ABSTRACT

CHIN, PAUL. Kinetics of Photocatalytic Degradation Using Titanium Dioxide Films. (Under the direction of Dr. David F. Ollis).

Titanium dioxide (TiO₂), a semiconductor metal oxide, has been used in heterogeneous photocatalysis for the destruction of organic, inorganic, and biological materials. The chief objectives of my doctoral research are to generate kinetic data and to develop engineering models for photocatalytic oxidation (PCO) using TiO₂ thin films for current challenges in “solid”-solid and air-solid environmental remediation. Three topics are studied in detail:

i. TiO₂ Photocatalytic Oxidation for Formaldehyde Removal from Air (Air-Solid)

Formaldehyde (CH₂O) is a toxic air contaminant present in industrial, commercial, and residential buildings. A novel rotating honeycomb adsorbent coupled with a PCO reactor was demonstrated by F. Shiraishi and coworkers for CH₂O oxidation. They showed that their cyclic adsorbent / PCO reactor could oxidize CH₂O to concentrations below the WHO guideline, but they made no attempt to model the system. In this project we modeled their batch system at transient and steady states. In addition, we applied the batch model kinetic parameters to design a continuous system for typical residential home challenges.

ii. TiO₂ Photobleaching of Dye Layers as a Field Analysis Method (“Solid”-Solid)

Technological advances in the past decade allow glass manufacturers to deposit thin, photoactive, nano-sized TiO₂ layers on glass billed as “self-cleaning” surfaces.
installation of such “self-cleaning” window glass for office buildings or residential homes will require the creation of analysis methods to characterize the initial and continuing catalyst activity variations with time and environmental conditions. In this project we characterized the PCO properties of commercial Pilkington Activ™ glass by oxidizing deposited organic dyes (a) to show visual decolorization and recovery of the aesthetic clarity of the glass and (b) to determine the light-driven reaction kinetics on Activ™ glass.

iii. TiO$_2$ Photooxidation of Deposited Soot Layers (“Solid”-Solid)

A major contribution to visual degradation of exterior surfaces in urban environments, especially the major cities of industrialized countries, is the deposition of particulate soot. Destruction of deposited soot layers by TiO$_2$ photocatalysis had been reported recently, but there was (a) an inability to deposit a soot layer of uniform thickness on the TiO$_2$ surface and (b) a lack of rigorous kinetic modeling. In this project we developed a method to apply a uniform, thin soot layer or a model soot on TiO$_2$ thin films. We also executed laboratory studies to collect kinetic data for PCO of soot deposits and demonstrated applicability of a series / parallel reaction network model to describe the kinetics of TiO$_2$ PCO on these porous carbonaceous layers.
Kinetics of Photocatalytic Degradation using Titanium Dioxide Films

by

Paul Chin

A dissertation submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the Requirements for the degree of Doctor of Philosophy

Chemical Engineering

Raleigh, North Carolina

April 2, 2008

APPROVED BY:

Dr. David F. Ollis
Chemical Engineering
Chair of Advisory Committee

Dr. George W. Roberts
Chemical Engineering

Dr. H. Henry Lamb
Chemical Engineering

Dr. Christine S. Grant
Chemical Engineering

Dr. Eric A. Stone
Statistics
DEDICATION  (致谢)

兹将本论文献给我的家人：母亲，父亲，哥哥，嫂子，和伴侣。感谢你们给予我的爱，支持，和奉献。

Translation from Chinese:

This dissertation is dedicated to my immediate family members:
my mom, dad, brother, sister-in-law, and spouse. Thank you for all of your love, support, and sacrifice throughout my life.
BIOGRAPHY

Paul Chin was born on November 30, 1979 in Hong Kong en route to the United States. Twenty-one days later he transitioned to the United States of America with his mother. He spent the first nine years of his life in Flushing, New York, and the latter nine years of his childhood in Burlington, Massachusetts. Paul was a part-time Chinese restaurant front desk worker, part-time hospital volunteer, part-time actor in crazy high school videos, but a full-time wise-cracking Bostonian.

After graduating with his high school diploma in 1997 from Burlington High School, he attended Cornell University for his undergraduate degree in Ithaca, New York. He volunteered substantially in his fraternity, Alpha Phi Omega, was active in the AIChE student chapter, and co-oped at Air Products and Chemicals, Inc. He graduated with his Bachelors of Science in Chemical Engineering in May 2001.

In August 2001, he enrolled as a graduate student in the chemical engineering department at North Carolina State University in Raleigh, North Carolina. He was heavily involved in graduate life, from vice president of the chemical engineering graduate student association to graduate recruiting captain. He obtained his Masters of Science (thesis) in June 2004, focusing on structured platinum/iron catalytic supports for PEM fuel cell applications. He was co-advised by Drs. George W. Roberts and James J. Spivey. His doctoral research, under the direction of Dr. David F. Ollis, focused on experimental and kinetic modeling of titanium dioxide thin films as a photocatalyst for environmental remediation. After graduation, he will pursue an industrial career in Boston, Massachusetts, or be drafted as a short stop for the Pawtucket Red Sox.
ACKNOWLEDGEMENTS

First and foremost, I would like to thank my advisor Dr. David F. Ollis for his direction and discussion. Without him I would not have achieved my goals for this dissertation. I also thank the State of North Carolina for funding this research project.

This Ph.D. research would not have been completed without the help of others at NC State. These people include Professors George W. Roberts and Christine S. Grant, A. Evren Ozcam, and Yazan A. Hussain for research advice. Characterization work was accomplished with help from Jeong-Seok Na and the Martin research group. We also thank the Genzer, Velev, Grant, Fedkiw, and Khan research groups for use of their equipment. Finally, we acknowledge Professor Marc A. Anderson and Jennifer Sanfilippo of his University of Wisconsin, Madison, group for advice on the preparation of TiO₂ sol-gel materials.

There is a special group of graduate student friends whom without their support and understanding in my life I would not have made it past my first year. Thank you Joan D. Patterson, Angelica M. Sanchez, Brian G. Prevo, and M. Omon Herigstad for making my seven years here wonderful. Additionally, I acknowledge the Roberts research group for their continual support, especially Laura Beth Dong and Nathanial A. Cain.

I am a firm believer of the work hard, play hard mentality, and sports fall in the latter category. I am grateful of my dodgeball team, Pimp’s Revenge, for giving me a constructive outlet to release my research aggressions. Past and current members include: Courtney and Travis Shillings, Joan Patterson, Matt Walker, Angelica Sanchez, Vinnie Verruto, Samantha Kwan, Erin Dunbar, Erin Phelps, Jamie Matsik, Andrew Loebl, Kristen
Roskov, Brendan Miller, Michael Weiger, Keith Gawrys, Sam and Jenn Keys, Dave Trettel, Nancy Santagata, and Casey Galvin. In addition, I thank the Wednesday night, Saturday morning, and Sunday afternoon volleyball players I had the pleasure to play with on a regular basis. Thank you for helping me keep my sanity and for all the welts on my body from the spikes.

I thank the Raleigh Toastmasters club, especially W. Stan Taylor, W. Rick Jernigan, and Adrienne L. Toghraie, for teaching me the skill set required to be a confident public speaker. The ability to get up in front of a crowd and to speak without breaking out in a massive sweat has helped me through my graduate career, and life in general.

Church has played an important role in my life in Raleigh, and I sincerely thank those whom I connected with at Sacred Heart Cathedral. It was a pleasure to coach these fine students in *Can’t Judge A Powder By Its Color*: Joseph Palko, Nicole Centeno, Alexandra Hubbell, and Becky Gamble. I thank Honor M. Gifford and the DeWolf family, especially my goddaughter Caroleen, for welcoming me when I first arrived to the parish family. Other friends in Christ include Jay Butler and Monsignor Gerard (Jerry) M. Sherba; both have helped me through my perpetual search for enlightenment. Last, I acknowledge those at Saint Michael’s Episcopal Church who have welcomed me and taught me about their faith, especially Reverend S. Greg Jones, Frank S. Haynes, and Marion B. “Chip” Chase III.

I would like to thank the Triangle Red Sox Nation, especially Sean G. Bunn, for becoming my adopted baseball family in a place where professional baseball can be as foreign a sport as cricket. I will carry the memories of the 2007 World Series with me as I leave my family of friends from there.
I acknowledge Haiou Yang for translating my *Dedication* section into Chinese.

I would like to thank my family members, especially my parents Yock Lai and Mee Chew, my brother Benjamin, and my sister-in-law Urvi. Without them I would not have made it this far in life. They have been there for me every step of the way, have always loved me unconditionally, and have aided me through all of my tough decisions.

Finally, I would like to thank my husband, Christopher A. Post, whom without his full love, support, and sacrifice I never would have realized my full potential. I thank him everyday of my life.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>LIST OF TABLES</th>
<th>...........................................................................................................................................................................</th>
<th>xii</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF FIGURES</td>
<td>...........................................................................................................................................................................</td>
<td>xiv</td>
</tr>
<tr>
<td>CHAPTER 1. BACKGROUND, MOTIVATION, AND GOALS</td>
<td>...........................................................................................................................................................................</td>
<td>1</td>
</tr>
<tr>
<td>1.1. Background</td>
<td>...........................................................................................................................................................................</td>
<td>2</td>
</tr>
<tr>
<td>1.1.1. Photocatalysts</td>
<td>...........................................................................................................................................................................</td>
<td>2</td>
</tr>
<tr>
<td>1.1.2. TiO₂ Photoactive Properties</td>
<td>...........................................................................................................................................................................</td>
<td>3</td>
</tr>
<tr>
<td>1.1.3. Photocatalytic Reaction Rates</td>
<td>...........................................................................................................................................................................</td>
<td>5</td>
</tr>
<tr>
<td>1.2. Motivation</td>
<td>...........................................................................................................................................................................</td>
<td>7</td>
</tr>
<tr>
<td>1.3. Goals</td>
<td>...........................................................................................................................................................................</td>
<td>8</td>
</tr>
<tr>
<td>1.4. References</td>
<td>...........................................................................................................................................................................</td>
<td>10</td>
</tr>
<tr>
<td>1.5. List of Figures</td>
<td>...........................................................................................................................................................................</td>
<td>15</td>
</tr>
<tr>
<td>CHAPTER 2. FORMALDEHYDE REMOVAL FROM AIR VIA A ROTATING ADSORBENT COMBINED WITH A PHOTOCATALYST REACTOR: KINETIC MODELING</td>
<td>...........................................................................................................................................................................</td>
<td>18</td>
</tr>
<tr>
<td>2.1. Abstract</td>
<td>...........................................................................................................................................................................</td>
<td>19</td>
</tr>
<tr>
<td>2.2. Nomenclature</td>
<td>...........................................................................................................................................................................</td>
<td>20</td>
</tr>
<tr>
<td>2.3. Introduction</td>
<td>...........................................................................................................................................................................</td>
<td>21</td>
</tr>
<tr>
<td>2.4. Experimental</td>
<td>...........................................................................................................................................................................</td>
<td>25</td>
</tr>
<tr>
<td>2.4.1. Experimental Apparatus</td>
<td>...........................................................................................................................................................................</td>
<td>25</td>
</tr>
<tr>
<td>2.4.2. Model and Parameter Estimation</td>
<td>...........................................................................................................................................................................</td>
<td>27</td>
</tr>
<tr>
<td>2.4.2.1. Adsorption-Desorption Equilibrium Constants</td>
<td>...........................................................................................................................................................................</td>
<td>27</td>
</tr>
<tr>
<td>2.4.2.2. Adsorption Rate Constant in the Airtight Chamber</td>
<td>...........................................................................................................................................................................</td>
<td>29</td>
</tr>
<tr>
<td>2.4.2.3. Desorption Rate Constants in the Small Box</td>
<td>...........................................................................................................................................................................</td>
<td>29</td>
</tr>
<tr>
<td>2.4.2.4. Reaction Rate Constant</td>
<td>...........................................................................................................................................................................</td>
<td>30</td>
</tr>
<tr>
<td>2.4.2.5. Overall Models</td>
<td>...........................................................................................................................................................................</td>
<td>34</td>
</tr>
</tbody>
</table>
CHAPTER 4. DECOLORIZATION OF ORGANIC DYES ON PILKINGTON ACTIV™ PHOTOCATALYTIC GLASS............................................................................................................. 82

4.1. Abstract ................................................................................................................. 83

4.2. Introduction ........................................................................................................... 84

4.3. Experimental ......................................................................................................... 88
   4.3.1. Materials ...................................................................................................... 88
   4.3.2. Characterization of Pilkington Activ™ Glass .............................................. 89
   4.3.3. Deposition Procedure .............................................................................. 90
   4.3.4. Testing Conditions .................................................................................. 91
   4.3.5. Data Analysis ........................................................................................ 92

4.4. Results and Discussion.......................................................................................... 92
   4.4.1. Atomic Force Microscopy ........................................................................ 92
   4.4.2. X-Ray Diffraction ..................................................................................... 93
   4.4.3. Photodecolorization of AB9 & RBk5 Dyes – Thin Multilayers ................. 94
   4.4.4. Decolorization Kinetics ........................................................................... 94
   4.4.5. Solar Experiments .................................................................................... 100
   4.4.6. Effect of Light Intensity .......................................................................... 102
   4.4.7. Photodecolorization of AB9 & RBk5 Dyes – Thick Multilayers .............. 105

4.5. Conclusions ......................................................................................................... 106

4.6. Acknowledgements ............................................................................................. 108

4.7. References ......................................................................................................... 108

4.8. List of Figures ..................................................................................................... 116

CHAPTER 5. KINETIC MODELING OF PHOTOCATALYZED SOOT OXIDATION ON TITANIUM DIOXIDE THIN FILMS................................. 125

5.1. Abstract ................................................................................................................. 126

5.2. Introduction ......................................................................................................... 126
CHAPTER 6. QUANTITATIVE PHOTOCATALYZED SOOT OXIDATION ON TITANIUM DIOXIDE ................................................................. 155

6.1. Abstract ........................................................................................................... 156

6.2. Introduction ....................................................................................................... 157

6.3. Experimental Setup .......................................................................................... 159
   6.3.1. TiO₂ Deposition ...................................................................................... 159
   6.3.2. Lamp Soot Deposition ......................................................................... 160
   6.3.3. Characterization of TiO₂ sol and Lamp Soot ........................................ 161
   6.3.4. Quartz Crystal Microbalance – Theory and Application .................... 162
   6.3.5. Experimental Reaction Setup ............................................................... 165
   6.3.6. Data Analysis and Kinetic Modeling .................................................... 166

6.4. Results and Discussion ..................................................................................... 168
   6.4.1. Atomic Force Microscopy (AFM) ......................................................... 168
   6.4.2. X-Ray Diffraction (XRD) ................................................................... 168
   6.4.3. Spectroscopic Ellipsometry (SE) ........................................................ 169
   6.4.4. UV-Vis Spectroscopy ......................................................................... 170
   6.4.5. Soot Photooxidation – Effect of Single and Multiple Soot Layers ...... 171
   6.4.6. Soot Photooxidation – Effect of TiO₂ thickness ................................... 173
   6.4.7. Soot Photooxidation – Kinetic Modeling .............................................. 177
LIST OF TABLES

Page Number

Table 2.1. A comparison of our pseudo-first order reaction rates ($k_{cat}$) and formal quantum efficiencies ($\delta$) to literature data....................................................42

Table 2.2. Summary of the parameters calculated or fitted in the model...................43

Table 3.1. Summary of the parameters calculated or fitted in the previous model......71

Table 3.2. Summary of parameters used in calculating the yearly heating and cooling costs...........................................................................................................71

Table 3.3. IAQ CH$_2$O concentrations as a function of desorption temperature for Case 1 ($Q_{SR,S} = 1.274$ m$^3$/min, $C_{SR} = 0.1$ mg/m$^3$, $\omega = 4$ rot/min, $f_{escape} = 0.20$). .........................................................................................................71

Table 4.1. Characteristics of dyes Acid Blue 9 and Reactive Black 5.................113

Table 4.2. Summary of kinetic parameters estimated from the two step series reaction model............................................................................................................114

Table 4.3. Summary of the variable UV light intensity parameters reported in the present work and previous literature............................................................115

Table 5.1. Initial and final parameter values for the “simple” model fitted to the CO$_2$ data of Mills et al. [1] for $p = 1$ and $p = 0.5$. ..................................................145

Table 5.2. Initial and final parameter values for the “simple” model fitted to the normalized mass loss data of Lee and Choi [2]. ($p = 1$, $\varepsilon_{soot} = 2.0$ $\mu$m$^{-1}$, only front irradiation solved).................................................................145

Table 5.3. Initial and final parameter values for the “initial” model fitted to the CO$_2$ formation data of Lee and Choi [2]. ($p = 1$, $\varepsilon_{soot} = 2.0$ $\mu$m$^{-1}$)...........145
### Table 6.1
Fitted parameter values for the series/parallel reaction model \((p = 1)\)......191

### Table 6.2
Formal quantum efficiencies for the series / parallel reaction model \((p = 1)\), where the incident light intensity is determined at the top of the soot layer \(\left( r_{\text{soot}} / I_{\text{soot}} \right) \) or the top of the TiO\(_2\) layer \(\left( r_{\text{soot}} / I_{\text{TiO}_2} \right)\). Initial \((t = 0)\) and maximum FQEs are reported.................................191
LIST OF FIGURES

Figure 1.1. Band positions of several semiconductors in contact with aqueous electrolyte at pH 1. The lower edge of the conduction band (red color) and upper edge of the valence band (green color) are presented along with the band gap in electron volts. The energy scale is indicated in electron volts using either the normal hydrogen electrode (NHE) or the vacuum level as a reference. Note that the ordinate presents internal and not free energy. On the right side the standard potentials of several redox couples are presented against the standard hydrogen electrode potential. (reproduced from Figure 2 of Grätzel [1]) ..........16

Figure 1.2. Schematic of anatase phase TiO$_2$ photocatalytic activation.........................17

Figure 2.1. A schematic of an air-purification system consisting of the photocatalytic reactor with a parallel array of nine blacklight-blue fluorescent lamps and the continuous adsorption and desorption apparatus with a ceramic-paper honeycomb rotor retaining activated carbon or zeolite fine particles (reproduced from Shiraishi et al. [29]). ......45

Figure 2.2. Shiraishi data and model of adsorption-desorption only at 180°C desorption temperature in the (a) airtight chamber and (b) the small box. ................................................................................................................46

Figure 2.3. Shiraishi data and model of adsorption-desorption only at 120°C and 150°C desorption temperatures in the (a) airtight chamber and (b) the small box. .....................................................................................................47

Figure 2.4. Shiraishi data and model of adsorption-desorption with photocatalytic reaction at 180°C desorption temperature in the (a) airtight chamber and (b) the small box. .................................................................48

Figure 2.5. Shiraishi data and model of adsorption-desorption with photocatalytic reaction at 120°C and 150°C desorption temperatures in the (a) airtight chamber and (b) the small box. .................................................................49
Figure 3.1. Simplified schematic of the simulated room, small box, and adsorbent rotor. ........................................................... 73

Figure 3.2. Schematic of the IAQ house with relevant parameters. ......................... 74

Figure 3.3. $C_{SR}$ as a function of (a) $f$ at $Q_{SR,S} = 1.274$ m$^3$/min, and $C_{SR}$ as a function of the normalized $Q_{SR,S}$ at (b) $f = 0.1$ and (c) $f = 1.0$. .......................... 75

Figure 3.4. Effect of $f$ on (a) $C_{SB}$, (b) $V_{SB}$, (c) $V_{CHR}$, and (d) $V_{rxr}$ for Case 1 ($Q_{SR,S} = 1.274$ m$^3$/min, $C_{SR} = 0.1$ mg/m$^3$, $\omega = 4$ rot/min, $f_{escape} = 0.20$, $T_{des} = 120$, 150, and 180°C)................................................................. 77

Figure 3.5. Effect of $\omega$ on (a) $C_{SB}$ and on (b) $V_{SB}$, $V_{CHR}$, and $V_{rxr}$ for Case 1 ($Q_{SR,S} = 1.274$ m$^3$/min, $C_{SR} = 0.1$ mg/m$^3$, $f = 0.1$, $f_{escape} = 0.20$, $T_{des} = 120^\circ$C). ................................................................. 79

Figure 3.6. Effect of $f_{escape}$ on (a) concentration and (b) volume for Case 3 ($Q_{SR,S} = 1.274$ m$^3$/min, $C_{SR} = 0.1$ mg/m$^3$, $\omega = 4$ rot/min, $f = 0.1$, $T_{des} = 120^\circ$C). .... 80

Figure 3.7. Effect of water vapor on (a) $V_{CHR}$, and (b) $V_{rxr}$ for Case 2 ($Q_{SR,S} = 1.274$ m$^3$/min, $C_{SR} = 0.1$ mg/m$^3$, $\omega = 4$ rot/min, $f_{escape} = 0.20$, $T_{des} = 120^\circ$C). ................................................................. 81

Figure 4.1. AFM images of 3mm Pilkington Activ$^{TM}$ glass in (a) a top-down view and (b) a topographical view, and 3mm Pilkington Optifloat$^{TM}$ clear glass in (c) a top-down view and (d) a topographical view................. 117

Figure 4.2. Smoothed XRD image of 3mm Pilkington Activ$^{TM}$ glass. A peak at $2\theta = 25.15^\circ$ corresponds to anatase phase TiO$_2$. ......................................................... 119

Figure 4.3. Absorbance versus wavelength as a function of time for dyes on Activ$^{TM}$ glass: (a) Acid Blue 9 and (b) Reactive Black 5. .................. 120

Figure 4.4. $\ln$(normalized absorbance) versus time for dyes (a) Acid Blue 9 and (b) Reactive Black 5. The squares represent data on Activ$^{TM}$ glass, the circles represent data on Optifloat$^{TM}$ glass (control), and the lines represent the two step series reaction model.............................................. 121
Figure 4.5. Solar experiments demonstrating visual decolorization of Acid Blue 9 on Activ™ glass from (a) 0 min to (b) 950 min. The grey dots represent the approximate location sampled by UV-Vis absorbance measurements.

Figure 4.6. The effect of UV light intensity on reaction rates for Acid Blue 9 decolorization on Activ™ glass: (a) ln(initial reaction rate) versus ln(UV light intensity); (b) $k_{app,0}$ as a function of UV light intensity.

Figure 4.7. Decolorization plots of thick multilayers (260 monolayers) of Reactive Black 5: (a) Absorbance versus wavelength as a function of time; (b) ln(normalized absorbance) versus time, where the points represent data and the line represents the model. The inset graph in (b) magnifies the 0-4000 min region.

Figure 5.1. Configurations for experiments run in (a) front irradiation mode and (b) back irradiation mode.

Figure 5.2. CO$_2$ generation from soot photocatalyzed oxidation as a function of irradiation time, adapted from Mills et al. [1]. (□) experimental data; (—) first order rate model: $N_{CO2} = 22.5(1 - e^{-0.003t})$.

Figure 5.3. Mills’ [1] $N_{CO2}$ data (□) and the “simple” model $N_{CO2}$ (—), $N_{soot}$ (—), and $N_{int}$ (•••) data at (a) $p = 1$ and (b) $p = 0.5$.

Figure 5.4. “Simple” model prediction for the work by Mills et al. [1] of the change in (a) incident UV light intensity passing through the soot layer as a function of time at $p = 1$ (—) and $p = 0.5$ (—), and (b) soot thickness as a function of time at $p = 1$ (◇) and $p = 0.5$ (○). The dotted and dashed horizontal lines in figure (a) represent the maximum theoretical values for $I^f$ and $I^{0.5}$, respectively.

Figure 5.5. Lee and Choi [2] normalized mass loss data as function of UV illumination time under front (▲) and back (◇) illumination modes, and a control experiment with no TiO$_2$ (○). The lines represent the “simple” model fit to the front (—) and back (—) illumination mode experiments. ($p = 1$, $\varepsilon_{soot} = 2.0 \, \mu m^{-1}$, only front irradiation solved).
Figure 5.6. “Simple” model prediction for the work by Lee and Choi [2] of the change in (a) incident UV light intensity passing through the soot layer as a function of time, and (b) soot thickness as a function of time. (▲) front illumination mode; (◇) back illumination mode \((p = 1, \varepsilon_{\text{soot}} = 2.0 \, \mu m^{-1}, \text{only front irradiation solved})\) .....................................................152

Figure 5.7. Lee and Choi [2] CO\textsubscript{2} formation data in pure O\textsubscript{2} (■), air (△), and He (●), and a control experiment with no TiO\textsubscript{2} (◇). The solid lines represent the “initial” model fit to the pure O\textsubscript{2} (―), air (−−), and He (· · ·) data, respectively. Figure (a) shows the original data of Lee and Choi [2], while figure (b) is the pure O\textsubscript{2} and air data with the He data subtracted from their \(N_{\text{CO2}}\) values. \((p = 1)\) ..................................................153

Figure 5.8. “Initial” model prediction for the work by Lee and Choi [2] of the change in (a) incident UV light intensity passing through the soot layer as a function of time, and (b) soot thickness as a function of time, in the CO\textsubscript{2} formation data. (□) pure O\textsubscript{2}; (○) air \((p = 1, \varepsilon_{\text{soot}} = 2.0 \, \mu m^{-1})\)...154

Figure 6.1. Schematic of the controlled soot deposition method using an analytical rotator to pass through a hurricane lamp flame....................................................194

Figure 6.2. Process flow schematic of the quartz crystal microbalance reaction experiments. ...............................................................................................195

Figure 6.3. A series / parallel reaction mechanism to describe soot photooxidation by TiO\textsubscript{2} ...........................................................................................................196

Figure 6.4. AFM images of a QCM crystal with four spin coats of TiO\textsubscript{2} sol, calcined at 350\textdegree C, in (a) a top-down view and (b) a topographical view. ......................................................................................................................197

Figure 6.5. Smoothed XRD image of a QCM crystal with four spin coats of TiO\textsubscript{2} sol, calcined at 350\textdegree C. The symbols represent different crystal structures. ...................................................................................................198

Figure 6.6. Spectroscopic ellipsometry results of TiO\textsubscript{2} sol spin coated on Si wafers: (a) TiO\textsubscript{2} thickness as a function of the number of spin coats; (b) optical absorption spectrum for the TiO\textsubscript{2} thin film calcined at
$350^\circ C$, graphed as $(\alpha h\nu)^2$ as a function of photon energy $(h\nu)$ for direct band gap transitions .................................................................199

Figure 6.7. UV-Vis spectroscopy results on quartz glass for (a) soot absorption $(\lambda = 350 \text{ nm})$ as a function of the number of passes through hurricane lamp flame for different analytical rotor speeds and distance from the top of the flame; (b) TiO$_2$ absorption for two, four, and eight spin coats of TiO$_2$ sol. .................................................................200

Figure 6.8. Visual results of soot oxidation for a QCM crystal spin coated four times with TiO$_2$ sol, then deposited with a single pass of hurricane lamp soot: (a) bare crystal, (b) TiO$_2$-coated crystal (pre-soot deposition), and soot/TiO$_2$/crystal after (c) 0 min and (d) 11,000 min of UV illumination time. .................................................................201

Figure 6.9. Soot photocatalyzed oxidation as a function of time for QCM crystals deposited with TiO$_2$, then soot: (a) four spin coats of TiO$_2$ sol, and one, two, four, and eight passes of soot using the analytical rotor; (b) zero (“blank”), two, four, and eight spin coats of TiO$_2$ sol, and a single pass through the lamp flame .................................................................202

Figure 6.10. Series / parallel reaction mechanism, described in Figure 6.3, for QCM crystals spin coated four times with TiO$_2$ sol. Model fit to the experimental data for and single and double passes through the lamp flame .................................................................203

Figure 6.11. Series / parallel reaction mechanism, described in Figure 6.3, for QCM crystals spin coated four times with TiO$_2$ sol. Model prediction using averaged fitted parameter values (Table 6.1) for one, two, four, and eight passes through the lamp flame .................................................................204

Figure 6.12. Carbon black oxidation on QCM crystals coated with Degussa P25 TiO$_2$: visual results are shown for (a) 0 min and (b) 32,000 min of UV illumination time; (c) mass loss as a function of time; (d) $ln[m(t)/m_0]$ versus time for $m_0 = 17.3 \mu g$ and $m_0 = 27.1 \mu g$. .................................................................205

Figure A1. Schematic of a one-dimensional diffusional flux problem. .................213
Figure B1. Simplified model of a quartz crystal microbalance. (a) At resonance, the wavelength $\lambda_q$ is equal to half of the quartz plate thickness. (b) An increase in the quartz plate thickness results in a decrease in the resonant frequency (an increase in the wavelength $\lambda_q$). (c) The mass of a deposited film is treated as an equivalent amount of the quartz mass. (figure reproduced from Lu and Czanderna)
CHAPTER 1

BACKGROUND, MOTIVATION, AND GOALS
1.1. **Background**

1.1.1 *Photocatalysts*

Various n-type semiconductor metal oxides, such as TiO$_2$, ZnO, CdS, SnO$_2$, and WO$_3$, have been tested for photocatalytic elimination of organic pollutants in water and air. The drawbacks to using these metal oxides are their (a) large band gap, often requiring near-UV light ($\lambda < 400$ nm) to induce electron photoexcitation, (b) instability in aqueous medium, leading to photocatalyst decomposition, and (c) high electron-hole recombination rates. Figure 1.1 illustrates the band gap positions for several semiconductors, reproduced from Grätzel [1]. Miyauchi and co-workers [2] tested 12 metal oxide (MO) thin films in air for surface wettability and oxidation of methylene blue coated on the MO surface. Only TiO$_2$, ZnO, and SnO$_2$ exhibited both photocatalytic oxidation (PCO) and photo-induced superhydrophilicity (PSH) qualities when illuminated under 2 mW/cm$^2$ UV irradiance, making them good catalyst candidates for “self-cleaning” surfaces in air. Zinc oxide in water self-deactivates when reacted with photogenerated holes to form Zn$^{2+}$ ions which dissolve into solution [3,4]. A similar photocorrosion effect is seen for CdS in solution, releasing toxic Cd$^{2+}$ into the aqueous medium [3,5]. Tin oxide has lower relative photoactivity compared to TiO$_2$ because of its wider band gap of 3.5-4.2 eV (350-300 nm) versus 3.2 eV (TiO$_2$), which utilizes a lesser fraction of UVA light [6]. Titanium dioxide is widely accepted as the best photocatalyst because of its chemical stability, strong oxidizing power, non-toxicity, and low cost. Generally regarded as a safe material (GRAS), TiO$_2$ can be found in household items such as toothpaste, pharmaceutical drugs, paints, and sunscreens [7]. The photoactive properties of TiO$_2$ are detailed below.
There are three main photoactive aspects of TiO$_2$: (1) photovoltaic generation of electricity [1]; (2) photocatalytic oxidation; (3) photo-induced surface wettability. Only the latter two aspects are relevant here, since our interest is adsorption and oxidative reaction of organic films.

The PCO property is activated by photocatalyst absorption of UV photons of energy greater than the TiO$_2$ band gap energy ($E_{BG}$). Electron photoexcitation from the TiO$_2$ valence band (VB) to the conduction band (CB) produces electron ($e^-_{CB}$) - hole ($h^+_{VB}$) pairs (Eq. 1a). For anatase phase TiO$_2$, $E_{BG} = 3.2$ eV ($\lambda = 385$ nm), while rutile phase TiO$_2$ has a $E_{BG} = 3.0$ eV ($\lambda = 410$ nm). The redox potential for $h^+_{VB}$ is $+2.53$V with respect to the standard hydrogen electrode (SHE), which is sufficiently oxidizing to overcome the $+2.27$V SHE binding energy of $e^-$ in OH$^-$ to form a hydroxyl radical $OH^*$ ($E_{B.VB}$) from water [8], shown in Eq. (1b). Similarly, $e^-_{CB}$ (-0.52V SHE redox potential) is sufficiently reductive to react with O$_2$ to form $O_2^-$ ($E_{B.CB} = -0.28$V SHE) [8], shown in Eq. (1c). The $O_2^-$ in turn may react with $H^+$ to form the perhydroxyl / hydroperoxyl radical $HO_2^*$ (Eq. 1d). All $E$ values are reported for pH = 7.

The overall PCO process is shown schematically in Figure 1.2. The mobile $OH^*$ reacts with adsorbed, oxidizable species to form volatile and/or water soluble products. The $HO_2^*$ is also reactive, but weaker than $OH^*$. The $HO_2^*$ also can combine with another $H^+$ to form yet less reactive H$_2$O$_2$. The full PCO reaction sequence for TiO$_2$ is detailed by Turchi and Ollis [9].
The TiO$_2$ PSH property, as designated by Fujishima et al. [8], has been rationalized by two proposed mechanisms. In one explanation, electrons reduce Ti(IV) cation sites to Ti(III) and holes oxidize $O_2^-$ anions to O$_2$. The molecular O$_2$ are ejected, creating surface vacancies on which water can adsorb as OH groups, giving the TiO$_2$ surface its hydrophilic nature [8,10]. This process is summarized in Eq. (2) taken from Mills et al. [10]. In fact, the illuminated TiO$_2$ surface exhibited amphiphilicity [11] caused by creation of alternating hydrophilic/hydrophobic domains. Fujishima and coworkers [8] showed that in the absence of UV illumination, the water contact angle for TiO$_2$ was $72^\circ \pm 1^\circ$ (hydrophobic), while UV illumination of 1 $\mu$W/cm$^2$ dropped the contact angle to $0^\circ \pm 1^\circ$ (hydrophilic).

$$\equiv \text{Ti-O-Ti} \equiv + H_2O \xrightleftharpoons{\Delta, h\nu \geq E_{BG}} \equiv \text{Ti-OH} \text{ HO-Ti} \equiv$$ (2)

Alternatively, Zubkov et al. [12] hypothesized that absorbed trace-level hydrocarbon contaminants on the initial TiO$_2$ surface were photooxidized by O$_2$ to reveal a wettable surface. A water droplet on hydrocarbon-covered TiO$_2$ experienced a sudden decrease ($< 1$ s) in contact angle after an initial period of hydrophobic behavior. This induction period occurred because the pre-absorbed hydrocarbon layer must be removed before the TiO$_2$ surface became wetted. Transmission FTIR experiments indicated that
chemisorbed H$_2$O or Ti-OH surface groups did not participate in the photochemistry of UV-induced TiO$_2$ hydrophilicity.

1.1.3 Photocatalytic Reaction Rates

The photocatalytic initial reaction rate is a function of the initial species concentration ($C_{i,\text{in}}$), the catalyst concentration/weight ($C_C$), and the rate of photon absorption ($P_\alpha$), shown in Eq. (3) [13]. As $C_C$ increases, the reaction rate increases until a maximum is achieved, corresponding to total absorption of incident light. No benefit is observed from further increasing $C_C$ because the additional (dark) catalyst does not participate in the photoreaction. The initial rate of reaction as a function of reactant species concentration generally follows a Langmuir-Hinshelwood rate form, whether in an air-solid [14,15] or a liquid-solid [9,16,17] system.

$$r_{i,\text{in}}^* = f(C_{i,\text{in}}) \cdot f(C_C) \cdot f(P_\alpha) \tag{3}$$

The rate of photon absorption, and hence the initial reaction rate, follows a power law dependency on the incident UV light intensity. Egerton and King [18] studied the intensity influence on TiO$_2$ PCO conversion of liquid isopropanol to acetone. At weak light supply rates (much less than 5 x $10^{15}$ quanta/sec), there was a linear relationship between light intensity and reaction rate. At strong light supply rates (much greater than 5 x $10^{15}$ quanta/sec), the reaction rate varied with the square root of the light intensity, and electron-hole recombination was suggested to be the dominant process. Their work and later analyses by Turchi and Ollis [9] have become the basis for a power-law light intensity
explanation of photocatalyzed kinetics, where $I$ is the UV light intensity and $p$ is the power-law dependency:

$$r_{\text{initial}} \propto I^p \begin{cases} \text{weak light intensity: (p = 1)} \\ \text{medium light intensity: (0.5 \leq p \leq 1)} \\ \text{strong light intensity: (p = 0.5)} \end{cases}$$

Eq. (4) contains a transition regime in between the two asymptotic values of $p = 0.5$ and 1. Peral and Ollis [14] determined $p = 0.7$ for vapor phase acetone oxidation with a UV irradiance in the range $3-40 \times 10^{15}$ photons/(cm$^2$ sec). Mills and Wang [19] degraded aqueous 2-chlorophenol using Degussa P25 TiO$_2$ dispersions and thin films with a UVA irradiance of $0.5-6.4 \times 10^{15}$ photons/(cm$^2$ sec), and reported $p = 0.64$ for a TiO$_2$ dispersion and $p \approx 1$ for a TiO$_2$ thin film. They argued that TiO$_2$ thin films, under reaction conditions identical to their dispersions, were subject to lower light intensities because aggregate TiO$_2$ particles of about 0.44 µm diameter partially screened UV light from the smaller, photoactive TiO$_2$ particles in direct contact with the solution.

Two other variables that affect the photocatalytic reaction rate in air are temperature and humidity. Reaction rate is roughly temperature independent, though electron-hole recombination may rise with increasing temperature, causing a decrease in photocatalyst activity. More importantly, a temperature increase will induce specie desorption from the TiO$_2$ surface, decreasing the rate of reaction at low specie concentrations [20]. Obee and Brown [15] saw a mixed positive/negative temperature effect (constant ppmv humidity) on oxidation rates under partial mass transfer influence: for gaseous toluene and 1,3-butadiene, oxidation rates increased when the temperature rose
from ~24°C to ~60°C, while oxidation of weakly bound formaldehyde decreased under similar conditions. Humidity has two influences on the reaction rate [14,15]. At minimal water concentrations, higher humidity increases the reaction rate because of increased OH\(^*\) production. For some compounds, excessive humidity decreases the reaction rate because water displaces weakly adsorbed pollutants (e.g., aldehydes, aromatics), inhibiting the reaction. This effect was observed by Peral and Ollis [14] for \(m\)-xylene destruction and for oxidation of toluene, 1,3-butadiene, and formaldehyde by Obee and Brown [15].

1.2. Motivation

Titanium dioxide (TiO\(_2\)), a semiconductor metal oxide, has been used in heterogeneous photocatalysis for destruction of organic, inorganic, and biological materials in aqueous and in air-solid systems. Both TiO\(_2\) powders and thin films have been studied extensively for the photocatalytic oxidation (PCO) of water pollutants [16,18,19,21,22], air contaminants [14,15,23-26], and layers of adsorbed organic compounds, such as dyes [27-30], carboxylic acids (e.g., stearic [10,31-33] and palmitic [34]), soot [35-37], and dried microorganisms [38].

The chief objectives of the research proposed in this project are to generate or utilize existing quantitative kinetic data and to develop engineering models for PCO using TiO\(_2\) thin films for current challenges in “solid”-solid and air-solid environmental remediation.
### 1.3. Goals

The following topics are studied in detail:

i. *TiO$_2$ Photocatalytic Oxidation for Formaldehyde Removal from Air (Air-Solid)*

Formaldehyde (CH$_2$O) is a toxic, organic indoor air contaminant present in industrial, commercial, and residential buildings. The World Health Organization (WHO) set the permissible CH$_2$O indoor air concentration at a very low level of 0.1 mg/m$^3$. Since the TiO$_2$ PCO kinetics are first order for CH$_2$O concentrations below 10 ppm [15], pre-concentration of CH$_2$O can increase its destruction rate and improve process performance.

A novel rotating honeycomb adsorbent coupled with a PCO reactor (photoreactor) was demonstrated by F. Shiraishi and coworkers [26] for CH$_2$O oxidation. They [26] showed that their cyclic adsorbent / photoreactor could oxidize CH$_2$O to concentrations below the WHO guideline, but they made no attempt to model the system. We have modeled [20] their batch system at transient and steady states. Additionally, we applied the batch model to design a continuous system for typical residential home air remediation challenges [39].

ii. *TiO$_2$ Photobleaching of Dye Layers as a Field Analysis Method ("Solid"-Solid)*

Technological advances in the past decade allow glass manufacturers to deposit thin layers of photoactive, nano-sized TiO$_2$ (10-20 nm) on glass, with trademark names such as Pilkington Activ$^\text{TM}$, PPG Sunclean$^\text{TM}$, and Saint-Gobain Bioclean$^\text{TM}$. These products are billed as “self-cleaning” surfaces because they utilize TiO$_2$ photocatalytic oxidation (PCO) and photo-induced superhydrophilicity (PSH) properties. The PCO
activity causes progressive oxidation of adsorbed oxidizable molecules and organic particulate matter, while the PSH property allows for water washing removal of partially oxidized molecules and particulates from the TiO\textsubscript{2} surface.

Field installation of such “self-cleaning” window glass for office buildings or residential homes will require the creation of field tests to characterize the initial and continuing catalyst activity variations with time and environmental conditions. We continued the recent work by Julson and Ollis [27,28] on PCO of a sub-monolayer dry dye layer on optically opaque TiO\textsubscript{2} powder layers to determine its potential as an analysis method to measure the PCO activity of commercial Pilkington Activ\textsuperscript{TM} TiO\textsubscript{2}-coated transparent (optically dilute) glass [40].

iii. \textit{TiO\textsubscript{2} Photooxidation of Deposited Soot Layers (“Solid”-Solid)}

A major contribution to visual degradation of exterior surfaces (e.g., buildings and statues) in urban environments, especially the major cities of industrialized countries, is the deposition of particulate soot from diesel automobiles, heavy equipment, forest fires, burning wastes [41], and other incomplete combustions of heavier liquid fuels.

Therefore, a recent area of TiO\textsubscript{2} research has focused on tackling this issue. Destruction of deposited soot layers by TiO\textsubscript{2} photocatalysis had been reported recently in these papers [35-37], but there was (a) an inability to deposit a soot layer of uniform thickness on the TiO\textsubscript{2} surface and (b) a lack of rigorous modeling to describe the PCO kinetics of soot disappearance. We developed a method to apply a uniform, thin soot layer on TiO\textsubscript{2} thin films. Laboratory studies were conducted to collect quantitative kinetic data
via quartz crystal microbalance monitoring, and a model was developed [42] to describe the kinetics of TiO₂ PCO on these porous carbonaceous layers.

Chapter 2 of this dissertation describes the batch modeling of the experimental data generated by Shiraishi et al. [26]. Chapter 3 extends this batch model to simulate a continuous system model for typical residential home challenges. Chapter 4 demonstrates PCO of organic dyes as a means for field characterization method of commercially available Pilkington Activ™ “self-cleaning” glass. Chapter 5 presents a new mixed series / parallel reaction mechanism to model the PCO soot data from Mills et al. [37] and Lee and Choi [35]. Chapter 6 employs the use of quartz crystal microbalance to collect extensive, quantitative data for soot oxidation by thin TiO₂ layers and to demonstrate use of the series / parallel model to incorporate variable soot and TiO₂ layer thicknesses [43]. Chapter 7 summarizes the global conclusions for the research objectives of this project.

1.4. References


1.5. List of Figures

Figure 1.1. Band positions of several semiconductors in contact with aqueous electrolyte at pH 1. The lower edge of the conduction band (red color) and upper edge of the valence band (green color) are presented along with the band gap in electron volts. The energy scale is indicated in electron volts using either the normal hydrogen electrode (NHE) or the vacuum level as a reference. Note that the ordinate presents internal and not free energy. On the right side the standard potentials of several redox couples are presented against the standard hydrogen electrode potential. (reproduced from Figure 2 of Grätzel [1])

Figure 1.2. Schematic of anatase phase TiO$_2$ photocatalytic activation.
Figure 1.1. Band positions of several semiconductors in contact with aqueous electrolyte at pH 1. The lower edge of the conduction band (red color) and upper edge of the valence band (green color) are presented along with the band gap in electron volts. The energy scale is indicated in electron volts using either the normal hydrogen electrode (NHE) or the vacuum level as a reference. Note that the ordinate presents internal and not free energy. On the right side the standard potentials of several redox couples are presented against the standard hydrogen electrode potential. (reproduced from Figure 2 of Grätzel [1])
Figure 1.2. Schematic of anatase phase TiO$_2$ photocatalytic activation.
CHAPTER 2

FORMALDEHYDE REMOVAL FROM AIR VIA A ROTATING ADSORBENT COMBINED WITH A PHOTOCATALYST REACTOR: KINETIC MODELING *

2.1. Abstract

A novel rotating honeycomb adsorbent coupled with a photocatalytic reactor demonstrated by F. Shiraishi, S. Yamaguchi, Y. Ohbuchi, Chemical Engineering Science 58 (2003) 929, is modeled here. In operation, the air pollutant formaldehyde was adsorbed from a simulated room (10 m$^3$) on to a slowly rotating honeycomb, which then passed slowly through a small chamber (0.09 m$^3$), in which locally recirculated, heated air desorbed the formaldehyde and carried it through a photocatalytic reactor which oxidized the desorbed material. The regenerated rotor-adsorbent then rotated back into the airtight chamber. This system was modeled at steady and transient states to determine adsorption, desorption, and photocatalyst pseudo-first order rate constants at the appropriate temperatures (ambient T for adsorption, T=120-180°C for desorption and photocatalysis). Intensity-corrected values for the photocatalytic rate constant $k_{cat}$ (cm$^2$/mW-s) deduced from fitting our model to Shiraishi’s data were in good agreement with those calculated from five literature reports for formaldehyde photocatalytic destruction.

**Keywords**: Photocatalysis, Volatile organic compounds, Formaldehyde, Titanium dioxide, TiO$_2$, Adsorption, Desorption, Regeneration, Thermal swing, Kinetic model, Sick Building Syndrome
2.2. Nomenclature

\( \delta \) Formal quantum efficiency (FQE)
\( \Phi_{overall} \) Quantum yield
\( h \) Planck’s constant \((6.63 \times 10^{-34} \text{ J s/phot})\)
\( \lambda \) Wavelength (nm)
\( c \) Speed of light in vacuum \((2.998 \times 10^8 \text{ m/s})\)
\( C_0 \) Initial \( \text{CH}_2\text{O} \) concentration in the airtight chamber \((\text{mg/cm}^3)\)
\( C_{AC} \) \( \text{CH}_2\text{O} \) concentration in the airtight chamber \((\text{mg/cm}^3)\)
\( C_{CHR} \) \( \text{CH}_2\text{O} \) concentration on the ceramic honeycomb rotor \((\text{mg/cm}^3)\)
\( C_{SB} \) \( \text{CH}_2\text{O} \) concentration in the small box \((\text{mg/cm}^3)\)
\( E \) Photon specific energy \((\text{mW})\)
\( E_{A,des} \) Activation energy for the \( \text{CH}_2\text{O} \) desorption rate constant between the ceramic honeycomb rotor and the small box \((\text{J/mol})\)
\( k_{ads}(T_{ads}) \) \( \text{CH}_2\text{O} \) adsorption rate constant between the ceramic honeycomb rotor and the airtight chamber \((\text{s}^{-1})\)
\( k_{ads}(T_{des}) \) \( \text{CH}_2\text{O} \) adsorption rate constant between the ceramic honeycomb rotor and the small box \((\text{s}^{-1})\)
\( k_{cat}(T_{des}) \) \( \text{CH}_2\text{O} \) pseudo-first order kinetic rate constant in the photocatalytic reactor \((\text{s}^{-1})\)
\( k_{des}(T_{ads}) \) \( \text{CH}_2\text{O} \) desorption rate constant between the ceramic honeycomb rotor and the airtight chamber \((\text{s}^{-1})\)
\( k_{des}(T_{des}) \) \( \text{CH}_2\text{O} \) desorption rate constant on the ceramic honeycomb rotor in the small box \((\text{s}^{-1})\)
\( k_{des,0} \) Pre-exponential factor for the \( \text{CH}_2\text{O} \) desorption rate constant between the ceramic honeycomb rotor and the small box
\( K_{AC-CHR}(T_{ads}) \) \( \text{CH}_2\text{O} \) adsorption equilibrium constant between the airtight chamber and the ceramic honeycomb rotor
\( K_{SB-CHR}(T_{des}) \) \( \text{CH}_2\text{O} \) adsorption equilibrium constant between the small box and the ceramic honeycomb rotor
\( r_{ads} \) Rate of \( \text{CH}_2\text{O} \) adsorption on the ceramic honeycomb rotor from the airtight chamber \(\{\text{mg/(m}^3\text{-s}\}\}\)
\( r_{cat} \) Rate of \( \text{CH}_2\text{O} \) photocatalyzed oxidation by TiO\(_2\) \(\{\text{mg/(m}^3\text{-s}\}\}\)
\( r_{des} \) Rate of \( \text{CH}_2\text{O} \) desorption on the ceramic honeycomb rotor to the small box \(\{\text{mg/(m}^3\text{-s}\}\}\)
\( t \) Time \((\text{s})\)
\( R \) Universal gas constant \(\{8.314 \text{ J/(mol·°K)}\}\)
\( V_{AC} \) Volume of the airtight chamber \((10 \text{ m}^3)\)
\( V_{CHR} \) Volume of the ceramic honeycomb rotor
\( V_{rxr} \) Volume of the photocatalytic reactor \((\sim0.014 \text{ m}^3)\)
\( V_{SB} \) Volume of the small box \((0.09 \text{ m}^3)\)
2.3. Introduction

The US Environmental Protection Agency (EPA) defines “sick building” syndrome (SBS) as a situation in which building occupants experience acute health conditions linked to time spent in a building, but where no specific diagnosis can be assigned to their illness [1]. Often the occupants’ symptoms disappear soon after leaving the building. Some causes of SBS are: inadequate ventilation, chemical contaminants from both indoor and outdoor sources, and biological contaminants. Volatile organic compounds (VOCs) are an example category of indoor chemical contaminants, and formaldehyde (CH₂O) levels are of widespread interest. To prevent or eliminate SBS, building air needs to be cleaned or properly refreshed, and/or the sources of VOC pollutants must be removed or modified.

Volatile organic compounds are a diverse class of organic indoor air contaminants and are present in industrial (petroleum, pharmaceutical, textile), commercial (offices, restaurants), and residential buildings [2]. A VOC is defined by the US EPA in the Code of Federal Regulations (CFR) [3] as any carbon compound (excluding certain compounds) participating in atmospheric photochemical reactions. Formaldehyde is an example VOC that has been linked to SBS [4]. It is found in many indoor products, such as pressed wood, paints, insulation, coated paper products, and combustible materials. It is a colorless, strong-smelling gas that can cause nausea, chest tightness, wheezing, skin rashes, and allergic reactions at 0.1 ppm levels [5]. It is a suspected human carcinogen, and has been shown to cause cancer in animals. The Occupational Safety and Health Administration (OSHA) workplace Time Weighted Average Permissible Exposure Limits (TWA-PEL) is 0.75 ppm, while the American Conference of Governmental Industrial
Hygienists (ACGIH) publishes a TWA Threshold Limit Value (TLV) of 0.3 ppm [6]. These time-weighted averages are for 8-hour workdays or 40-hour workweeks.

Techniques for VOC control in exhaust airstreams include incineration, oxidation, wet scrubbing, ozonation, and adsorption [6,7]. Of these techniques, VOC adsorption on a solid surface has the most promise for reducing SBS via treatment of ventilation air. The quantity of VOCs bound to the adsorbent is dependent on: available adsorbent surface area; VOC concentration; temperature; VOC chemical structure; physical properties of adsorbent and VOC; adsorbent capacity or regenerated capacity; and contact time [7]. Two common adsorbents for indoor VOC removal are activated carbon and zeolites. Activated carbon is predominantly used to remove hydrocarbons and non-polar gases, and zeolites for polar gases and vapors [7]. Zeolites have been shown to remove benzene, \( n \)-hexane, and \( \text{CH}_2\text{O} \) from indoor air [8]. A typical activated carbon has a large surface area (1400 m\(^2\)/gr) and a modest density (0.55 gr/cm\(^3\)). It is used to retain VOCs with molecular weights over 45 and boiling points above 0°C, and is easily regenerated thermally [7]. Formaldehyde is a polar compound; its retentivity on activated carbon at 20°C and 1 atm is \(~3\%\) [9], where retentivity is defined as the maximum amount (wt%) of adsorbed vapor retained by the carbon after the ambient gas concentration reduces to zero.

Volatile organic compound removal from air using TiO\(_2\) as a photocatalyst has been widely explored. Peral and Ollis [10] degraded trace levels of gas-phase acetone, 1-butanol, \( \text{CH}_2\text{O} \), and \( m \)-xylene on Degussa P25 TiO\(_2\). Other studies have been conducted with \( \text{CH}_2\text{O} \) as a reactant [11-17]. Moreover, other VOCs (e.g., ethanol, acetaldehyde,
methyl formate) are known to produce CH$_2$O as an intermediate species [18-22] during photocatalytic oxidation (PCO).

Ceramic honeycombs have been examined as catalyst supports for PCO. Honeycombs offer a number of advantages over pellet-shaped particles, including attrition resistance and low pressure drop even at high flow rates [2]. Suzuki [23] studied TiO$_2$ coated on cordierite monoliths for air purification in vehicles. Sauer and Ollis [22,24] coated anatase TiO$_2$ on ceramic monoliths and oxidized acetone, ethanol, and acetaldehyde in air. Son et al. [25] designed a combination of plasma with photocatalyst cordierite honeycomb substrate for removal of propane, propene, toluene, m-xylene, ammonia, trimethylamine, and methylmercaptane.

Honeycomb monoliths have also been used as supports for thermally regenerable adsorbents. In one configuration, a rotating honeycomb adsorbent is used to cycle through process (adsorption) and regeneration (desorption) zones to remove contaminants. In the adsorption or process zone, organic impurities are removed from the inflowing stream by adsorption on the rotor. In the subsequent high temperature regeneration zone, these impurities desorb from the rotor into a second, isolated air flow. Some rotor sorbent configurations include a cooling zone to rapidly decrease the honeycomb temperature just following the regeneration zone. Researchers have studied rotating zeolite-coated honeycombs for VOC removal [26,27]. For removal from air of acetone, isopropyl alcohol, propylene glycol monomethyl ether acetate, and propylene glycol methyl ether, Chang et al. [26] found an optimal rotation speed of 3-4.5 rotations per hour for a process temperature of 40°C and a regeneration temperature of 180°C. Mitsuma et al. [27]
developed an optimal rotation speed empirical formula for cyclohexanone adsorption on a ceramic honeycomb rotor impregnated with a high silica zeolite. For 30 and 200 ppm cyclohexanone concentrations, the optimal rotation speed was a function of the desorption gas stream velocity, the rotor width, and the ratio of the monolith cross-sectional area in the process zone to the monolith area in the desorption zone. Typical values ranged from 20-50 rotations/hour.

Combination PCO reactor-adsorbent systems have also been examined. Ao and Lee [28] studied toluene and nitrogen oxide removal using TiO₂ immobilized on an activated carbon filter. Combining adsorption, thermal regeneration and photocatalysis, Shiraishi et al. [29] developed a novel air-purification system consisting of a rotating honeycomb, loaded with zeolite or activated carbon, combined with a TiO₂ reactor in order to remove, and eventually to photocatalytically oxidize, the air contaminant CH₂O. In a batch system (airtight chamber) with initial CH₂O levels of 0.55-0.75 mg/m³, this system achieved the 0.1 mg/m³ CH₂O guideline set by the World Health Organization in 10 minutes, and reached nearly zero concentration after 90 minutes. Our work constructs an engineering model for their combined adsorbent - PCO reactor system.

Except for CH₂O source removal in indoor products, the technology developed by Shiraishi et al. [29] is believed to be the best option in removing existing levels of CH₂O. Their system decreases the CH₂O concentration in a simulated room below the WHO guideline, in addition to oxidizing the CH₂O in a small PCO reactor. Adsorption-only systems to a sorbent material require frequent replacement or regeneration of the sorbent. Increased ventilation of fresh air and removal of exhaust air require an increase in energy
consumption because air is not recirculated. Energy is expended to cool or heat the fresh air to the desired temperature, and the CH$_2$O-containing air is exhausted outdoors, polluting the atmosphere. Ozonation can be used to oxidize CH$_2$O, but ozone can damage the respiratory system.

We report the development of a kinetic model for a novel (rotating adsorbent) - (photocatalyst reactor). The combination adsorbent-catalyst system allows for rapid air contaminant removal (air to adsorbent) followed by desorption into a small volume photoreactor, where the consequent 3-5x contaminant concentration increase allows for the use of a smaller reactor than a photocatalyst-only system would require.

2.4. Experimental

2.4.1 Experimental Apparatus

The process modeled includes two independent, continuous flow systems interconnected by a rotating, cylindrical ceramic honeycomb. The rotation cycles the honeycomb rotor through a low temperature process (adsorption) and a high temperature regeneration (desorption) zone to remove CH$_2$O from chamber air. A diagram of the experimental system is reproduced in Figure 2.1 [29]. In greater detail, the system comprises of an airtight chamber (“highly tight room” in the Shiraishi article), a cylindrical honeycomb ceramic rotor, a small box chamber, and a photocatalytic reactor contained therein. The volumes of the airtight chamber (simulated room) and small box are 10 and 0.09 m$^3$, respectively. The rotating honeycomb passes alternately through the airtight chamber and the small box chamber containing the PCO reactor (~0.014 m$^3$). The
combination system provides a greater than 4x increase in CH$_2$O initial concentration compared to the airtight chamber. The higher CH$_2$O concentration in the small box reduces the required size of the PCO reactor accordingly.

The rotor (300 mm diameter, 50 mm thickness) is made of ceramic honeycomb laminates with a 3 mm corrugation pitch. Shiraiishi et al. [29] deposited a zeolite (ZSM-5) or activated carbon (coconut husk) on the rotor to adsorb CH$_2$O. They found activated carbon to be a better adsorbent for CH$_2$O, so our model examines only their data for this system. The rotation speed of their honeycomb is not specified, but it is assumed slow enough that the higher temperature in the small box does not elevate the airtight chamber temperature.

The photocatalytic reactor consists of nine 6-W blacklight blue fluorescent lamps enclosed in Pyrex glass tubes. The lamps emit primarily in the UVA (300-400 nm) wavelengths. The Pyrex tubes are 230 mm long and 28 mm in internal diameter. A thin film of TiO$_2$ is deposited on the inside surface of the glass tubes, concentric to the lamps. The total superficial photocatalyst surface area is 0.182 m$^2$. The distance from the lamp surface to the TiO$_2$ photocatalyst film is 3.5 mm. The lamp intensity at the TiO$_2$ surface is estimated by our calculations as 9 mW/cm$^2$.

At the start of a batch adsorption-desorption experiment [29], an initial dose of CH$_2$O was added to the airtight chamber. Independent air streams recirculated within the 10 m$^3$ chamber and the 0.09 m$^3$ small box, with no fresh air added at any time. In the simple adsorption-desorption experiments, CH$_2$O is transferred from the airtight chamber to the small box via adsorption to, and desorption from, the rotor until steady-state is
reached. In the batch adsorption-desorption with reaction experiments, the PCO reactor is placed in the small box and is operated concurrently with the rotating honeycomb.

2.4.2 Model and Parameter Estimation

The model development and parameter evaluation method is discussed in the following sections.

2.4.2.1 Adsorption-Desorption Equilibrium Constants

Data from the simple adsorption-desorption experiments from Shiraishi et al. [29] are used to calculate the adsorption equilibrium constants $K_{AC-CHR}$ and $K_{SB-CHR}$ at ambient and desorption/regeneration temperatures, respectively. The total quantity of CH$_2$O in the system is constant because no reaction occurs in these experiments. A CH$_2$O mole balance is used to calculate the amount of CH$_2$O adsorbed on the honeycomb rotor.

\[
V_{AC}C_0 = V_{AC}C_{AC} + V_{SB}C_{SB} + V_{CHR}C_{CHR} 
\]

The experimental conditions state that $5/6$ of the rotor resides in the airtight chamber, while $1/6$ is located in the small box. This separation is used to split the amount of CH$_2$O on the rotor. This is an approximation because the adsorption and desorption temperatures are different. At higher temperatures, more CH$_2$O desorbs from the rotor. Therefore, the amount of CH$_2$O on the hot rotor in the small box is smaller than we estimate.

Moles of CH$_2$O on the cold rotor in airtight chamber = \( \left( \frac{5}{6} V_{CHR} \right) C_{CHR} \)
Moles of CH₂O on the hot rotor in small box = \( \left( \frac{1}{6} V_{CHR} \right) C_{CHR} \)

A simple rate expression is developed for CH₂O adsorption on and desorption from the rotor. For the low CH₂O levels of interest (\(< 3 \text{ mg/m}^3\) or \(< 2.4 \text{ ppm}\)), we assume both adsorption and desorption to be first order in CH₂O on a sparsely covered surface.

**Adsorption Side:** \( \text{CH}_2\text{O}_{\text{airtight chamber (gas)}} \xrightleftharpoons[k_{\text{ads}}(T_{\text{ads}})]{k_{\text{des}}(T_{\text{des}})} \text{CH}_2\text{O}_{\text{rotor (ads)}} \)

\[ -V_{AC} \frac{dC_{AC}}{dt} = \frac{5}{6} V_{CHR} \frac{dC_{CHR}}{dt} = V_{AC} k_{\text{ads}}(T_{\text{ads}}) C_{AC} - \frac{5}{6} V_{CHR} k_{\text{des}}(T_{\text{des}}) C_{CHR} \]  

(3)

**Desorption Side:** \( \text{CH}_2\text{O}_{\text{rotor (ads)}} \xrightleftharpoons[k_{\text{ads}}(T_{\text{ads}})]{k_{\text{des}}(T_{\text{des}})} \text{CH}_2\text{O}_{\text{small box (gas)}} \)

\[ V_{SB} \frac{dC_{SB}}{dt} = -\frac{1}{6} V_{CHR} \frac{dC_{CHR}}{dt} = \frac{1}{6} V_{CHR} k_{\text{des}}(T_{\text{des}}) C_{CHR} - V_{SB} k_{\text{ads}}(T_{\text{ads}}) C_{SB} \]  

(4)

For adsorption-desorption only experiments, a steady state is predicted, at which time the net change in concentrations is zero. In this case, equations (3) and (4) are equal to zero and the adsorption equilibrium constants (ratio of rate constants) are solved from the system steady-state data. In the adsorption-desorption only experiments, Shiraishi and coworkers [29] stated that after 900 seconds (15 min), the CH₂O concentration in both rooms remained relatively unchanged. A system steady-state, corresponding approximately to an adsorption-desorption equilibrium between the chamber, rotor, and box, had been achieved. Thus, we solve for \( K_{AC-CHR} \) and \( K_{SB-CHR} \) using the data after 900 seconds. The K values are averaged using the data points from 1800-7200 seconds (30-120 min). The small decrease in CH₂O concentration at longer time (10800 s) is neglected.
The adsorption equilibrium constant is dependent on temperature. Hence, we find only one $K_{AC-CHR}$ constant ($T_{ads} =$ ambient) of 3.28, but three $K_{SB-CHR}$ constants ($T_{des} = 120^\circ C, 150^\circ C, 180^\circ C$) of 4.76, 4.07, and 2.70, respectively.

### 2.4.2.2 Adsorption Rate Constant in the Airtight Chamber

Given $K_{AC-CHR}$, equation 3 can be rearranged in terms of $K_{AC-CHR}$ instead of $k_{des}(T_{ads})$. This allows us to solve for $k_{ads}(T_{ads})$ because $K_{AC-CHR}$ is calculated from the method described above. The derivative term is obtained by the Differentiate function in Microcal Origin. All adsorption experiments were conducted at one temperature ($T_{ads}$), presumably ambient.

$$-V_{AC} \frac{dC_{AC}}{dt} = k_{ads}(T_{ads}) \left\{ V_{AC}C_{AC} - \frac{5}{6}V_{CHR}C_{CHR} \right\} \left( \frac{K_{AC-CHR}(T_{ads})}{K_{AC-CHR}(T_{ads})} \right)$$  \hspace{1cm} (7)

### 2.4.2.3 Desorption Rate Constants in the Small Box

The desorption rate constant $k_{des}(T_{des})$ is fitted to the Shiraishi data. An Arrhenius form is assumed for $k_{des}$. With $k_{des,0}$ taken as $10^{13}$ s$^{-1}$, the $E_{A,des}$ fitted to the data is 107 kJ/mol (25.6 kcal/mol). The pre-exponential factor for desorption is the same order of magnitude as reported in the literature for first-order desorption kinetics [30,31].
fitted activation energy of desorption is a typical value for weakly chemisorbed molecules on TiO$_2$. Lewandowski and Ollis [30] used the TPO/TPD data of Larson and Falconer [32] to estimate an $E_{A,\text{des}}$ between 23-28 kcal/mol for benzene, toluene, and xylene. Chemisorbed molecules characteristically have desorption activation energies greater than 50-100 kJ/mol (12-24 kcal/mol) [33]. Aldehydes are known to chemisorb weakly on TiO$_2$ (versus alcohols or carboxylic acids), hence their common appearance as reaction intermediates [22,32]. Our fitted $E_{A,\text{des}}$ falls within or just above these estimations. With these $k_{\text{des,0}}$ and $E_{A,\text{des}}$ values, three $k_{\text{des}}$ are calculated, one for each desorption temperature (i.e., 120°C, 150°C, 180°C).

$$k_{\text{des}}(T_{\text{des}}) = k_{\text{des,0}} \exp \left( \frac{-E_{A,\text{des}}}{RT_{\text{des}}} \right)$$  \hspace{1cm} (8)

2.4.2.4 Reaction Rate Constant

Our photocatalytic rate constant $k_{\text{cat}}(T_{\text{des}})$ is also fitted to the Shiraishi et al. [29] data from the combined, simultaneous operation of the rotating honeycomb and PCO reactor. A pseudo-first order reaction rate is assumed for CH$_2$O destruction. Obee and Brown [11] report that the CH$_2$O oxidation rate is first order at ambient temperatures for CH$_2$O concentrations pertinent to problematic buildings, which include the Shiraishi et al. [29] conditions (~0.5-2.0 ppmv). At 180°C (453 K) desorption temperature, the best fit for $k_{\text{cat}}$ is $2.38 \times 10^{-2}$ s$^{-1}$. At 120°C (393 K) and 150°C (423 K) the best fits for $k_{\text{cat}}$ are $1.19 \times 10^{-1}$ and $1.06 \times 10^{-1}$ s$^{-1}$, respectively.
The negative influence of temperature on apparent rate constant is rationalized as follows: a catalyzed reaction following a Langmuir-Hinshelwood rate form (as do most air contaminants including CH₂O) will provide a reaction rate form at low concentrations of

\[
\frac{r_{cat} = -k_{cat}C_{SB}V_{rrx}}{r_{cat} = -k_{rxn}K_{ads}C_{SB}V_{rrx}} = \frac{-k_{rxn} \exp \left( \frac{-E_{ads,TiO_2}}{RT} \right)}{k_{des,TiO_2,0} \exp \left( \frac{-E_{des,TiO_2}}{RT_{des}} \right)} C_{SB}V_{rrx} \]  

(9)

\[
\frac{r_{cat} \approx -k_{rxn} \frac{k_{ads,TiO_2,0}}{k_{des,TiO_2,0}} \exp \left( \frac{E_{app}}{RT_{des}} \right) C_{SB}V_{rrx}}{k_{cat} \approx k_{rxn} \frac{k_{ads,TiO_2,0}}{k_{des,TiO_2,0}} \exp \left( \frac{E_{app}}{RT_{des}} \right)} \]  

thus,

\[
k_{cat} \approx \frac{k_{rxn} \frac{k_{ads,TiO_2,0}}{k_{des,TiO_2,0}} \exp \left( \frac{E_{app}}{RT_{des}} \right)}{\Delta H_{ads,TiO_2}} \approx \frac{k_{rxn} \frac{k_{ads,TiO_2,0}}{k_{des,TiO_2,0}} \exp \left( \frac{E_{app}}{RT_{des}} \right)}{E_{des,TiO_2}}
\]

(if we assume \( k_{rxn} \) of a free radical (e.g., OH) to be approximately independent of temperature). Using the fitted \( k_{cat} \) values variation with temperature, we estimate the apparent activation energy of CH₂O desorption on TiO₂ \( (E_{app}) \) as 39 kJ/mol (9.3 kcal/mol). We expect a zero-to-small value for \( E_{ads,TiO_2} \) (e.g., CH₂O may need to displace weakly bound water) and a substantial value for \( E_{des,TiO_2} \) (e.g., 20-30 kcal/mol). We expect the term \( (E_{des,TiO_2}/T_{des} - E_{ads,TiO_2}/T_{ads}) > 0 \), thus \( k_{cat} \) will decrease with temperature, reflecting a decreased CH₂O coverage on the TiO₂ with increased temperature. A summary of our \( k_{cat} \) values and those in the literature is found in Table 2.1. Authors of the literature reported
here used various reactor geometries, so we chose a reactor volume basis \( V_{rxr} \) to simplify calculations.

We compare in Table 2.1 the reaction rate constants evaluated in this study with those in the literature. Reaction rates are dependent on the catalyst manufacturer and the UV light intensity, among other factors. We derived pseudo-first order kinetic rate constants from CH\(_2\)O data for PCO collected by other researchers, using CH\(_2\)O concentrations similar to those of Shiraishi (~2 ppm at STP). Data from Obee [12] and Obee and Brown [11] are used to derive a first order \( k_{cat} \) of 5.8 x 10\(^{-4}\) and 2.2 x 10\(^{-3}\) s\(^{-1}\), respectively, for UV light intensities ranging from 0.33-9.3 mW/cm\(^2\). Data from Noguchi et al. [15] and Ao et al. [17] are also used to calculate a \( k_{cat} \) of 2.1 x 10\(^{-3}\) and 6.8 x 10\(^{-4}\) s\(^{-1}\), respectively, for UV light intensities between 0.75-1.0 mW/cm\(^2\). Ching et al. [16] found first order \( k_{cat} \) values of 1.5 x 10\(^{-3}\) and 2.6 x 10\(^{-3}\) s\(^{-1}\) using solar and UV light intensities of 0.6 and 1.56 mW/cm\(^2\), respectively. The \( k_{cat} \) in our study ranges from 2.38 x 10\(^{-2}\) to 1.19 x 10\(^{-1}\) s\(^{-1}\). Shiraishi et al. [29] reported a UV light intensity of 15 \( \mu \)W/cm\(^2\), which is low for nine 6W blacklight-blue fluorescent lamps. Instead, our calculations estimate an intensity of 9 mW/cm\(^2\) for their data, assuming 30\% blacklight-blue emission efficiency. The brand of TiO\(_2\) catalyst used in the Shiraishi study is not listed. The two brands used by other authors discussed above are Degussa P25 or Ishihara Sangyo. Our calculated \( k_{cat} \) values fall on the high end and above the range derived from the authors above.

The \( k_{cat} \) derived from various authors’ data are normalized by their UV light intensity to account for this variation. Ching et al. [16] and Sauer and Ollis [22] report that at low UV intensities, the reaction rate is proportional to the irradiance \( (I) \). At medium to
higher UV intensities, the reaction rate is often proportional to $I^n$, where $0.5 < n < 1$. If all the reported irradiances for CH$_2$O PCO are low intensity, we may divide $k_{cat}$ by their irradiances (mW/cm$^2$). The normalized $k_{cat}$ for the authors discussed above range from $2.4 \times 10^{-4}$ to $2.5 \times 10^{-3}$ cm$^2$/mW-s at ambient temperatures (Table 2.1). The normalized $k_{cat}$ values in our study range from $2.6 \times 10^{-3}$ to $1.3 \times 10^{-2}$ cm$^2$/mW-s. Again, our values are on the high end and above the range derived from other authors’ data. We note that other reports pertain to ambient temperature photocatalysis, versus Shiraishi et al. [29] for which $T_{(reaction)} \sim T_{(desorption: 120-180°C)}$.

At high UV intensities, photodissociation (photolysis) of CH$_2$O can occur and potentially complicate interpretation of PCO data for CH$_2$O. The fitted $k_{cat}$ in our study is a bulk term that includes both photocatalytic and any photolytic effects. Obee and Brown [11] explored this issue, finding a linear relationship between UV flux and CO evolution from CH$_2$O photolysis. At 7 mW/cm$^2$, they observed no CO evolution in a stream with initial 3.3 ppmv CH$_2$O. At 25 mW/cm$^2$, they observed 0.10 ppmv CO evolution. Assuming a linear relationship, the data from Shiraishi et al. [29] would produce 0.03 ppmv CO from photolysis at 9 mW/cm$^2$. Thus, less than 1.5% of the CH$_2$O would photodissociate, using a 1:1 CH$_2$O:CO relationship. This 1:1 ratio is similar to the Obee and Brown [11] reported data, and predicted by Okabe [34]. Moreover, Ching et al. [16] found the photolytic rate constant to be $\sim 10x$ smaller than the photocatalytic rate constant at a solar irradiance of 0.6 mW/cm$^2$. Hence, we believe the photolytic contribution to CH$_2$O disappearance is negligible in Shiraishi’s data, and is not included in our model.
2.4.2.5 **Overall Models**

After all of the parameters are calculated or fitted, two equations result for each model: one equation for the airtight chamber, and one for the small box. Equation 7 is used for CH$_2$O adsorption on the rotor from the airtight chamber. In the adsorption-desorption only model, equation 4 is rearranged to estimate CH$_2$O desorption from the rotor to the small box (equation 10). In the desorption/reaction model, equation 11 includes the PCO reaction in the small box. Table 2.2 summarizes all of the calculated and fitted parameters in the two models.

\[
V_{SB} \frac{dC_{SB}}{dt} = k_{des} \left( T_{des} \right) \left\{ \frac{1}{6} V_{CHR} C_{CHR} - K_{SB-CHR} \left( T_{des} \right) V_{SB} C_{SB} \right\} \quad \text{(without reaction)} \tag{10}
\]

\[
V_{SB} \frac{dC_{SB}}{dt} = k_{des} \left( T_{des} \right) \left\{ \frac{1}{6} V_{CHR} C_{CHR} - K_{SB-CHR} \left( T_{des} \right) V_{SB} C_{SB} \right\} - k_{cat} \left( T_{des} \right) V_{rxr} C_{SB} \quad \text{(with reaction)} \tag{11}
\]

2.5. **Calculated Results and Discussion**

2.5.1 *Adsorption-Desorption Only Model*

Figure 2.2 shows the model and Shiraishi data in both rooms at 180°C desorption temperature. In the airtight chamber, the adsorption model fits the data well; it predicts the initial $C_{AC}(t)$ profile (0-1800 s) accurately. At longer times, the adsorption equilibrium value $C_{AC}(\text{equil})$ is smaller than predicted. In the small box, the desorption model provides a reasonable fit to the data. The model predicts the initial $C_{SB}(t)$ profile (0-300 s) well. The monotonic decrease in this data under dark conditions between 3600-10800 seconds may be caused by an effect that is not considered. For example, slow dimerization of
CH₂O to paraformaldehyde may occur on the adsorbent. Similar data for the model and Shiraishi data at 120°C and 150°C desorption temperatures are found in Figure 2.3. At all desorption temperatures, the residual error between our model and the Shiraishi data falls within ±0.07 mg/m³ in the airtight chamber, and ±0.3 mg/m³ in the small box with the exception of two data points.

2.5.2 Adsorption-Desorption and Reaction Model

The model described above is modified to include the PCO reactor in the small box. Figure 2.4 shows the model and Shiraishi data in both rooms at 180°C desorption temperature. In the airtight chamber, the adsorption model follows the trend of the data. At 10800 seconds (180 min), both the data and the model approach zero for \( C_{AC} \), as expected because CH₂O is continuously oxidized photocatalytically in the small box. In the small box, the reaction model also provides a reasonable fit to the desorption and reaction data. The model qualitatively describes the increase and subsequent decrease in \( C_{SB} \) caused by the reaction. Results for the model and Shiraishi data at 120°C and 150°C desorption temperatures are found in Figure 2.5. At all desorption temperatures, the residual error falls within ±0.05 mg/m³ in the airtight chamber, and ±0.3 mg/m³ in the small box.

The fitted values of \( k_{cat} \) for the 120°C and 150°C desorption temperatures are almost an order of magnitude larger than the 180°C value. Shiraishi et al. [29] attributed a marked loss in photocatalytic activity (and consequently a decrease in \( k_{cat} \)) at 180°C to unknown substances, liberated from the activated carbon rotor, and strongly adsorbed on
the glass surface of the TiO$_2$ reactor. Such a film formation would decrease the intensity of light arriving at the photocatalyst surface, and thus the resultant decrease in $k_{cat}$. An alternate explanation is that the $k_{cat}$ used here is a bulk term which includes both CH$_2$O adsorption on TiO$_2$ and the true reaction rate constant, as described above. Adsorption decreases with increasing temperature, lowering CH$_2$O coverage. There are similar order of magnitude decreases in $k_{cat}$ and $K_{SB}$ with increasing temperature, consistent with the idea that $k_{cat}$ is dominated by the temperature dependence of adsorption.

The quantum yield ($\Phi_{overall}$) is defined as the rate of photoreaction divided by the rate of light absorption [35]. The latter is difficult to estimate using the Shiraishi data. Incident light from the lamp may be absorbed, reflected, or scattered upon reaching the catalyst surface. Instead, a formal quantum efficiency (FQE) of the system is calculated, defined as [35,36]

$$\delta = \frac{\text{rate of photocatalyzed reaction (molecules/second)}}{\text{incident light intensity (photons/second)}}$$

(12)

The FQE is always less than the quantum yield because it incorporates all incident light. The FQE is calculated for the Shiraishi data by making two estimations: 1) the reaction rate is first order in CH$_2$O, and 2) 1 mW/cm$^2$ corresponds to $\sim$2 x $10^{15}$ photons/(s-cm$^2$) at 350 nm wavelength, as calculated using the Planck relation and the wave theory of light [37]

$$E = h\nu$$

(13)

$$\lambda\nu = c$$

(14)
\[
\text{# photons cm}^{-2}\text{sec}^{-1} = \frac{E}{h(c/\lambda)} 
\]

where \( E \) is the total incident photon energy (mW), \( h \) is Planck’s constant (6.63 \times 10^{-34} \text{J\cdot s/photon}), \( c \) is the speed of light in vacuum (2.998 \times 10^8 \text{m/s}), and \( \lambda \) is the wavelength (nm). We calculate the maximum FQEs for the Shiraishi reaction data to be 6 \times 10^{-3} at 180°C, and 2 \times 10^{-3} molecules/photon at 120°C and 150°C desorption temperatures. A comparison of our FQEs for the Shiraishi data with other literature is found in Table 2.1. Our calculated FQEs for the Shiraishi data are lower than those of other authors.

The model developed here for the combined rotating adsorbent - PCO reactor system developed by Shiraishi et al. [29] gives a technique for evaluation of the adsorption, desorption, and reaction rate constants, and the adsorption equilibrium constants. This engineering kinetic model can be broadly applied to design related systems with different adsorption/desorption temperatures, adsorbent materials, and room (chamber) sizes.

### 2.6. Conclusions

A reaction engineering model is developed for the novel combination of a rotating honeycomb adsorbent with a photocatalytic reactor. The model assumes the adsorption, desorption, and reaction steps to be first order with respect to CH\(_2\)O. All model parameters were evaluated from the batch data of Shiraishi et al. [29]. Two models are developed: adsorption-desorption only, and adsorption-desorption with PCO reaction. Both models qualitatively describe the observed behavior of gas phase CH\(_2\)O concentrations vs. time.
In the adsorption-desorption only experiments, the model describes both transient and asymptotic steady-state values in the airtight chamber and the small box. In the adsorption-desorption with reaction experiments, the model again adequately represents the data. The pseudo-first order reaction rate constants determined via model fitting fall in the same range as derived in five literature studies.

2.7. **Acknowledgements**

The authors acknowledge support from the State of North Carolina for funding of this research. The authors also thank the Park Foundation Scholarship at North Carolina State University for funding Lao Yang.

2.8. **References**


Table 2.1. A comparison of our pseudo-first order reaction rates ($k_{cat}$) and formal quantum efficiencies ($\delta$) to literature data.

<table>
<thead>
<tr>
<th>UV Flux (mW/cm²)</th>
<th>Reaction Temp (°C)</th>
<th>$k_{cat}$ (s⁻¹)</th>
<th>Normalized $k_{cat}$ (cm²/{mW-s})</th>
<th>FQE b</th>
<th>Catalyst Manufacturer</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>This Article</td>
<td>9</td>
<td>120-180</td>
<td>(2.38 \times 10^{-2}) to (1.19 \times 10^{-1})</td>
<td>(2.6 \times 10^{-3}) to (1.3 \times 10^{-2})</td>
<td>(6 \times 10^{-4}) to (2 \times 10^{-3})</td>
<td>--</td>
</tr>
<tr>
<td>Obee and Brown a, c</td>
<td>9.3</td>
<td>~22-24</td>
<td>(2.2 \times 10^{3})</td>
<td>(2.4 \times 10^{4})</td>
<td>(1.5 \times 10^{2})</td>
<td>Degussa P25</td>
</tr>
<tr>
<td>Obee a</td>
<td>0.33</td>
<td>~22</td>
<td>(5.8 \times 10^{-4})</td>
<td>(1.8 \times 10^{-3})</td>
<td>(1.2 \times 10^{-1})</td>
<td>Degussa P25</td>
</tr>
<tr>
<td>Noguchi et al. a</td>
<td>1</td>
<td>~22</td>
<td>(2.1 \times 10^{3})</td>
<td>(2.1 \times 10^{3})</td>
<td>(6 \times 10^{-2})</td>
<td>Ishihara Sangyo</td>
</tr>
<tr>
<td>Ching et al.</td>
<td>0.6 (solar)</td>
<td>Room Temp</td>
<td>(1.5 \times 10^{3})</td>
<td>(2.4 \times 10^{3})</td>
<td>(2 \times 10^{-3})</td>
<td>Self prepared &amp; Degussa P25</td>
</tr>
<tr>
<td>Ao et al. a</td>
<td>0.75</td>
<td>Room Temp</td>
<td>(6.8 \times 10^{-4})</td>
<td>(9.1 \times 10^{-4})</td>
<td>--</td>
<td>Degussa P25</td>
</tr>
</tbody>
</table>

* Pseudo-first order $k_{cat}$ values were estimated from literature data
* Formal quantum efficiencies were estimated from literature data
* Obee and Brown ran experiments at multiple temperatures, but only the room temperature data is reported here
Table 2.2. Summary of the parameters calculated or fitted in the model.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$k_{ads}(T_{ads})$ (s$^{-1}$)</th>
<th>$k_{des,0}$ (s$^{-1}$)</th>
<th>$E_{A,des}$ (kJ/mol)</th>
<th>$k_{des}(T_{des})$ (s$^{-1}$)</th>
<th>$K_{AC-CHR}$</th>
<th>$K_{SB-CHR}$</th>
<th>$k_{cat}(T_{des})$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T$_{ads}$</td>
<td>4.33 x 10$^{-4}$</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>3.28</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>120°C</td>
<td>--</td>
<td>10$^{13}$</td>
<td>107</td>
<td>0.0607</td>
<td>--</td>
<td>4.76</td>
<td>0.119</td>
</tr>
<tr>
<td>150°C</td>
<td>--</td>
<td>10$^{13}$</td>
<td>107</td>
<td>0.618</td>
<td>--</td>
<td>4.07</td>
<td>0.106</td>
</tr>
<tr>
<td>180°C</td>
<td>--</td>
<td>10$^{13}$</td>
<td>107</td>
<td>4.63</td>
<td>--</td>
<td>2.70</td>
<td>0.0238</td>
</tr>
</tbody>
</table>
2.9. List of Figures

Figure 2.1. A schematic of an air-purification system consisting of the photocatalytic reactor with a parallel array of nine blacklight-blue fluorescent lamps and the continuous adsorption and desorption apparatus with a ceramic-paper honeycomb rotor retaining activated carbon or zeolite fine particles (reproduced from Shiraishi et al. [29]).

Figure 2.2. Shiraishi data and model of adsorption-desorption only at 180°C desorption temperature in the (a) airtight chamber and (b) the small box.

Figure 2.3. Shiraishi data and model of adsorption-desorption only at 120°C and 150°C desorption temperatures in the (a) airtight chamber and (b) the small box.

Figure 2.4. Shiraishi data and model of adsorption-desorption with photocatalytic reaction at 180°C desorption temperature in the (a) airtight chamber and (b) the small box.

Figure 2.5. Shiraishi data and model of adsorption-desorption with photocatalytic reaction at 120°C and 150°C desorption temperatures in the (a) airtight chamber and (b) the small box.
Figure 2.2
Figure 2.3
Figure 2.5
CHAPTER 3

DESIGN APPROACHES FOR A CYCLING ADSORBENT / PHOTOCATALYST SYSTEM FOR INDOOR AIR PURIFICATION: FORMALDEHYDE EXAMPLE

3.1. Abstract

A kinetic model for a cycling adsorbent/photocatalyst combination for formaldehyde removal in indoor air [1] was previously developed in our lab, demonstrating agreement with lab-scale batch operation data of Shiraishi, Yamaguchi, and Ohbuchi [2]. Model parameters evaluated included adsorption equilibrium and rate constants for the adsorbent (activated carbon) honeycomb rotor, and catalytic rate constant for pseudo-first-order formaldehyde destruction in the titanium-dioxide photoreactor.

The present paper explores design consequences for this novel system. In particular, the batch parameter values are used to model both adsorbent and photocatalyst behavior for continuous operation in typical residential home challenges. Design variables, including realistic make-up air fractions, adsorbent honeycomb rotation speed, and formaldehyde source emission rates, are considered to evaluate the ability of the system to achieve World Health Organization pollutant guidelines. In all circumstances, the size of the required rotating adsorbent bed and photoreactor for single stage operation, and the resultant formaldehyde concentration in the home is calculated. The ability of how well such a system might be accommodated within the typical dimensions of commercial ventilation ducts is also considered.

**Key Words:** Indoor air quality, Photocatalysis, Formaldehyde, Titanium dioxide, TiO₂, Adsorption, Desorption, Regeneration, Model, Design
### 3.2. Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{CHR}$</td>
<td>CH$_2$O concentration on the ceramic honeycomb rotor (mg/cm$^3$)</td>
</tr>
<tr>
<td>$C_F$</td>
<td>CH$_2$O concentration in the feed after recirculated/make-up air (mg/cm$^3$)</td>
</tr>
<tr>
<td>$C_M$</td>
<td>CH$_2$O concentration in the make-up air stream (mg/cm$^3$)</td>
</tr>
<tr>
<td>$C_S$</td>
<td>CH$_2$O concentration source emission at steady state (µg/m$^3$)</td>
</tr>
<tr>
<td>$C_{SR}$</td>
<td>CH$_2$O concentration in the simulated room (mg/cm$^3$)</td>
</tr>
<tr>
<td>$C_{SR,S}$</td>
<td>CH$_2$O concentration in the supply air entering the simulated room (mg/cm$^3$)</td>
</tr>
<tr>
<td>$C_{SB}$</td>
<td>CH$_2$O concentration in the small box (mg/cm$^3$)</td>
</tr>
<tr>
<td>$c_{fuel}$</td>
<td>Fuel cost ($/unit fuel)</td>
</tr>
<tr>
<td>$DD_c$</td>
<td>Degree days data for cooling (°F days)</td>
</tr>
<tr>
<td>$DD_h$</td>
<td>Degree days data for heating (°F days)</td>
</tr>
<tr>
<td>$f$</td>
<td>Fraction of make-up air</td>
</tr>
<tr>
<td>$f_{escape}$</td>
<td>Fraction of CH$_2$O (emission rate) which escapes into the house</td>
</tr>
<tr>
<td>$k_{ads}(T_{ads})$</td>
<td>CH$_2$O adsorption rate constant between the ceramic honeycomb rotor and the simulated room (min$^{-1}$)</td>
</tr>
<tr>
<td>$k_{cat}(T_{des})$</td>
<td>CH$_2$O pseudo-first order kinetic rate constant in the photocatalytic reactor (min$^{-1}$)</td>
</tr>
<tr>
<td>$k_{des}(T_{des})$</td>
<td>CH$_2$O desorption rate constant on the ceramic honeycomb rotor in the small box (min$^{-1}$)</td>
</tr>
<tr>
<td>$K_{SR-CHR}(T_{ads})$</td>
<td>CH$_2$O adsorption equilibrium constant between the simulated room and the ceramic honeycomb rotor</td>
</tr>
<tr>
<td>$K_{SB-CHR}(T_{des})$</td>
<td>CH$_2$O adsorption equilibrium constant between the small box and the ceramic honeycomb rotor</td>
</tr>
<tr>
<td>$L$</td>
<td>Product loading rate (m$^2$/m$^3$)</td>
</tr>
<tr>
<td>$N$</td>
<td>Air exchange rate (h$^{-1}$)</td>
</tr>
<tr>
<td>$q_{fuel}$</td>
<td>Available fuel heat (BTU/unit fuel)</td>
</tr>
<tr>
<td>$q_{latent}$</td>
<td>Latent energy load from cooling of water (kW)</td>
</tr>
<tr>
<td>$Q_M$</td>
<td>Ventilation air flow rate in the make-up stream (m$^3$/min)</td>
</tr>
<tr>
<td>$Q_{SR,D}$</td>
<td>Ventilation air flow rate in the discharge stream (m$^3$/min)</td>
</tr>
<tr>
<td>$Q_{SR,R}$</td>
<td>Ventilation air flow rate in the recirculation stream (m$^3$/min)</td>
</tr>
<tr>
<td>$Q_{SR,S}$</td>
<td>Ventilation air flow rate in the supply stream of the simulated room (m$^3$/min)</td>
</tr>
<tr>
<td>$R$</td>
<td>Universal gas constant (8.314 J/(mol·°K))</td>
</tr>
<tr>
<td>$S$</td>
<td>Source emission rate of CH$_2$O (mg/min or µg/m$^2$·h)</td>
</tr>
<tr>
<td>$t$</td>
<td>Time (min)</td>
</tr>
<tr>
<td>$t_{op}$</td>
<td>Operating time (h/week)</td>
</tr>
<tr>
<td>$V_{SR}$</td>
<td>Volume of the simulated room (300 m$^3$)</td>
</tr>
<tr>
<td>$V_{CHR}$</td>
<td>Volume (bulk) of the ceramic honeycomb rotor (m$^3$)</td>
</tr>
<tr>
<td>$V_{rxr}$</td>
<td>Volume of the photocatalytic reactor (m$^3$)</td>
</tr>
<tr>
<td>$V_{SB}$</td>
<td>Volume of the small box (m$^3$)</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Rotation speed of the ceramic honeycomb rotor (rot/min)</td>
</tr>
</tbody>
</table>
3.3. Introduction

Indoor air quality (IAQ) has been a health hazard concern since the early 1990s. The primary causes for IAQ problems in residential homes are gas and particle release from pollution sources, such as paint [3], wallpaper [4], carpet [5], and cleaning products [6]. Studies show that pollutant concentration indoors can be higher than outdoors [7] in both developed and developing countries, a circumstance of concern because people spend about 87% of their time enclosed indoors [8].

One class of gas releases in homes is volatile organic compounds (VOCs). Compounds such as formaldehyde (CH\textsubscript{2}O) and derivative aldehydes (e.g., acetaldehyde), derivative benzenes (e.g., styrene, xylene), alkanes/alkenes, and alcohols [5], are example VOCs that can cause poor IAQ, and a condition called “sick building syndrome” (SBS). Formaldehyde has been studied exhaustively as a problem indoor air pollutant. Not only does CH\textsubscript{2}O contribute to poor IAQ, but other VOCs (e.g., ethanol, acetaldehyde) decompose to CH\textsubscript{2}O as an intermediate species [9,10]. It is sufficiently important to IAQ that Sherman and Hodgson [11] suggest its use as a basis for residential ventilation design rates. Formaldehyde exposure levels are regulated by the World Health Organization (WHO), the Occupational Safety and Health Administration (OSHA), and the American Conference of Governmental Industrial Hygienists (ACGIH). The main source of CH\textsubscript{2}O emissions in homes is wood products [11-13].

There are three primary methods to improve IAQ: (1) source control, (2) improved ventilation, and (3) remediation. Current source control consists of voluntary standards for
particleboard construction. The maximum CH$_2$O emission for most particleboards is 0.30 ppm, with 0.20 ppm for particleboard flooring products (e.g., underlayment), as stated by ANSI A208.1-1999 [14]. Increasing air ventilation can introduce hazardous pollutants from outdoor air, especially in urban areas [15], and increase energy consumption for humidification and heating/cooling of fresh air to the desired temperature. Increasing ventilation rates does not guarantee lower CH$_2$O concentration because of seasonal temperature and relative humidity effects on CH$_2$O emission rates [12].

Of these three main control methods, remediation is the best option for CH$_2$O removal in residential homes. Adsorption by carbonaceous material is the most common remediation technique for cleaning air. Asada et al. [16] studied the use of charcoal as an adsorbent for harmful gases and odorants that cause SBS or “chemical sensitivity.” Rotating adsorbents feature alternating adsorption and desorption zones. Both activated carbon and silica zeolites have been coated on ceramic honeycomb and explored as adsorbent rotor for VOC removal. Mitsuma et al. [17] developed an empirical formula for the optimal rotation speed for cyclohexanone adsorption on a silica zeolite-coated honeycomb rotor. For 30 and 200 ppm cyclohexanone concentrations, the optimal rotation speed was found to be a function of desorption gas stream velocity, rotor width, and ratio of the monolith cross-sectional area in the process zone to the monolith area in the desorption zone. Typical rotation rates ranged from 20-50 per hour.

Shiraishi et al. [2] demonstrated the use of a cyclic activated carbon adsorbent in combination with a titanium dioxide (TiO$_2$) photocatalyst for photocatalytic oxidation (PCO) of CH$_2$O. Previous work in our research group [1] developed a kinetic model for
the rotating adsorbent / PCO system constructed by Shiraishi et al. [2]. The model parameters evaluated include adsorption equilibrium and rate constants for the adsorbent rotor, and pseudo-first-order PCO rate constants at multiple temperatures (120, 150, 180°C). The present paper applies our kinetic model to design a continuous flow adsorbent / PCO system using realistic values for CH2O concentrations, house volume, and ventilation rates. The model system is tested to ascertain the feasibility of achieving the 0.1 mg/m³ (0.081 ppm at STP) WHO guideline for CH2O. Different parameters (e.g., CH2O emission rate, desorption temperature, make-up air fraction, rotation speed) are varied to determine their effect on CH2O concentrations and volumes of the cycling adsorbent, photoreactor, and small box. Our model can incorporate software with more complex emission patterns, such as RISK [18] and EXPOSURE [19].

3.4. Experimental

3.4.1 Experimental Apparatus

The original Shiraishi et al. [2] system consists of a 10 m³ simulated room (SR) and a 0.09 m³ small box (SB) containing a photoreactor, shown in Figure 3.1. A cylindrical rotating adsorbent (activated carbon on ceramic honeycomb) carries adsorbed pollutant from the simulated room into the small box, where a recirculating hot air stream drives pollutant desorption, and subsequent destruction by the photocatalyst in the small box. The “regenerated” adsorbent ceramic honeycomb rotor (CHR) rotates back into the simulated room to repeat the cycle of adsorption (SR), desorption (SB), and
photocatalyzed oxidation (PCO). Shiraishi et al. [2] used batch operation to demonstrate their system concept for integrated adsorption/desorption/PCO of CH$_2$O.

The present paper uses our kinetic model to describe a continuous operation shown in Figure 3.2. The system considered is based on the well-mixed model for a typical house with air recirculation [20]. The dimensions of the simulated room are those for an EPA test house tested by Sparks et al. [19]. The house volume ($V_{SR}$) is 300 m$^3$ (~10,600 ft$^3$), with floor area of 123 m$^2$ (1,325 ft$^2$) and wall area of 188 m$^2$ (~2,025 ft$^2$). Sparks et al. [19] treated their seven-room house as three rooms, but for our modeling purposes, we combine all rooms into one. Previous work [21] on another EPA test house show minimal pollutant concentration variations between each room, except where the pollutant source is located.

The simulated room has a supply and exit volumetric flow rate, $Q_{SR,S}$ and $Q_{SR,E}$, respectively, with corresponding CH$_2$O supply and exit concentrations, $C_{SR,S}$ and $C_{SR}$, respectively. The source term $S$ in the simulated room is the CH$_2$O emission rate. A portion of the exit air is discharged ($Q_{SR,D}$). The remaining exit air is recirculated ($Q_{SR,R}$). Additional make-up air ($Q_M$) is added to the system to maintain a constant volumetric flow rate in the simulated room ($Q_{SR,D} = Q_M$). Therefore, the air flow entering and leaving the system are equal ($Q_{SR,S} = Q_{SR,E}$). The fraction of make-up air ($f$) is defined as the ratio of make-up air to exit air volumetric flow rates ($Q_M/Q_{SR,E}$).

With these definitions, the simulated room CH$_2$O mass balance is a first-order linear ODE:

$$\text{(rate)} = \text{(source)} + [(\text{inflow}) - (\text{outflow})]$$

(1)
The small box balance depends on both rotor speed \( \dot{\omega} \) (rot/min) and the catalytic rate constant \( k_{\text{cat}} \):

\[
V_{\text{SR}} \frac{dC_{\text{SR}}}{dt} = S + \left( Q_{\text{SR},S} C_{\text{SR},S} - Q_{\text{SR},E} C_{\text{SR}} \right)
\]

The mass balance for adsorbed formaldehyde \( C_{\text{CHR}} \) at flow stream conditions includes net adsorption from the flowing streams and net removal by rotation into the small box:

\[
V_{\text{HR}} \frac{dC_{\text{CHR}}}{dt} = \dot{\omega} V_{\text{CHR}} \left( C_{\text{CHR}} - K_{\text{SB-CHR}} (T_{\text{des}}) C_{\text{SB}} \right) - k_{\text{cat}} (T_{\text{des}}) V_{\text{rxr}} C_{\text{SB}}
\]

where \( C_{\text{CHR}} = K_{\text{SR-CHR}} (T_{\text{ads}}) C_{\text{SR},s} \)

\[
(\text{rate}) = [(\text{rotation in from SR}) - (\text{rotation out to SR})] - (\text{PCO reaction})
\]

\[
V_{\text{SB}} \frac{dC_{\text{SB}}}{dt} = \dot{\omega} V_{\text{CHR}} \left( C_{\text{CHR}} - K_{\text{SB-CHR}} (T_{\text{des}}) C_{\text{SB}} \right) - k_{\text{cat}} (T_{\text{des}}) V_{\text{rxr}} C_{\text{SB}} \tag{2}
\]

where \( C_{\text{CHR}} = K_{\text{SR-CHR}} (T_{\text{ads}}) C_{\text{SR},s} \)

The recirculated and make-up air are mixed downstream of the simulated room \((Q_{\text{SR},s}, C_{F})\), and enter the ceramic honeycomb rotor \((V_{\text{CHR}}, C_{\text{CHR}})\), where \( \text{CH}_2\text{O} \) adsorbs \((k_{\text{ads}}(T_{\text{ads}}), K_{\text{SR-CHR}})\) on the activated carbon honeycomb at ambient conditions \((T_{\text{ads}})\). The rotor effluent stream \((Q_{\text{SR},s}, C_{\text{SR},s})\) returns to the simulated room. The adsorbent honeycomb rotor carries adsorbed \( \text{CH}_2\text{O} \) from the simulated room to the small box \((V_{\text{SB}}, C_{\text{SB}})\), where an internal, recirculating heated air stream heats the rotor to a temperature \((T_{\text{des}})\) ranging from 120-180°C. Formaldehyde desorbs from the honeycomb into the small box gas phase because of the elevated temperature \((k_{\text{des}}(T_{\text{des}}), K_{\text{SB-CHR}})\). Finally, the photoreactor \((V_{\text{rxr}})\) in the small box oxidizes \( \text{CH}_2\text{O} \) at a pseudo-first-order reaction rate,
with a temperature dependent reaction rate constant \(k_{cat}(T_{des})\) listed in Table 3.1, along with the other parameters calculated from the previous model [1].

3.4.2 Model and Parameter Estimations

The model development and parameter evaluation method are discussed in the following sections. There are 5 design parameters \((C_{SR,S}, C_{SB}, V_{CHR}, V_{SB}, \text{and } V_{rxr})\) and 5 equations (Eq. (1), (2), (3), (5), and (6)) to solve. The tunable parameters are \(Q_{SR,S}, f, \sigma, S, \text{and } f_{escape}\), the fraction of emitted CH\(_2\)O which escapes into the house.

3.4.2.1 Simulated Room

The simulated room CH\(_2\)O mass balance (Eq. (1)) includes an emission source term \(S\) (generation) and a continuous inflow/outflow of the room. The design parameter in Eq. (1) is \(C_{SR,S}\). The system is assumed to be a well-mixed room with no transport resistances, as described in “Indoor Air Quality Engineering” by Heinsohn and Cimbala [20]. The source term \(S\) for CH\(_2\)O emission occurs only from particleboard underlayment flooring because it has the highest surface area (123 m\(^2\)). Formaldehyde emissions from cabinets and countertops have minimal impact because of their low surface area compared to flooring. Formaldehyde adsorption/desorption from gypsum board [22] (e.g., drywall) is neglected. Air infiltration from the outdoors or exfiltration to the outdoors is neglected. The make-up air \((Q_M, C_M)\) has no CH\(_2\)O (i.e., \(C_M = 0\)).

Three cases are considered in this article. Case 1 assumes a source term \(S\) strength of 119 \(\mu\)g/(m\(^2\)-h) (0.244 mg/min CH\(_2\)O), taken from Kelly et al. [4] for 5/8” particleboard
underlayment under typical conditions. Case 2 and 3 are derived from ANSI A208.1-1999 [14] maximum values of 0.20 and 0.30 ppm (250 and 370 µg/m³ at STP, respectively) CH₂O steady state concentrations. Emission rates are calculated from ASTM E 1333-96 [23] (Eq. (4)), where \( C_S \) is the steady state CH₂O concentration (µg/m³), \( N \) is the air exchange rate (h⁻¹), and \( L \) is the product loading rate in the chamber (m²/m³). For most particleboard grades, \( L \) is 0.425 m²/m³ [14]. Kelly et al. [4] assumes an \( N \) of 0.50 h⁻¹, which gives an \( S \) of 290 µg/(m²-h) (0.595 mg/min) for a \( C_S \) of 0.20 ppm (Case 2) and 440 µg/(m²-h) (0.902 mg/min) for a \( C_S \) of 0.30 ppm (Case 3).

\[
S = \frac{C_S N}{L}; \quad \text{where} \quad N = \frac{Q_{SR,s}}{V_{SR}}
\]  

(4)

Bare particleboard underlayment is often covered by tiles, carpet, or hardwood flooring. Therefore, not all emitted CH₂O releases immediately into the house. The fraction of the emission rate (\( f_{\text{escape}} \)) entering the simulated room is assumed to be 20% for the base case. Incorporating \( f_{\text{escape}} \) changes \( S \) to 0.049, 0.12, and 0.18 mg/min CH₂O for Case 1, Case 2, and Case 3, respectively.

3.4.2.2 Small Box

The small box encloses the photoreactor. The CH₂O small box mass balance (Eq. (2)) includes three terms: the adsorbent honeycomb rotation in from and out to the ventilation duct, and a first-order irreversible PCO reaction. The small box is operated at 3 different desorption temperatures (\( T_{\text{des}} \)): 120, 150, and 180°C. The design parameters in
Eq. (2) are $C_{SB}$, $V_{CHR}$, $V_{SB}$, and $V_{rxr}$. We take the ratios of ($V_{CHR}/V_{SB}$) and ($V_{rxr}/V_{SB}$) to be constant, according to the Shiraishi et al. [2] dimensions (Eq. (5) and (6)). No attempt is made to evaluate the cost of heating up the small box.

$$V_{CHR}/V_{SB} = 0.0393$$  \hspace{1cm} (5)

$$V_{rxr}/V_{SB} = 0.152$$  \hspace{1cm} (6)

### 3.4.2.3 Ceramic Honeycomb Rotor

The ceramic honeycomb rotor contains the activated carbon adsorbent. The CH$_2$O mass balance (Eq. (3)) includes an adsorption rate from the ventilation duct air stream to the adsorbent honeycomb, and adsorbent honeycomb rotation out to and in from the small box. The design parameters in Eq. (3) are $C_{SR,S}$, $C_{SB}$, and $V_{CHR}$. The rotor speed was not stated in the Shiraishi et al. [2] article. A base case $\omega$ of 4 rot/min is assumed as a reasonable rate. Per Shiraishi et al. [2] we assume that 1/6 of the rotor volume $V_{CHR}$ lies within the small box, and 5/6 is in the ventilation duct.

Activated carbon is used to absorb many chemicals present in ventilation air [16,24], including CH$_2$O. The CH$_2$O concentration on the rotor, $C_{CHR}$, may decrease if there is a significant presence of other pollutants. In addition, activated carbon adsorbs water vapor [25,26]. The experiments run by Shiraishi et al. [2] did not contain water. Our original model [1] neglected the effect of water vapor / relative humidity (R.H.) on the adsorbent CH$_2$O capacity, but this present article explores the effect of water on adsorbent honeycomb and photoreactor volumes.
3.5. Results and Discussion

3.5.1 No Remediation

In the absence of the photoreactor, no remediation occurs in the house, transforming Eq. (1) into Eq. (7). This equation is solved analytically using the integrating factor to yield Eq. (8). The steady-state $C_{SR}$ is calculated by setting the derivative in Eq. (7) equal to zero, or setting time $t$ to infinity in Eq. (8).

$$V_{SR} \frac{dC_{SR}}{dt} + C_{SR} \left[ Q_{SR,E} - Q_{SR,S} (1-f) \right] = S + Q_{SR,S} C_M f$$

(7)

$$C_{SR} (t) = \frac{S + Q_{SR,S} C_M f}{Q_{SR,E} - Q_{SR,S} (1-f)} \left[ 1 - \exp \left( - \frac{Q_{SR,E} - Q_{SR,S} (1-f)}{V_{SR}} t \right) \right]$$

(8)

If we fix $Q_{SR,S}$ to 1.274 m$^3$/min, the minimum ventilation rate for our conditions as specified by American Society of Heating, Refrigerating, and Air-Conditioning Engineers (ASHRAE) Standard 62.2-2004 [27], a make-up air ratio $f$ between 0.4-1.4 is required to achieve the WHO guideline of 0.1 mg/m$^3$ (Figure 3.3a). A value of 0.4 for $f$, as in Case 1, is high but not unreasonable. Case 2 is unrealistic because $f = 0.95$ to achieve the WHO guideline. It is physically impossible to achieve the WHO guideline for Case 3 because for any $f > 1$, the recirculation air flow is negative, indicating direct bypassing of make-up air into the exhaust stream.

Alternatively, we fix $f$ at two values, 0.1 and 1.0, to see what $Q_{SR,S}$ values are required to achieve the WHO guideline. The ASHRAE Standard 62.2-2004 [27] does not regulate the value of $f$ in residential homes, so we assume $f = 0.1$ as a reasonable fraction. We normalize $Q_{SR,S}$ to the floor area of the house to generalize the model. For the model
home with 123 m$^2$ floor area and $f = 0.1$ (Figure 3.3b), the best case scenario (Case 1) requires a 4x increase in the minimum $Q_{SR,S}$, while the worst case scenario (Case 3) requires a 15x increase in the minimum $Q_{SR,S}$. At $f = 1.0$ (Figure 3.3c), Case 1 only requires 0.4x of the minimum $Q_{SR,S}$, while Case 3 requires a 1.5x increase in the minimum $Q_{SR,S}$.

We estimate a yearly annual cost to heat up and to cool down ventilation air using a modified equation from the ACGIH Industrial Ventilation Manual [28], Eq. (9), where $DD_h$ and $DD_c$ are the degree day data for heating and cooling (°F days), respectively, $t_{op}$ is the operating time (h/week), $c_{fuel}$ is the cost of fuel ($/unit fuel)$, $q_{fuel}$ is the available fuel heat (BTU/unit fuel), and $q_{latent}$ is the water latent energy load from cooling (kW) estimated from the ASHRAE Handbook [29]. The estimated variables in Eq. (9) are shown in Table 3.2. Data for $DD_h$ and $DD_c$ in North Carolina are taken from the NOAA National Climactic Data Center [30] from 2003-2005 and 2004-2005, respectively.

$$\text{Yearly Cost ($)} = \frac{(0.154)Q_{SR,S}DD_h t_{op} c_{fuel}}{q_{fuel}} + \left(\frac{(0.154)Q_{SR,S}DD_c t_{op} c_{fuel}}{q_{fuel}} + \frac{q_{latent} t_{op} c_{fuel}}{q_{fuel}}\right)$$

(9)

For $f$ of 0.1 and 1.0, the yearly costs for heating and cooling for Case 2 and Case 3 are 2.5x and 3.8x higher than Case 1, respectively, regardless of fuel type. The annual cost is 3.3x greater when operating at a higher $Q_{SR,S}$ and an $f$ of 0.1 instead of a lower $Q_{SR,S}$ and an $f$ of 1.0.
3.5.2 Adsorbent / Photocatalyst System

3.5.2.1 Effect of Make-up Air Fraction, f

Eq. (1)-(3) are solved at steady state conditions to determine the design variables for several T_{des} in the small box. We fix Q_{SR,S} to 1.274 m^3/min, the minimum ventilation rate for our conditions. Concentration C_{SR,S} is solved from Eq. (1) when we set C_{SR} to the 0.1 mg/m^3 WHO guideline. The small box mass balance is solvable when \( \dot{\omega} \) is specified and Eq. (5) and (6) are incorporated. Table 3.3 shows various calculated concentrations as a function of desorption temperature for Case 1.

Figure 3.4 shows C_{SB} (a), V_{SB} (b), V_{CHR} (c), and V_{rxr} (d), as a function of f for Case 1. As f increases, C_{SB} remains flat while V_{CHR}, V_{SB}, and V_{rxr} decrease. As f approaches 0.383, all volumes equal zero, or no remediation is needed to achieve the WHO guideline. At f = 0.1, V_{SB} is 1.92 m^3 at 120°C T_{des} and 1.89 m^3 at 150°C, or about the volume of a clothes washer and dryer. The corresponding V_{CHR} and V_{rxr} are 0.075 and 0.29 m^3 for 120 and 150°C T_{des}.

There is no substantial difference in calculated concentration and volumes between T_{des} of 120 and 150°C. This result allows us to operate the small box at lower T_{des} without paying larger concentration or volume penalties. The amount of energy expended to heat the small box is less costly. The model data at 180°C desorption temperature is unreasonably different from 120 and 150°C. The volumes required to achieve the WHO guideline are much larger at 180°C because of a slow reaction rate at 180°C caused by a
loss of photocatalytic activity [2] or significant CH$_2$O desorption from the TiO$_2$ catalyst surface [1]. Similar results are found for Case 2 and Case 3.

3.5.2.2 Effect of Rotation Speed, $\omega$

The rotation speed $\omega$ is studied at $f = 0.1$ for Case 1. Figure 3.5 shows the effect of $\omega$ on $C_{SB}$ and volumes. Rotation speeds slower than 1 rot/min cause $V_{SB}$ to be greater than 5 m$^3$. The effect of $\omega$ on volumes diminishes past 4 rot/min. At large $\omega$, the pseudo-steady state $V_{SB}$ is about 1 m$^3$. Increasing $\omega$ from 10 to 20 rot/min decreases $V_{SB}$ only 0.23 m$^3$. Similarly, increasing $\omega$ from 10 to 20 rot/min increases $C_{SB}$ to 6.1 x 10$^{-3}$ for 120°C. The 150°C desorption temperature results are not shown, but they are similar to the 120°C results. Overall, $\omega$ has a larger effect on $C_{SB}$ than on volume. The volumes start to level off at speeds greater than 10 rot/min.

3.5.2.3 Effect of CH$_2$O Escape Fraction, $f_{escape}$

The effect of $f_{escape}$ on concentration and volume in Case 3 is graphed in Figure 3.6. As $f_{escape}$ increases, the concentrations decrease (except for $C_F$) while volumes increase. As $S$ increases, there is less CH$_2$O allowable in the supply stream to satisfy the WHO guideline of $C_{SR} = 0.1$ mg/m$^3$. A decrease in $C_{SR,S}$ also causes $C_{SB}$ and $C_{CHR}$ to decrease, and the photoreactor volume required to oxidize CH$_2$O becomes larger as $C_{SB}$ decreases. Consequently, $V_{CHR}$ and $V_{SB}$ increase because of Eq. (5) and (6).

The small box and rotor volumes approach zero when $f_{escape} < 0.14\%$ because no remediation is necessary to achieve the WHO guideline. In contrast, as $f_{escape}$ approaches
14%, the volumes grow exponentially large, and no physically valid solution exists beyond \( f_{\text{escape}} = 14\% \). This occurs because \( S \) is too large to achieve a positive \( C_{SR,S} \) in Eq (1) given the constraint \( C_{SR} = 0.1 \text{ mg/m}^3 \).

### 3.5.2.4 Effect of Water Vapor

The adsorbent honeycomb rotor volume \( V_{\text{CHR}} \) is divided by the factor 0.83 to include water adsorption on the activated carbon according to Rong et al. [25], based on the ratio of adsorbed CH\(_2\)O with pre-adsorbed water vapor versus that without water at 20°C and 50% R.H. (Rong et al. [25] data uses 100% R.H.). The photoreactor volume \( V_{\text{rxr}} \) is divided by the factor 0.82 to account for water adsorbed on the TiO\(_2\) surface at 25°C, 50% R.H. (~11,000 ppmv humidity). This factor is the smallest ratio of (CH\(_2\)O oxidation rate at ~11,000 ppmv humidity) / (maximum CH\(_2\)O oxidation rate) from the Obee and Brown [31] and Obee [32] data without mass transfer resistances. Water adsorption should increase the catalyst volume because of adsorption site competition between water and formaldehyde.

Figure 3.7 shows the effect of water vapor on \( V_{\text{CHR}} \) and \( V_{\text{rxr}} \) in Case 2. Water vapor has no effect on small box concentration or volume because only Eq. (5) and (6) are affected by water. Both \( V_{\text{CHR}} \) and \( V_{\text{rxr}} \) increase when water vapor is added, though the effect is insignificant as \( f \) approaches 0.90 where the volumes are reasonable. For example, at \( f = 0.90 \) (\( V_{SB} = 2.1 \text{ m}^3 \)), the difference in \( V_{\text{rxr}} \) for the case with water and without water is only 0.07 m\(^3\), and 0.02 m\(^3\) for \( V_{\text{CHR}} \).
3.6. Conclusions

This paper applies the batch experimental work of Shiraishi et al. [2] and the kinetic model developed in our lab [1] to design a formaldehyde adsorbent / PCO system for residential homes. The model consists of three CH₂O mass balances (simulated room, ceramic honeycomb rotor, small box) and two volume ratios. Three cases for the CH₂O source strength $S$ are considered. Case 1 is taken from Kelly et al. [4] for 5/8” particleboard underlayment at typical conditions. Case 2 and Case 3 are maximum CH₂O particleboard emission rates derived from ANSI A208.1-1999 [23]. All emission rates are calculated at a room air change rate of 0.5 h⁻¹ and a floor specific area of 0.425 m²/m³.

With no remediation, the required make-up air fraction at the minimum supply ventilation air flow rate for our house conditions ranges from 0.4-1.4. Only Case 1 yields a reasonable make-up air fraction of 0.4 for residential homes. At a make-up air fraction of 0.1, flow rates ranging from 4x to 15x higher than the minimum supply ventilation air flow rate are required for Cases 1 through 3. At a make-up air fraction of 1.0, flow rates ranging from 0.4x to 1.5x the minimum supply ventilation air flow rate are required for Cases 1 through 3.

With the adsorbent / PCO system, $V_{SB}$ is about the size of a clothes washer and dryer (1.9 m³) for Case 1. This is a reasonable volume for residential home application. The adsorbent honeycomb rotation speed $\omega$ has a larger effect on small box concentration than on volume. The small box volume starts to level off at $\omega$ greater than 10 rot/min. The source strength $S$ (varied by $f_{escape}$) has a significant effect on concentrations and volumes. Large values of $S$ make it impossible to achieve the WHO guideline at the
minimum $Q_{SR,S}$. Addition of water vapor to the model increases the size of $V_{CHR}$ and $V_{rxr}$.

There is no substantial difference between the data at 120°C and 150°C, allowing us to operate at the lower $T_{des}$. The data at 180°C is unreasonable because of the slow reaction rate in the photoreactor.

3.7. Acknowledgements

The authors acknowledge support from the State of North Carolina for funding of this research.

3.8. References


68


### Table 3.1. Summary of the parameters calculated or fitted in the previous model.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$k_{ads}$ ($T_{ads}$) (min$^{-1}$)</th>
<th>$k_{des}$ ($T_{des}$) (min$^{-1}$)</th>
<th>$K_{SR-CHR}$</th>
<th>$K_{SB-CHR}$</th>
<th>$k_{cat}$ ($T_{des}$) (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{ads}$</td>
<td>0.0260</td>
<td>--</td>
<td>3.28</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>120°C</td>
<td>--</td>
<td>3.64</td>
<td>--</td>
<td>4.76</td>
<td>7.13</td>
</tr>
<tr>
<td>150°C</td>
<td>--</td>
<td>37.1</td>
<td>--</td>
<td>4.07</td>
<td>6.34</td>
</tr>
<tr>
<td>180°C</td>
<td>--</td>
<td>278</td>
<td>--</td>
<td>2.70</td>
<td>1.43</td>
</tr>
</tbody>
</table>

### Table 3.2. Summary of parameters used in calculating the yearly heating and cooling costs.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
<th>Variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>North Carolina DD_h (°F days)</td>
<td>3407</td>
<td>$c_{fuel}$ (natural gas) ($/ft^3$)</td>
<td>$0.007$</td>
</tr>
<tr>
<td>North Carolina DD_c (°F days)</td>
<td>1479</td>
<td>$q_{fuel}$ (natural gas) (BTU/ft$^3$)</td>
<td>900</td>
</tr>
<tr>
<td>$t_{op}$ (h/week)</td>
<td>92</td>
<td>$c_{fuel}$ (electricity) ($/kWh$)</td>
<td>$0.085$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$q_{fuel}$ (electricity) (BTU/kWh)</td>
<td>3415</td>
</tr>
</tbody>
</table>

### Table 3.3. IAQ CH$_2$O concentrations as a function of desorption temperature for Case 1 ($Q_{SR,S} = 1.274$ m$^3$/min, $C_{SR} = 0.1$ mg/m$^3$, $\omega = 4$ rot/min, $f_{escape} = 0.20$).

<table>
<thead>
<tr>
<th>CH$_2$O Concentration</th>
<th>$T_{des} = 120^\circ$C</th>
<th>$T_{des} = 150^\circ$C</th>
<th>$T_{des} = 180^\circ$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{SR,S}$ (mg/m$^3$)</td>
<td>0.062</td>
<td>0.062</td>
<td>0.062</td>
</tr>
<tr>
<td>$C_{SR,S}$ (ppm)$^a$</td>
<td>0.050</td>
<td>0.050</td>
<td>0.050</td>
</tr>
<tr>
<td>$C_{CHR}$ (mg/m$^3$)</td>
<td>0.203</td>
<td>0.203</td>
<td>0.203</td>
</tr>
<tr>
<td>$C_{SB}$ (mg/m$^3$)</td>
<td>0.017</td>
<td>0.020</td>
<td>0.050</td>
</tr>
</tbody>
</table>

$^a$ ppm values calculated using ideal gas law at standard pressure.
3.9. List of Figures

Figure 3.1. Simplified schematic of the simulated room, small box, and adsorbent rotor.

Figure 3.2. Schematic of the IAQ house with relevant parameters.

Figure 3.3. $C_{SR}$ as a function of (a) $f$ at $Q_{SR,S} = 1.274$ m$^3$/min, and $C_{SR}$ as a function of the normalized $Q_{SR,S}$ at (b) $f = 0.1$ and (c) $f = 1.0$.

Figure 3.4. Effect of $f$ on (a) $C_{SB}$, (b) $V_{SB}$, (c) $V_{CHR}$, and (d) $V_{rxr}$ for Case 1 ($Q_{SR,S} = 1.274$ m$^3$/min, $C_{SR} = 0.1$ mg/m$^3$, $\omega = 4$ rot/min, $f_{escape} = 0.20$, $T_{des} = 120, 150, \text{ and } 180^\circ\text{C}$).

Figure 3.5. Effect of $\omega$ on (a) $C_{SB}$ and on (b) $V_{SB}$, $V_{CHR}$, and $V_{rxr}$ for Case 1 ($Q_{SR,S} = 1.274$ m$^3$/min, $C_{SR} = 0.1$ mg/m$^3$, $f = 0.1$, $f_{escape} = 0.20$, $T_{des} = 120^\circ\text{C}$).

Figure 3.6. Effect of $f_{escape}$ on (a) concentration and (b) volume for Case 3 ($Q_{SR,S} = 1.274$ m$^3$/min, $C_{SR} = 0.1$ mg/m$^3$, $\omega = 4$ rot/min, $f = 0.1$, $T_{des} = 120^\circ\text{C}$).

Figure 3.7. Effect of water vapor on (a) $V_{CHR}$, and (b) $V_{rxr}$ for Case 2 ($Q_{SR,S} = 1.274$ m$^3$/min, $C_{SR} = 0.1$ mg/m$^3$, $\omega = 4$ rot/min, $f_{escape} = 0.20$, $T_{des} = 120^\circ\text{C}$).
Simulated Room (SR)
T ~ Ambient
10 m³

Small Box (SB)
w/ Photoreactor
T ~ 120-180°C
0.09 m³

Figure 3.1
Figure 3.2
Figure 3.3

(a) Graph showing the concentration of SR (mg/m³) as a function of the fraction (f) for different cases with specified parameters.

(b) Graph showing the concentration of SR (mg/m³) as a function of the normalized SR flow rate (Q_{SR}/A_{SR}} m³/(m²·min)) for different cases with specified parameters.

Legend:
- Case 1: S(t) = 0.049 mg/min, Q_{SR} = 1.274 m³/min
- Case 2: S(t) = 0.119 mg/min, Q_{SR} = 1.274 m³/min
- Case 3: S(t) = 0.180 mg/min, Q_{SR} = 1.274 m³/min
- WHO guideline (0.1 mg/cm³)

10% make-up air (f = 0.1)
Figure 3.3
Figure 3.4
Figure 3.4
Figure 3.5
Figure 3.6
Figure 3.7
CHAPTER 4

DECOLORIZATION OF ORGANIC DYES ON PILKINGTON ACTIV™ PHOTOCATALYTIC GLASS

* Work published in Chin and Ollis, Catalysis Today 2007, 123, 177-188.
4.1. Abstract

The air-solid photocatalytic degradation of organic dye films Acid Blue 9 (AB9) and Reactive Black 5 (RBk5) is studied on Pilkington Activ™ glass. The Activ™ glass comprises of a colorless TiO₂ layer deposited on clear glass. The Activ™ glass is characterized using Atomic Force Microscopy (AFM) and X-Ray Diffraction (XRD). Using AFM, the TiO₂ average agglomerate particle size is 95 nm, with an apparent TiO₂ thickness of 12 nm. The XRD results indicate the anatase phase of TiO₂, with a calculated crystallite size of 18 nm.

Dyes AB9 and RBk5 are deposited in a liquid film and dried on the Activ™ glass to test for photodecolorization in air, using eight UVA blacklight-blue fluorescent lamps with an average UVA irradiance of 1.4 mW/cm². A novel horizontal coat method is used for dye deposition, minimizing the amount of solution used while forming a fairly uniform dye layer. About 35-75 monolayers of dye are placed on the Activ™ glass, with a covered area of 7-10 cm². Dye degradation is observed visually and via UV-Vis spectroscopy.

The kinetics of photodecolorization satisfactorily fit a two-step series reaction model, indicating that the dye degrades to a single colored intermediate compound before reaching its final colorless product(s). Each reaction step follows a simple irreversible first-order reaction rate form. The average \( k_1 \) is 0.017 and 0.021 min⁻¹ for AB9 and RBk5, respectively, and the corresponding average \( k_2 \) is 2.0 x 10⁻³ and 1.5 x 10⁻³ min⁻¹. Variable light intensity experiments reveal a \( p = 0.44 \pm 0.02 \) exponent dependency of initial decolorization rate on the UV irradiance. Solar experiments are conducted outdoors with an average temperature, water vapor density, and UVA irradiance of 30.8°C, 6.4 g water /
m$^3$ dry air, and 1.5 mW/cm$^2$, respectively. For AB9, the average solar $k_1$ is 0.041 min$^{-1}$ and $k_2$ is 5.7 x 10$^{-3}$ min$^{-1}$.

**Keywords**: Photocatalysis, Dyes, Acid Blue 9, Reactive Black 5, Titanium Dioxide, TiO$_2$, Decolorization, Activ$^\text{TM}$

### 4.2. Introduction

Technological advances in the past decade allow glass manufacturers to deposit thin photoactive TiO$_2$ layers on glass, with trademark names such as Activ$^\text{TM}$ [1], Sunclean$^\text{TM}$ [2], and Bioclean$^\text{TM}$ [3]. These products are billed as “self-cleaning” surfaces because they utilize TiO$_2$ photocatalytic oxidation (PCO) and photo-induced superhydrophilicity (PSH) properties. The PCO activity causes progressive oxidation of adsorbed oxidizable molecules and particulate matter, while the PSH property allows for water washing removal of partially oxidized molecules and particulates from the photocatalytic surface.

The PCO property of self-cleaning glass is activated by absorption of UV light of energy higher than the TiO$_2$ band gap energy ($E_{BG}$). Electron photoexcitation from the TiO$_2$ valence band (VB) to the conduction band (CB) produces electron ($e^-_{CB}$) - hole ($h^+_{VB}$) pairs (Eq. 1a). For anatase phase TiO$_2$, $E_{BG} = 3.2$ eV ($\lambda = 385$ nm), while rutile phase TiO$_2$ has $E_{BG} = 3.0$ eV ($\lambda = 410$ nm). The redox potential for $h^+_{VB}$ is +2.53V with respect to the standard hydrogen electrode (SHE), which is enough energy to overcome the +2.27V SHE binding energy to form $OH^*$ ($E_{B,VB}$) [4], shown in Eq. (1b). Similarly, $e^-_{CB}$ (-0.52V

84
SHE redox potential) can react with $O_2$ to form $O_2^-$ ($E_{B,CB} = -0.28$ V SHE) [4], shown in Eq. (1c). The $O_2^-$ may combine with $H^+$ to form $O_2H^*$ (Eq. 1d). These oxygen containing radicals are responsible for adsorbate oxidation to volatile and/or water soluble products, generating the “self-cleaning” effect. The full reaction sequence for TiO$_2$ photocatalysis is detailed elsewhere [5]. Similar to the PCO property, the PSH mechanism of TiO$_2$ is activated by UV light. Two mechanisms have been proposed elsewhere [4,6] to describe the ability of TiO$_2$ to change from a hydrophobic to a hydrophilic surface after UV illumination.

\[
\begin{align*}
  &\text{TiO}_2 \xrightarrow{h_{BG}} e_{CB}^- + h_{VB}^+ \quad (E_{BG} = 3.0-3.2 \text{ eV}) \\
  &h_{VB}^+ + H_2O \rightarrow OH^+ + H^+ \quad (E_{VB} = 2.27 \text{ V SHE}) \\
  &e_{CB}^- + O_2 \rightarrow O_2^- \quad (E_{B,CB} = -0.28 \text{ V SHE}) \\
  &O_2^- + H^+ \rightarrow O_2H^* 
\end{align*}
\]

We continue here our exploration of photocatalyzed dye degradation in air-solid systems because of its potential as a field analysis method to characterize initial and continuing photocatalytic activity of installed “self-cleaning” window glass. Research to date on organic dye degradation by TiO$_2$ has focused on aqueous-solid systems, since dye wastewater treatment is a current environmental challenge. There have been few papers [7-9] on air-solid dye systems. Vinodgopal and coworkers [7] studied dye photosensitization of Acid Orange 7 (AO7) on Degussa P25 TiO$_2$ in an air-solid system. Diffuse reflectance laser flash photolysis experiments at sub-bandgap wavelengths ($\lambda = 532$ nm) yielded dye degradation of samples exposed to air, but negligible degradation of degassed samples. Yang et al. [8] oxidized Acid Blue 9 (AB9) on nano-sized TiO$_2$ in
aqueous and air-solid systems. Their aqueous results were fit to a first-order kinetic model, but they did not propose a kinetic model for their air-solid data. Julson and Ollis [9,10] researched decolorization in air of dyes Reactive Blue 19, Reactive Black 5 (RBk5), AB9, and AO7 on Degussa P25 TiO₂ and alumina (Alu C Al₂O₃) powders. Minimal homogeneous photo-degradation on Al₂O₃ was reported, but on TiO₂, the PCO decolorization data was fit to a two step series reaction model, described in detail later.

Thin films of TiO₂ [11-21] have been coated on a variety of surfaces for air and water remediation. Doushita and Kawahara [12] coated glass substrates with a TiO₂ sol-gel solution using the spin coat method and fired the substrate to 318°C to give TiO₂ an anatase structure. They mixed methylene blue and AB9 with polyvinyl alcohol binder, water, and ethanol, and then deposited the solution on the TiO₂ thin films. Binder degradation was negligible for UV illumination times less than 10 min, but the radical species such as OH⁻ and O₂H⁻ presumably diffused within the binder layer to react with the entrapped dyes. They proposed a diffusion-reaction model, but made no attempt to fit the model to their data.

Sitkiewitz and Heller [13] applied 0.3 ± 0.1 µm TiO₂ layers on glass slides by spin coating a sol-gel solution. Vapor phase benzene and condensed phase stearic acid were oxidized separately over 4 hr test periods. In the presence of H₂O and O₂, the CO₂ generation rate for both pollutants was linear with a zero order rate constant of 10⁻² µmol CO₂/(hr-cm² TiO₂) for UV irradiances (λ = 365 nm) varying from 0.3-5.8 mW/cm², while minimal or no CO₂ was produced in the absence of O₂ or H₂O. The CO₂ generation rate
was proportional to the square root of irradiance for UVA values ranging from ~0.1-6.0 mW/cm².

Romeas et al. [14] sprayed ~580 nm thick layers of palmitic acid, a C₁₅ molecule, on glass plates dip-coated with TiO₂ and an unstated photostable binder. They observed zero order kinetics with a rate constant of 

\[ 0.60 \pm 0.12 \ \mu \text{mol} / \text{hr} \] of palmitic acid at 0.7-1 mW/cm² irradiance and 18-22°C temperature conditions. The zero order kinetics was rationalized by constant saturation of the TiO₂ surface by palmitic acid, and a negligible diffusion resistance for O₂ supply. Identified intermediate products included C₈-C₁₂ carboxylic acids on the glass plate, and various lower MW alkanes, alcohols, aldehydes, ketones, and C₁-C₁₃ carboxylic acids in the vapor phase.

Pilkington Activ™ “self-cleaning” glass has been investigated by Mills et al. [21] for oxidation of stearic acid films. For thick layers of stearic acid (61-75 monolayers), the initial kinetics were zero-order for disappearance of the integrated area of CH₂- and CH₃-group IR bands. In the absence of stearic acid, contact angle measurements on Activ™ glass showed that 45 min of UV light exposure decreased the water contact angle from 67° (hydrophobic) to 0° (hydrophilic). Complete dark recovery of the water contact angle after UV illumination required 120-150 hr. To date, only Mills et al. [21] have tested the commercial Activ™ glass for stearic acid destruction.

Our present work further characterizes the PCO properties of Activ™ glass using organic dyes (rather than stearic or palmitic acid) deposited in a liquid film, then dried on the Activ™ glass, and subsequently oxidized (a) to show visual decolorization and
recovery of the aesthetic clarity of the glass, and (b) to determine the light-driven reaction kinetics on Activ™ glass.

4.3.  Experimental

4.3.1  Materials

The dyes Brilliant Blue FCF (C.I. Acid Blue 9, or AB9) and Remazol Black B (C.I. Reactive Black 5, or RBk5) were purchased from Fisher Scientific and used as received. The composition, structure, and optical characteristics of AB9 and RBk5 are reported in Table 4.1. The 10 cm (l) x 10 cm (w) x 0.3 cm (h) Pilkington Activ™ TiO2-coated glass and the Pilkington Optifloat™ clear glass (non-photocatalytic control reference) were gifts from Pilkington PLC and were cut into 10 cm (l) x 2.5 cm (w) x 0.3 cm (h) pieces. A Jelight Company Inc. Model #42 ultraviolet-ozone (UVO) cleaner was used to remove any initial organic contaminants on the glass surface. A KD Scientific KDS100 syringe pump with a linear motor ranging from 1-100 mL/hr (2.12-212 µm/sec) allowed dye solution deposition on the glass surfaces.

The laboratory photoreactor, described elsewhere [9], consisted of eight parallel General Electric 20W UVA blacklight-blue fluorescent lamps (peak emission λ = 365 nm) mounted in a 66 cm (l) x 46 cm (w) x 71 cm (h) enclosed, painted wooden box. A small fan brought in fresh air and maintained ambient temperature conditions. The UVA light intensity (320-390 nm) was measured by a Control Company Traceable™ UV Light Meter, and temperature and relative humidity (R.H.) measurements were obtained with a Traceable™ Memory Hygrometer/Thermometer.
Dye decolorization was followed (a) photographically using a Canon Powershot S30 3.2 megapixel digital camera and (b) optically via absorbance data from a Jasco V-550 UV-Visible spectrophotometer. The clean Activ™ glass surface was characterized by Atomic Force Microscopy (AFM) and X-Ray Diffraction (XRD), as described below.

4.3.2 Characterization of Pilkington Activ™ Glass

The average TiO$_2$ particle size and apparent thickness (height) were determined using a Digital Instruments Dimension™ 3000 AFM, with a NanoScope IIIa controller and a vibration-shielded hood. The AFM imaging was performed in contact and tapping modes. The tapping mode employed an OTESPA model Si cantilever from Veeco Probes with a 7 nm nominal tip radius and a 12-103 N/m spring constant. The contact mode employed a DNP-S20 model Si$_3$N$_4$ cantilever from Veeco Probes with a 10 nm nominal tip radius and 0.06-0.58 N/m spring constant. All measurements were done on 1 µm x 1 µm area under ambient conditions, with 256 samples per image and a scan rate of 1 Hz. In tapping mode, the drive frequency was 330 kHz. The surface root-mean-square roughness ($R_q$) and the maximum height ($R_{max}$) are defined as the standard deviation of the surface height ($Z$) and the largest $Z$ difference within the image area, respectively.

Atomic spacing and crystallite size were determined using an Inel XRG 3000 X-ray diffractometer that employed Cu Kα$_1$ radiation ($\lambda = 1.5405$ Å). Data was collected using a CPS-120 detector over $0^\circ < 2\theta < 69^\circ$ angles. The data was calibrated with respect to a potassium alum standard. The characteristic d-spacing between atomic planes ($d$) is calculated from Bragg’s Law (Eq. 2), where $\theta_B$ is the Bragg angle (° or rad) and $\lambda$ is the
radiation wavelength. The crystallite size ($x$) is obtained from the Scherrer equation (Eq. 3), where $K$ is the prefactor coefficient ranging from 0.9-1.0 (assumed to equal one) and $\beta$ is the full width at half maximum. The Scherrer equation is derived for cubic crystal configuration, but it provides a good estimate for different geometries [22] (anatase and rutile: tetragonal; brookite: orthorhombic [23]). The effects of instrument broadening, microstrain, and faulting are ignored in Eq. (3).

$$\lambda = 2d \sin \theta_b$$  \hspace{1cm} (2)  

$$x = \frac{K\lambda}{\beta \cos \theta_b}$$ \hspace{1cm} (3)

4.3.3 Deposition Procedure

Two and ten millimolar (mM) concentration solutions of AB9 and RBk5 in DI water were prepared. The Activ™ glass was placed in the UVO cleaner for 10 minutes to remove surface contaminants and to make the surface hydrophilic. Then the dye solutions were deposited on the Activ™ glass using a rapid convective assembly method developed by Prevo and Velev [24]. Their novel horizontal, moving “dip coat” method formed a fairly uniform dye layer and minimized the quantity of dye solution used. The dye coverage on the glass could be controlled by adjusting the dye concentration, motor speed, or injection volume.

For our experiments, a 15 $\mu$L injection volume of 2 or 10 mM AB9 or RBk5 in DI water was placed between the Activ™ glass and the deposition slide. The deposition slide was fitted with a Teflon spacer to reduce scraping of the TiO$_2$ thin film. The linear motor spread the dye injection volume across the slide at a velocity of 10.6 $\mu$m/sec (5 mL/hr) at
ambient lab air conditions (T = 21-24°C; R.H. = 20-50%) unless noted otherwise. The terms “thin” and “thick” multilayers describe the deposition of 2 and 10 mM dye solutions, respectively, corresponding to 40-75 and 150-260 layers of dye on the subsequent dried surface. Control experiments were run on the Optifloat™ glass following the same dye deposition procedure used for the Activ™ glass.

4.3.4 Testing Conditions

The dried, dye-coated Activ™ and Optifloat™ glass samples were placed in the laboratory photoreactor, where typical experiments were run at a UVA light intensity of 1.4 mW/cm² achieved by placing the glass samples 24 cm below the lamps. Experiments were stopped at given time intervals, and absorbance data was collected from 390-800 nm using the UV-Vis spectrophotometer. The spectra scan stopped at 390 nm to prevent photocatalyzed reaction propagation by TiO₂. Light intensity-influenced experiments on the Activ™ glass were conducted in the laboratory photoreactor. Light intensity was varied by adjusting the distance of the Activ™ glass samples from the lamps. The three resulting light intensities were 1.8-1.9, 0.70-0.77, and 0.08-0.10 mW/cm². In all indoor photoreactor experiments, the measured lab air temperature was 22°C ± 2°C and the water vapor density was 7 ± 2 g/m³ dry air (approx. 25-50% relative humidity).

Solar experiments on the Activ™ glass were run outdoors at midday (1000-1700 hrs) for up to 3 days on the top floor of a parking deck in Raleigh, North Carolina. The uncontrolled UVA light intensity varied from 0.30-2.05 mW/cm² under sunny and cloudy spring conditions. The average outside temperature was 31°C, with a standard deviation of
4°C and a minimum and maximum of 20°C and 39°C, respectively. The average vapor density was 7 g water / m³ dry air (22% relative humidity), with a standard deviation of 3 g/m³ and a minimum and maximum of 2 and 11 g/m³, respectively (approx. 6-35% relative humidity).

4.3.5 Data Analysis

Dye decolorization was observed visually, and digital photographs were taken at various time intervals. UV-Vis absorbance data was collected and related to dye concentration using the Beer-Lambert Law (Eq. 4), where Abs is the absorbance, \( \alpha \) is the molar absorptivity at wavelength \( \lambda \) (L/mol-cm or cm²/mol) of each colored compound (i.e., dye and intermediate), \( b \) is the path length (cm), \( C \) is the colored compound solution concentration (mol/L), and \( C_{app} \) is the colored compound molar value per unit glass surface area covered by the compound (mol/cm²).

\[
Abs = \alpha bC = \alpha C_{app}
\]  

(4)

4.4 Results and Discussion

4.4.1 Atomic Force Microscopy

Figure 4.1 shows AFM images of the Activ™ and Optifloat™ glass. The \( R_q \) values for the Activ™ and Optifloat™ glass were 2.3 and 0.4 nm, respectively. The \( R_{max} \) for the Activ™ glass was 21.1 nm versus only 4.5 nm for the Optifloat™ glass. These results indicate greater roughness on the Activ™ glass, and verify a coated layer on the Activ™ surface compared to the smoother Optifloat™ clear glass. According to Mills [21], their
SEM images showed broad TiO$_2$ domes of about 30 nm diameter on Activ$^\text{TM}$. From the top-down view in Figure 4.1a, our average TiO$_2$ particle diameter is 95 nm with a standard deviation of 30 nm. Our TiO$_2$ diameter was calculated from 30 random measurements of the broad dome shapes. Our measured particle diameter is 3x larger than Mills’ value, but this difference may be caused by overlapping TiO$_2$ peaks that cannot be resolved from the top-down view. Overlapping TiO$_2$ hemispherical peaks are seen in the topographical view (Figure 4.1b) and the sectional view (not shown).

From the sectional AFM view (not shown) averaged over 7 measurements, the TiO$_2$ thickness is 12 nm. This value is similar to those reported by Mills et al. [21] (15 nm) and the Sanderson and Knowles patent [25] (10-20 nm).

### 4.4.2 X-Ray Diffraction

Figure 4.2 shows the smoothed XRD results from the Activ$^\text{TM}$ glass, with the Optifloat$^\text{TM}$ clear glass results subtracted as a baseline. There is considerable noise, but a clear peak at 25.15° corresponds to a d-spacing of 3.54 Å using Bragg’s Law (Eq. 2). Anatase phase TiO$_2$ has its highest intensity at the (101) plane with $d = 3.52$ Å ($2\theta_B = 25.28°$ for Cu K$\alpha_1$ radiation) [26]. Brookite phase TiO$_2$ also has its highest intensity at $d = 3.51$ Å ($2\theta_B = 25.35°$ for Cu K$\alpha_1$ radiation) [26]. Since no other peaks are seen for brookite phase TiO$_2$ (90% and 80% maximum intensities at $d = 2.90$ and 3.47 Å, respectively), we conclude that TiO$_2$ is in the anatase phase. No peaks are seen associated with rutile phase TiO$_2$. We use the Scherrer equation (Eq. 3) to approximate the TiO$_2$ crystallite thickness. From Figure 4.2, the estimated $\beta$ is 0.51° (0.009 rad) and thus $x = 18$
nm, similar to previously reported values ranging from 10-20 nm for Activ™ glass [21,25].

4.4.3 Photodecolorization of AB9 & RBk5 Dyes – Thin Multilayers

Degradation of AB9 and RBk5 is tracked by UV-Vis spectroscopy, as shown in Figure 4.3a and Figure 4.3b, respectively. Photographs also are obtained (not included), revealing visual decolorization. Using the Prevo/Velev [24] deposition method, we are unable to achieve sub-monolayer coverage on the Activ™ glass because of its low surface area. To deposit sub-monolayer coverage, only 1 nmol dye can be deposited. For a 10 µL injection volume, this is about 0.1 mM dye solution. Such a small amount of dye is undetectable by UV-Vis spectroscopy because it is masked by absorption from the glass substrate. Therefore, we used a uniform deposition of 2 mM dye corresponding to 40-45 monolayers of AB9 and 60-75 monolayers of RBk5 on the Activ™ glass, with a glass area ranging from 7.5-9.5 cm² and a dye area of (1-2) x 10¹⁰ cm²/mol dye [27]. A monotonic decrease in absorbance is seen for AB9 (λmax = 629 nm) and RBk5 (λmax = 597 nm) as UV illumination time increases, which corresponds to dye decolorization.

4.4.4 Decolorization Kinetics

A simple reaction mechanism for decolorization of AB9 and RBk5 sub-monolayer dry deposits on TiO₂ powders has been published previously [9], including a derivation of a time-dependent absorbance kinetic model for the two step, series reaction. Briefly, the
simplified reaction involves colored dye conversion to a colored pseudo-intermediate compound continuing on to its colorless final product(s) (Eq. 5).

\[
\text{(colored) Dye } \xrightarrow{k_1} \text{(colored) Intermediate } \xrightarrow{k_2} \text{(colorless) Product}
\]  

The total absorbance measured by UV-Vis contains contributions from both dye and intermediate compounds. The absorbance kinetic model is shown in Eq. (6), where \( \text{Abs}_0 \) is the initial absorbance at 0 min, \( \alpha_D \) and \( \alpha_I \) are the dye and pseudo-intermediate molar absorptivities, respectively, \( k_1 \) is the first-order reaction rate constant from dye to intermediate (min\(^{-1}\)), \( k_2 \) is the first-order reaction rate constant from intermediate to product (min\(^{-1}\)), and \( t \) is the UV illumination time (min). The parameters \( k_1, k_2, \) and \( \alpha_I/\alpha_D \) are estimated using the asymptotic forms of Eq. (6) at short times where \( t \to 0 \) (Eq. 7) and at long times (large \( t \)) (Eq. 8). We assumed that \( k_1 > k_2 \) and that homogeneous photolytic effects are negligible [9].

\[
\begin{align*}
\text{Abs}(t) &= \text{Abs}_0 \left[ \frac{\alpha_I}{\alpha_D} \frac{k_1}{k_2 - k_1} \right] \left[ \exp(-k_1 t) - \exp(-k_2 t) \right] + \exp(-k_1 t) \\
\frac{\text{Abs}(t)}{\text{Abs}_0} - 1 &= k_1 t \left( \frac{\alpha_I}{\alpha_D} - 1 \right) & t \to 0 \\
\ln \left( \frac{\text{Abs}(t)}{\text{Abs}_0} \right) &= \ln \left( -\frac{\alpha_I}{\alpha_D} \frac{k_1}{k_2 - k_1} \right) - k_2 t & t \to \text{large}
\end{align*}
\]  

The fit for the two step series reaction model using the asymptote analyses is shown in Figure 4.4. The model fits the AB9 data (Figure 4.4a) slightly better than the RBk5 data (Figure 4.4b). A summary of the kinetic parameters evaluated from Figure 4.4
data (Table 4.2) shows that $k_1$ and $k_2$ values are similar for each dye, indicating an insensitivity to dye type. This behavior was also observed in our previous work with sub-monolayer deposits on TiO$_2$ powders [9]. Using all the data, the same kinetic parameters also are evaluated with the nonlinear curve fit function of Microcal Origin$^\text{®}$. The function utilizes the Levenberg-Marquardt (LM) algorithm to determine the best fit, and requires Eq. (6) and initial parameter estimates as input, where the latter are those obtained from the asymptote analyses. The respective parameter values fitted over the entire data range using the LM algorithm are the same order of magnitude as found by the asymptote analyses (see rows 1-4 in Table 4.2).

To achieve 90% dye decolorization, or $\ln(Abs/Abs_0) \approx -2.5$ in Figure 4.4, AB9 takes $\sim$850 min versus $\sim$1200 min for RBk5. Possible influences include: (a) RBk5 has a higher MW and thus higher carbon content compared to AB9 (Table 4.1); (b) the RBk5 disazo structure or its intermediate may be less reactive than the triphenylmethane framework in AB9 or its reaction intermediates. The latter possibility is supported by the fact that the pseudo-intermediate decolorization rate constant, $k_2$, is smaller for RBk5 than AB9 (Table 4.2).

Previous dye PCO work in our lab [9] for opaque (Abs $\geq$ 2) TiO$_2$ powder layers used the same absorbance kinetic model for sub-monolayer deposits of dyes AB9, RBk5, RB19, and AO7, and found an average $k_1$ and $k_2$ of 0.13 min$^{-1}$ and 0.0014 min$^{-1}$, respectively, and a $\alpha_d/\alpha_I$ of 0.56 for the indirect analysis data and 0.19 for the direct analysis data (Table 4.2). A comparison of the present dye multilayer results to previous sub-monolayer work revealed similar $k_2$ and $\alpha_d/\alpha_I$ values, while an order of magnitude
difference was seen in $k_j$. Three explanations are considered for the smaller $k_j$ on Activ™ glass.

First, the TiO$_2$ preparation method and phases are different. The previous work [9] used Degussa P25 TiO$_2$ powder, a 70:30 mixture of anatase: rutile phases. The Activ™ glass was coated by chemical vapor deposition of a SiO$_2$ blocking layer and then a TiO$_2$ layer formed from titanium chloride and ethyl acetate precursors [25]. The Activ™ TiO$_2$ layer is comprised solely of anatase phase. Previous literature cited an advantageous effect of mixing anatase and rutile on the reaction rate [28-30], but the mechanism was ambiguous. Bickley et al. [31] studied the Degussa P25 structure and postulated a synergistic effect of the thin rutile overlayer on the anatase particles, creating an increased efficiency in electron-hole separation by transferring valence band holes from anatase to rutile. Hurum et al. [32] used electron paramagnetic resonance spectroscopy (EPR) to hypothesize a conduction band electron transfer from rutile to a lower energy anatase lattice trapping site. Conversely, Datye et al. [33] reported no mixing of anatase and rutile phases in Degussa P25, and theorized that well-developed crystallinity in each phase resulted in a decrease in electron-hole recombination. Regardless of the mechanism, Ohno and coworkers found (a) a 3x higher acetone production rate from aqueous phase 2-propanol oxidation on Degussa P25 versus pure rutile [28], and (b) a 10x and 3x increase in liquid phase naphthalene oxidation on Degussa P25 versus pure anatase and pure rutile, respectively [29].

Second, the TiO$_2$ layer on the Activ™ glass is very thin (10-20 nm) and does not absorb all incident UVA light. Peill and Hoffmann [34] calculated from the Beer-Lambert
law that 2 μm and 5 μm thick TiO$_2$ layers coated on fiber-optic cables absorbed 45% and 95% of the refracted UV light, assuming a $\alpha C$ of 0.3 μm$^{-1}$ or 0.6 μm$^{-1}$, respectively. Julson and Ollis [9] stated that 5 μm was approximately 0.5% of the total TiO$_2$ powder layer thickness for their Direct Analysis data. Thus, about 100% UV light was absorbed in their TiO$_2$ layer. Mills et al. [21] estimated an absorbance of 0.065 (14%) at 365 nm for the TiO$_2$ layer on the Activ$^\text{TM}$ glass. This corresponds to reduction in TiO$_2$ photon absorption from our previous work (100%) on opaque TiO$_2$ powders to our present work (14%) with Activ$^\text{TM}$ glass. The number of photoexcitations and the rate of electron-hole separation per unit area diminish, leading to decreased reaction kinetics. If we normalize all $k_1$ values from the asymptote analyses to the calculated % UV light absorbed, then our previous and present work collapse to the same ratio of $k_1 / I_{abs} = 0.14 \text{ min}^{-1} / \% \text{ photon absorbed}$. Third, the dyes RBk5 and AB9 may absorb incident UV light (internal filter effect), decreasing the number of photons that reach the TiO$_2$ layer. Tang and Chen [35] postulated similar behavior for TiO$_2$ oxidation of aqueous RBk5 solutions in an annular photoreactor. They stated that higher RBk5 concentrations increased the solution opacity and reduced the number of incident photons that reached the TiO$_2$ surface, leading to a decrease in TiO$_2$ electron photoexcitation. Julson and Ollis [9] applied a sub-monolayer dye coverage, and noted that the dyes did not absorb photons appreciably. In contrast, the present work has coated 40-75 monolayers of dye, potentially decreasing the incident UVA and thus the TiO$_2$ photon absorption rate. Standard solutions were tested for dye absorption in the UV range. Reactive Black 5 has a maximum at $\lambda_{max} = 392$ nm with a
molar absorptivity $\alpha_{RBk5, 392nm} \approx 2830 \text{ L/(mol cm)}$ ($2.83 \times 10^6 \text{ cm}^2/\text{mol}$), while Acid Blue 9 peaks at $\lambda_{\text{max}} = 408 \text{ nm}$ with $\alpha_{AB9, 408nm} \approx 8730 \text{ L/(mol cm)}$ ($8.73 \times 10^6 \text{ cm}^2/\text{mol}$). From the molarity and injected volume of the dye solution, and the Activ\textsuperscript{TM} area covered by the dye, we estimate $C_{app}$ as $(3-4) \times 10^{-9} \text{ mol/cm}^2$. The corresponding dye absorbance of UV light is calculated from the Beer-Lambert law, with a maximum of 3-6% UVA absorption. This effect is likely the least important among the three proposed, because $\alpha$ is not too large in the UVA range, and our dyes form only thin multilayers for all but one case in Table 4.2.

In conclusion, the primary difference between our current and previous work is the % UVA absorption. Normalization of our rate constants to the variable % light absorption leads to nearly identical rate constant $k_1$ for the prior sub-monolayer and current multilayer experiments.

Control experiments on the dye-coated Optifloat\textsuperscript{TM} glass, shown as circles in Figure 4.4a, b, reveal an unexpected decolorization of both dyes. Previous work by Julson and Ollis [9] using the same photoreactor as our experiments observed negligible homogeneous photodegradation of a sub-monolayer coverage of the same dyes, AB9 and RBk5, on Al\textsubscript{2}O\textsubscript{3} powder, a photo-inert support, under 480 min of 1.3 mW/cm\textsuperscript{2} UV light illumination. In contrast, there is 50% and 15% AB9 and RBk5 decolorization, respectively, after 480 min of UV irradiance on the Pilkington Optifloat\textsuperscript{TM} glass, leading us to assume there may be a photoactive material in the float glass. Semiconductor oxides, such as Fe\textsubscript{2}O\textsubscript{3} and SnO\textsubscript{2}, can be added to float glass for color/tint. Miyauchi and co-workers [36] reported methylene blue dye degradation on SnO\textsubscript{2} thin films under 100 min of 2 mW/cm\textsuperscript{2} UVA irradiance. Though Miyauchi et al. [36] stated that Fe\textsubscript{2}O\textsubscript{3} is photo-
inactive for methylene blue degradation up to 100 min, their figure showed a slight
decrease in absorbance. It is possible that appreciable dye degradation on Fe\textsubscript{2}O\textsubscript{3} can occur
over a period of 2000 min UV illumination. Given our results and the previous literature,
we hypothesize the float glass may be photoactive, but not to the extent of the TiO\textsubscript{2}-coated
Activ\textsuperscript{TM} glass. Further studies on float glass will be conducted in our lab to clarify this
effect.

Mills et al. [21] and Sanderson and Knowles [25] state that with Activ\textsuperscript{TM} glass, a
25-40 nm thick silicon oxide, presumably SiO\textsubscript{2}, blocking layer exists between the float
glass and the TiO\textsubscript{2} thin film. This blocking layer prevents metal migration from the float
glass to the TiO\textsubscript{2} layer. Therefore, we assume there is no other photoactive material on the
surface of the Activ\textsuperscript{TM} glass except TiO\textsubscript{2}, and the multilayer dye decolorization kinetics
measured in Figure 4.4a, b are solely for PCO by TiO\textsubscript{2}.

4.4.5 Solar Experiments

Solar tests to decolorize AB9 were conducted outdoors; example results are shown
in Figure 4.5. For a uniform deposition of 2 mM AB9, there are 55 monolayers on the
Activ\textsuperscript{TM} glass. The AB9 achieves 95\% decolorization in 480 min of solar UV
illumination. These results are faster than the indoor laboratory experiments, which take
about 850 min to achieve 90\% AB9 decolorization. The number of incident photons is
estimated for indoor and outdoor experiments by assuming 1 mW/cm\textsuperscript{2} corresponds to \(~1.8
x \, 10^{15} \) photons/(cm\textsuperscript{2} sec) for a emission wavelength of 365 nm, as calculated using the
Planck relation and the wave theory of light [37]:
\[ E = h \nu = \frac{hc}{\lambda} \]

(9)

\[
\text{mol photons} \quad \frac{\text{cm}^2}{\text{sec}} = \frac{\left( \frac{E}{\text{cm}^2 \text{-sec}} \right)}{\left( \frac{hc}{\lambda} \right) / N_A} = \frac{I}{\left( \frac{hc}{\lambda} \right) / N_A} \]

(10)

where \( E \) is the total incident photon energy (J), \( I \) is the UVA irradiance (mW/cm\(^2\)), \( h \) is Planck’s constant \((6.63 \times 10^{-34} \text{ J* s/photon})\), \( c \) is the speed of light in vacuum \((2.998 \times 10^8 \text{ m/s})\), \( \lambda \) is the wavelength (nm), and \( N_A \) is Avogadro’s number \((6.023 \times 10^{23} \text{ photons/mol})\).

The number of UVA incident photons reaching the Activ\textsuperscript{TM} surface is similar for 480 min of exposure, regardless if tested in the controlled laboratory photoreactor with \(1.23 \times 10^{-4} \text{ mol photons/cm}^2\) \((1.4 \text{ mW/cm}^2 \text{ irradiance})\) or \(1.47 \times 10^{-4} \text{ mol photons/cm}^2\) in the solar experiments \(\text{(time-weighted value because of variable irradiance)}. \) Though total UVA exposure was similar in both cases, the solar experiments decolorized faster. This may be partly accounted for by sunlight UVB photons which also photoexcite TiO\(_2\), while the laboratory photoreactor emits only UVA photons in the 315-400 nm range. About 4\% of ground level UV light is dermatological UVB \((\text{dUVB, 290-320 nm})\) while dermatological UVA \((\text{dUVA, 320-400 nm})\) makes up the remaining 96\% [38].

Additionally, the temperature and humidity are slightly higher outdoors. The TiO\(_2\) reaction rate is roughly temperature independent, though electron-hole recombination may rise with increasing temperature. Obee and Brown [39] saw a mixed positive/negative temperature effect on oxidation rates under partial mass transfer influence: for gaseous toluene and 1,3-butadiene, oxidation rates increased when the temperature rose from \(~24^\circ\text{C}\) to \(~60^\circ\text{C}\), while formaldehyde oxidation rates decreased under similar conditions. Humidity has two influences on the reaction rate [39,40]. At minimal water
concentrations, higher humidity increases the reaction rate because of increased OH\textsuperscript{•} production. For some compounds, excessive humidity decreases the reaction rate because water displaces weakly adsorbed pollutants (e.g., aldehydes, aromatics), inhibiting the reaction. This effect was observed by Peral and Ollis [40] for m-xylene destruction and for oxidation of toluene, 1,3-butadiene, and formaldehyde by Obee and Brown [39]. Even though indoor and outdoor experiments exhibited similar water vapor densities of 6.4 g/m\textsuperscript{3} (8000 ppmv at STP, 28% relative humidity at 25°C), the outdoor humidity fluctuated more. At 8000 ppmv, Obee and Brown [39] observed a small negative slope for trace level contaminants, i.e., < 3 ppmv, but at higher concentrations, i.e., 8 ppmv toluene, they saw a monotonic positive slope upon changing the humidity from 0 to 20,000 ppmv. Thus, a slight humidity effect, in combination with ground level UVB light, may explain why our solar experiments decolorized AB9 somewhat quicker than the indoor experiments.

The AB9 solar experiments involved variable UV irradiance, so we expected the model (Eq. 6) to fit the data less well. Nonetheless, the solar absorbance data fit well to the two step series reaction model; the calculated $k_1$ and $k_2$ standard deviations are an order of magnitude smaller than their values. These AB9 kinetic parameters are shown in Table 4.2, where $k_1$ and $k_2$ for the solar tests are roughly double the laboratory photoreactor tests.

4.4.6 Effect of Light Intensity

Experiments were carried out to demonstrate the effect of light intensity on the reaction rate in our dye multilayer films. Egerton and King [41] studied the intensity influence on TiO\textsubscript{2} PCO of liquid isopropanol to acetone. At weak light supply rates (less
than $5 \times 10^{15}$ quanta/sec), there was a linear relationship between light intensity and reaction rate. At strong light supply rates (greater than $5 \times 10^{15}$ quanta/sec), the reaction rate varied with the square root of the light intensity, and electron-hole recombination was suggested to be the dominant process. Their work and later analyses by Turchi and Ollis [5] have become the basis for a power-law light intensity explanation of photocatalyzed kinetics, where $I$ is the UV light intensity and $p$ is the power-law dependency:

\[
\begin{align*}
  r_{\text{initial}} \propto I^p & \quad \text{weak light intensity: } (p = 1) \\
  & \quad \text{medium light intensity: } (0.5 \leq p \leq 1) \\
  & \quad \text{strong light intensity: } (p = 0.5) \\
\end{align*}
\]

Eq. (11) contains a transition regime in between the two asymptotic values of $p = 0.5$ and 1. Peral and Ollis [40] determined $p = 0.7$ for acetone vapor phase oxidation with a UV irradiance ranging from $(3-40) \times 10^{15}$ photons/(cm$^2$ sec). Mills and Wang [42] degraded aqueous 2-chlorophenol using Degussa P25 TiO$_2$ dispersions and thin films with a UVA irradiance of $(0.5-6.4) \times 10^{15}$ photons/(cm$^2$ sec). They reported $p = 0.64$ for a TiO$_2$ dispersion and $p \approx 1$ for a TiO$_2$ thin film. They argued that TiO$_2$ thin films, under identical reaction conditions to their dispersions, were subject to lower light intensities because aggregate TiO$_2$ particles of about 0.44 µm diameter partially screened UV light from the smaller, photoactive TiO$_2$ particles in direct contact with the solution. Their TiO$_2$ thin films were coated on the reaction vessel inner wall, and since the UVA lamps enclosed the reactor, the TiO$_2$ films were irradiated from the back.

For our uniform dye deposition of 2 mM AB9, there are 35-45 monolayers on the Activ$^\text{TM}$ glass. The UV light intensity ranges from 0.08-1.9 mW/cm$^2$, and we neglect
intermediates by using only initial times (0-10 min). The series rate expression simplifies to a first-order irreversible reaction: 

\[-r_{\text{initial}} = k_{\text{app,0}} C_0\]

where \(k_{\text{app,0}}\) is the apparent rate constant (min\(^{-1}\)) and \(C_0\) is the initial dye concentration (mol/L). The intensity variation results are shown in Figure 4.6a, where the three data points are best fit to Eq. (11) with \(p = 0.44\) and a standard error of 0.02. This is close to the asymptotic regime of strong UV light intensity, which is unexpected.

Mills and Wang [42] stated that for TiO\(_2\) dispersions, the transition regime for Degussa P25 was \((2-3) \times 10^{15}\) ultra-band gap photons/(cm\(^2\) sec). The number of incident photons approaching the Activ\(^\text{TM}\) surface in the present work is listed in Table 4.3. Our values of \(1.4 \times 10^{15}\) and \(3.5 \times 10^{15}\) photons/(cm\(^2\) sec) are similar those estimated by Mills and Wang [42] for the transition regime, while \(0.17 \times 10^{15}\) photons/(cm\(^2\) sec) is below their transition regime. The Activ\(^\text{TM}\) glass follows their dispersion data because our TiO\(_2\) particle diameters are small (less than 0.1 \(\mu m\)). Mills and Wang [42] estimated their thin film TiO\(_2\) particle diameters to be \(\sim 0.44\) \(\mu m\), four times larger than the Activ\(^\text{TM}\) TiO\(_2\) particles.

Ching et al. [43] presented an empirical correlation for the effect of UV light intensity on the gas phase formaldehyde oxidation rate for a transparent sol-gel TiO\(_2\) thin film deposited on glass tubes. Using UVA irradiances ranging from 0-1.6 mW/cm\(^2\), they suggested Eq. (12) where \(k_{\text{app,0}}\) was the apparent rate constant (min\(^{-1}\)) and \(k_a\) (min\(^{-1}\)) and \(k_b\) (cm\(^2\)/mW) accounted for the effects of UV exposure time \(t\) (min) and UV irradiance \(I\) (mW/cm\(^2\)), respectively. We applied Eq. (12) to the LM algorithm of Microcal Origin\(^\circledast\) using our intensity influenced kinetic data for dyes, finding the best fit \(k_a\) and \(k_b\) values of
0.036 min\(^{-1}\) and 3.4 cm\(^2\)/mW, respectively (Figure 4.6b). Our values differed considerably from those reported by Ching et al. [43] for formaldehyde oxidation \((k_a = 0.408\ \text{min}^{-1}; k_b = 0.383\ \text{cm}^2/\text{mW})\), even though their calculated 13.6% UVA absorption plus scattering on sol-gel TiO\(_2\) is similar to our 14% absorption on the Activ\(^{\text{TM}}\) glass at 365 nm.

\[
\frac{C}{C_0} = \exp\left[-k_{\text{app},0} t\right] = \exp\left[-k_a t (1 - e^{-k_b t})\right]
\]

\[
k_{\text{app},0} = k_a \left(1 - e^{-k_b t}\right)
\]

(12)

4.4.7 Photodecolorization of AB9 & RBk5 Dyes – Thick Multilayers

Thick dye multilayers were uniformly deposited on the Activ\(^{\text{TM}}\) glass using 10 mM solutions of RBk5 and AB9, corresponding to 260 and 150 monolayers, respectively. The linear motor was set to 4 mL/hr (8.48 µm/sec) and run at ambient lab air conditions \((T = 25^\circ\text{C}, \ R.H. = 33\%)\). Figure 4.7 shows the decolorization of RBk5 thick multilayers on Activ\(^{\text{TM}}\) glass. Similar results are seen on the AB9 dye. The absorbance peak for the thick multilayers in Figure 4.7a is 4-5x greater than the thin multilayers in Figure 4.3b, consistent with the mass loading increase, and the time needed for 90% decolorization is 10x greater on the thick multilayers (i.e., \(~1050\ \text{min vs. } ~10800\ \text{min}\)). Thus the % decolorization kinetics are slower on thick multilayers, shown in Figure 4.7b, with \(k_1 = 0.0085\ \text{min}^{-1}\), \(k_2 = 0.00012\ \text{min}^{-1}\), and \(\alpha_I/\alpha_D = 0.65\) (Table 4.2). Vinodgopal et al. [7] observed faster AO7 photosensitized degradation at low coverage \((0.02 \text{ mmol AO7/g TiO}_2)\) than at high coverage \((0.10 \text{ mmol AO7/g TiO}_2)\), attributed to a larger ratio of photon dose-to-dye molecules. Three explanations for the slower kinetics observed in thicker layers are considered.
First, RBk5 and AB9 will absorb more incident UV light which decreases the number of photons reaching the TiO$_2$ layer, as discussed in the third explanation of the decolorization kinetics section. We estimate that a maximum of 9% and 20% UVA (or approaching UVA) light is absorbed by RBk5 and AB9, respectively. As time progresses, the dye layer decreases and more photons reach the TiO$_2$ film.

Second, one intermediate may inadequately describe the system. There are certainly multiple intermediates in the true reaction mechanism. We extended our series kinetic model (Eq. 6) to two intermediate compounds, with additional $k_3$ and $\alpha_{I2}$ series terms. Using the LM algorithm of Microcal Origin$^\text{®}$, we calculate $k_1 = 0.053 \text{ min}^{-1}$, $k_2 = 0.0033 \text{ min}^{-1}$, and $k_3 = 0.00012 \text{ min}^{-1}$, with $\alpha_{I1}/\alpha_D = 0.92$ and $\alpha_{I2}/\alpha_D = 0.65$. These $k_1$ and $k_2$ values are the same order of magnitude as the thin multilayer values.

Third, inorganics in the original dye may accumulate and progressively deactivate TiO$_2$ sites. Both RBk5 and AB9 contain N, S, and Na. If these inorganics appear as nonvolatile products (e.g., NH$_4^+$, NO$_3^-$, SO$_3^-$, SO$_4^{2-}$, Na$^+$), they may build up and contribute to apparent deactivation.

A combination of these three effects should account for why the kinetic rate constants were slower for thick dye multilayers.

4.5. Conclusions

Pilkington Activ™ glass was tested for decolorization of organic dye multilayer films of Reactive Black 5 and Acid Blue 9 in an air-solid system. Dye deposition on the glass was carried out by a horizontal coat method. Characterization of the Activ™ glass
using Atomic Force Microscopy yielded a TiO$_2$ average particle diameter of 95 nm and an average thickness of 12 nm. X-ray diffraction results revealed only anatase phase TiO$_2$. A TiO$_2$ crystallite thickness of 18 nm was estimated using the Scherrer equation.

Dye layer decolorization was observed visually and using UV-Vis spectroscopy. A monotonic decrease in absorbance was seen with increasing UV illumination time. The kinetics for thin and thick dye multilayers were fitted to a two step series reaction model previously developed in our lab for dye sub-monolayers dried onto TiO$_2$ powders. In the simplified reaction scheme, the colored dye formed a colored intermediate before its colorless final product. The model fitted our multi-layer data adequately for both RBk5 and AB9 using the asymptote analyses at $t \to 0$ and at long times (large t). The Levenberg-Marquardt algorithm was utilized to check the kinetic parameter values obtained from the asymptote analyses, and yielded new parameter values of the same order of magnitude as the asymptotic approach.

Solar experiments on the Activ$^\text{TM}$ glass decolorized AB9 faster than the laboratory photoreactor experiments after 480 min of UV exposure. The number of incident photons reaching the Activ$^\text{TM}$ surface was similar for both indoor and outdoor experiments. Our simple kinetic model fitted the solar data well even though the UV light intensity varied with time. We hypothesize that the additional UVB photons in the solar spectrum, and the higher water vapor density outdoors account for the solar versus blacklight-blue activity differences.

Light intensity-influenced laboratory experiments showed a $p = 0.44 \ (\pm 0.02$ standard error) power-law dependency of the initial decolorization rate on the UV light
intensity. This indicated that the experiments occurred in the “strong” light intensity regime. The pseudo-first order initial rate constant also was fitted to a previous empirical equation incorporating the effects of illumination time and light intensity.

4.6. Acknowledgements

The authors thank the State of North Carolina for funding of this research, and Pilkington Glass plc for their generous material support. We carried out dye deposition with the syringe pump and UV-Vis spectrophotometer measurements in the Velev research lab, Department of Chemical and Biomolecular Engineering, NC State. Characterization XRD and AFM measurements were run by Mike Capracotta and Jeong-Seok Na, respectively, at NC State.

4.7. References


### Table 4.1. Characteristics of dyes Acid Blue 9 and Reactive Black 5.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Chemical Structure</th>
<th>$M_W$ (g/mol)</th>
<th>Abs Peaks ($\lambda$)</th>
<th>Molar Absorptivity ($\alpha$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid Blue 9</td>
<td>$C_{37}H_{34}N_2Na_2O_9S_3$ acid triphenylmethane dye</td>
<td>792.9</td>
<td>629 nm, 408 nm</td>
<td>86600 L/(mol cm), 8730 L/(mol cm)</td>
</tr>
<tr>
<td>Reactive Black 5</td>
<td>$C_{26}H_{21}N_5Na_4O_{19}S_6$ reactive vinylsulphone disazo dye</td>
<td>991.8</td>
<td>597 nm, 392 nm</td>
<td>27600 L/(mol cm), 2830 L/(mol cm)</td>
</tr>
<tr>
<td>Dye</td>
<td>Dye Coverage Type</td>
<td>Analysis Type</td>
<td>$k_1$ (min$^{-1}$)</td>
<td>$k_2$ (min$^{-1}$)</td>
</tr>
<tr>
<td>------------------------------</td>
<td>------------------</td>
<td>---------------</td>
<td>------------------</td>
<td>------------------</td>
</tr>
<tr>
<td>Reactive Black 5 (laboratory experiment)</td>
<td>Thin</td>
<td>Asymptote</td>
<td>0.021</td>
<td>0.0015</td>
</tr>
<tr>
<td>Reactive Black 5 (laboratory experiment)</td>
<td>Multilayer</td>
<td>Analysis</td>
<td>0.035</td>
<td>0.0021</td>
</tr>
<tr>
<td>Acid Blue 9 (laboratory experiment)</td>
<td>Thin</td>
<td>Asymptote</td>
<td>0.017</td>
<td>0.0020</td>
</tr>
<tr>
<td>Acid Blue 9 (laboratory experiment)</td>
<td>Multilayer</td>
<td>Algorithm</td>
<td>0.029</td>
<td>0.0026</td>
</tr>
<tr>
<td>Acid Blue 9 (solar experiment)</td>
<td>Thin</td>
<td>Asymptote</td>
<td>0.041</td>
<td>0.0057</td>
</tr>
<tr>
<td>Acid Blue 9 (Julson &amp; Ollis [9], indirect analysis data)</td>
<td>Multilayer</td>
<td>Analysis</td>
<td>0.0085</td>
<td>0.00012</td>
</tr>
<tr>
<td>Reactive Black 5 (Julson &amp; Ollis [9], direct analysis data)</td>
<td>Multilayer</td>
<td>Asymptote</td>
<td>0.12</td>
<td>0.0021</td>
</tr>
<tr>
<td>Acid Blue 9 (Julson &amp; Ollis [9], direct analysis data)</td>
<td>Sub-monolayer</td>
<td>Asymptote</td>
<td>0.16</td>
<td>0.0007</td>
</tr>
<tr>
<td>Reactive Black 5 (Julson &amp; Ollis [9], indirect analysis data)</td>
<td>Sub-monolayer</td>
<td>Asymptote</td>
<td>0.12</td>
<td>0.0022</td>
</tr>
<tr>
<td>Acid Blue 9 (Julson &amp; Ollis [9], direct analysis data)</td>
<td>Sub-monolayer</td>
<td>Asymptote</td>
<td>0.14</td>
<td>0.0007</td>
</tr>
</tbody>
</table>
Table 4.3. Summary of the variable UV light intensity parameters reported in the present work and previous literature.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Irradiated Area (cm²)</th>
<th>UV Light Intensity (mW/cm²)</th>
<th>UV Light Intensity (photons/cm² sec)</th>
<th>UV Supply Rate (photons/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This Work</td>
<td>11.3</td>
<td>0.09</td>
<td>$0.17 \times 10^{15}$</td>
<td>$1.9 \times 10^{15}$</td>
</tr>
<tr>
<td></td>
<td>9.45</td>
<td>0.75</td>
<td>$1.4 \times 10^{15}$</td>
<td>$13 \times 10^{15}$</td>
</tr>
<tr>
<td></td>
<td>10.4</td>
<td>1.9</td>
<td>$3.5 \times 10^{15}$</td>
<td>$36 \times 10^{15}$</td>
</tr>
<tr>
<td>Egerton and King</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>$10^{13}-10^{19}$</td>
</tr>
<tr>
<td>[41]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mills and Wang</td>
<td>120.5</td>
<td>--</td>
<td>$(0.50-6.4) \times 10^{15}$</td>
<td>--</td>
</tr>
<tr>
<td>[42]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peral and Ollis</td>
<td>7.7</td>
<td>--</td>
<td>$(3-40) \times 10^{15}$</td>
<td>--</td>
</tr>
<tr>
<td>[40]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.8. List of Figures

Figure 4.1. AFM images of 3mm Pilkington Activ™ glass in (a) a top-down view and (b) a topographical view, and 3mm Pilkington Optifloat™ clear glass in (c) a top-down view and (d) a topographical view.

Figure 4.2. Smoothed XRD image of 3mm Pilkington Activ™ glass. A peak at $2\theta = 25.15^\circ$ corresponds to anatase phase TiO$_2$.

Figure 4.3. Absorbance versus wavelength as a function of time for dyes on Activ™ glass: (a) Acid Blue 9 and (b) Reactive Black 5.

Figure 4.4. $ln$(normalized absorbance) versus time for dyes (a) Acid Blue 9 and (b) Reactive Black 5. The squares represent data on Activ™ glass, the circles represent data on Optifloat™ glass (control), and the lines represent the two step series reaction model.

Figure 4.5. Solar experiments demonstrating visual decolorization of Acid Blue 9 on Activ™ glass from (a) 0 min to (b) 950 min. The grey dots represent the approximate location sampled by UV-Vis absorbance measurements.

Figure 4.6. The effect of UV light intensity on reaction rates for Acid Blue 9 decolorization on Activ™ glass: (a) $ln$(initial reaction rate) versus $ln$(UV light intensity); (b) $k_{app,0}$ as a function of UV light intensity.

Figure 4.7. Decolorization plots of thick multilayers (260 monolayers) of Reactive Black 5: (a) Absorbance versus wavelength as a function of time; (b) $ln$(normalized absorbance) versus time, where the points represent data and the line represents the model. The inset graph in (b) magnifies the 0-4000 min region.
Figure 4.1
Figure 4.3

(a) Acid Blue 9

(b) Reactive Black 5
Figure 4.4
Figure 4.5

Acid Blue 9

0 min  950 min

(a)  (b)
Figure 4.6
Figure 4.7
CHAPTER 5

KINETIC MODELING OF PHOTOCATALYZED SOOT OXIDATION ON TITANIUM DIOXIDE THIN FILMS

5.1. Abstract

Recent research [1,2] has demonstrated photocatalytic oxidation of “soot” by titanium dioxide thin films. However, little attention has been paid to developing kinetic models of photocatalyzed soot destruction. We develop here a series/parallel kinetic model for soot oxidation and use it to analyze the CO$_2$ data of Mills et al. [1] and the mass loss data of Lee and Choi [2]. The model assumes two oxidation pathways: a single step yielding CO$_2$ directly, and a serial sequence through a solid intermediate species, which is subsequently oxidized to CO$_2$. We extend this simple model to include variable O$_2$ partial pressure, which is used to evaluate the initial CO$_2$ data of Lee and Choi [2]. These models fit the experimental CO$_2$ data of Mills et al. [1] and Lee and Choi [2] well. The simple kinetic model also describes the mass loss data of Lee and Choi [2] for the front mode of sample irradiation.

Keywords: Photocatalysis, UV-irradiated TiO$_2$, Titania, Soot, Decomposition, Oxidation, Destruction, Gas-Phase, Kinetic Model

5.2. Introduction

Titanium dioxide (TiO$_2$), a semiconductor metal oxide, often is used as a heterogeneous photocatalyst for oxidative destruction of organic, inorganic, and biological materials. Both powders and thin films of TiO$_2$ have been studied extensively for photocatalytic oxidation (PCO) of water pollutants [3,4], air contaminants [5-7], and layers of adsorbed organic compounds, such as dyes [8,9], carboxylic acids [10-12], dried
microorganisms [13], and “soot” [1,2,14]. The deposition of particulate soot arising from diesel automobiles, heavy equipment, forest fires, burning wastes [15], and other incomplete combustion processes is a major contributor to visual degradation of exterior surfaces, e.g., of buildings and statues, especially in the major cities of industrialized countries.

The possibility of “self-cleaning” building and glass surfaces leads naturally to consideration of soot. To date, only three articles have addressed TiO$_2$ photooxidation of soot. Lee and Choi [2] flame-deposited 2 µm soot layers by burning $n$-hexane near 1 µm thin films of Degussa P25 TiO$_2$ coated on glass plates. Using 1.5 mW/cm$^2$ UV irradiance ($300 < \lambda < 400 \text{ nm}$) for 0-32 hr, they explored front and back illumination (Figure 5.1a, b). The decrease of normalized (soot) mass $m/m_0$ was faster when the incident UV light impinged on the uncoated side (back irradiation) rather than the soot-coated side (front irradiation), presumably because light absorption by soot reduced the UV flux reaching the photocatalyst. In various atmospheres, the early (0-40 min) CO$_2$ formation was measured using a gas chromatograph equipped with a flame ionization detector. In a He atmosphere, CO$_2$ was generated. This suggests that a small amount of either O$_2$ or CO$_2$ may have been adsorbed on the soot. The CO$_2$ formation was faster in pure O$_2$ than in air, suggesting a rate dependency on the O$_2$ partial pressure. No kinetic model was proposed for either mass loss or CO$_2$ formation.

Research in the Mills group [1,14] used “T-lite” paraffin-based candles to produce soot layers averaging 0.5 µm thickness on top of 0.9-4 µm TiO$_2$ films which had been pre-deposited on microscope slides. Using front illumination, Lee, McIntyre, and Mills [14]
visually demonstrated photo-destruction of soot coated (a) directly on the TiO₂ surface, (b) laterally alongside the illuminated TiO₂ surface, and (c) remotely on a quartz glass 175 µm away from and parallel to the illuminated TiO₂ surface. Mills et al. [1] performed soot photooxidation experiments using a FTIR gas cell to measure volatile carbonaceous species, such as CO₂, under 4.28 mW/cm² UVA irradiation (λ_{max} = 365 nm), 101.3 kPa O₂ gas flow, and front irradiation mode (Figure 5.1a). They suggested a first order kinetic model to describe the moles of CO₂ (N_{CO₂}) generated from soot as a function of irradiation time (t). However, they did not show a comparison of the model, \( N_{CO₂} = 22.5(1 - e^{-0.003t}) \), to the data. Figure 5.2, a plot of their equation and data, shows that the model does not capture the CO₂ data well between 300 to 900 hr. The decrease in the rate of CO₂ generation from 300 to 600 hr suggests the possibility of a non-volatile intermediate species which is subsequently oxidized to CO₂. Also, the thinning soot layer at longer times may have allowed an increased UV irradiation incident on the TiO₂, leading to the CO₂ generation rate increase seen from 600 to 900 hr.

To date, there is no satisfactory kinetic model for the TiO₂ photocatalyzed kinetics for soot disappearance. In this article, a series/parallel kinetic mechanism for soot destruction is developed to describe quantitatively the experimental data of Lee and Choi [2] and Mills et al. [1]. The models provide reasonable fits to the CO₂ formation data from these two articles [1,2].
5.3. **Model Development and Parameter Evaluation**

Two models are developed. The “simple” model describes the CO$_2$ generation data of Mills et al. [1] ($0 < t < 1100$ hr) and the mass loss ($m/m_0$) data from Lee and Choi [2] ($0 < t < 30$ hr). These experiments were conducted in air, so there was no variation of O$_2$ partial pressure ($P_{O_2}$). Also, the amount of O$_2$ was in large excess over soot. The “initial” model includes the effect of O$_2$ partial pressure, and is fitted to the CO$_2$ formation data obtained by Lee and Choi [2] at short times ($t \leq 40$ min) with He, air, and pure O$_2$ atmospheres. All fitted and standard error values are estimated by using Solver in Excel® and OriginLab Origin® 7, respectively.

5.3.1. “Simple” Model

Scheme 1. A “simple” series / parallel reaction mechanism to describe soot photooxidation by TiO$_2$.

![Scheme 1](image)

Scheme 1 shows a mixed reaction system for soot photooxidation which assumes the existence of a non-volatile intermediate species. In Scheme 1, $k_1$ is the rate constant (hr$^{-1}$) for direct soot oxidation to CO$_2$, $k_2$ is the rate constant (hr$^{-1}$) for intermediate formation from soot, and $k_3$ is the rate constant (hr$^{-1}$) for CO$_2$ generation from the intermediate species. All reaction steps are assumed first order and irreversible. The reaction rate expressions for the change in the moles of soot ($N_{soot}$), intermediate ($N_{int}$), and
CO$_2$ ($N_{CO2}$) as a function of UV irradiation time ($t$) are shown in Eqs. (1a), (2a) and (3a), respectively. These equations are integrated analytically to yield Eqs. (1b), (2b), and (3b), where $N_{soot,0}$ is the moles of soot at $t = 0$. The initial moles of $N_{int}$ and $N_{CO2}$ are assumed to be zero. Lee and Choi [2] expressed some of their experimental data as normalized mass loss, which we obtained by summing Eq. (1b) and (2b), yielding Eq. (4). We assume the molecular weights of the soot and intermediate species are the same (Eq. 4).

$$\frac{dN_{soot}}{dt} = -k_1 N_{soot} - k_2 N_{soot} = -(k_1 + k_2) N_{soot}$$  \hspace{1cm} (1a)

$$N_{soot} = N_{soot,0} \exp[-(k_1 + k_2) t]$$ \hspace{1cm} (1b)

$$\frac{dN_{int}}{dt} = k_2 N_{soot} - k_3 N_{int}$$ \hspace{1cm} (2a)

$$N_{int} = \frac{k_2}{k_1 - (k_1 + k_2)} N_{soot,0} \left\{ \exp[-(k_1 + k_2) t] - \exp(-k_3 t) \right\}$$ \hspace{1cm} (2b)

$$\frac{dN_{CO2}}{dt} = k_1 N_{soot} + k_3 N_{int}$$ \hspace{1cm} (3a)

$$N_{CO2} = N_{soot,0} \left\{ 1 - \frac{k_3 - k_1}{k_3 - (k_1 + k_2)} \exp[-(k_1 + k_2) t] + \frac{k_2}{k_3 - (k_1 + k_2)} \exp(-k_3 t) \right\}$$ \hspace{1cm} (3b)

$$\frac{m}{m_0} \approx \frac{N_{soot} + N_{int}}{N_{soot,0}} = \exp[-(k_1 + k_2) t] + \frac{k_2}{k_3 - (k_1 + k_2)} \left\{ \exp[-(k_1 + k_2) t] - \exp(-k_3 t) \right\}$$ \hspace{1cm} (4)

All experiments by Mills et al. [1] and some by Lee and Choi [2] were executed in front irradiation mode, shown in Figure 5.1a. Therefore, $k_1$, $k_2$, and $k_3$ must be modified to account for the time-varying effect of soot absorption of UV light. Peral and Ollis [6] and Julson and Ollis [8] modeled the effect of light intensity profile on the apparent reaction rate constant within TiO$_2$ powder layers. We modify their intensity-dependent TiO$_2$ rate constant form for soot instead, as shown in Eq. (5).
\[ k_i = k_{0,i}I^p = k_{0,i} \left\{ I_0 \exp \left[ -\epsilon_{\text{soot}} \delta_{\text{soot}}(t) \right] \right\}^p \quad \text{where } i = 1, 2, 3 \] (5)

Here \( k_{0,i} \) is the intensity-independent kinetic rate constant \((cm^2/mW-hr\) or \((cm^2/mW)^{1/2}/hr\)), \( I_0 \) is the light intensity \((mW/cm^2)\), \( \epsilon_{\text{soot}} \) is the apparent UV absorption coefficient of soot \((\mu m^{-1})\), \( \delta_{\text{soot}}(t) \) is the soot layer thickness \((\mu m)\), and \( p \) is the exponent for rate constant dependence on light intensity, described in detail below. We estimate \( \delta_{\text{soot}}(t) \) by relating the change in soot thickness to the measured carbon loss, i.e., amount of CO\(_2\) generated using the data of Mills et al. [1] or the \( m/m_0 \) data of Lee and Choi [2]. The assumptions in this relationship, seen in Eq. (6), are (a) the \( \delta_{\text{soot}} \) and \( \epsilon_{\text{soot}} \) terms include both soot and intermediate species, (b) \( \epsilon \) is the same for the soot and intermediate, and (c) the only gaseous product formed is CO\(_2\).

\[
\delta_{\text{soot}}(t) = \delta_{\text{soot}}(0) \left[ \frac{\delta_{\text{soot}}(t)}{\delta_{\text{soot}}(0)} \right] \approx \delta_{\text{soot}}(0) \left[ \frac{m(t)}{m_0} \right] \approx \delta_{\text{soot}}(0) \left[ \frac{CO_{2,\text{final}} - CO_{2}(t)}{CO_{2,\text{final}} - CO_{2}(0)} \right] \] (6)

Researchers [16-18] have examined the effect of light intensity on reaction rate. Turchi and Ollis [16] obtained \( 0.5 < p < 1.0 \) from theoretical considerations. At high photogenerated hole concentrations \([h^+]\), the apparent rate constant varied as the square root of the light intensity, while at low \([h^+]\) the apparent rate constant was proportional to the light intensity. A transition regime from first-order to half-order kinetics occurred as light intensity increased. Early experimental results of Egerton and King [17] for the PCO of liquid isopropanol to acetone showed that at weak light supply rates (less than \( 5 \times 10^{15} \) quanta/sec), there was a linear relationship between light intensity and reaction rate. At
strong light supply rates (greater than $5 \times 10^{15}$ quanta/sec), the reaction rate varied with the square root of the light intensity, and electron-hole recombination was suggested to be the dominant process. Both exponents, $p = 0.5$ and $p = 1$, are evaluated here.

The “simple” model requires a maximum of 5 parameters to be fitted: $N_{\text{soot},0}$, $k_{0,1}$, $k_{0,2}$, $k_{0,3}$, and $\varepsilon_{\text{soot}}$. All parameters were obtained using the Solver function in Microsoft Excel®. The “simple” model is used to fit the CO$_2$ generation data from Mills et al. [1] and the $m/m_0$ data of Lee and Choi [2]. Other parameters may affect the reaction rate (e.g., humidity, temperature, TiO$_2$ thickness, TiO$_2$ porosity). However, they were not studied experimentally and therefore cannot be included in the model.

5.3.2. “Initial” Model

The “initial” model includes the influence of O$_2$ partial pressure ($P_{O2}$), but does not account for the oxidation of soot to intermediate, or for oxidation of intermediate to CO$_2$. Thus, this model is useful only at very short times. The reaction scheme for the “initial” model is shown in Scheme 2.

Scheme 2. An “initial” parallel reaction mechanism to describe the photocatalyzed oxidation of soot by TiO$_2$ at short times in various atmospheres.

To account for the “short time” CO$_2$ formation data from Lee and Choi [2], three parameters are needed: the rate constant, $k_1$, the order of the reaction ($n$) for oxidation of
soot to CO$_2$, and the apparent rate constant for reaction of pre-adsorbed O$_2$ in the soot, yielding CO$_2$ in an inert atmosphere ($k_d$). Since $k_d$ (hr$^{-1}$) is only important at the very beginning of the reaction, (i.e., no significant change in soot thickness), we assume that $k_d$ is intensity-independent. We obtain $k_d$ values using the He data from Lee and Choi [2] by modeling the removal of a finite quantity of pre-adsorbed O$_2$ as an irreversible reaction, first order in soot. The effect of $P_{O2}$ on the rates of soot oxidation and CO$_2$ formation are shown in Eq. (7) and (8), respectively.

The value of $n$ is determined from the CO$_2$ formation data by taking the ratio of $N_{CO2}$, Eq. (8b), in air and pure O$_2$ and making three assumptions: (a) the ratio of $P_{O2}$ in air over pure O$_2$ ($P_{O2,air}/P_{O2,O2}$) is 0.21, (b) a two-term Maclaurin series expansion of Eq. (8b) is sufficiently accurate at short times, and (c) $N_{soot,0}$, $k_1$, $n$, and the total system pressure have the same values in air and pure O$_2$. The order, $n$, can be calculated from Eq. (9), where $N_{CO2,air}$ and $N_{CO2,air}$ are the CO$_2$ formation data in pure O$_2$ and air, respectively.

$$\frac{dN_{soot}}{dt} = -k_1 N_{soot} P_{O2}^n$$  \hspace{1cm} (7a)$$
$$N_{soot} = N_{soot,0} \exp(-P_{O2}^n k_1 t)$$  \hspace{1cm} (7b)$$
$$\frac{dN_{CO2}}{dt} = k_1 N_{soot} P_{O2}^n$$  \hspace{1cm} (8a)$$
$$N_{CO2} = N_{soot,0} \left\{1 - \exp\left(-P_{O2}^n k_1 t\right)\right\}$$  \hspace{1cm} (8b)$$
$$\frac{N_{CO2,air}}{N_{CO2,air}} \approx \frac{N_{soot,0} P_{O2,air}^n k_1 t}{N_{soot,0} P_{O2,air}^n k_1 t} = \left(\frac{P_{O2,air}}{P_{O2,air}}\right)^n = \left(\frac{P_{total}}{0.21 \times P_{total}}\right)^n = \left(\frac{1}{0.21}\right)^n$$  \hspace{1cm} (9)
5.4. Results and Discussion

5.4.1. Fit to Mills et al. [1] CO₂ generation data

The “simple” model is fit to the CO₂ generation data using 5 parameters. The initial guesses and final fitted values from Excel Solver® are listed in Table 5.1. The initial guesses for \( k_{0,1} \), \( k_{0,2} \), and \( k_{0,3} \) were estimated using rough slope calculations of Mills’ CO₂ generation data, while the initial value of \( N_{\text{soot},0} \) was estimated from the mass loss of Mills’ soot film, measured before and after UV illumination. The initial value of \( \varepsilon_{\text{soot}} \) was estimated from the Lee and Choi [2] measurements of \( n \)-hexane soot at 350 nm.

Figure 5.3 compares the CO₂ generation data against the model for \( p = 0.5 \) and \( p = 1 \). The calculated moles of residual soot (\( N_{\text{soot}} \)) and intermediate (\( N_{\text{int}} \)) are also shown. The model (solid line) captures the “slowing” and subsequent acceleration of the CO₂ generation rate between 200-1000 hr for both \( p = 1 \) (Figure 5.3a) and \( p = 0.5 \) (Figure 5.3b), with an average relative error = 3%. The model fits are nearly identical for the two light intensity exponents. Both versions of the model predict that \( N_{\text{soot}} \) is essentially consumed after 400 hr, and that a maximum in \( N_{\text{int}} \) occurs between 200-300 hr. The model predicts a higher \( N_{\text{soot},0} \) (26.2 µmol) compared to Mills’ value (22.5 µmol). After the end of his experiment, Mills observed a good match between \( N_{\text{CO}_2} \) and the measured mass loss from the TiO₂-soot film before and after irradiation. This mass balance confirms that CO₂ is the main volatile product in soot photooxidation; however, it does not prove that the soot (or non-volatile intermediate) is completely oxidized.

The model predicts that about 3.5 µmol of \( N_{\text{int}} \) remained on the TiO₂ surface at the end of Mills’ experiment. The photographs from Mills et al. [1] appeared to show a clear
microscope slide after 45 days (1080 hr), but there might have been a colorless intermediate(s) remaining on the surface. For dyes, another optically dense reactant in photocatalysis, decolorization in solution is typically rapid compared to mineralization [4,9]. Visible color comes from chromophore groups in a compound. These chromophores often arise from conjugated π systems where electrons are delocalized, with a minimum of 8 conjugated double bonds. Therefore at high $N_{\text{soot}}$ and $N_{\text{int}}$ values, the solids on the surface can appear black. As $N_{\text{soot}}$ and $N_{\text{int}}$ decrease, their electron delocalization and double bond conjugation should also decrease, causing them to become colorless at longer times because they do not absorb in the visible light wavelengths. Alternatively, carbon may leave the surface as volatile species other than CO$_2$, though the FTIR-gas cell results of Mills et al. [1] did not find evidence of gaseous species other than CO$_2$ during soot PCO. In contrast, Romeas et al. [11] reported substantial amounts of lower molecular weight (C$_1$-C$_{15}$) alkanes, alcohols, aldehydes, ketones, and carboxylic acids in the vapor phase during PCO of palmitic acid (C$_{16}$) multilayers on UV-illuminated TiO$_2$-coated glass plates.

Figure 5.4a shows the predicted change in UV light intensity arriving at the TiO$_2$ surface ($I^p$) as a function of front illumination time, calculated from Eq. (5). At $t = 0$, the calculated irradiance is less than 0.5 mW/cm$^2$ for both $p = 1$ and $p = 0.5$, which means soot absorbs 90% and 95% of the incident UV light, respectively. After 1100 hr of UV irradiation, soot is completely oxidized but the intermediate species still absorbs a portion of the incident UV light. Correspondingly, in Figure 5.4b we calculate a continuous decrease in soot thickness, $\delta_{\text{soot}}$, from 0.5 μm to 70 nm at 1100 hr. The change in $\delta_{\text{soot}}$ is
nearly identical for \( p = 1 \) and \( p = 0.5 \). Though Figure 5.3 depicts \( N_{\text{soot}} \) reaching zero by 400 hr, there is still a contribution of \( N_{\text{int}} \) to \( \delta_{\text{soot}} \).

5.4.2. *Fit to Lee and Choi [2] normalized mass loss data*

The “simple” model is fit to the normalized mass loss data from Lee and Choi [2] using 3 parameters. We solve *only* for the front irradiation data so that we can compare these parameter values to the work of Mills et al. [1]. The \( k \) values are fitted to Eq. (4), and listed in Table 5.2. We keep \( \varepsilon_{\text{soot}} \) constant at 2.0 \( \mu \text{m}^{-1} \) for consistency with the soot absorption measurements of Lee and Choi [2]. Only the weak light intensity case \( (p = 1) \) is considered since no difference is seen previously with the Mills et al. [1] work.

Figure 5.5 shows that the model fits the front irradiation data using this regression technique, while it captures only the last 2 data points when applied to the back irradiation mode. For modeling purposes, the last 2 data points are the most important because they describe the time required for complete soot oxidation. The model prediction of temporal changes in incident UV light intensity passing through the soot layer and in \( \delta_{\text{soot}} \) are depicted in Figure 5.6a and Figure 5.6b, respectively. As expected, the UV light intensity is constant in back irradiation mode, while a slow increase from 0.018 to 0.24 mW/cm\(^2\) is observed in front irradiation mode over the span of 32 hr. The change in \( \delta_{\text{soot}} \), calculated using Eq. (6), follows the same pattern as the experimental mass data.

Three other regression techniques are applied to fit our model to their data:

- Estimate \( k_{0.1}, k_{0.2}, \) and \( k_{0.3} \) simultaneously for front and back irradiation modes, while holding \( \varepsilon_{\text{soot}} \) constant at 2 \( \mu \text{m}^{-1} \).
• Solve the three $k$ parameters using the mass loss data under back irradiation mode where we can neglect $\varepsilon_{\text{soot}}$, then evaluate $\varepsilon_{\text{soot}}$ from the front irradiation mass data using $k$ values from the former analysis. We assume $\varepsilon$ from the glass slide is negligible for the back irradiation mode.

• Vary four parameters ($k_{0,1}$, $k_{0,2}$, $k_{0,3}$, $\varepsilon_{\text{soot}}$) simultaneously for front and back irradiation modes.

None of these techniques generate fitted parameters that satisfactorily fit both the back and front irradiation data or only the back irradiation data. Two explanations may explain this mismatch between our kinetic model and the experimental data of Lee and Choi [2]. First, there are only 4 data points for 32 hours of data. Relatively small experimental errors can create apparent trends that cannot be captured by a physically-based model. Second, it is surprising to see a large decrease in normalized mass between 15 to 25 hr for both the front and back irradiation data; we expect this large decrease to occur at different times. The fact that this latter statement happens in the same time period for both irradiation modes leads us to believe that this large decrease in normalized mass may be an experimental artifact. Furthermore, the increased rate of mass loss towards the end of the back irradiation data was unexpected because the $k$ values should be intensity-independent (Figure 5.6a). However, one explanation is that the glass may absorb UV light, which is not accounted for in the model. For example, float (i.e., window) glass absorbs a large portion of UVA (320-390 nm) light. Lee and Choi [2] did not specify the type of glass used in their experiments.

A comparison of the fitted parameters for the two studies reveals that the $k$ values and $\varepsilon_{\text{soot}}$ for Lee and Choi [2] are 100-300x and 2x greater, respectively, than Mills et al.
138

Although both researchers examine the photocatalyzed oxidation of “soot” on “TiO2,” these large differences in parameter values show that catalyst and contaminant properties (e.g., soot structure, soot porosity, TiO2 thickness, TiO2 phase) affect the kinetic rate constants and molar absorptivity.

5.4.3. Fit to Lee and Choi [2] CO2 formation data

The “initial” model is fitted to the CO2 formation data under pure O2, air, and He using two parameters: \( k_{0,1} \) and \( k_4 \), which is intensity-independent. The value of \( n \) in Eq. (9) is calculated by taking the ratio of the pure O2 to the air data from 0-40 min.

The effect of pre-adsorbed O2 on the CO2 formation from soot photooxidation is shown in the He data in Figure 5.7a. The He data is fit to a first order irreversible reaction with a \( k_4 \) of 5.0 hr\(^{-1}\). To remove the effect of pre-adsorbed O2, the He data is subtracted from the air and pure O2 data, illustrated in Figure 5.7b. Lee and Choi [2] do not specify their pretreatment procedure, therefore we reasonably assume that the moles of pre-adsorbed O2 is the same for the He, pure O2, and air data. Work by Kim et al. [19] demonstrated non-selective adsorption on activated carbon (e.g., soot); similar amounts of O2 and N2 were adsorbed per gram of activated carbon at 1 atm and 293 K.

The reaction order \( n \) is calculated as 0.8 using the CO2 data in Figure 5.7b, assuming the same amount of trace O2 in all three cases. This value is within the range (0.5 \( \leq n \leq 1.0 \)) previously reported in the literature [20-22] for the traditional thermal catalytic oxidation of diesel soot. Ciambelli et al. [20] determined a \( n = 0.5 \) dependency on the reaction rate for diesel soot and Degussa CB-330 carbon black using a Cu/V/K catalyst
at 101 kPa total pressure and 593 K, while Fino and coworkers [21] reported 0.68 ≤ \( n \) ≤ 1.0 when they tested 3 Cs/V catalysts for the combustion of Cabot Ltd. Monarch 700, Elftex 435, and Elftex 125 carbon blacks at 573-723 K.

We can solve explicitly for one value of \( k_{0,1} \) using Eq. (8b) if we assume that \( P_{O_2,O_2} \) is about 4 times greater than \( P_{O_2,air} \) and the total pressure is the same in both sets of experiments. We estimate \( N_{soot,0} \) as 2.2 µmol from the soot thickness and area of 2.4 µm and 0.55 cm², respectively, given by Lee and Choi [2], a soot bulk density of 0.2 g/cm³, and a carbon molecular weight of 12 g/mol. The soot bulk density is a median value from Degussa Printex-U® carbon black, a compound which has been used as a model diesel soot [22-24]. The data in Figure 5.7b is linear, meaning the exponent term of \( k_1 \) (Eq. 5) is negligible because minimal soot is oxidized. Therefore, we fix \( \varepsilon_{soot} \) to 2.0 µm⁻¹, estimated by Lee and Choi[2] at 350 nm absorbance or transmittance, instead of fitting it as a parameter. This \( \varepsilon_{soot} \) is assumed to be a representative value for 300 < \( \lambda \) < 400 nm. The value of \( k_{0,1} \) is solved via simultaneous use of the pure O₂ and air data, and the model is represented as solid lines in Figure 5.7b. The single parameter value for \( k_{0,1} \), listed in Table 5.3, is able to fit both the pure O₂ and air data well. The solid and dashed lines in Figure 5.7a are the kinetic model fits to the pure O₂ and air data, respectively, when we add the model prediction from Figure 5.7b with the first order reaction (\( k_4 \)) for the He data. Overall, the model can describe the CO₂ formation data for both graphs in Figure 5.7.

Figure 5.8 illustrates the calculated change in light intensity (Figure 5.8a) and soot thickness (Figure 5.8b) for the 40 minutes of CO₂ data. As expected, the changes in these variables are insignificant. The model predictions in Figure 5.7 and Figure 5.8 are for \( p = \)
1, which is a good estimate because the incident UV irradiance approaching the TiO$_2$ is calculated as 0.012-0.013 mW/cm$^2$. These light intensities are well within the linear regime studied by Egerton and King [17] and discussed by Turchi and Ollis [16].

5.4.4. **Mass Transfer Influences**

The role of mass transfer to the TiO$_2$ surface is often negligible in gas-solid PCO systems [25]. Mass transfer influences on the PCO reaction rate are considered when studying low concentrations of volatile organic compounds (VOCs) [5,7] or competitive adsorption between VOCs and water [6]. We examine the possibility of O$_2$ diffusion-limited conditions in the Mills et al. [1] and Lee and Choi [2] studies by estimating their systems as zero O$_2$ surface concentration and a one-dimensional ($x$) semi-infinite medium with an O$_2$ concentration $C_0$ (mol/cm$^3$) and a diffusion coefficient $D$ (cm$^2$/s) [26]. Fick’s second law, Eq. (10), is applied assuming $D$ and density are constant:

$$\frac{\partial C}{\partial t} - D \frac{\partial^2 C}{\partial x^2} = 0 \tag{10}$$

$$M_t = 2C_0 \sqrt{\frac{D t}{\pi}} \tag{11}$$

where $M_t$ is the total amount of O$_2$ that has left the medium (mol/cm$^2$) at time $t$. We calculate $D$ for gas pairs of non-polar, non-reactive molecules using the Lennard-Jones potential [27], with $D = 0.21$ cm$^2$/s for Mills et al. [1] under $P_{O2} = 1$ atm and $T = 298$ K, and $D = 0.23$ cm$^2$/s for Lee and Choi [2] under $P_{O2} = 0.21$ atm and $T \approx 318$ K. Using the ideal gas law, $C_0$ is 41 mol/cm$^3$ for Mills et al. [1] and 8.0 mol/cm$^3$ for Lee and Choi [2].
Assuming a one hour basis \( (t = 3600 \text{ s}) \) for Eq. (11), we estimate a maximum \( M_t = 1260 \text{ mol/cm}^2 \) for Mills et al. [1] or 3140 mol using the 2.5 cm\(^2\) area \((A)\) of the cover slide. Since Mills et al. [1] does not specify the soot area we have to use the TiO\(_2\)-covered area. The initial soot reaction rate using the “simple” model is \( 1.4 \times 10^{-7} \text{ mol/hr} \), much slower than the \( M_t \) for \( \text{O}_2 \) diffusion to the TiO\(_2\)/soot surface. Similarly, for Lee and Choi we obtain a maximum \( M_t*A = 144 \text{ mol} \) for a 0.55 cm\(^2\) glass plate area, which is orders of magnitude faster than the initial soot reaction rate of \( 1.1 \times 10^{-7} \text{ mol/hr} \) for the “simple” model and \( 8.0 \times 10^{-11} \text{ mol/hr} \) for the “initial” model. Therefore, we can neglect mass transfer resistances for these two systems. Derivation of the one-dimensional flux equation can be found in Appendix A.

5.5. Conclusions

Titanium dioxide photooxidation of soot is a complex process requiring a series / parallel kinetic model to adequately describe the \( \text{CO}_2 \) generation and normalized mass loss data available in the literature. The two models also predict the temporal changes in \( N_{\text{int}}, \ N_{\text{soot}}, \ \delta_{\text{soot}}, \ \text{and} \ I. \) The “simple” model is able to fit the \( \text{CO}_2 \) generation data of Mills et al. [1] over a period of 1100 hr using 5 parameters: \( k_{0,1}, k_{0,2}, k_{0,3}, \varepsilon_{\text{soot}}, \) and \( N_{\text{soot},0}. \) This model also captures the normalized mass loss data of Lee and Choi [2] when evaluated only for the front irradiation data. The \( \varepsilon_{\text{soot}} \) and \( k \) values derived from the model are much larger for Lee and Choi [2] compared to Mills et al. [1].

The “initial” model fits the \( \text{CO}_2 \) data of Lee and Choi [2] under pure \( \text{O}_2, \) air, and He. We predict the \( \text{CO}_2 \) formation rate to have a 0.8 exponent dependency on the \( \text{O}_2 \)
partial pressure. Only one \( k_{0,1} \) value is used to model the pure \( \text{O}_2 \) and air data after subtracting the effect of pre-adsorbed \( \text{O}_2 \) on \( N_{\text{CO}_2} \). Mass transfer calculations reveal negligible \( \text{O}_2 \) diffusion influence on the soot reaction rate for both research studies.

5.6. Acknowledgments

The authors thank the State of North Carolina for funding of this research.

5.7. References


Table 5.1. Initial and final parameter values for the “simple” model fitted to the CO$_2$ data of Mills et al. [1] for $p = 1$ and $p = 0.5$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Initial Estimate</th>
<th>Fitted Value</th>
<th>Standard Error</th>
<th>Initial Estimate</th>
<th>Fitted Value</th>
<th>Standard Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_{soot,0}$ (mol)</td>
<td>2.26 x 10$^{-5}$</td>
<td>2.62 x 10$^{-5}$</td>
<td>9.5 x 10$^{-7}$</td>
<td>2.26 x 10$^{-5}$</td>
<td>2.62 x 10$^{-5}$</td>
<td>1.1 x 10$^{-6}$</td>
</tr>
<tr>
<td>$\varepsilon_{soot}$ ($\mu$m$^{-1}$)</td>
<td>2.0</td>
<td>4.4</td>
<td>5.3 x 10$^{-2}$</td>
<td>2.0</td>
<td>8.3</td>
<td>0.1</td>
</tr>
<tr>
<td>$k_{0,1}$</td>
<td>7.4 x 10$^{-4}$</td>
<td>4.0 x 10$^{-3}$</td>
<td>2.4 x 10$^{-4}$</td>
<td>5.6 x 10$^{-4}$</td>
<td>7.5 x 10$^{-3}$</td>
<td>4.7 x 10$^{-4}$</td>
</tr>
<tr>
<td>$k_{0,2}$</td>
<td>1.3 x 10$^{-4}$</td>
<td>7.1 x 10$^{-3}$</td>
<td>4.9 x 10$^{-4}$</td>
<td>1.5 x 10$^{-3}$</td>
<td>1.4 x 10$^{-2}$</td>
<td>9.4 x 10$^{-4}$</td>
</tr>
<tr>
<td>$k_{0,3}$</td>
<td>2.0 x 10$^{-4}$</td>
<td>4.8 x 10$^{-4}$</td>
<td>5.0 x 10$^{-5}$</td>
<td>4.2 x 10$^{-4}$</td>
<td>9.6 x 10$^{-4}$</td>
<td>9.0 x 10$^{-5}$</td>
</tr>
</tbody>
</table>

$^a$ When $p = 1$ and $p = 0.5$, $k_{0,1}$, $k_{0,2}$, and $k_{0,3}$ have units of cm$^2$/mW-hr and (cm$^2$/mW)$^{1/2}$/hr, respectively.

Table 5.2. Initial and final parameter values for the “simple” model fitted to the normalized mass loss data of Lee and Choi [2]. ($p = 1$, $\varepsilon_{soot} = 2.0$ $\mu$m$^{-1}$, only front irradiation solved)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Initial Estimate</th>
<th>Fitted Value</th>
<th>Standard Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{0,1}$ (cm$^2$/mW-hr)</td>
<td>6.2 x 10$^{-1}$</td>
<td>8.7 x 10$^{-1}$</td>
<td>2.2 x 10$^{-1}$</td>
</tr>
<tr>
<td>$k_{0,2}$ (cm$^2$/mW-hr)</td>
<td>3.0</td>
<td>2.0</td>
<td>8.2 x 10$^{-1}$</td>
</tr>
<tr>
<td>$k_{0,3}$ (cm$^2$/mW-hr)</td>
<td>4.8 x 10$^{-2}$</td>
<td>7.6 x 10$^{-2}$</td>
<td>1.4 x 10$^{-2}$</td>
</tr>
</tbody>
</table>

Table 5.3. Initial and final parameter values for the “initial” model fitted to the CO$_2$ formation data of Lee and Choi [2]. ($p = 1$, $\varepsilon_{soot} = 2.0$ $\mu$m$^{-1}$)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Initial Estimate</th>
<th>Fitted Value</th>
<th>Standard Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$</td>
<td>--</td>
<td>0.8</td>
<td>--</td>
</tr>
<tr>
<td>$k_{0,1}$ (cm$^2$/mW-hr)</td>
<td>6.2 x 10$^{-1}$</td>
<td>1.9 x 10$^{-1}$</td>
<td>7.8 x 10$^{-3}$</td>
</tr>
<tr>
<td>$k_d$ (hr$^{-1}$)</td>
<td>3.5 x 10$^{-2}$</td>
<td>5.0</td>
<td>0.3</td>
</tr>
</tbody>
</table>
5.8. List of Figures

Figure 5.1. Configurations for experiments run in (a) front irradiation mode and (b) back irradiation mode.

Figure 5.2. CO₂ generation from soot photocatalyzed oxidation as a function of irradiation time, adapted from Mills et al. [1]. (□) experimental data; (—) first order rate model: \( N_{CO2} = 22.5(1 - e^{-0.003t}) \)

Figure 5.3. Mills’ [1] \( N_{CO2} \) data (□) and the “simple” model \( N_{CO2} \) (—), \( N_{soot} \) (—), and \( N_{int} \) (···) data at (a) \( p = 1 \) and (b) \( p = 0.5 \).

Figure 5.4. “Simple” model prediction for the work by Mills et al. [1] of the change in (a) incident UV light intensity passing through the soot layer as a function of time at \( p = 1 \) (—) and \( p = 0.5 \) (—), and (b) soot thickness as a function of time at \( p = 1 \) (◇) and \( p = 0.5 \) (○). The dotted and dashed horizontal lines in figure (a) represent the maximum theoretical values for \( I^1 \) and \( I^{0.5} \), respectively.

Figure 5.5. Lee and Choi [2] normalized mass loss data as function of UV illumination time under front (▲) and back (◇) illumination modes, and a control experiment with no TiO₂ (○). The lines represent the “simple” model fit to the front (—) and back (—) illumination mode experiments. (\( p = 1, \varepsilon_{soot} = 2.0 \mu m^{-1}, \) only front irradiation solved)

Figure 5.6. “Simple” model prediction for the work by Lee and Choi [2] of the change in (a) incident UV light intensity passing through the soot layer as a function of time, and (b) soot thickness as a function of time. (▲) front illumination mode; (◇) back illumination mode (\( p = 1, \varepsilon_{soot} = 2.0 \mu m^{-1}, \) only front irradiation solved)

Figure 5.7. Lee and Choi [2] CO₂ formation data in pure O₂ (◼), air (△), and He (●), and a control experiment with no TiO₂ (◇). The solid lines represent the “initial” model fit to the pure O₂ (—), air (—), and He (···) data, respectively. Figure (a) shows the original data of Lee and Choi [2], while figure (b) is the pure O₂ and air data with the He data subtracted from their \( N_{CO2} \) values. (\( p = 1 \))

Figure 5.8. “Initial” model prediction for the work by Lee and Choi [2] of the change in (a) incident UV light intensity passing through the soot layer as a function of time, and (b) soot thickness as a function of time, in the CO₂ formation data. (□) pure O₂; (○) air (\( p = 1, \varepsilon_{soot} = 2.0 \mu m^{-1} \))
Figure 5.1
Figure 5.2
Figure 5.3
Figure 5.4
Figure 5.5
Figure 5.6
Figure 5.7
Figure 5.8

(a) Graph showing the variation of $I_0 e^{-\frac{t}{\tau_{\text{post}}}}$ (mW/cm²) with time (min) for Pure O₂ and Air.

(b) Graph showing the variation of $\delta_{\text{soot}}$ (µm) with time (min) for Pure O₂ and Air.
CHAPTER 6

QUANTITATIVE PHOTOCATALYZED SOOT OXIDATION ON TITANIUM DIOXIDE *

6.1. Abstract

We report here the photocatalytic oxidation of deposited hurricane lamp soot by titanium dioxide (TiO$_2$). Sol-gel derived TiO$_2$ was coated on quartz crystal microbalance (QCM) elements. Characterization by spectroscopic ellipsometry ($SE$) and atomic force microscopy (AFM) revealed low surface roughness of 0-17%, and $SE$ showed a linear variation of the TiO$_2$ thickness versus the number of sol-gel spin coats. Anatase and rutile phase structures were observed using X-ray diffraction (XRD) after TiO$_2$ film calcination at 350°C.

Soot was deposited on the calcined TiO$_2$ film using an analytical rotor passing through a hurricane lamp flame, and subsequently irradiated with near-UV light ($\lambda_{\text{max}} = 365$ nm). The TiO$_2$ layer thickness and subsequent mass of soot deposited were varied independently to determine their effects on the reaction rate. Varying the soot mass on the TiO$_2$-coated QCM crystals revealed a range of behavior over 20,000 min, ranging from total soot destruction of a single pass soot layer to minimal oxidation of an eight pass soot layer, the latter caused by soot screening of the incident UV light. A series / parallel reaction mechanism [1] developed to describe previous literature data on TiO$_2$-catalysed soot photooxidation was successfully employed to capture the longer time changes in presumably graphitic soot mass as a function of UV illumination time from 1,000-20,000 min and of soot layer thickness. Short time soot mass loss is attributed to oxidation of organic carbons deposited on the graphitic soot components. This kinetic model can be used to predict the rate of TiO$_2$-catalyzed soot destruction as a function of near-UV illumination time and initial soot layer thickness.
Keywords: Titania, Photocatalysis, Soot, Kinetic Model, Oxidation, Diffusion, Carbon Black, Formal Quantum Efficiency

6.2. Introduction

The development of “self Cleaning” surfaces of glass [2-4], tiles [5], and even buildings [6] using TiO$_2$ photocatalytic oxidation (PCO) logically demands consideration of likely organic deposits, including soot. To date, four articles addressed TiO$_2$ PCO of soot [1,7-9], but only two reported quantitative data [7,8] and no kinetic model was proposed. We have generated two soot kinetic models [1] to describe mass loss data of Lee and Choi [7] and CO$_2$ generation data of Mills et al. [8]. A comparison of the two studies reveals that although both research groups examined the TiO$_2$ PCO of “soot,” the large differences in fitted parameter values [1] show that soot characteristics affect the kinetic rate constants and molar absorptivity of such deposits.

The soot composition is categorized primarily as three components [10-14]: (a) graphitic or inorganic carbon; (b) organic carbon, such as unburned hydrocarbons (HCs), soluble organic fractions (SOFs), or volatile organic fractions (VOFs); (c) inorganic material (e.g., sulfates, water, ash), especially in diesel soot. We explore here only on the first two components. The organic carbons can constitute a significant portion of the total soot; for example, fuel SOFs can represent 20% of the particulate emissions in diesel engine exhaust [11]. The organic carbons are removed thermally from the soot surface more readily than to the graphitic carbon. Temperature-programmed desorption (TPD)
experiments by Ahlström and Odenbrand [14] and Querini et al. [15] confirmed hydrocarbon removal from diesel soot at temperatures from 200-400°C and below 300°C, respectively. The organic carbons are assumed to surround and fill the micropores of graphitic carbon [12]. Electron microscope images of soot particles reveal the porous nature of soot [16-18]. Ahlström and Odenbrand [14] observed an increase in the BET specific area of diesel soot from 35 to 270 m²/g as the sample degassing (N₂) temperature increased from 100 to 600°C. They attributed this increase to desorption of water and volatile unburned HCs from the soot.

For model development, we summarize the earlier literature on a related process, the thermal catalytic oxidation of soot, which exhibits different reaction rates for the organic and graphitic portions of soot carbons [13,19-22]. Neeft et al. [19] observed high reaction rates for the initial 10-20% soot conversion compared to later reaction times for both diesel soot and Degussa Printex-U, a carbon black often used as a model soot. They ascribe the fast reaction to oxidation of the more reactive compounds, such as adsorbed hydrocarbons. Research by de Soete [20] displayed faster oxidation of n-hexadecane and α-ethynaphthalene soots than of their char counterparts, where the char is produced by thermal desorption of the volatiles in the initial soot under N₂ atmosphere at 1100°C. The char SOFs are more than an order of magnitude lower than those for the original soot. Ahlström and Odenbrand [22] plotted the ratio of combustion rates for degassed (600°C, N₂, 1 hr) to fresh diesel soot and noted a ratio of 0.4 for temperatures lower than 350°C. The lowered combustion rate after sample degassing pretreatment was caused by the lack of unburned HCs. Neri et al. [13] tested various metal oxide catalysts and determined
Fe$_2$O$_3$ to be a better HC oxidation catalyst, while V$_2$O$_5$ and CuO catalysts were better for inorganic carbon oxidation compared to non-catalyzed soot oxidation. They suggested that in the presence of a thermal catalyst, HCs are more readably combusted than graphitic carbon. Finally, Darcy et al. [21] developed a soot oxidation reaction rate consisting of a “fast” oxidation of VOFs from diesel soot and a “slow” oxidation of the low-reactive (i.e., inorganic carbon) diesel soot portion. Their model was applied to both catalyzed and non-catalyzed soot oxidation data.

The research completed for both thermal catalytic oxidation and PCO of soot have shown that results can vary considerably depending on the chemical and physical characteristics of the soot being analyzed. The objective of this study is to develop a reproducible system that will deposit soot on top of a TiO$_2$ layer and allow reliable determination of PCO soot kinetics. Once we generate a reliable technique for soot layer deposition, we can alter process variables such as soot and TiO$_2$ loadings to determine their effects on reaction rate, and further test the utility of our soot series / parallel reaction rate mechanism and model.

6.3. Experimental Setup

6.3.1. TiO$_2$ Deposition

Titanium dioxide sol-gel solutions were synthesized using “method 2” of Xu and Anderson [23]. In brief, 16.5 mL titanium isopropoxide (TTIP, Sigma Aldrich) was added to 200 mL of 0.71 vol% nitric acid (HNO$_3$, Fisher Scientific) in deionized (DI, Millipore Milli-Q) water. The TTIP suspension was peptized at room temperature for three days.
The resultant TiO$_2$ sol was dialyzed in a SPECTRA/POR molecular porous membrane (Spectrum Laboratories, Inc.) until a final pH value of 3.5 was achieved.

The final TiO$_2$ sol was deposited on quartz crystals and silicon substrates using a spin coater (Headway Research, Inc. PWM32-PS-R790 spinner system) set at 1000 rpm, with a 500 rps ramp rate and a 500 s termination step. The number of TiO$_2$ spin coats varied from 0 to 8, with a firing step of 100°C for 1 hour between each coat. After all TiO$_2$ spin coats were deposited on each QCM crystal, the sample was calcined at 350°C for 3 hours with a ramp up rate of 3°C/min, then cooled to room temperature over 4 hours at an approximate rate of 5°C/min. A Jelight Company Inc. Model #42 ultraviolet-ozone (UVO) cleaner was used to remove any initial organic contaminants on the QCM crystal surface prior to TiO$_2$ deposition.

6.3.2. Lamp Soot Deposition

Soot was deposited from a hurricane lamp (Ultra-Pure Oil Lamp with 99% Ultra-Pure Paraffin Candle and Lamp Liquid, Lamplight Farms) with a 1.8 cm linear flame, as depicted in Figure 6.1. A modulated speed rotator (MSR) / controller (AFMSRX analytical rotator, Pine Instrument Company) was used to deposit soot on the QCM crystal in a controlled fashion. A smooth alligator clip (1 1/8” smooth test clips, copper, Radioshack) was attached to the MSR to fasten the QCM crystal to the device. The rotation speed varied from 5 to 10 rpm ($\bar{v}$=7-15 cm/s; $\omega$=27-56 °/s), and the QCM crystal passed 0.2 to 0.5 cm below the top of the undisturbed hurricane lamp flame. For our experiments, the analytical rotor ran at 10 rpm and 0.5 cm into the flame.
6.3.3. **Characterization of TiO$_2$ sol and Lamp Soot**

Following 350°C calcination, TiO$_2$ roughness was determined by AFM (Dimension 3000, Digital Instruments), with imaging performed in tapping mode (drive frequency: 330 kHz) employing a Si cantilever (Veeco Probes). Measurements were done on 1 µm x 1 µm and 10 µm x 10 µm areas under ambient conditions, with 512 samples per image and 0.5 Hz scan rate. The surface root-mean-square roughness ($R_q$) and the maximum height ($R_{max}$) calculated by AFM software are defined as the standard deviation of the surface height ($Z$) and the largest $Z$ difference within the image area, respectively.

Titania crystal structure was determined using XRD (XRG 3000, Inel Inc.) employing Co K$\alpha_1$ radiation ($\lambda = 1.7890$ Å). Data was collected using a CPS-120 detector over $0^\circ < 2\theta < 125^\circ$, and converted to Cu K$\alpha_1$ radiation ($\lambda = 1.5405$ Å) with a range of $0^\circ < 2\theta < 100^\circ$. The data was calibrated with respect to a silicon standard.

The TiO$_2$ film thickness was ascertained by ellipsometry (VASE spectroscopic ellipsometer, J. A. Woollam). The Bruggemann effective medium approximation (BEMA) was employed between 450-1100 nm to model the measured $\psi$ and $\Delta$ (both in degrees) Stokes parameters related to the polarization change of light interaction with a sample, and correlated to the ratio of complex Fresnel reflection coefficients. For the BEMA, the film was modeled as a two-component mixture of solid TiO$_2$ and void volume, where the latter material fraction was fitted. Interfacial roughness / inhomogeneity was added as an additional fitted parameter to capture peak broadening. Ellipsometry measurements were
completed for TiO$_2$ sol deposited on Si wafers (polished, 500-550 µm thick, Silicon Wafer Microelectronics, Inc.).

To calculate the calcined TiO$_2$ film band gap for an allowed direct transition ($E_{BG,d}$), a generalized oscillator model consisting of 3 Tauc-Lorentz models and 1 Gaussian model was used to fit the refractive index ($n$) and extinction coefficient ($k$) as a function of wavelength ($\lambda$). We were unable to use the BEMA model to determine $E_{BG,d}$ because the two-component mixture only modeled $k(\lambda)$ for $\lambda > 400$ nm. The direct band gap equation is shown in Eq. 1 [24], where $h$ is Planck’s constant ($6.63 \times 10^{-34}$ J*s), $\nu$ is the frequency (s$^{-1}$), and $\alpha$ is the absorption coefficient, where $\alpha = 4\pi k/\lambda$.

\[
h\nu = E_{BG,d} + (\alpha h\nu)^2
\] (1)

Soot and TiO$_2$ absorption spectra were measured by UV-Visible spectrometer (Jasco V-550) in the $\lambda$ range of 300-800 nm. Visual imaging of soot oxidation was recorded using a Canon Powershot S30 3.2 megapixel digital camera.

6.3.4. Quartz Crystal Microbalance – Theory and Application

The quartz crystal microbalance (QCM) is a frequency sensitive technique used to monitor mass changes in our surface studies. The primary component to QCM is its thin quartz crystal plate, with a thin metal electrode attached to each side of the plate. The electrode material is often gold (Au), but other metals (e.g., Ti, Zn, Pt, Ni, Si, C) can be used. When an electrode is subjected to an alternating electric field, the quartz crystal vibrates at its resonance frequency. The resonance frequency is sensitive to these
properties on the electrode surface: (a) mass changes, (b) mechanical stresses and damping from the density and viscosity of the adjacent fluid, (c) other environmental influences, such as temperature and pressure [25], and (d) surface roughness of the QCM crystal. The total frequency change ($\Delta f$), Eq. (2), is equal to the sum of the frequency changes caused by each of the five influences described above [26-28], where subscripts $m$, $T$, $P$, $\eta$, and $r$ represent mass, temperature, pressure, viscosity, and roughness, respectively, and $f_q$ is the fundamental quartz crystal resonance frequency. All $f$ values are reported in Hz.

$$\Delta f = f - f_q = \Delta f_m + \Delta f_T + \Delta f_P + \Delta f_\eta + \Delta f_r$$

(2)

$$\Delta f_m = \frac{-2nf_q^2}{(\mu_q \rho_q)^{1/2}} \Delta m_f = \left( -nf_q \right) \Delta m_f$$

(3)

The Sauerbrey equation, Eq. (3), relates the QCM frequency shift to the change in mass adsorbed on the quartz crystal surface [29]. Equation (3) strictly holds for a uniform, rigid, thin film deposit, where $\Delta f_m$ is the frequency change related to mass, $n$ is the number of quartz plate sides with adsorbed mass, $\Delta m_f$ is the mass change per unit area (g/cm$^2$), $\mu_q$ is the quartz shear modulus (2.947 x 10$^{11}$ g/cm·s$^2$), $\rho_q$ is the quartz density (2.648 g/cm$^3$), and $C_q$ is a constant based on the type of quartz crystal (Hz/ng·cm$^2$). This constant is roughly 0.0566 and 0.0815 Hz/(ng·cm$^2$) for 5 and 6 MHz QCM crystals at 20°C, respectively. The Sauerbrey equation is valid for (a) mass loadings less than 2% of the mass/frequency of the bare QCM crystal [30] and (b) the coated film elasticity has a negligible effect on the QCM crystal’s resonance resistance compared to the film viscosity.
Calculations (not shown) prove that both assumptions are valid for our system. Derivation of the Sauerbrey equation is found in Appendix B.

Quartz crystal frequency variations may also be caused by changes in its surrounding fluid, for example, of density, viscosity, pressure, and temperature. The influence of density and viscosity on frequency ($\Delta f_\eta$) were derived by Kanazawa and Gordon [32] for Newtonian fluids, but their effects would be negligible in our air-solid system. Frequency increases linearly [28] or parabolically [30] with pressure ($\Delta f_P$), but we neglect this influence because we run an isobaric system operating at near standard pressure. We also ignore QCM crystal roughness ($\Delta f_r$) because polished crystals are used in our system. Average electrode surface roughness is 5 nm for polished crystals versus 1800 nm for unpolished crystals.

The temperature impact on frequency for AT-cut (35°15' with respect to the crystal axes [33]) crystals is shown in Eq. (4), where $\Delta f_T$ is the frequency change related to temperature, $T$ is the temperature (°C) and $a_0$-$a_3$ are empirical temperature coefficients [26,34]. This effect also should be negligible in our air-solid system run at 20-40°C using an AT-cut quartz crystal [25]. Experimental data from the QCM manufacturer for a clean, AT-cut, 5 MHz crystal optimized for 25°C was fitted to Eq. (4), yielding $a_3 = 0.0005$, $a_2 = -0.045$, $a_1 = 1.35$, $a_0 = -13.5$, and a -0.5 Hz < $\Delta f_T$ < 0.5 Hz shift for 20°C and 40°C, respectively. This frequency shift is negligible compared to our observed $\Delta f$ values of greater than 100 Hz.

$$\Delta f_T = a_3 T^3 + a_2 T^2 + a_1 T + a_0$$  (4)
Our QCM phase lock oscillators (PLO), crystal holders, and 1” diameter crystals (5 MHz crystals, Au electrode, part #149257-1; 6 MHz crystals, Pt electrode, part #149281-1) were purchased from Inficon (formerly Maxtek, Inc.). All crystals are AT-cut and optimized for 25°C operating temperature.

6.3.5. Experimental Reaction Setup

Figure 6.2 is a process flow schematic of the reaction experiments. Zero air (8 ppm H\textsubscript{2}O, 1 ppm THC) flows through a moisture trap and is piped into a refrigerator (model 3927 incubator, Forma Scientific) containing the QCM crystal holder. A variable area rotameter (K-03216-12 flowmeter, Cole Parmer) controls the volumetric zero-air flow rate at 55 mL/min. A quartz flow chamber was manufactured to shield the QCM crystal from exposure to laboratory air and to create a controlled atmosphere surrounding the crystal. The 1 5/16” diameter, 1/16” thick quartz discs (Prism Research Company, Raleigh, NC) contained two 1/16” holes drilled through the disc. Two 1/16” OD stainless steel pipes (Swagelok) are inserted into the holes to allow zero-air flow into and out of the chamber.

A spot lamp (100 W Black-Ray B-100A, UVP, LLC) positioned 9+” above the crystal holder emits UVA light (300 < \( \lambda \) < 400 nm, \( \lambda_{\text{max}} = 365 \) nm). A cooling fan is used to help maintain the refrigerator cavity at uniform temperature, and a UV shield (Safety Shield 6350, Naglene) in front of the UV spot lamps protects the user. Vibration dampening pads are positioned below the crystal holders to prevent any external vibrations from causing a frequency shift.
Soot PCO occurs within the UV-illuminated flow chamber, and the effluent gas (zero-air feed plus oxidation products, presumably CO$_2$ and H$_2$O) is vented into the refrigerator cavity. The QCM PLOs are interfaced with a controller and data acquisition software (NI SC-2345 signal conditioning connector box and LabView version 8.20, respectively, National Instruments) for data collection of crystal frequency and voltage (53131A 225 MHz universal counter and 34401A 6$^{1/2}$ digital multimeter, respectively, Agilent Technologies), and refrigeration temperature (K thermocouple, Omega Engineering). The zero-air flow temperature and relative humidity (R.H.) are measured using a thermohygrometer (Traceable memory hygrometer / thermometer model 4185, Control Company) interfaced with a computer using data acquisition software (Control Company). A pressure transducer (Omega Engineering) measures the air flow pressure. All experiments are run between 28°C ± 2.5°C and 0 psig, with trace H$_2$O in the air flow.

6.3.6. Data Analysis and Kinetic Modeling

The mixed series/parallel network model for soot photooxidation we proposed previously [1] is reproduced in Figure 6.3. The resulting kinetic model (Eqs. 5a, 5b, 6) [1] is the “simple” model we previously employed for the photocatalyzed soot mass loss data of Lee and Choi [7]. These equations (Eq. 5a, 5b) describe the mass rate change in adherent soot and adsorbed intermediate compounds, where $m_{soot}$ and $m_{int}$ are the soot and intermediate masses (ng), respectively. These equations are solved analytically to give the change in soot and intermediate masses as a function of time, where the rate constants $k_1$, $k_2$, and $k_3$ (min$^{-1}$) are functions of incident UV light intensity arriving at the TiO$_2$ top
surface. The fractional remaining mass is the dimensionless $m(t)/m_0$, with solution given in Eq. (6).

$$\frac{dm_{\text{soot}}}{dt} = -k_1 m_{\text{soot}} - k_2 m_{\text{soot}} = -(k_1 + k_2) m_{\text{soot}}$$  \quad (5a)$$

$$\frac{dm_{\text{int}}}{dt} = k_2 m_{\text{soot}} - k_3 m_{\text{int}}$$  \quad (5b)$$

$$\frac{m}{m_0} \approx \frac{m_{\text{soot}} + m_{\text{int}}}{m_{\text{soot,0}}} = \exp\left[-(k_1 + k_2)t\right] + \frac{k_2}{k_1 - (k_1 + k_2)}\left\{\exp\left[-(k_1 + k_2)t\right] - \exp(-k_2 t)\right\}$$  \quad (6)$$

Since soot deposited above the TiO$_2$ thin film will absorb some UV light, the rate constants are corrected for absorbance by the soot layer (Eq. 7), and the intensity $I_0$ refers to that reaching the top of the soot layer.

$$k_i = k_{0,i} I^p = k_{0,i} \left\{I_0 \exp\left[-\varepsilon_{\text{soot}} \delta_{\text{soot}}(t)\right]\right\}^p$$ \quad \text{where } i = 1, 2, 3$$  \quad (7)$$

The change in soot thickness, $\delta_{\text{soot}}(t)$ (µm), is related to the change in measured mass loss, seen in Eq. (8).

$$\delta_{\text{soot}}(t) \approx \delta_{\text{soot}}(0) \left[\frac{m(t)}{m_0}\right]$$  \quad (8)$$

This model has two fixed parameters: (a) the initial soot thickness $\delta_{\text{soot}}(0)$, and (b) the exponent for rate constant dependence on light intensity, $p$. We choose $p = 1$, but previous work [1] shows relative insensitivity to different values from $0.5 \leq p \leq 1$. Additionally, there are four fitted parameters: the intensity-independent kinetic rate constants $k_{0,1}, k_{0,2}, k_{0,3}$ (cm$^2$/mW–min), and the apparent UV absorption coefficient of soot,
Mathematical analyses for model fitting were completed using the Solver function in Excel® (Microsoft), Origin (OriginLab), or Matlab (The Mathworks, Inc.).

6.4. Results and Discussion

6.4.1. Atomic Force Microscopy (AFM)

Figure 6.4 shows the QCM crystal with 4 spin coats of TiO₂ sol calcined at 350°C. The surface height root mean square for Figure 6.4a is 3.7 nm. In this 10 µm x 10 µm area, the overall standard deviation in height differential is less than 5% of total TiO₂ thickness. In general, the surface roughness for our TiO₂-coated samples is low.

6.4.2. X-Ray Diffraction (XRD)

The XRD result for the Au electrode QCM crystal with four spin coats of TiO₂ sol calcined at 350°C is shown in Figure 6.5. Minor differences between the XRD peaks and the powder diffraction file data [35] are caused by Si calibration shifts. The most intense diffraction peak belongs to the quartz crystal (2θ = 26.8°), while the next four largest peaks are identified with the Au electrode. Three peaks (2θ = 25.0°, 37.8°, 53.9°) are recognized as anatase phase TiO₂, while a shoulder peak (2θ = 28.0°) may be related to rutile phase TiO₂. Therefore, we assume a predominately anatase phase TiO₂ crystallinity for our sol, which is expected for sol-gel derived TiO₂ calcined at temperatures from 350-500°C [36-41]. Specifically, Fu et al. [41] detected 90% anatase / 10% rutile structure and 71 Å TiO₂ crystallite size using a similar sol-gel preparation technique (dialysis pH = 4,
calcination temperature = 300°C, pelletized TiO₂). For calcination above 500°C, the resultant predominant phase is rutile [41].

6.4.3. **Spectroscopic Ellipsometry (SE)**

To determine TiO₂ film thickness, SE was used to model the optical parameters \( n \) (refractive index) and \( k \) (extinction coefficient). The original model assumed a single-component TiO₂ material, which yielded a poor fit to \( \Psi \) and \( \Delta \). We then used the BEMA two-component model of TiO₂ and void volume, which captured well the peaks for \( \Psi \) and \( \Delta \) as a function of \( \lambda \). In addition, surface inhomogeneity was added as an additional parameter to account for peak broadening. Figure 6.6a shows the results of TiO₂ film thickness as a function of the number of TiO₂ spin coats on Si wafers. Overall, the mean square error ranged from 1-3, with void volumes of 3-6% and surface roughness of 0-17%. The higher the number of spin coats, the higher the void volume and surface roughness. A simple linear fit captures the data well, thus each resulting spin coat deposited 20 nm (200 Å) of TiO₂ film on the Si wafer. This test shows that we can deposit a reproducible amount of TiO₂ on a substrate using a spin coater. Similar SE measurements of TiO₂ films on QCM crystals as the substrate yielded poor model fits to \( \psi \) and \( \Delta \). This latter result occurs because the Au electrode significantly absorbs light in the wavelength range studied, an effect not included in the model. Nonetheless, we may assume that our TiO₂ layers deposited on the QCM varied linearly with the number of spin coats, as shown for Si wafers (Figure 6.6a).
Additionally, we can use SE to determine the band gap energy $E_{BG,d}$ for the TiO$_2$ film on Si. A generalized oscillator model was used to determine $k(\lambda)$ for the calcined, TiO$_2$-coated Si wafer. Figure 6.6b shows the optical absorption spectrum (Eq. 1), graphed as $(\alpha h\nu)^2$ for direct transitions, as a function of photon energy $(h\nu)$. The shape of the data allows for two direct band gap transitions. Fitting a linear curve to the steepest data, we estimate two $E_{BG,d}$ of 2.99 eV ($\lambda \sim 415$ nm) and 3.23 eV ($\lambda \sim 385$ nm). These $E_{BG,d}$ correlate well to the bulk band gaps of rutile phase (3.05 eV or $\lambda \sim 407$ nm) and anatase phase (3.26 eV or $\lambda \sim 380$ nm) TiO$_2$ crystallinity [42], respectively. The dual crystal structure arising from the band gap transitions correspond nicely with the XRD peaks.

6.4.4. UV-Vis Spectroscopy

We used UV-Vis spectroscopy to determine the soot layer absorption ($\lambda = 350$ nm) as a function of the number of deposition passes through the hurricane lamp (Figure 6.7a). These results show that we can linearly and reproducibly deposit soot using a hurricane lamp. We can control the amount of soot deposited on the QCM crystal by varying any of four parameters: (a) the number of passes through the hurricane lamp, (b) the speed of the analytical rotor, (c) the flame height, and (d) sample position in the flame. For photocatalyzed sample preparation, we choose a 10 rpm rotor speed and a sample distance of 0.5 cm into the flame because we obtain a range from approximately 50%-1% UV transmission ($\lambda = 350$ nm) through the soot layer when we prepare samples by one, two, four, and eight passes through the lamp flame (Figure 6.7a). Absorption spectra for the TiO$_2$ sol is exhibited in Figure 6.7b, and the analysis is discussed in a later section.
6.4.5. *Soot Photooxidation – Effect of Single and Multiple Soot Layers*

Soot oxidation was studied using samples experiencing one, two, four and eight passes of deposited soot. The TiO$_2$ loading was kept constant at 4 spin coats, or 80 nm thickness. Figure 6.8 shows the visual change in the QCM crystal for the different deposition steps, as well as after TiO$_2$ soot oxidation. Figure 6.8a is a photo of a bare QCM crystal, while Figure 6.8b shows a TiO$_2$-coated QCM crystal. Figure 6.8c depicts a single pass of soot deposited on the TiO$_2$-covered QCM crystal. Figure 6.8d represents soot photooxidation after 11,000 min of UV illumination, and shows an image very similar to Figure 6.8b, corresponding to a soot-free TiO$_2$ surface.

The change in soot mass as a function of time for the four different soot loadings appears in Figure 6.9a. Several experiments were duplicated to check reproducibility. For the single and double passes through the hurricane lamp, the mass change $\Delta m$ ultimately levels off at longer time, indicating complete soot oxidation. In each case, the final frequency value was similar to the frequency of the soot-free crystal, providing independent verification of the mass balance for total soot photooxidation. The one pass $\Delta m$(total) is about 3,000 ng, and the two pass result is 6,200 ng, showing consistent deposition rates for these two samples.

For the four pass sample, photooxidation is incomplete even after 14,000 min (~10 days) of UV illumination. From the Sauerbrey equation, we estimate 55% soot oxidation of this sample. Using a simple linear fit of the data from 8,000-14,000 min, we estimate an additional 22,000 min (~15 days) is needed for complete photooxidation.
For eight passes through the hurricane lamp, the soot film is visibly opaque. The $\Delta m$ initially decreases with UV illumination time, and then shows a steady increase from 1,000-15,000 min before leveling off. From Figure 6.7a, eight passes through the hurricane lamp yields a soot absorbance ($\lambda = 350$ nm) of 1.98, or 1% UV transmission. Therefore, minimal soot PCO occurs because the soot screens nearly all UV light incident to the TiO$_2$ layer. There appears to be two distinct regions to this data: (a) initial rapid desorption, followed by (b) adsorption and/or photooxidation. The short, fast desorption phase is from 0-700 min, where presumably any volatile organic material on the soot surface leaves. The subsequent adsorption/oxidation phase lasts from 1,000-15,000 min, as indicated by a steady increase in mass on the QCM crystal. The data in this region can be fit by a simple linear equation: $\Delta m = 0.0604^*t - 483.69$.

We propose two explanations for the adsorption/oxidation phase. First, trace H$_2$O from the feed air stream can adsorb on the soot, causing the mass increase rate of 0.0604 ng/min. This value translates to 0.0384 ppmv of H$_2$O in the flowing air of 55 mL/min, which is within reasonable limits for trace H$_2$O in the feed air, even after passing through the moisture trap. We expect a minimum of 0.4 ppmv in the air stream according to our in-line thermohygrometer measurements. This value is a rough approximation because these values are outside the specified detection limits (10-95% R.H., greater than $\pm$ 4% error for R.H. $< 10$%) of the thermohygrometer. Previous researchers detected water adsorption on oxygenated surface sites for soot [43-46] and activated carbon [47,48].

Second, the soot may experience non-catalyzed, homogeneous photooxidation to create additional oxygenated organic functionalities and/or compounds on the soot surface.
Photons in the near-UV range have energies ranging from 300-400 kJ/mol, which are sufficient to cause C-C and C-H bond dissociations to form free radicals [49]. The radicals should quickly react with nearby molecular oxygen, and eventually can form carboxylic and carbonyl groups. For example, it is common to see photooxidation of plastics (e.g., polystyrene, polyethylene terephthalate) by sunlight, causing a discoloration [49] or a “yellowing” effect.

For UV-illumination times after 15,000 min, $\Delta m$ levels off at 350 ng. In any event, these effects would not change the ultimate $\Delta m$ values of one and two passes soot experiments, because no soot remains as $t$ approaches 20,000 min. It may make a modest contribution to the $m(t)$ curve shape, which we have not included here in our modeling.

6.4.6. Soot Photooxidation – Effect of TiO$_2$ thickness

We next altered the number of TiO$_2$ sol spin coats from zero to eight coating layers, and held soot deposition to one pass through the lamp flame. The TiO$_2$ thickness was 0 nm, 40 nm, 80 nm, and 160 nm, for zero, two, four, and eight coats, respectively (Figure 6.6a).

Figure 6.9b shows the change in soot mass as a function of time for the different TiO$_2$ loadings. For the “blank” experiment with no TiO$_2$ layer, an initial mass change of -50 ng corresponds to thermal desorption or vaporization of organics on the soot and TiO$_2$ surfaces. After a short flat period to 2,000 min, a monotonic increase in the mass change to 150 ng at 13,000 min is seen. Similar to the previous data with eight passes through the lamp flame, we assume H$_2$O adsorption and/or homogeneous photooxidation on the soot
layer. The “blank” experiment data suggests minimal $\Delta m$ shift caused by the near-UV light for single soot pass, so we do not include this contribution in our modeling.

For two coats of TiO$_2$ sol, the time required for complete oxidation is 17,000-18,000 min, or about double the time needed for four coats of TiO$_2$ sol (9,000 min), but the soot loading deposited on the two TiO$_2$ coat data is nearly 60% higher than the four TiO$_2$ coat. The data for four and eight coats of TiO$_2$ sol show nearly identical soot loadings. We expected that the eight coat TiO$_2$ sol would react soot faster than the four coats of TiO$_2$ sol. We postulate two explanations for why this phenomenon occurs.

First, the UV light absorption ($\lambda = 300$-400 nm) for the different TiO$_2$ thicknesses may be similar. Quartz glass slides were coated with two, four, and eight spin coats of TiO$_2$ sol, then were calcined at 350°C for 1 hour, same procedure as for the QCM crystals. The UV-Vis spectroscopy results (Figure 6.7b) show that for $\lambda > 350$ nm, the UV-Vis results are comparable for all three TiO$_2$ coatings (oddly, the $\text{Abs}$ for 2TiO$_2$sol was greater than 4TiO$_2$sol and 8TiO$_2$sol between $350 \text{ nm} < \lambda < 400 \text{ nm}$). We average the integrated $\text{Abs}$ from $300 \text{ nm} < \lambda < 400 \text{ nm}$ (the spectral range of the UV bulb) and obtain $\text{Abs}$ values of 0.18, 0.19, and 0.35 for two, four, and eight TiO$_2$ layers, respectively. If we weight the $\text{Abs}$ values using a Gaussian distribution ($A = 40.89$, $\sigma = 33.32$, $\mu = 350$) for the $I(\lambda)$ emission of the UV lamp, the average integrated $\text{Abs}$ from $300 \text{ nm} < \lambda < 400 \text{ nm}$ is 0.06, 0.04, and 0.08 for two, four, and eight TiO$_2$ layers, respectively. Two pieces of information about the TiO$_2$ sol used in this work are obtained from the UV-Vis data: (a) more UV light is absorbed for the 2TiO$_2$sol coating than the 4TiO$_2$sol coating, which is counterintuitive; (b) the 8TiO$_2$sol coating absorbs double the amount of UV light than the
4TiO$_2$sol coating. Consequently, the UV-Vis results do not explain why the 8TiO$_2$sol and 4TiO$_2$sol experiments are nearly identical, though the TiO$_2$ sol for the UV-Vis and soot oxidation data were deposited at separate times and used different solutions, thus the sol viscosity may vary. We move to the next explanation.

While the two, four, and eight spin coats of TiO$_2$ exhibit different TiO$_2$ thicknesses, the surface area in direct contact with soot may not vary significantly between the three samples. Research on the direct, lateral, and remote oxidation of organics by TiO$_2$ show a dominant reaction rate for direct oxidation compared to lateral or remote oxidation methods [7,9,50,51]. Lee et al. [9] deposited 0.5 $\mu$m thick candle soot on TiO$_2$ and TiO$_2$-free films and observed complete destruction of soot in direct contact with the TiO$_2$ film in 4.5 hours. Lateral oxidation of the soot film required 155 hours, or a 35x increase in reaction time versus direct oxidation, and remote oxidation of a soot film 175 $\mu$m from the TiO$_2$ layer needed 305 hours, or 70x longer compared to direct oxidation. Lee and Choi [7] monitored the oxidation of $n$-hexane soot on TiO$_2$ and claimed that direct oxidation of soot must occur first prior to lateral soot oxidation. Haick and Paz [51] observed fast ($t < 20$ min) degradation of octadecytrichlorosilane (OTS) coated on TiO$_2$ when UV light is exposed to TiO$_2$, attributed to direct oxidation. Slower OTS degradation rates at longer times ($t = 240$-1,000 min) were caused by lateral oxidation of OTS on a non-UV illuminated TiO$_2$ surface. Kubo et al. [50] calculated the quantum yield of H$_2$O$_2$ production, assumed to be the diffusing species for remote oxidation, as $1.8 \times 10^{-7}$, which is considerably lower than, for example, direct oxidation of soot, calculated as $1.1 \times 10^{-4}$ by Mills et al. [8].
Therefore, we expect that the soot in contact with the surface TiO$_2$ layer to exhibit the fastest oxidation and that free radical generation and migration from the bulk TiO$_2$ to its surface is negligible. Under this assumption, we do not expect large differences in soot oxidation rate for different TiO$_2$ thicknesses because of similar soot/TiO$_2$ contact area for all cases. Our SE results of 3-6% TiO$_2$ void volume and 0-17% surface roughness confirm that (a) a minimal amount of soot will enter the TiO$_2$ layer because of its low porosity and (b) there are only minor inhomogeneities in the TiO$_2$ surface for different thicknesses.

In addition to direct soot oxidation on the TiO$_2$ surface, we may be neglecting a flux component of the surface free radical to the soot for reaction to occur. A diffusion-reaction mechanism was proposed by Doushita and Kawahara [52] for TiO$_2$ photodegradation of Acid Blue 9 dye dispersed in a polyvinyl alcohol (PVA) binder. They explicitly solved a diffusion-reaction system using a simple first-order reaction at steady-state ($\frac{dm_{\text{OH}^*}}{dt} = 0$), and simulated $k_{\text{reaction}}/D_{\text{OH}^*\text{air}}$ ratios from 0.01-100 to model free radical concentration distributions, but did not compare the model to their data. Similar multi-regime results were seen in heterogeneous thermal catalytic oxidation of carbon blacks, often used as a model soot. Previous literature [53-57] describes “loose” and “tight” contact modes; in “loose” contact the thermal catalyst and carbon black are mixed with a spatula or stirring rod, while in “tight” contact the catalyst and carbon black are mixed in a mechanical ball mill. Results show that in “loose” mode the catalytic oxidation activity is diminished at lower combustion temperatures compared to “tight” mode because of the poor contact between the catalyst and carbon black. Average results represent a 100 K increase in combustion temperature (e.g., 850 K instead of 750 K) when operating under
“loose” versus “tight” contact mode. We can apply this logic to our soot photooxidation work – our soot deposition from the hurricane lamp is in “loose” contact with the TiO₂ layer. Hence, the role of migrating free radicals may play an important role when we attempt to create a comprehensive model.

6.4.7. Soot Photooxidation – Kinetic Modeling

The series / parallel reaction mechanism, described in Figure 6.3 and Eqs. (5)-(8), was used to model the soot data that exhibited complete photooxidation. Figure 6.10 shows model fits for four spin coats of TiO₂ sol and one or two passes through the hurricane lamp. Table 6.1 reports the results of the four fitted parameters for the soot data modeled. Overall, for each $k_{0,i}$ and $\varepsilon_{soot}$, the fitted parameter values for each experiment fall within the same order of magnitude. The average relative error between the model and the data ranged from 2-5% for $t > 1,000$ min. We neglect the initial 1,000 min because of the significant mass loss in this short time, which is not captured in our reaction mechanism. Two phenomena may contribute to this early decrease in $\Delta m$.

First, a QCM frequency shift is seen when UV light is shone on the QCM crystal for $t < 30$ min. Tests on bare and soot-coated QCM crystals (not shown) reveal a frequency change when UV light initially hits the crystal, shifting $\Delta m = -300$ ng to -650 ng. We assume this is related to surface thermal desorption; alternating blocking and allowing UV light to reach the crystal did not alter the $\Delta m$ considerably after the initial presumed desorption.
Second, the rest of the initial $\Delta m$ loss ($30 \text{ min} < t < 1,000 \text{ min}$) likely relates to the photolytic oxidation into volatile oxygenates of unburned HCs, SOFs or VOFs in direct contact with the TiO$_2$. The organic carbons would deposit directly on the porous soot [12] and may contact most of the TiO$_2$ surface as well. It is reasonable to believe that the $\Delta m$ loss in this regime is attributed to HC and SOF/VOF degradation because (a) it is more readily accessible to the TiO$_2$ and (b) the organic carbons are easier to react than the graphitic carbons in soot. These results parallel the different kinetic reaction rates and regimes seen for the thermal catalytic oxidation of organic and graphitic carbon [13,19-21]. Moreover, previous literature on adsorbed organic layers, such as stearic acid [38,58-60] or palmitic acid [61], deposited on TiO$_2$ thin films has shown burn off times ranging from 250 min to over 700 min. Sitkiewitz & Heller [60] used a 300 nm TiO$_2$ sol-gel film for the destruction of a 200 nm stearic acid ($C_{18}H_{36}O_2$) layer, but stopped their experiment after 240 min. They estimated a zero-order kinetic rate constant of 0.21 nmol ($-CH_2-$) / [cm$^2$-min-(mW/cm$^2$)], assuming 1 mol CO$_2$ produced per carbon reacted. Romeas et al. [61] similarly observed an apparent zero-order kinetics of 5.3 nmol ($-CH_2-$) / [cm$^2$-min-(mW/cm$^2$)] for the destruction of a 580 nm thick palmitic acid layer. Over 900 min was needed for complete film mineralization. These reaction times for adsorbed high molecular weight hydrocarbons are comparable to our short time organic carbon PCO data.

6.4.8. Soot Photooxidation – Model Predictions

The series / parallel model can be used to predict the UV illumination time required for soot oxidation using four spin coats of TiO$_2$ and one, two, four, and eight passes
through the lamp flame (Figure 6.11). The model predicts complete soot oxidation for a single and double passes of deposited soot. For four passes through the lamp flame, the model predicts only partial soot oxidation of $\Delta m = -1450$ ng or 13% soot oxidation after 20,000 min of UV illumination. Soot oxidation is negligible for eight passes of deposited soot because it screens nearly all UV light from the TiO$_2$ top layer, with $\Delta m = -60$ ng or 0.25% soot oxidation after 20,000 min. Qualitatively, the model predicts trends similar to the actual data: (a) complete soot oxidation of one and two passes of deposited soot; (b) partial soot oxidation for four passes of deposited soot, and (c) negligible soot oxidation for eight passes through the lamp flame.

We can use the reaction rates calculated from the series / parallel model to determine the formal quantum efficiency ($\phi$), defined in Eq. (11). We calculate that 1 mW/cm$^2$ of near-UV light ($\lambda = 365$ nm) is 1.8 photons/(cm$^2$-sec) [62]. A full description of the FQE computation is described previously [63]. Table 6.2 lists the calculated initial FQEs for our soot oxidation data. Two types of FQEs are calculated, one for the light intensity incident to the soot layer, $(r_{\text{soot}}/I_{\text{soot}})_{\text{initial}}$ and $(r_{\text{soot}}/I_{\text{soot}})_{\text{max}}$, where $I_{\text{soot}} = 1.3 \times 10^{16}$ photons/sec, and one incident to the TiO$_2$ layer corrected for soot screening $(r_{\text{soot}}/I_{\text{TiO}_2})$, where $I_{\text{TiO}_2}$ changes with UV illumination time.

\[
\phi = \frac{\text{rate of photocatalyzed reaction (molecules/second)}}{\text{incident light intensity (photons/second)}} = \left( \frac{r_{\text{soot}}}{I_{\text{soot}}} \right) \text{ or } \left( \frac{r_{\text{soot}}}{I_{\text{TiO}_2}} \right) \quad (11)
\]
The maximum FQEs occur at initial times for \( \frac{r_{soot}}{I_{TiO_2}} \), and they are all in the same order of magnitude of \( 3.5 \times 10^{-3} \) molecules reacted / incident photons. For \( \frac{r_{soot}}{I_{soot}} \), the maximum FQEs do not occur at initial times because the reaction rate is slow. The \( \frac{r_{soot}}{I_{soot}} \) max values are comparable to those of \( \frac{r_{soot}}{I_{TiO_2}} \), while the \( \frac{r_{soot}}{I_{soot}} \) initial are nearly an order of magnitude smaller than the maximum \( \frac{r_{soot}}{I_{TiO_2}} \) values, reflecting considerable light absorption by the soot layer. Mills and coworkers [8] performed soot PCO experiments using a FTIR gas cell to measure volatile carbonaceous species, such as CO\(_2\), under 4.28 mW/cm\(^2\) near-UV irradiation and 101.3 kPa O\(_2\) gas flow. They calculated a \( \frac{r_{soot}}{I_{soot}} \) initial FQE of \( 1.1 \times 10^{-4} \) molecules / photon, which is similar to our reported \( \frac{r_{soot}}{I_{soot}} \) initial.

6.4.9. **Carbon Black Photooxidation** (Preliminary Results)

As stated in the previous section, literature [55,57,64-67] has shown that certain carbon blacks, such as Degussa Printex-U [19,56,68,69], have been used as a model soot for tests of thermal and thermal catalyzed oxidation. In addition to studying soot deposited from a hurricane lamp, we tested the ability of TiO\(_2\) to destroy carbon black, specifically Printex-U since it has been studied by many researchers.

The experimental procedure follows: 10 wt% Degussa P25 TiO\(_2\) suspension in ethanol was spin coated twice on the QCM crystals. The TiO\(_2\)-coated crystals were fired at 100°C between each coat. No calcination was required for Degussa P25 because it exhibited an 80:20 crystallinity ratio of anatase:rutile already. Next, a 1 vol% Degussa
Printex-U suspension in toluene was spin coated on top of the TiO$_2$ layer. Finally, the coated crystal was baked at 350°C for 1 hour to remove any organic liquids entrapped from the suspension. The crystal was placed in the QCM holder and exposed to UV light.

Figure 6.12a, b show visual results of carbon black photocatalyzed oxidation at 0 and 32,000 min, respectively. Figure 6.12a shows that spin coating carbon black yields a semi-uniform layer, but the presence of agglomerated carbonaceous particles is also observed. Figure 6.12c depicts the mass loss as a function of time. After 32,000 min (~23 days) of UV illumination, $\Delta m = 17.3 \, \mu g$. From the Sauerbrey equation, we estimate an initial $\Delta m = 27.1 \, \mu g$ of carbon black deposited on the crystal. Therefore, only 65% of the carbon black is oxidized. Note that the initial rapid loss in $\Delta m$ for $t < 1,000$ min does not occur for (350°C calcined) carbon black compared to the soot (Figure 6.9a,b). This is expected because the oxygen, and presumably unburned HC, content is low in carbon blacks [18,70,71]. Elemental analysis by Neeft et al. [70] and Vonarb et al. [71] characterize Printex-U as 92 wt% carbon, 3 wt% oxygen, 0.6 wt% hydrogen, and a balance of nitrogen, sulfur, and trace metals. This finding corroborates our hypothesis that the initial $\Delta m$ loss for the soot data is likely derived from organic carbon destruction.

Application of the series / parallel reaction mechanism generated a poor fit to the data. The shape of the data mimics a first-order reaction rate mechanism, though it is difficult to ascertain since the carbon black is not completely oxidized. Figure 6.12d illustrates $\ln[m(t)/m_0]$ for the carbon black data. If $m_0$ is assumed as 17.3 $\mu g$ from the experimental data (dash-dot curve), then a linear curve is obtained for $t < 30,000$ min, indicating a first-order reaction. Instead, if $m_0 = 21.1 \, \mu g$ (dash curve) calculated from the
Sauerbrey equation, then the curve is nonlinear. A two- and three-step series first-order reaction mechanism, where the carbon black photocatalytically reacted to one or two intermediate compound(s), respectively, before oxidizing to CO₂, was used to fit the carbon black data using $m_0 = 21.1 \, \mu g$. Neither models adequately described the data. Further carbon black research is required to elucidate the PCO pathway.

**6.5. Conclusions**

Soot photocatalyzed oxidation was studied quantitatively using single- and multi-layer soot and TiO₂ thin films deposited on QCM crystals. Characterization of the sol-gel derived TiO₂ thin films showed (a) low surface roughness, (b) a linear dependence of TiO₂ layer thickness with number of spin coats, and (c) anatase and rutile phase crystallinity. By varying the amount of soot deposited on the TiO₂-coated crystals, experiments revealed a range of behaviors from complete mineralization of soot (single and double passes of soot deposition), partial oxidation up to 15,000 min (four deposition passes), and minimal oxidation of soot up to 20,000 min (eight deposition passes) caused by soot screening of the incident UV light. Water vapor adsorption on and/or homogeneous photooxidation of the soot are postulated for the slow increase in $\Delta m$ for non reactive circumstances: 1 soot / no TiO₂ (no photocatalyst), and 8 soot / TiO₂ (opaque soot layer). Varying the TiO₂ thickness did not demonstrate significant changes in the soot destruction rate because oxidation of soot in direct contact with TiO₂ is the dominant reaction compared to lateral and remote soot oxidation, and the soot / TiO₂ contact area is independent of TiO₂ thickness.
The series / parallel reaction mechanism was successfully utilized to describe the reaction kinetics of soot photooxidation for $t > 1,000$ min. All three rate constants between each experiment studied were the same order of magnitude. For short times where $t < 1,000$ min, two phenomena appear to have occurred which are not captured by our model: (1) early thermal desorption from TiO$_2$ / soot surface ($t < 30$ min); (2) destruction and removal of organic carbons readily accessible and in direct contact to the TiO$_2$ film ($t < 1,000$ min). We can use the kinetic model to predict the change in $\Delta m$ as a function of UV illumination time for varying soot loadings. Finally we illustrate photocatalytic TiO$_2$ oxidation of carbon black, often studied as a model soot, and show that its kinetic behavior is quite different from that of the lamp soot.

6.6. Acknowledgments

The authors thank the State of North Carolina for funding of this research, North Carolina State University colleagues Yazan A. Hussain (post-doctorate) for advice and general discussion on the quartz crystal microbalance and A. Evren Ozcam (graduate student) for advice on spectroscopic ellipsometry. We also thank Professor Marc A. Anderson and Jennifer Sanfilippo of his University of Wisconsin, Madison, group for advice on the preparation of TiO$_2$ sol-gel materials.

6.7. References


[26] Wang, D. X.; Mousavi, P.; Hauser, P. J.; Oxenham, W.; Grant, C. S.; Quartz crystal microbalance in elevated temperature viscous liquids: Temperature effect compensation


Table 6.1. Fitted parameter values for the series/parallel reaction model ($p = 1$).

<table>
<thead>
<tr>
<th>Experiment Data</th>
<th>$k_{0.1}$ (cm$^2$/(mW-min))</th>
<th>$k_{0.2}$ (cm$^2$/(mW-min))</th>
<th>$k_{0.3}$ (cm$^2$/(mW-min))</th>
<th>$\varepsilon_{\text{soot}}$ (µm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4TiO$_2$ sol, 1 soot</td>
<td>5.56 x 10$^{-5}$</td>
<td>1.66 x 10$^{-6}$</td>
<td>3.33 x 10$^{-7}$</td>
<td>3.72</td>
</tr>
<tr>
<td>4TiO$_2$ sol, 2 soot</td>
<td>4.04 x 10$^{-5}$</td>
<td>9.05 x 10$^{-7}$</td>
<td>5.33 x 10$^{-7}$</td>
<td>3.00</td>
</tr>
<tr>
<td>2TiO$_2$ sol, 1 soot</td>
<td>2.74 x 10$^{-5}$</td>
<td>2.20 x 10$^{-6}$</td>
<td>5.66 x 10$^{-7}$</td>
<td>3.69</td>
</tr>
<tr>
<td>8TiO$_2$ sol, 1 soot</td>
<td>7.37 x 10$^{-5}$</td>
<td>1.99 x 10$^{-6}$</td>
<td>1.27 x 10$^{-7}$</td>
<td>5.00</td>
</tr>
<tr>
<td><strong>Average Values</strong></td>
<td>4.92 x 10$^{-5}$</td>
<td>1.69 x 10$^{-6}$</td>
<td>3.90 x 10$^{-7}$</td>
<td>3.85</td>
</tr>
</tbody>
</table>

Table 6.2. Formal quantum efficiencies for the series / parallel reaction model ($p = 1$), where the incident light intensity is determined at the top of the soot layer ($r_{\text{soot}}/I_{\text{soot}}$) or the top of the TiO$_2$ layer ($r_{\text{soot}}/I_{\text{TiO}_2}$). Initial ($t = 0$) and maximum FQEs are reported.

<table>
<thead>
<tr>
<th>Experiment Data</th>
<th>Initial FQE ($r_{\text{soot}}/I_{\text{soot}}$)$_{\text{initial}}$</th>
<th>Maximum FQE ($r_{\text{soot}}/I_{\text{soot}}$)$_{\text{max}}$</th>
<th>Initial &amp; Maximum FQE ($r_{\text{soot}}/I_{\text{TiO}_2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4TiO$_2$ sol, 1 soot</td>
<td>6.26 x 10$^{-4}$</td>
<td>8.03 x 10$^{-4}$</td>
<td>3.10 x 10$^{-4}$</td>
</tr>
<tr>
<td>4TiO$_2$ sol, 2 soot</td>
<td>9.30 x 10$^{-4}$</td>
<td>9.53 x 10$^{-4}$</td>
<td>3.95 x 10$^{-3}$</td>
</tr>
<tr>
<td>2TiO$_2$ sol, 1 soot</td>
<td>5.92 x 10$^{-4}$</td>
<td>6.13 x 10$^{-4}$</td>
<td>1.97 x 10$^{-3}$</td>
</tr>
<tr>
<td>8TiO$_2$ sol, 1 soot</td>
<td>7.54 x 10$^{-4}$</td>
<td>8.81 x 10$^{-4}$</td>
<td>3.82 x 10$^{-3}$</td>
</tr>
</tbody>
</table>
6.8. List of Figures

Figure 6.1. Schematic of the controlled soot deposition method using an analytical rotator to pass through a hurricane lamp flame.

Figure 6.2. Process flow schematic of the quartz crystal microbalance reaction experiments.

Figure 6.3. A series/parallel reaction mechanism to describe soot photooxidation by TiO₂.

Figure 6.4. AFM images of a QCM crystal with four spin coats of TiO₂ sol, calcined at 350°C, in (a) a top-down view and (b) a topographical view.

Figure 6.5. Smoothed XRD image of a QCM crystal with four spin coats of TiO₂ sol, calcined at 350°C. The symbols represent different crystal structures.

Figure 6.6. Spectroscopic ellipsometry results of TiO₂ sol spin coated on Si wafers: (a) TiO₂ thickness as a function of the number of spin coats; (b) optical absorption spectrum for the TiO₂ thin film calcined at 350°C, graphed as (αhv)² as a function of photon energy (hv) for direct band gap transitions.

Figure 6.7. UV-Vis spectroscopy results on quartz glass for (a) soot absorption (λ = 350 nm) as a function of the number of passes through hurricane lamp flame for different analytical rotor speeds and distance from the top of the flame; (b) TiO₂ absorption for two, four, and eight spin coats of TiO₂ sol.

Figure 6.8. Visual results of soot oxidation for a QCM crystal spin coated four times with TiO₂ sol, then deposited with a single pass of hurricane lamp soot: (a) bare crystal, (b) TiO₂-coated crystal (pre-soot deposition), and soot/TiO₂/crystal after (c) 0 min and (d) 11,000 min of UV illumination time.

Figure 6.9. Soot photocatalyzed oxidation as a function of time for QCM crystals deposited with TiO₂, then soot: (a) four spin coats of TiO₂ sol, and one, two, four, and eight passes of soot using the analytical rotator; (b) zero (“blank”), two, four, and eight spin coats of TiO₂ sol, and a single pass through the lamp flame.
Figure 6.10. Series / parallel reaction mechanism, described in Figure 6.3, for QCM crystals spin coated four times with TiO$_2$ sol. Model fit to the experimental data for and single and double passes through the lamp flame.

Figure 6.11. Series / parallel reaction mechanism, described in Figure 6.3, for QCM crystals spin coated four times with TiO$_2$ sol. Model prediction using averaged fitted parameter values (Table 6.1) for one, two, four, and eight passes through the lamp flame.

Figure 6.12. Carbon black oxidation on QCM crystals coated with Degussa P25 TiO$_2$: visual results are shown for (a) 0 min and (b) 32,000 min of UV illumination time; (c) mass loss as a function of time; (d) $ln[\frac{m(t)}{m_0}]$ versus time for $m_0 = 17.3$ µg and $m_0 = 27.1$ µg.
Figure 6.1
Figure 6.2
Figure 6.3
Figure 6.5
Figure 6.6
Figure 6.7
Figure 6.8
Figure 6.9
Figure 6.10
Figure 6.11
Figure 6.12
Figure 6.12
CHAPTER 7

CONCLUSIONS
7.1. Conclusions

The chief objectives of the research on TiO₂ photocatalysis carried out in this dissertation were:

- to create an engineering model for a combination cyclic adsorbent / photoreactor batch system and apply it to design a continuous system for typical residential home air purification challenge for formaldehyde control.
- to characterize the photocatalytic activity of novel commercial window glass for dye oxidation and to develop a kinetic model suitable for field assay of photocatalyst activity via dye oxidation in air.
- to develop a kinetic model for photocatalyzed soot oxidation from recent but sparse literature data, and to generate more quantitative, reproducible experimental data via quartz crystal microbalance study of the change in the observed reaction rate caused by the influence of (a) soot layer and (b) titania catalyst thicknesses.

Overall, the three goals stated above were achieved and described in Chapters two through six. The three main research projects studied in detail all utilized TiO₂ thin films (i.e., less than 1 µm thickness) as a remediation method for removal of the organic pollutants formaldehyde, azo and triphenylmethane dyes, and soot. The films were deposited by dip coat, spin coat, or chemical vapor deposition (e.g., Pilkington Activ™ glass), and various analysis methods were employed for each project.

For formaldehyde destruction, previous literature data by Shiraiishi et al. [1] was used to successfully model their lab-scale adsorbent / photoreactor system. Kinetic rate parameters were calculated for adsorption, desorption, and first-order PCO reaction [2].
These values were used for scale-up to model a continuous system for typical residential homes as a function of 5 different environmental and physical parameters [3].

For the Pilkington Activ™ glass, we employed the photocatalytic degradation of organic dyes Acid Blue 9 and Reactive Black 5 as a field analysis method to characterize initial and continuing photoactivity of installed “self-cleaning” window glass. Specifically, the dyes were used to show visual decolorization and recovery of the aesthetic clarity of the glass, and to determine the light-driven reaction kinetics on Activ™ glass using a two-step series reaction mechanism [4].

For the soot photooxidation work, we constructed two kinetic models [5] to describe the data of Mills et al. [6] and Lee and Choi [7]. The “simple” model is a mixed series / parallel reaction mechanism for soot PCO to CO₂, while the “initial” model includes the influence of O₂ partial pressure for initial reaction times. We extended their work by using an analytical rotor to reproducibly and controllably deposit soot using a hurricane lamp. The effects of (a) incident UV light screening by soot deposited on top of the TiO₂ layer and (b) the TiO₂ thickness on the rate of soot photooxidation were studied and successfully modeled [8]. Our research constitutes the first detailed reaction engineering model of a well defined soot-photocatalyst system.

7.2. References


APPENDICES
APPENDIX A

DERIVATION OF ONE-DIMENSIONAL DIFFUSIONAL FLUX TO A SURFACE FROM A SEMI-INFINITE MEDIUM
**Figure A1.** Schematic of a one-dimensional diffusional flux problem.

The subject of mass transfer in the photocatalyzed soot oxidation system can be characterized by the diffusion of $O_2$ from the medium (i.e., air) to the TiO$_2$/soot surface. We use the continuity equation with (a) no reaction term and (b) only one-dimensional diffusion (i.e., no flux in $y$ and $z$ directions). Assume $D$, $\rho$ are constant and Fick’s first law holds in our system. This is Fick’s second law.

\[
\frac{\partial C}{\partial t} - D \frac{\partial^2 C}{\partial x^2} = 0
\]  
(A1)

We solve this problem by similarity transform. Two additional variables, $Y$ and $\eta$ are defined.

\[
Y = \frac{C - C_0}{C_1 - C_0}
\]  
(A2)

\[
\eta = \frac{x}{2\sqrt{Dt}}
\]  
(A3)
We apply the chain rule to Eq. (A3) to determine the derivative, but dC and d\(\eta\) are both functions of variables \(x\) and \(t\), so partial derivatives must be taken. Grouping similar terms for\(dx\) and \(dt\), we differentiate to \(f(\eta)\) to calculate the partial derivatives for \(dC\).

\[
\frac{\partial C}{\partial x} = f'(\eta)\frac{\partial}{\partial x}\left[\frac{x}{2\sqrt{D_t}}\right] = \frac{f'(\eta)}{2\sqrt{D_t}}
\]

\[
\frac{\partial C}{\partial t} = f'(\eta)\frac{\partial}{\partial t}\left[\frac{x}{2\sqrt{D_t}}\right] = f'(\eta)\left(-\frac{\eta}{2t}\right)
\]

(A4a)

(A4b)

We now have the first derivative of \(C\) with respect to \(t\), shown in Eq. (A4b), but we need to calculate the second derivative of \(C\) with respect to \(x\). We define another variable, \(\Psi\). Again, we must apply the chain rule to calculate the derivatives of \(dC/dx\) and \(\Psi\). Since \(\Psi\) is a function of \(\eta\), we must differentiate \(d\eta\) again as a function of \(x\) and \(t\). The second partial derivative of \(C\) as a function of \(x\) is shown in Eq. (A6).

\[
\frac{\partial C}{\partial x} = f'(\eta)\frac{\partial \eta}{\partial x} = \Psi(\eta,x,t)
\]

(A5)

\[
\frac{\partial^2 C}{\partial x^2} = \frac{\partial^2 f}{\partial \eta^2}\left(\frac{1}{4Dt}\right) = \frac{f''(\eta)}{4Dt}
\]

(A6)

We input all of the terms into Fick’s second law (Eq. A1) to get our transformed equation (Eq. A7).

\[
\frac{\partial^2 Y}{\partial \eta^2} + \frac{\partial Y}{\partial \eta}(2\eta) = 0
\]

(A7)
The initial and boundary conditions also must be transformed. The first and second conditions collapse into the same condition:

**IC:** \( C(x > 0, t = 0) = C_0 \) \quad \quad Y(\eta \to \infty) = 0

**BC:** \( C(x \to \infty, t \geq 0) = C_0 \) \quad \quad Y(\eta \to \infty) = 0

**BC:** \( C(x = 0, t = 0) = C_1 \) \quad \quad Y(\eta \to 0) = 1

This linear ODE is simplified by defining another variable, \( p \), and substituting \( p \) into Eq (A7). This equation is integrated easily to a solution for \( Y \), where \( C \) and \( \gamma \) are integration constants. This solution is commonly known as the error function, \( \text{erf}(x) \).

\[
p = \frac{\partial Y}{\partial \eta}
\]

(A8)

\[
\frac{\partial p}{\partial \eta} + (2\eta) p = 0
\]

(A9)

\[
Y(\eta) = \gamma \text{erf}(\eta) + C
\]

(A10)

From the definition of the error function, we know that \( \text{erf}(0) = 0 \) and \( \text{erf}(\infty) = 1 \).

**IC:** \( Y(\eta \to 0) = 1 \) \quad \quad \quad C = 1

**BC:** \( Y(\eta \to \infty) = 0 \) \quad \quad \quad \gamma = -1

Replacing variables \( Y \) and \( \eta \) with \( C, x, \) and \( t \) (Eq. A2 and A3), we obtain the complete solution. Returning to our original problem of no initial surface concentration (i.e., \( C_1 = 0 \)), we now get Eq. (A11).

\[
C(x,t) = C_0 \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)
\]

(A11)
We want to calculate the rate of loss of the diffusing substance from the semi-infinite medium to the surface when \( C_1 = 0 \), defined as \((D^* dc/dx)_{x=0}\). The derivative of the error function shown in Eq. (A12). Note that the \((d\eta/dx)\) term is often written as \((dx/dx)\) and is assumed equal to 1, but that is not the case here because \( \eta \) is a function, not a simple variable.

\[
\frac{\partial}{\partial x} \left[ \text{erf} \left( \eta \right) \right] = \frac{2}{\sqrt{\pi}} \left( \frac{\partial \eta}{\partial x} \right) e^{-\eta^2} \quad \text{(A12)}
\]

\[
\frac{\partial C}{\partial x} = C_0 \left[ \frac{2}{\sqrt{\pi}} \exp \left[ -\left( \frac{x}{2\sqrt{Dt}} \right)^2 \right] \frac{\partial}{\partial x} \left( \frac{x}{2\sqrt{Dt}} \right) \right] = C_0 \frac{2}{\sqrt{\pi Dt}} \exp \left( -\frac{x^2}{4Dt} \right) \quad \text{(A13)}
\]

\[
\left( D \frac{\partial C}{\partial x} \right)_{x=0} = \frac{DC_0}{\sqrt{\pi Dt}} \quad \text{(A14)}
\]

To calculate the total amount of diffusing substance which has left the medium at time \( t \) per unit area \( (M_t) \), we integrate Eq. (A14) from 0 to \( t \) and arrive at our final equation.

\[
M_t = \int_0^t \left( D \frac{\partial C}{\partial x} \right)_{x=0} \, dt = 2C_0 \sqrt{\frac{Dt}{\pi}} \left[ \text{=} \right] \frac{M}{L^2} \quad \text{(A15)}
\]

References


APPENDIX B

DERIVATION OF THE SAUERBREY EQUATION FOR THE QUARTZ CRYSTAL MICROBALANCE
The Sauerbrey equation is used to relate the frequency shift of a quartz crystal resonator to the added mass on the quartz crystal. There are many quartz vibrational modes (e.g., longitudinal, lateral, torsional), but when the quartz crystal operates under its fundamental thickness-shear mode (TSM) it is the most sensitive to changes in mass. An idealized model of the quartz crystal microbalance (QCM) and how additional mass changes its resonance frequency is shown in Figure B1, reproduced from Lu and Czanderna.

To operate under TSM, Eq. B1 must be satisfied, where \( t_q \) is the quartz crystal thickness and \( \lambda_q \) is the wavelength of the shear-mode elastic wave in the thickness direction. The effect of electrodes deposited on the quartz crystal surface is ignored in this equation. If we relate the quartz crystal shear wave velocity \( v_q \) to the resonant frequency
(f_q) and \( \lambda_{q} \), then Eq. B1 transforms to Eq. B2, and taking the derivative of the latter yields Eq. B3.

\[
t_{q} = \frac{\lambda_{q}}{2} \quad \text{(B1)}
\]

\[
f_{q} t_{q} = \frac{\nu_{q}}{2} \quad \text{where } \lambda_{q} f_{q} = \nu_{q} \quad \text{(B2)}
\]

\[
\frac{df_{q}}{f_{q}} = -\frac{dt_{q}}{t_{q}} \quad \text{(B3)}
\]

The relationship between \( f_{q} \) and \( t_{q} \) can also be expressed in terms of mass (Eq. B4), where \( M_{q} \) is the crystal mass. For small changes in mass, the uniformly deposited film can be treated as a mass change of the quartz crystal (Eq. B5), where \( \Delta M_{f} \) is the small mass change of the deposited film. Thus, any change in \( \Delta M_{f} \) is associated with a change in the resonant frequency between the film-coated quartz crystal (\( f_{c} \)) and \( f_{q} \), as shown in Eq. B6. Mass can be defined per unit area for the quartz crystal (\( m_{q} \)) and the deposited film (\( m_{f} \)). For spatially uniform materials, the areal density is equal to its bulk density \( \rho_{i} \) multiplied by its thickness \( t_{i} \) (Eq. B8). Combining Eq. B7 and B8 and substituting Eq. B2 for \( t_{q} \) yields Eq. B9.

\[
\frac{df_{q}}{f_{q}} = -\frac{dM_{q}}{M_{q}} \quad \text{(B4)}
\]

\[
\frac{df_{q}}{f_{q}} = \frac{\Delta M_{f}}{M_{q}} \quad \text{(B5)}
\]

\[
\left( f_{c} - f_{q} \right) \frac{1}{f_{q}} = \frac{\Delta M_{f}}{M_{q}} \quad \text{(B6)}
\]
\[ \frac{(f_c - f_q)}{f_q} = -\frac{\Delta m_f}{m_q} \]  
\[ m_i = t, \rho_i \]  
\[ \Delta m_f = \rho_f \Delta t_f = -\frac{(f_c - f_q) \rho_q v_q}{2f_q^2} \]

Rearranging Eq. B9 gives Eq. B10, where \( \Delta f_m \) is the frequency change related to the deposited film mass \( (f_c - f_q) \). Since the elastic shear modulus \( (\mu_q) \) is equal to the product of its density \( (\rho_q) \) and its shear wave velocity \( (v_q) \) squared (Eq. B11) for a standing wave, we modify Eq. B10 to its more common form, the Sauerbrey equation (Eq. B12), where \( n \) is the number of film-coated sides on the quartz crystal and \( C_q \) is a constant based on the quartz crystal properties.

There are situations where the Sauerbrey equation does not hold, for example, when the added mass \( (a) \) is not rigidly or evenly deposited, \( (b) \) slips on the surface, or \( (c) \) is too thick. The important assumption made by Sauerbrey is that the coated film mass behaves the same way as a quartz crystal with an identical mass increment. Consequently, the Sauerbrey equation is only strictly applicable to uniform, rigid, thin film deposits on the quartz crystal.

\[ \Delta f_m = (f_c - f_q) = -\frac{2f_q^2}{\rho_q v_q} \Delta m_f \]  
\[ \mu_q = \rho_q v_q^2 \]  
\[ \Delta f_m = -nC_q m_f = \frac{-2nf_q^2}{\left(\mu_q \rho_q \right)^{1/2}} \Delta m_f \]
References
