spectra also reflect the sharp contrast in crystallographic properties observed in the previous SEM micrographs. In Figure 9 it is observed that NanoActive yields no detectable diffraction pattern while Degussa yields anatase and rutile patterns that are in excellent agreement with the characteristic anatase and rutile diffraction patterns of TiO$_2$. For clarity, characteristic anatase and rutile 2θ peaks are labeled along the top abscissa with red and blue vertical bars, respectively.
Figure 9: XRD spectra of as received NanoActive and Degussa P25.

4.1.1.4 Nitrogen Adsorption

Nitrogen adsorption was utilized to elucidate differences in surface area and porosity of NanoActive and Degussa P25. Specifics related to adsorption measurement conditions are described in Section 3.2.4. The adsorptions isotherms in Figure 10 exhibit hysteresis patterns characteristic of mesoporosity. Microporosity was also observed but only for the NanoActive titania. The specific surface area measurements for NanoActive and Degussa are $437 \pm 27$ and $34 \pm 8 \text{ m}^2/\text{gm}$, respectively.
Figure 10: Nitrogen adsorption isotherms for NA and P25 at 77 K.

In order to further elucidate mesoporous differences, pore size distribution curves were determined via the Horvath-Kawazoe (HK) method. For simplicity, cylindrical pore geometry was assumed. The pore size distribution curves, shown in Figure 11, show that Degussa P25 possesses both a larger pore geometry and a larger distribution of pore size across the entire mesopore range. NanoActive, on the other hand, possesses a smaller pore geometry and pore size range. Despite this sharp contrast in mesoporosity, the total pore volumes of both materials indicate they are quite similar (.296 vs .271 cm³/gm, P25 to NA). These values were calculated via the MP method using a 1 nm film thickness. The similar pore volumes of the two materials suggest that, despite large differences in pore geometry, the NanoActive possesses a greater quantity of pores (meso
and micro) as total pore volume is ultimately a cumulative sum of individual pore volumes.

![Differential Pore Volume vs. Mesopore Radius](image)

**Figure 11**: Pore size distributions of as received NanoActive and Degussa TiO$_2$ in the mesopore range.

### 4.1.2 Infrared Spectrum of Neat Liquid CEES

Infrared analysis of neat liquid CEES was done in order to provide a representative spectra of CEES as well as to verify chemical purity. The acquired spectrum is shown below in Figure 12 and was found to yield a spectrum matching that of S. D. Christesen. [14] For clarity, vertical bars are plotted along the bottom to identify expected CEES peaks.
Figure 12: IR absorption spectra of neat, liquid CEES. Minor peaks have been excluded for clarity.
4.2 Assessment of Thermal Annealing Affects

The pre-activation process utilized introduced changes to surface area and crystal properties of the NanoActive material while it did not affect Degussa in any appreciable manner. The following subsections elucidate this observation in further detail.

4.2.1 X-Ray Diffraction

XRD spectroscopy was employed to assess the extent of crystallographic changes upon pre-activation of the NA and P25 samples. Oxidation and reduction was not found to alter the crystallography of P25 while it substantially altered the NA. The initially amorphous NanoActive TiO₂ yielded anatase crystallites measuring roughly 11 nm in mean diameter.

4.2.1.1 NanoActive TiO₂

XRD spectra comparing the oxidized and reduced NanoActive TiO₂ samples to the original, as received material are shown in Figure 13. For clarity, the characteristic anatase 2θ peaks are labeled with red vertical bars along the top abscissa. Diffraction peaks appearing as a consequence of the aluminum stage employed during analysis are intentionally cut off and labeled along the top abscissa with an “Al” symbol. It is apparent from Figure 13 that upon completion of thermal annealing, the samples are no longer amorphous in character but instead exist as anatase TiO₂. Due to an overlap with the much stronger Al peak at 38°, the three anatase diffraction peaks centered about 37° are not discretely visible in the oxidized and reduced samples. However, the wider full-
width-at-half-maximum (FWHM) of the $38^\circ$ Al peak for the oxidized/reduced samples compared to the initial TiO$_2$ Al peak FWHM suggests that these peaks are present.

![Anatase Pattern](image)

Figure 13: XRD spectra comparing oxidized and reduced NanoActive TiO$_2$ to the initial, un-annealed material.

4.2.1.2 Degussa P25

XRD spectra comparing oxidized and reduced Degussa P25 samples to the initial, as received material are shown in Figure 14. Again, the characteristic anatase and rutile $2\theta$ peaks are labeled along the top abscissa with red and blue vertical bars. Diffraction peaks appearing as a consequence of the aluminum stage employed during analysis are intentionally cut off and labeled along the top abscissa with an “Al” symbol. Comparison
of annealed and un-annealed samples indicates there are no crystallographic differences among the three and that, for all intents and purposes, these samples are identical.

![Anatase/Rutile Patterns](image)

Figure 14: XRD spectra comparing oxidized and reduced samples of Degussa P25 TiO$_2$ to the initial, as received material.

4.2.1.3 Resulting Crystallite Dimensions

Mean crystallite diameters, t (nm), of the annealed and un-annealed TiO$_2$ samples are tabulated in Table 5. These diameters were calculated by applying the Scherrer equation to the anatase and rutile peaks of highest relative intensities. In this case there are two that meet this criterion for anatase (25.4°, 48.0°) and only one for rutile (27.4°).
Oxidation or reduction of the initially amorphous NanoActive TiO$_2$ at 400 °C yields anatase crystallites that are roughly 10 nm in diameter. For Degussa P25, no crystallographic changes were observed. The P25 crystallite diameters of the starting material are virtually identical to that of the annealed samples (about 22 nm anatase and 36 nm rutile in all instances).

Table 5: Mean crystallite diameters of variously annealed NanoActive and Degussa P25 samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pre-activated Condition</th>
<th>Resulting Phase</th>
<th>Diffraction Peak 2θ (deg)</th>
<th>Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NanoActive</td>
<td>As Received</td>
<td>Amorphous</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Oxidized</td>
<td>Anatase 25.4</td>
<td>11</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Anatase 48</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Reduced</td>
<td>Anatase 25.4</td>
<td>11</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Anatase 48</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>Degussa P25</td>
<td>As Received</td>
<td>Anatase 25.4</td>
<td>22</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Anatase 48</td>
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<td>20</td>
</tr>
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<td></td>
<td>Rutile 27.4</td>
<td>36</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>Oxidized</td>
<td>Anatase 25.4</td>
<td>23</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Anatase 48</td>
<td>22</td>
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<td></td>
<td>Rutile 27.4</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>Reduced</td>
<td>Anatase 25.4</td>
<td>24</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Anatase 48</td>
<td>21</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Rutile 27.4</td>
<td>36</td>
<td>36</td>
</tr>
</tbody>
</table>

4.2.2 Surface Areas after Thermal Annealing

Liquid nitrogen adsorption was utilized to determine whether the initial thermal annealing of the TiO$_2$ catalysts introduced any changes to the specific surface areas of these titania samples. Oxidized and reduced samples of NanoActive and Degussa P25
were annealed as described previously and their adsorption isotherms were subsequently measured.

4.2.2.1 NanoActive TiO₂

As shown in Figure 15, the initial thermal annealing step dramatically reduces the adsorptive capacity of NanoActive TiO₂. The surface area of the as received material decreases from 437 ± 27 m²/gm to about 90 ± 13 m²/gm upon annealing. This reduction in adsorptivity is independent of annealing in O₂ or H₂.

![Figure 15: The adsorption isotherms of the annealed and un-annealed NanoActive.](image)

Changes in mesoporosity were observed as well. The full adsorption isotherm of reduced NanoActive TiO₂ (Figure 16) suggests that the hysteresis associated with mesoporous adsorption has changed in a manner that reflects significant loss in specific surface area and a slight change in mesoporosity. A plot of the pore size distribution for
the reduced NA sample (Figure 17) confirms this and suggests that thermal annealing reduces micropores while retaining or producing mesopores in the 25-50 nm range. Total pore volume decreases from the initial .271 cm$^3$/gm down to .046 cm$^3$/gm. The formation of new mesopores accompanied by the loss of total pore volume suggests a substantial loss in microporosity.

![Figure 16: Full N$_2$ adsorption isotherms before and after annealing NanoActive TiO$_2$.](image-url)
Figure 17: Pore size distribution for NA before and after annealing.

4.2.2.2 Degussa P25

Annealing the Degussa samples (Figure 18) altered surface areas though these changes were slight. The small magnitude of these changes suggests that oxidation and reduction are interacting with residual impurities on the surface of P25. No pore size distribution was measured as BET adsorption and XRD analysis indicated that pre-activation yielded little change to these Degussa samples.
Figure 18: Comparison of the adsorption isotherms for annealed and as received Degussa samples.

4.2.2.3 Summary of Resulting Surface Areas

Table 6 and Figure 19 summarize the observed effects of thermal pre-activation in oxygen or hydrogen. NanoActive TiO$_2$ surface areas exhibit an 80% reduction whereas P25 is virtually unchanged.

Table 6: Mean surface areas for NanoActive/Degussa under different annealing conditions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean Surface Area (m$^2$/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As Received</td>
</tr>
<tr>
<td>Degussa</td>
<td>34 ± 8</td>
</tr>
<tr>
<td>NanoActive</td>
<td>437 ± 27</td>
</tr>
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</table>
4.3 Reactions of CEES on TiO$_2$

Reactions of CEES on TiO$_2$ were observed utilizing an in situ FTIR setup as described in Section 3.2.1. The spectral behavior indicated that only strong adsorption of the CEES species was being observed at room temperature conditions. This was readily observed with P25 samples. Reactivity was observed on NA and P25 at temperatures above 200°C.

4.3.1 Ambient Condition Interactions

The adsorption of CEES onto oxidized and reduced NanoActive samples yields little spectral information (Figure 20). The –OH band that is broadly observed from about 3700-3200 cm$^{-1}$ in Figure 20A arises from hydrogen bonding of densely packed...
neighboring hydroxyl groups [28, 29] as well as from isolated Ti-OH stretching vibrations [29, 37, 38, 39]. The broadening of the methyl region in Figure 20C at 2 hrs is also indicative of intramolecular hydrogen bonding. [22] The two peaks of primary interest, 1264 cm\(^{-1}\) (S-CH\(_2\)) and 1214 cm\(^{-1}\) (CH\(_2\)-Cl) are readily observed in Figure 20B though they weaken with time. Their relative heights remain constant throughout the four hours and suggest no reaction is occurring, only adsorption into the surface of the oxidized NanoActive.

Oxidized NanoActive

Reduced NanoActive

Figure 20: IR spectra of CEES adsorbed at room temperature onto oxidized and reduced NanoActive samples.
Peak resolution in Figure 20D is very weak and does not offer significant insight towards understanding its spectral behavior. Weak peak resolution is common to all NanoActive samples, particularly those dessicated under wet conditions. This poor resolution is attributed to the particle size of the NA agglomerates. With a mean agglomerate size of 5 μm, this places the particles well above the 1 μm threshold upon which scattering losses become significant. [28, 29, 40, and 41] These scattering losses result in poor transmission that is chronically observed in this work when dealing with NanoActive samples.

The adsorption of CEES onto oxidized and reduced Degussa samples (Figure 21), particularly for the oxidized sample, suggests that there is no reaction occurring and that we are instead observing CEES bands indicative of physical adsorption into the surface of the TiO₂. For both the oxidized and reduced samples, no new peaks appeared upon adsorption of CEES.

The 1264 cm⁻¹ (S-CH₂) and 1214 cm⁻¹ (CH₂-Cl) bands are readily observed in both P25 samples (Figure 21B, D). As observed with NanoActive, their relative heights are constant throughout the experiment, again suggesting that only CEES adsorption is occurring. Methyl broadening suggests there is strong hydrogen bonding occurring on the reduced surface (Figure 21C) but not on the oxidized surface (Figure 21A).
4.3.2 CEES Adsorption Followed by Progressive Heating

Progressive heating of NanoActive and Degussa samples with adsorbed CEES suggest that reactivity occurs at temperature above 200°C. Evidence for strong CEES adsorption through the chlorine moiety of CEES was also observed. As described in the
previous sections, NA samples yielded poor infrared spectra due to beam scattering affects. Two sets of NanoActive samples were stored at a relative humidity below 10 % and at 54 % RH dessication conditions in order to study the effects of increased water adsorption on the surface of TiO₂. The subsequent experiments yielded no significant findings for NA and, as a result, were not carried out on P25.

4.3.2.1 Wet Oxidized NanoActive

Little is observed in the FTIR spectra of these oxidized NanoActive samples dessicated at a relative humidity of 54 % (Figure 22). Vibrational peaks attributed to CEES are only broadly discernable particularly in the 1200 cm⁻¹ region. The reduced appearance the of spectral features of CEES is largely due to the factors identified in Section 4.3.1.1

![Figure 22: Spectra of wet, oxidized NanoActive samples obtained on heating from ambient temperature to 300°C.](image)
4.3.2.2 Wet Reduced NanoActive

Similar results were observed for the reduced NanoActive samples also dessicated at a relative humidity of 54%. All alkyl related spectral features are poorly visible at 3000 cm⁻¹ and not visible at all in the 1200 cm⁻¹ region (Figure 23).

![Figure 23: Spectra of wet, reduced NanoActive samples obtained on heating from ambient temperature to 300°C.](image)

4.3.2.3 Dry Oxidized NanoActive

Spectral activity is observed in the form of increasing -OH dissociation as well as spectral broadening of the CH₃ stretching modes (Figure 24A). This pattern continues for the duration of the experiment. In the CH₂ region, Figure 24B, the two major peaks of equal magnitude corresponding to CH₂ wagging vibrational modes appear as expected at 1264 and 1214 cm⁻¹ (for reference compare to the red reference spectra). While initially present, the latter band permanently disappears upon heating to 100 °C without the co-appearance of any new bands to reflect molecular changes that occurred to the lost CH₂ group. Thus, it is suspected that strong adsorption occurs through the CH₂-Cl moiety of
CEES, in agreement with the prior findings of Panayotov and Yates Jr. [26] The general broadening of the dissociated -OH and CH$_3$ stretching modes in Figure 24A are similar to that observed previously.

![Figure 24: Spectra of dry, oxidized Nanoscale TiO$_2$ samples obtained on heating from ambient temperature to 300°C.](image)

**4.3.2.4 Dry Reduced NanoActive**

Unlike the oxidized sample, little activity is observed in the –OH region of Figure 25A as its spectral features change little throughout the experiment. At ambient temperature, the presence of adsorbed CEES is weakly observed, particularly in the methyl stretching region. The two major peaks previously described at 1264 and 1214 cm$^{-1}$ are also present in Figure 25B and exhibit the same behavior as observed with the oxidized samples (i.e. the CH$_2$ wag band is initially present at ambient temperature and permanently disappears upon heating to 100 °C and above). Unlike the oxidized sample, however, the presence of an additional peak is immediately observed at 1244 cm$^{-1}$ and...
does not disappear until 300 °C. This band could be attributed to number of functional groups including carboxyls, sulfoxides, or sulfonic acids. [42, 43, and 44] Unfortunately, too many functional groups share this characteristic vibrational region to allow conclusive peak identification through IR alone.

Figure 25: Spectra of dry, reduced Nanoscale TiO₂ samples obtained on heating from ambient temperature to 300°C.

4.3.2.5 Dry Oxidized P25

Spectral activity is immediately observed upon the addition of CEES to dry oxidized P25. Upon heating, there is an increasing –OH dissociation indicating removal of dissociated and undissociated surface H₂O. The CH₃ and CH₂ vibrational modes, shown in Figure 26A and B, are generally better resolved than they were on NA and persists until 400°C as opposed to the 300°C observed previously. This behavior was found to be typical of Degussa samples. Both figures suggest that there is no chemical
activity between the CEES and the P25. No band is observed at 1214 cm\(^{-1}\), indicating chemisorption of CEES through the CH\(_2\)-Cl moiety.

**Figure 26: Spectra of dry, oxidized Degussa samples obtained on heating from ambient temperature to 400°C.**

**4.3.2.6 Dry Reduced P25**

CEES addition to reduced P25 is illustrated in Figure 27. Spectral activity is immediately observed upon CEES addition. The resulting spectra closely resemble what was observed for CEES on dry, oxidized P25 (see Figure 26) and further suggest that CEES is chemisorbing through the CH\(_2\)-Cl moiety.
Given that the thermal annealing steps used to activate the TiO$_2$ significantly alter the properties of the NanoActive material, FTIR experiments were conducted on the as received NA. The spectra presented below in Figure 28A and B show spectral behavior similar to the annealed NanoActive samples. In the CH$_2$ region, the 1214 cm$^{-1}$ peak corresponding to CH$_2$ wagging vibration is weakly observed in a manner that is very similar to the annealed NanoActive samples. Unlike the annealed samples, there is a new band at 1190 cm$^{-1}$ that could be a result of the disappearance of the 1214 cm$^{-1}$ band, though this requires further analysis in order to be confirmed. Revisiting Figure 24 and Figure 25 suggests there may be a small peak at 1190 cm$^{-1}$ on these samples as well but it is very weakly present. It does not seem that the thermally annealed and un-annealed NA samples are very different in their reactivity towards CEES.
Figure 28: Spectra of as received NanoActive samples obtained on heating from ambient temperature to 500°C.

4.3.3 Summary of CEES Interactions Observed on NA and P25

The spectral findings obtained through IR suggest that little happens upon adding CEES to Degussa P25 TiO$_2$ and NanoActive TiO$_2$ at room temperature. The common behavior observed above room temperature suggests that surface activity is acting in a manner that reflects chemisorption via the CH$_2$-Cl moiety. No chemisorption through the S-CH$_2$ moiety is observed. This agrees closely with Panayotov and Yates Jr. [26] as their work found strong evidence of surface adsorption through the CH$_2$-Cl moiety of CEES with no subsequent evidence suggestive of S-CH$_2$ surface interactions.

Given the uncertainty in vibrational assignments as pointed out in Section 2.4.2, particular attention must be given to correctly identify the 1214 cm$^{-1}$ band. The vibrational assignments for 1214 cm$^{-1}$ as listed in Table 4 suggest a discrepancy for this particular band as Mawhinney [18] attributes it to a CH$_2$-Cl vibration while Sosa et al. [15] and S. D. Christesen [14] do not identify this band as an explicit CH$_2$-Cl band but instead as a combination band that belongs to the C$_2$-CH$_2$ and C$_4$-CH$_2$ wagging vibrations.
that belong to the chlorinated side of CEES (see Figure 29). At the same time, the 1264 cm\(^{-1}\) band is primarily assigned to that same C\(_2\)-CH\(_2\) vibration that co-produces the 1214 cm\(^{-1}\) band. Therefore, any changes occurring as a result of the disappearance of the C\(_2\)-CH\(_2\) vibrations will simultaneously reduce the peak height at 1264 and 1214 cm\(^{-1}\). Since a decrease is only observed at 1214 cm\(^{-1}\) without any accompanying change at 1264 cm\(^{-1}\), this must mean that the molecular behavior responsible for this disappearance is not related to the C\(_2\)-CH\(_2\) vibration. Thus, the observed changes at the 1214 cm\(^{-1}\) band indicates chemisorption occurring at the Cl moiety only.

Figure 29: The 2-chloroethyl ethyl sulfide model used by Sosa et al to distinguish individual atomic vibrational contributions. Adapted from [15].
5.0 CONCLUSIONS

The thermal activation procedure was found to induce changes to the physical properties of NanoActive while P25 remained unchanged. The magnitude of these changes was irrespective of oxidation or reduction. Pre-activation of the amorphous NA yielded anatase crystallites of a 10 nm mean diameter. Crystallite formation was accompanied by a decrease in surface areas and pore volume by 80 % and 17 %, respectively.

Infrared analysis suggests little happens upon the adsorption of CEES to Degussa P25 and NanoActive TiO₂ at room temperature, regardless of pre-activation or dessication conditions. Evidence suggesting chemical activity at temperatures above ambient (> 200 °C) was observed and confirmed by preliminary differential scanning calorimetry data (see Section 6.0). At temperatures above ambient, strong chemisorption via the CH₂-Cl moiety is observed on all NA and P25 samples dessicated under dry conditions. Wet dessication conditions yielded little information overall, particularly for the NA samples due to spectroscopic limitations related to the particle size of NanoActive TiO₂.

While these samples exhibit very different responses to the thermal pre-activation procedure, these resulting surfaces do not show any improvement in reactivity when compared to the original sample. Since no chemical activity is observed until temperature exceeding 200°C, it is concluded that neither P25 nor NA are desirable as catalytic adsorbents for CWA decontamination at ambient conditions.
6.0 RECOMMENDATIONS

The current IR spectra do not conclusively show that reactions are occurring. Further calorimetric analysis will provide evidence to permit a conclusive determination of observed chemical activity.

Augmenting the IR chamber with a GC inlet will aid in species identification, particularly those that are not IR active. Identification of these adsorbed species will provide information useful in identifying whether the observed reactions are occurring through a hydrolytic or a nucleophilic mechanism. In knowing which mechanism is occurring, reaction dependence on undissociated surface H₂O can be ruled in or out of the picture.
7.0 NOMENCLATURE

2-CEES, CEES 2-chloroethyl ethyl sulfide; Cl-CH₂-CH₂-S-CH₂-CH₃

DES diethyl sulfide; H₃C-CH₂-S-CH₂-CH₃

HD sulfur mustard, bis(2-chloroethyl) sulfide, 2,2’-dichlorodiethyl sulfide, β,β’-dichlorodiethyl sulfide; Cl-CH₂-CH₂-S-CH₂-CH₂-Cl

NA NanoScale NanoActive™ TiO₂

P25 Degussa Aeroxide® P25 TiO₂

Greek

ν IR stretching mode

γ IR scissoring mode

δ IR deformation mode

ω IR wagging mode

τ IR twisting mode

ρ IR rocking mode

Superscripts

(CH₃)ₘₙ CH₃ asymmetric vibration
(CH₂)ᵢₚ CH₂ in plane vibration
(CH₃)ₒᵢ CH₃ out of plane vibration
(CH₃)ₛ CH₃ symmetric vibration
8.0 REFERENCES


[33] Brevett, C. A. S., R. J. Willey, B. MacIver, and G. W. Wagner, Reactivity of CEPS (2-Chloroethyl Phenyl Sulfide) on Silica and Titania Surfaces as Detected by 13C SSMAS NMR, unpublished results


