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DEVELOPMENT AND CHARACTERIZATION OF HIGH TEMPERATURE
SELECTIVE, TITANIA-BASED GAS SENSORS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By
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ABSTRACT

Selective titania-based sensors for the high temperature detection of carbon monoxide were developed and characterized. Two approaches to making the sensors selective were taken: the addition of dopants to the anatase phase of TiO$_2$ and the mixing of p-type and n-type TiO$_2$ to make composite sensors.

Upon exposure to both CO and CH$_4$, sensors made of TiO$_2$ (anatase) and TiO$_2$ doped with La$_2$O$_3$ show a resistance change, with the response to CO larger than the response to CH$_4$. When CuO is added to the sensor, the sensitivity to methane is minimal, while the sensor still maintains sensitivity to CO. The samples were studied with diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) in order to determine a sensing mechanism. La$_2$O$_3$, which was added to the sensor to inhibit the transformation of the anatase phase to the rutile phase of TiO$_2$ during sample preparation, is shown to form a LaO$_x$ surface phase on TiO$_2$, which strongly adsorbs CO$_2$ and carbonate-type species. The adsorptive properties of the LaO$_x$ surface phase allows for the observation of the intermediates of the reactions of CO and CH$_4$ on the surface of the TiO$_2$ and CuO at high temperatures. CO oxidation on the anatase/La$_2$O$_3$/CuO sample resulted in the formation of large amounts of carbonate species on the surface of the sample, while the
reaction of methane produced negligible carbonate species. This suggests that the CH₄ may be rapidly oxidizing on the copper oxide without interaction with the titania or La₂O₃, thus producing minimal resistance change and few infrared observable species. CO oxidation also occurred partially on the CuO surface but significant reaction also occurred on the anatase surface and produced a change in resistance.

The anatase phase of TiO₂ sensors shows an n-type response to CO and CH₄ while the rutile phase shows a p-type response under the same conditions. The sensing behavior of composite sensors was examined at 600 °C. A composite mixture of 75% rutile and 25% anatase selectively responds to CO over CH₄. SEM micrographs of the sample show that both the anatase and rutile particles are percolating in this sample, resulting in an electrical response that is a combination of both material's responses.

Sol-gel titania was investigated as a material for gas sensors. Characterization of the sol-gel derived powders by XRD and electron microscopy showed that under the high temperature required for the sensor preparation, the TiO₂ is rutile and approximately 100 nm in size. The electrical behavior of the sol-gel titania was n-type. Both thick film and thin film sensors made from the sol-gel titania were more sensitive to CO than titania sensors made from commercial material. The sensitivity of the thin films could be tailored by changing the film thickness by applying multiple coatings of the sol through spin coating.
Dedicated to Mom and Dad
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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>ii</td>
</tr>
<tr>
<td>Dedication</td>
<td>iv</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>v</td>
</tr>
<tr>
<td>Vita</td>
<td>vii</td>
</tr>
<tr>
<td>List of Tables</td>
<td>xiii</td>
</tr>
<tr>
<td>List of Figures</td>
<td>xv</td>
</tr>
<tr>
<td>Chapters:</td>
<td></td>
</tr>
<tr>
<td>1. Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.1. Types of Gas Sensors</td>
<td>2</td>
</tr>
<tr>
<td>1.1.1. Potentiometric-Type Sensor</td>
<td>3</td>
</tr>
<tr>
<td>1.1.2. Amperometric Sensors</td>
<td>4</td>
</tr>
<tr>
<td>1.1.3. Conductometric-Type Sensors</td>
<td>5</td>
</tr>
<tr>
<td>1.2. Metal Oxide Gas Sensors</td>
<td>7</td>
</tr>
<tr>
<td>1.2.1. Bulk Conductivity Changes</td>
<td>8</td>
</tr>
<tr>
<td>1.2.2. Surface Conductivity Changes</td>
<td>11</td>
</tr>
<tr>
<td>1.2.3. Conductivity in Polycrystalline Samples</td>
<td>12</td>
</tr>
<tr>
<td>1.2.4. Sensing Other Gases</td>
<td>14</td>
</tr>
<tr>
<td>1.3. Optimizing Metal Oxide Gas Sensors</td>
<td>15</td>
</tr>
</tbody>
</table>

viii
1.3.1. Metal Oxides for Gas Sensing ..............................................................16
1.3.2. Addition of Dopants to Metal Oxide Gas Sensors .......................18
1.3.3. Sensitivity and Material Preparation ..............................................20
1.3.4. Data Analysis Methods .................................................................24

1.4. TiO$_2$ as a Gas Sensor .................................................................26

References .................................................................................................28

2. Anatase/La$_2$O$_3$/CuO Selective Carbon Monoxide Sensor ...............47

2.1 Experimental ......................................................................................49
2.1a. Sample Preparation ........................................................................49
2.1b. Electrical Measurements ...............................................................50
2.1c. Sample Characterization .................................................................50

2.2 Sensor Characterization .................................................................52
2.3 Sensing Behavior ..............................................................................53
2.4 Adsorption of CO and CH$_4$ on the titania surface .........................55
2.5 Reaction Intermediates ......................................................................58
2.6 Nature of ALC: Role of La$_2$O$_3$ .......................................................62
2.7 Sensing Mechanism ..........................................................................63
2.8 Response Times ................................................................................68
2.9 Sample Aging .....................................................................................68
2.10. Conclusion ......................................................................................70

References .................................................................................................71

3. Characterization of surface species on titania-based samples ..........95

3.1 Experimental ....................................................................................97
3.2 TiO$_2$ ...............................................................................................98
3.3 TiO$_2$/CuO ......................................................................................100
3.4 La$_2$O$_3$ ........................................................................................101
3.4.1 CO$_2$ on La$_2$O$_3$ ......................................................................102
3.4.2 CO on La$_2$O$_3$ .........................................................................103
3.4.3 CH$_4$ on La$_2$O$_3$ ....................................................................104
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5</td>
<td>Anatase/La$_2$O$_3$ (AL)</td>
<td>105</td>
</tr>
<tr>
<td>3.5.1</td>
<td>CO$_2$ on Anatase/La$_2$O$_3$</td>
<td>105</td>
</tr>
<tr>
<td>3.5.2</td>
<td>CO on Anatase/La$_2$O$_3$</td>
<td>107</td>
</tr>
<tr>
<td>3.5.3</td>
<td>CH$_4$ on Anatase/La$_2$O$_3$</td>
<td>108</td>
</tr>
<tr>
<td>3.6</td>
<td>Anatase/La$_2$O$_3$/CuO (ALC)</td>
<td>109</td>
</tr>
<tr>
<td>3.6.1</td>
<td>CO$_2$ on Anatase/La$_2$O$_3$/CuO</td>
<td>110</td>
</tr>
<tr>
<td>3.6.2</td>
<td>CO on Anatase/La$_2$O$_3$/CuO</td>
<td>111</td>
</tr>
<tr>
<td>3.6.3</td>
<td>CH$_4$ on Anatase/La$_2$O$_3$/CuO</td>
<td>112</td>
</tr>
<tr>
<td>3.7</td>
<td>Chemistry of Surface Carbonates</td>
<td>112</td>
</tr>
<tr>
<td>3.8</td>
<td>Reactivity of CO/CH$_4$ on Anatase</td>
<td>115</td>
</tr>
<tr>
<td>3.9</td>
<td>Reactivity of CO/CH$_4$ on TiO$_2$/CuO</td>
<td>116</td>
</tr>
<tr>
<td>3.10</td>
<td>Reaction of CO$_2$ with La$_2$O$_3$, AL and ALC</td>
<td>117</td>
</tr>
<tr>
<td>3.11</td>
<td>Reaction of CO with AL and ALC</td>
<td>118</td>
</tr>
<tr>
<td>3.12</td>
<td>Reaction of CH$_4$ with AL and ALC</td>
<td>119</td>
</tr>
<tr>
<td>3.13</td>
<td>Conclusion</td>
<td>119</td>
</tr>
<tr>
<td>References</td>
<td></td>
<td>121</td>
</tr>
</tbody>
</table>

4. Anatase and Rutile Composite Sensors | 146  |
<p>| 4.1   | Experimental | 148  |
| 4.2   | Sensing Behavior of Pure Anatase and Rutile | 149  |
| 4.3   | Mixing of p-n Composites | 150  |
| 4.3.1 | X-ray Diffraction | 150  |
| 4.3.2 | Scanning Electron Microscopy | 152  |
| 4.3.3 | Sample reproducibility | 153  |
| 4.4   | Sensing Behavior of p-n Composites | 153  |
| Discussion | | 154  |
| 4.5   | Differences in the Semiconducting Behavior of Anatase and Rutile | 156  |
| 4.6   | Percolation in p-n Composites | 160  |
| 4.6.1 | 25% Rutile | 161  |
| 4.6.2 | 50% Rutile | 162  |
| 4.6.3 | 75% Rutile | 163  |</p>
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.7 Modeling of pn Composite Sensors</td>
<td>164</td>
</tr>
<tr>
<td>4.8 Conclusion</td>
<td>166</td>
</tr>
<tr>
<td>References</td>
<td>167</td>
</tr>
<tr>
<td>5. Sol-Gel Sensors</td>
<td>187</td>
</tr>
<tr>
<td>5.1 Sol-Gel Chemistry</td>
<td>189</td>
</tr>
<tr>
<td>5.2 Experimental</td>
<td>192</td>
</tr>
<tr>
<td>5.3 Effect of Heat Treatment on Sol-Gel Derived TiO₂ Powders</td>
<td>193</td>
</tr>
<tr>
<td>5.3.1 X-ray Diffraction Analysis</td>
<td>194</td>
</tr>
<tr>
<td>5.3.2 Electron Microscopy</td>
<td>196</td>
</tr>
<tr>
<td>5.4 Effect of Heat Treatment on Doped Sol-Gel Titania</td>
<td>197</td>
</tr>
<tr>
<td>5.4.1 X-ray Diffraction Studies</td>
<td>198</td>
</tr>
<tr>
<td>5.4.2 Electron Microscopy</td>
<td>199</td>
</tr>
<tr>
<td>5.5 Thick Film Sensors</td>
<td>200</td>
</tr>
<tr>
<td>5.6 Thin Film Sensors</td>
<td>203</td>
</tr>
<tr>
<td>5.6.1 Characterization of Thin Films</td>
<td>203</td>
</tr>
<tr>
<td>5.6.1a Raman Spectroscopy</td>
<td>204</td>
</tr>
<tr>
<td>5.6.1b Scanning Electron Microscopy</td>
<td>205</td>
</tr>
<tr>
<td>5.6.2 Sensing Measurements</td>
<td>205</td>
</tr>
<tr>
<td>5.7 Sensitivity Difference between Sol-Gel and commercial TiO₂</td>
<td>206</td>
</tr>
<tr>
<td>5.8 Phase Transformation and Grain Growth of TiO₂</td>
<td>208</td>
</tr>
<tr>
<td>5.8.1 Effect of pH</td>
<td>210</td>
</tr>
<tr>
<td>5.8.2 Effect of La³⁺ dopant</td>
<td>212</td>
</tr>
<tr>
<td>5.8.3 Effect of Cu²⁺ dopant</td>
<td>214</td>
</tr>
<tr>
<td>5.9 Effect of Sample Preparation on Thick Film Sensor Response</td>
<td>214</td>
</tr>
<tr>
<td>5.9.1 Effect of pH and Heat Treatment on Pure Sol-Gel Titania Sensors</td>
<td>215</td>
</tr>
<tr>
<td>5.9.2 Effect of Dopants on Thick Film Sensors</td>
<td>216</td>
</tr>
<tr>
<td>5.9.3 n-Type Response of Sol-Gel Rutile</td>
<td>216</td>
</tr>
<tr>
<td>5.10 Effect of Thickness on Thin Film Sensors</td>
<td>218</td>
</tr>
<tr>
<td>5.11 Comparison of Commercial Titania and Sol-Gel Sensors</td>
<td>219</td>
</tr>
<tr>
<td>5.12 Conclusion</td>
<td>220</td>
</tr>
</tbody>
</table>
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1 Relationship between the pO\textsubscript{2} dependence of the conductivity and the dominant defect type in TiO\textsubscript{2}</td>
<td>33</td>
</tr>
<tr>
<td>1.2 Metal oxides that have been used for gas sensing</td>
<td>34</td>
</tr>
<tr>
<td>1.3 Examples of CO sensors that use dopants to improve selectivity</td>
<td>35</td>
</tr>
<tr>
<td>1.4 CO sensors made of thin films and/or nanocrystalline materials</td>
<td>36</td>
</tr>
<tr>
<td>2.1 Absolute and relative resistance of titania-based sensors to CO at 600 °C. 5%\textsubscript{O\textsubscript{2}}/N\textsubscript{2}</td>
<td>76</td>
</tr>
<tr>
<td>2.2 Absolute and relative resistances of titania-based sensors to CH\textsubscript{4} at 600°C. 5%\textsubscript{O\textsubscript{2}}/N\textsubscript{2}</td>
<td>76</td>
</tr>
<tr>
<td>3.1 Literature assignments of adsorbed species on TiO\textsubscript{2}</td>
<td>124</td>
</tr>
<tr>
<td>3.2 Literature assignments of adsorbed species on La\textsubscript{2}O\textsubscript{3}</td>
<td>125</td>
</tr>
<tr>
<td>3.3 Literature assignments of adsorbed species on CuO</td>
<td>126</td>
</tr>
<tr>
<td>3.4 Summary of infrared data for La\textsubscript{2}O\textsubscript{3} dispersed in KBr</td>
<td>127</td>
</tr>
<tr>
<td>3.5 Summary of infrared data for anatase/La\textsubscript{2}O\textsubscript{3}</td>
<td>128</td>
</tr>
<tr>
<td>3.6 Summary of infrared data for anatase/La\textsubscript{2}O\textsubscript{3}/CuO</td>
<td>129</td>
</tr>
<tr>
<td>4.1 Summary of sensing behavior of anatase-rutile composite to carbon monoxide at 600 °C. 5%\textsubscript{O\textsubscript{2}}/N\textsubscript{2}</td>
<td>169</td>
</tr>
<tr>
<td>4.2 Summary of sensing behavior of anatase-rutile composite to methane at 600 °C. 5%\textsubscript{O\textsubscript{2}}/N\textsubscript{2}</td>
<td>169</td>
</tr>
<tr>
<td>5.1 Effect of temperature and pH on sol-gel TiO\textsubscript{2}</td>
<td>225</td>
</tr>
<tr>
<td>5.2 Effect of Dopants on sol-gel TiO\textsubscript{2}</td>
<td>226</td>
</tr>
<tr>
<td>5.3 Summary of sensing behavior of undoped sol-gel titania at 600 °C. 5%\textsubscript{O\textsubscript{2}}/N\textsubscript{2}</td>
<td>227</td>
</tr>
</tbody>
</table>
5.4 Summary of the effect of dopants and heat treatment temperatures on the sensing response of sol-gel titania sensors at 600 °C and 5%O₂/N₂.............228

5.5 Summary of thin film sol-gel sensor response to CO and CH₄..............................229

A.1 Summary of measured temperature of infrared chamber as compared to the setpoint temperature.................................................................283
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Schematic diagram of a potentiometric gas sensor</td>
</tr>
<tr>
<td>1.2</td>
<td>Schematic Diagram of an amperometric gas sensor</td>
</tr>
<tr>
<td>1.3</td>
<td>Schematic diagram of resistive type gas sensors</td>
</tr>
<tr>
<td>1.4</td>
<td>Band diagrams for a metal oxide semiconductor</td>
</tr>
<tr>
<td>1.5</td>
<td>Representation of oxygen adsorption on a metal oxide semiconductor</td>
</tr>
<tr>
<td>1.6</td>
<td>Different sintering levels in polycrystalline semiconductor samples</td>
</tr>
<tr>
<td>1.7</td>
<td>Formation of a Schottky barrier at the contact of two grains</td>
</tr>
<tr>
<td>1.8</td>
<td>Example of the effect of dopants on metal oxide gas sensors</td>
</tr>
<tr>
<td>1.9</td>
<td>Map of sensitivity vs. temperature change for selective detection of gases</td>
</tr>
<tr>
<td>1.10</td>
<td>Response of sensors to different gases with pulsed temperature operation</td>
</tr>
<tr>
<td>2.1</td>
<td>Scale drawing of sensing substrate</td>
</tr>
<tr>
<td>2.2</td>
<td>Schematic of apparatus used for sensing measurements</td>
</tr>
<tr>
<td>2.3</td>
<td>Unit cells of anatase and rutile</td>
</tr>
<tr>
<td>2.4</td>
<td>XRD patterns of the TiO₂ and TiO₂/CuO after an 800 °C heat treatment</td>
</tr>
<tr>
<td>2.5</td>
<td>XRD patterns of doped anatase after heat treatment at 800 °C</td>
</tr>
<tr>
<td>2.6</td>
<td>X-ray diffraction pattern of anatase/La₂O₃/CuO before preparation of sensing film and after sensing measurement</td>
</tr>
<tr>
<td>2.7</td>
<td>SEM micrographs of titania-based sensor</td>
</tr>
<tr>
<td>2.8</td>
<td>TEM micrograph of CuO particle on anatase</td>
</tr>
<tr>
<td>2.9</td>
<td>Response of titania-based sensors to CO and CH₄ at 600 °C and 5%O₂/N₂</td>
</tr>
<tr>
<td>2.10</td>
<td>Aging of titania-based sensor over time to CO exposure</td>
</tr>
<tr>
<td>2.11</td>
<td>Aging of titania-based sensor over time to CH₄ exposure</td>
</tr>
</tbody>
</table>
2.12 Recovery response of titania-based sensors at 600 °C and 5%O_2/N_2 .......... 88
2.13 Response of anatase/La_2O_3/CuO sensor to CH_4 in a background gas of 500 ppm CO/5%O_2/N_2 at 600 °C ................................................................. 89
2.14 Effect of oxygen on the relative resistance change of titania sensors .......... 90
2.15 Infrared data at room temperature after exposure to CO at a heater setting of 800 °C ................................................................. 91
2.16 Infrared data for the CO_2 reaction at a heater setting of 800 °C .............. 92
2.17 Infrared data for the CO reaction at a heater setting of 800 °C .............. 93
2.18 Infrared data for the CH_4 reaction at a heater setting of 800 °C ............ 94
3.1 Infrared spectra of anatase upon exposure to CO ...................................... 130
3.2 Infrared spectra of anatase upon exposure to CH_4 .................................. 131
3.3 Infrared spectra of TiO_2/CuO upon exposure to CO ............................... 132
3.4 Infrared spectra of TiO_2/CuO upon exposure to CH_4 ............................ 133
3.5 Infrared spectra of La_2O_3 upon exposure to CO_2 ................................. 134
3.6 Infrared spectra of La_2O_3 upon exposure to CO ..................................... 135
3.7 Infrared spectra of La_2O_3 upon exposure to CH_4 .................................. 136
3.8 Infrared spectra of La_2O_3 with CH_4 showing the hydroxyl region .......... 137
3.9 Infrared spectra of anatase/La_2O_3 upon exposure to CO_2 ..................... 138
3.10 Infrared Spectra of anatase/La_2O_3 upon exposure to CO ....................... 139
3.11 Infrared Spectra of anatase/La_2O_3 upon exposure to CH_4 .................. 140
3.12 Infrared spectra of anatase/La_2O_3/CuO upon exposure to CO_2 ............ 141
3.13 Infrared spectra of anatase/La_2O_3/CuO upon exposure to CO .............. 142
3.14 Infrared spectra of anatase/La_2O_3/CuO upon exposure to CH_4 .......... 143
3.15 Mechanism of CO and CH_4 oxidation on anatase ................................. 144
3.16 Illustration of adsorbed species on anatase/La_2O_3 and anatase/La_2O_3/CuO following reaction with CO ................................................................. 145
4.1 Effect of oxygen on the resistance of titania sensors ............................... 170
4.2 Response of TiO_2 sensors to CO and CH_4 at 600 °C and 5%O_2/N_2 .......... 171
4.3 XRD of anatase-rutile composite mixtures after 800 °C heat treatment ...... 172
4.4 XRD patterns of 25% Rutile composite ............................................... 173
4.5 X-ray diffraction patterns of 25% rutile sensor with layers of sensing
film removed................................................................................................................. 174
4.6 X-ray diffraction pattern of 50% rutile sensors ....................................................... 175
4.7 X-ray diffraction patterns of 75% rutile sensor ....................................................... 176
4.8 SEM micrographs of TiO₂ that has been heat treated at 800 °C............................ 177
4.9 SEM micrographs of 25% Rutile composite sensors............................................... 178
4.10 SEM micrograph of 50% rutile composite sensor ............................................... 179
4.11 SEM Micrographs of 75% rutile sample at two different magnifications 180
4.12 Response of p-n composite sensors to CO at 5%O₂/N₂, 600 °C............................ 181
4.13 Response of p-n composite sensors to CH₄ at 5%O₂/N₂, 600 °C .......................... 182
4.14 Bar graph representation of percolation in anatase-rutile composite at
750 ppm CO (in 5%O₂/N₂) at 600 °C...................................................................... 183
4.15 Schematic drawing of insulator-conductor composites ........................................ 184
4.16 Sensing response of 75% Rutile sensor at 5%O₂/N₂, 600 °C .............................. 185
4.17 Results of model of composite................................................................................ 186
5.1 Procedure for making sol-gel materials ................................................................. 230
5.2 TEM micrographs of as-dried sol-gel TiO₂ ............................................................. 231
5.3 The effect of heat treatment temperature on sol-gel TiO₂ ...................................... 232
5.4 The effect of heat treatment on sol-gel TiO₂ of pH sensor ........................................ 233
5.5 XRD of pH=1.44 sol-gel after heat treatment.......................................................... 234
5.6 TEM micrographs of sol-gel TiO₂ taken during in situ experiments....................... 235
5.7 TEM micrographs of sol-gel TiO₂ that has been heat treated to
600 °C ex situ................................................................................................................ 236
5.8 SEM micrographs of pH = 2.56 sol-gel TiO₂ after 700 °C heat treatment............. 237
5.9 SEM micrographs of pH=1.44 sol-gel TiO₂ after 700 °C heat treatment.............. 238
5.10 SEM micrograph of pH=1.44 sol-gel TiO₂ after 800 °C heat treatment .............. 239
5.11 The effect of La doping on sol-gel TiO₂ after a 1hr. 500 °C heat
treatment .................................................................................................................... 240
5.12 The effect of La doping on sol-gel TiO₂ after 1 hr at 700 °C heat
treatment .................................................................................................................... 241
5.13 The effect of La doping on sol-gel TiO₂ after 1 hr at 800 °C heat
treatment .................................................................................................................... 242
5.14 The effect of pH on La-doped sol-gel TiO₂ ............................................................ 243
5.15 Effect of pH and La\textsuperscript{3\textsuperscript{+}} doping on sol-gel TiO\textsubscript{2} at 800 °C ................................................................. 244
5.16 Effect of Cu\textsuperscript{2\textsuperscript{+}} doping on sol-gel titania after 500 °C and 700 °C heat treatments for 1 hour ........................................................................................................... 245
5.17 SEM micrographs of La-doped sol-gel TiO\textsubscript{2} after 800 °C heat treatment ............................................................ 246
5.18 SEM micrograph of Cu-doped sol-gel TiO\textsubscript{2} after 700 °C heat treatment ................................................................. 247
5.19 Sol-gel TiO\textsubscript{2} sensor response with heat treatment at 700 °C for 1 hour ................................................................. 248
5.20 Effect of sol-gel powder heat treatment temperature on the sensing response at 600 °C. 5% O\textsubscript{2}/N\textsubscript{2} ........................................................................................................ 249
5.21 Effect of on-substrate heat treatment on the sensing response at 600 °C. 5%O\textsubscript{2}/N\textsubscript{2} ........................................................................................................ 250
5.22 Effect of La-doping on gas sensitivity of sol-gel titania sensors at 600 °C. 5%O\textsubscript{2}/N\textsubscript{2} ........................................................................................................ 251
5.23 Effect of powder heat treatment temperature on gas sensitivity of La-doped sol-gel titania sensors ........................................................................................................ 252
5.24 Effect of Cu-doping on the gas sensitivity of sol-gel titania sensors at 600 °C. 5%O\textsubscript{2}/N\textsubscript{2} ........................................................................................................ 253
5.25 Effect of on-substrate heat treatment temperature on the gas sensitivity of Cu-doped sol-gel titania sensors ........................................................................................................ 254
5.26 Raman spectra of sol-gel TiO\textsubscript{2} films ........................................................................................................ 255
5.27 SEM micrograph of top view of sol-gel TiO\textsubscript{2} sensing film ........................................................................................................ 256
5.28 SEM micrograph of cross-section of sol-gel TiO\textsubscript{2} film ........................................................................................................ 257
5.29 Effect of film thickness sensor response at 600 °C. 5%O\textsubscript{2}/N\textsubscript{2} ........................................................................................................ 258
5.30 Change in baseline sensor resistance as a function of sensor thickness at 600 °C. 5%O\textsubscript{2}/N\textsubscript{2} ........................................................................................................ 259
5.31 The effect of increased heat treatment time on thin film sensor response ........................................................................................................ 260
5.32 Comparison of sensor response of thick film sol-gel and commercial anatase at 600 °C. 5%O\textsubscript{2}/N\textsubscript{2} ........................................................................................................ 261
5.33 Comparison of sensor response of thick film sol-gel and commercial rutile at 600 °C. 5%O\textsubscript{2}/N\textsubscript{2} ........................................................................................................ 262
5.34 Comparison of thin film sol-gel TiO\textsubscript{2} response with commercial anatase sensor response at 600 °C. 5%O\textsubscript{2}/N\textsubscript{2} ........................................................................................................ 263
5.35 Comparison of recovery response of different TiO\textsubscript{2} sensors ........................................................................................................ 264
A.1 Schematic of Transmission Spectroscopy ........................................................................................................ 284
A.2 Reflection of light from a surface ........................................................................................................ 285
A.3 Depiction of light flux used for derivation of Kubelka Munk expression... 286
A.4 Schematic diagram of environmental DRIFTS chamber ......................... 288
A.5 Temperature profile for DRIFTs step experiment ................................. 288
A.6 Single channel reflectance of KBr ......................................................... 289
A.7 Single channel Spectra of Anatase/La₂O₃/CuO upon exposure to CH₄ and N₂ ............................................................. 290
A.8 Correction of data using KBr as background at 25 °C .......................... 291
A.9 Correction of data using KBr as background at 800 °C ....................... 292
A.10 Kubelka Munk spectra obtained by using ALC under N₂ as r₀ ........... 293
A.11 Correction of 25 °C diffuse reflection data by relative reflectance method .................................................................................. 294
A.12 Correction of 800 °C diffuse reflection data by relative reflectance method .................................................................................. 295
A.13 Correction of 25 °C DRIFTS Data by single channel method .............. 296
A.14 Correction of 800 °C DRIFTS data by single channel method ............ 297
A.15 Comparison of diffuse reflectance spectra corrected by different methods .................................................................................. 298
CHAPTER 1

INTRODUCTION

A Brief Review of Gas Sensor Technology

Gas sensors have become an integral part of our daily lives. Oxygen sensors are present in automobile exhaust gas lines that control the air to fuel ratio so that engines can run efficiently and with low emissions. In homes, carbon monoxide gas sensors alert residents of the emission of the deadly gas from fireplaces and furnaces. Even food is monitored in order to detect spoilage, or residual chemicals in packing materials [1].

There are a number of areas that are of interest to both gas sensor researchers and to sensor users. As the regulations for automotive emissions are tightened, auto manufacturers are putting more effort into developing sensors to monitor automotive emissions. Alternatives to the combustion engine, such as diesel engines, and fuel cells are also being researched to improve fuel economy, but lead to new challenges in sensor development. In both of these cases, the oxygen sensors found in today's automobiles have limited utility. Diesel engines produce significant amounts of NOx, and a sensor for this type of emissions would be more suitable for combustion control. In fuel cells, CO is
an undesired product of methanol reforming, poisoning the platinum catalysts of the fuel
cell. The application of a CO sensor could be useful in control of the methanol reforming
process, reducing the production of CO.

Apart from the automotive industry, there are other areas where gas sensors are of
benefit. Utility industries, which use combustion processes as a means of producing
energy, could utilize carbon monoxide and NOₓ sensors that monitor incomplete
combustion. The information obtained by the sensor could then control the process. The
chemical manufacturing industry also uses gas sensors as a means of monitoring
production lines.

1.1 Types of Gas Sensors

There are many types of gas sensors that have been made to detect carbon
monoxide. Optical sensors detect gases based on a color change or development of
fluorescence of a probe molecule [2]. Physical sensors, such as Surface Acoustic Wave
Devices and Quartz Crystal Microbalances, become chemical sensors when coated with
polymers, self-assembled monolayers or other chemically selective materials. Finally,
there are numerous electrochemical sensors. These sensors show an electrical response
(resistance change, potential drop, etc.) to a chemical change. Of these many sensor
types, the electrochemical sensors are the only ones that can be applied at higher
temperatures because they can be made from semiconducting ceramics. The most
common types of electrochemical sensors include potentiometric, amperometric and
conductometric sensors, though numerous other devices, from field effect transistors
Potentiometric sensors are, in essence, miniaturized electrochemical cells where the response is based on the potential difference between a reference and sensing electrode. Typically a solid-state or polymeric material is used as the electrolyte, and the potential difference between the two electrodes is measured. Figure 1.1 shows a schematic of a potentiometric-type sensor made of Yttria-stabilized Zirconia (YSZ) that is used for oxygen sensing. One electrode of the sensor is exposed to a constant oxygen atmosphere to act as a reference, while the other electrode (sensing electrode) is exposed to a changing oxygen atmosphere. The difference in the oxygen concentration at the two electrodes results in a potential that usually follows Nernst's Law:

$$E = \frac{RT}{nF} \ln \frac{pO_2(a)}{pO_2(b)}$$  (1.1)

where T is the temperature, R is the gas constant, n is the number of electrons involved (4 for $O_2$ reduction), F is the Faraday constant, and $pO_2(a)$ and $pO_2(b)$ are the oxygen partial pressures on either side of the electrolyte.

Oxygen sensors made of YSZ are used for controlling the air to fuel ratio in automobiles. Potentiometric sensors made of oxygen ion conducting ceramics can also be used for sensing other gases, such as carbon monoxide [7]. By coating one electrode with a catalyst, CO can be oxidized to $CO_2$, changing the relative oxygen concentration at one electrode. Pt, RuO$_2$, [8] CdO and SnO$_2$ [7] have been used as catalysts for this type of
CO sensing. Often these sensors show non-Nernstian behavior. This non-Nernstian behavior occurs when both CO and O₂ are present in the gas phase, and the result is a mixed potential, with two processes occurring at the three-phase boundary, one oxidation, the other reduction [8-10]. In addition to YSZ, materials such as ceria have been investigated as the electrolyte [10].

1.1.2 Amperometric Sensors

Amperometric sensors operate on a similar principle to potentiometric sensors, except that instead of measuring a potential change based on relative oxygen concentration, a potential is applied to the sensor causing oxygen to be pumped from one side of the sensor to the other. Figure 1.2 shows a schematic of an amperometric device. As is the case with potentiometric sensors, two electrodes sandwich an ion conducting ceramic such as YSZ. However, a voltage is applied across the two electrodes which results in O₂ being reduced at one electrode, and O²⁻ being pumped through the electrolyte. The current resulting from the pumping of O²⁻ is typically independent of the oxygen partial pressure [11]. If in addition, there is a diffusion barrier (in the case of the figure, a channel) that restricts the flow of the ambient gas into the volume in front of one of the electrodes then at a high enough applied voltage, the chamber preceding this same electrode will be depleted of O₂, and the current is now dependent on the rate oxygen can diffuse through the channel to the electrode [12]. In other words, the device is operating
at the diffusion limit. At the diffusion limit the current ($I_d$) is proportional to the partial pressure of oxygen according to the following expression [13]:

$$I_d = \frac{nFDA}{RT} \cdot P_{O_2} \tag{1.2}$$

where $n$ is the number of electrons in the redox process (4 for $O_2$). $A$ is the cross-section of the diffusion channel. $l$ is the channel length. $D$ is the diffusion coefficient of $O_2$. $T$ is the temperature. $F$ is the Faraday constant and $R$ is the molar gas constant.

Amperometric sensors can also be made sensitive to gases other than oxygen by the use of coatings on the electrodes. The coating typically serves a dual purpose, acting both as a CO oxidation catalyst and as a diffusion barrier. Catalyst mixtures such as CuO/Al$_2$O$_3$/ZnO used as amperometric sensor coatings have shown linear responses from 500 ppm to 1800 ppm CO between 700° and 800 °C [12].

Visser et al. use a variation of an amperometric-type cell, where the oxygen is pumped at a controlled rate to a chamber containing a secondary gas sensing element [14]. This allows careful control of the oxygen concentration for sensors that respond not only to reducing gases such as CO, but to oxygen as well.

1.1.3 Conductometric-Type Sensors

A second type of electrochemical sensor is the resistive (or conductometric)-type gas sensor. In this case a semiconducting material shows a change in its resistance in response to the analyte gas. These types of sensors can be made from different types of materials. Polymers are popular for low temperature applications, but suffer from interference from humidity since they must be operated at temperatures below 50 °C [1].
Ceramic materials that show semiconducting properties can also be used for this type of sensor. Many metal oxides, depending on the temperature and atmosphere, show semiconducting behavior. These materials are of interest to sensor researchers because of their stability at high temperatures, and they are often resistant to many of the harsh conditions of some sensing environments. The most notable success in metal oxide semiconductor (MOS) sensor development has been in SnO$_2$ gas sensors. SnO$_2$-based sensors are found in numerous applications, including the carbon monoxide detectors that are found in many homes today. Other materials, such as ZnO and TiO$_2$ have also been investigated as potential sensor materials.

MOS sensors can be made as monolithic devices, pellets or as thick and thin films [13]. Monolith-type sensors, such as the one shown in Figure 1.3 often have an embedded heater for controlling the temperature. Monoliths and pellet sensors need to be well sintered so that the sensor will be a rigid body. Thick film sensors are usually made by depositing a polycrystalline sample onto a substrate which has a pair of gold or platinum electrodes. A number of electrode arrangements and geometrical designs can be used as depicted in Figure 1.3 b and 1.3c. Four-point probe sensors are used to obtain accurate resistance measurements across relatively large samples, while interdigitated electrode patterns minimize the distance between electrodes, reducing the overall measured resistance [13].
1.2 Metal Oxide Semiconductor Gas Sensors

Metal oxides typically have wide bandgaps which should make them insulating in nature, but due to defects in their structures, may show semiconducting behavior. Oxygen vacancies, cation interstitials and impurity atoms are all defects that are present in metal oxides, and their formation necessitates charge compensation by either electrons or holes in the bulk material (as expressed using Kröger Vink notation, where \( e^\ast = \) free electron, \( h^\ast = \) free hole, \( V = \) vacancy, subscript = lattice position, \( i = \) interstitial, and superscript indicates charge at lattice position. \( ^\ast = \) positive, \( ^\prime = \) negative):

\[
\begin{align*}
O_0 & \rightarrow V_0^{\ast\ast\ast\ast} + \frac{1}{2}O_2 + 2e^- \\
M_M & \rightarrow V_M^{\prime\prime\prime\prime} + M_i^{\ast\ast\ast\ast}
\end{align*}
\]

(1.3)  
(1.4)

These defects result in the formation of donor (n-type) and acceptor (p-type) states forming in the band gap, as shown in Figure 1.4. The overall conductivity is related to the sum of the conducting species in the material and is expressed as:

\[
\sigma = n\mu_e e + p\mu_p e
\]

(1.5)

where \( \sigma \) is the conductivity, \( n \) and \( p \) are the concentrations of electrons and holes, respectively, and \( \mu_e \) and \( \mu_p \) are their mobilities. The concentration of charge carriers varies with temperature, having an Arrhenius dependence:

\[
n \propto \exp\left[ -\frac{E_F}{kT} \right]
\]

(1.6)

where \( k \) is the Boltzmann constant, and \( E_F \) is the Fermi Energy. The Fermi Energy is \( \frac{1}{2} \) the energy between the bottom of the conduction band and the top of the valence band for a material with no defect states (Figure 1.4a), so the temperature required to substantially populate the conduction band with charge carriers is quite high. In a metal oxide that has
defect states in the band gap (Figure 1.4b and c), the Fermi level shifts, and the concentration of charge carriers (for and n-type semiconductor) is now:

\[ n = \text{[donor]} \exp \left( -\frac{E_d}{2kT} \right) \]  \hspace{1cm} (1.7)

with \( E_d \) the energy between the donor level and conduction band. A similar expression can be written for a p-type semiconductor. This smaller energy difference makes it easier (lower temperatures required) to substantially populate the conduction band.

In addition to the temperature, the conductivity of a semi-conducting metal oxide has a dependence on the ambient gas concentration. The behavior of oxygen is the most widely understood, and it can influence the bulk conductivity, or may be limited to a surface localized effect.

### 1.2.1 Bulk Conductivity Changes

There is an equilibrium between the presence of oxygen in the gas phase and in the bulk as expressed in equation 1.3, so it follows that the ambient oxygen concentration can have an effect on the bulk electron concentration. This \( \text{pO}_2 \) dependence is related to the type of defect present, whether it is a doubly or singly ionized oxygen vacancy, or a titanium interstitial atom. In the case of a metal oxide such as TiO\(_2\), the generation of a doubly ionized oxygen vacancy can be expressed more specifically as [15]:

\[
\begin{align*}
2 \text{Ti}_{\text{i}} + \text{O}_0 & \rightarrow 2\text{Ti}_{\text{i}}' + \frac{1}{2} \text{O}_2 + \text{V}_0^{**} \\
2 \text{Ti}_{\text{i}}' & \rightarrow 2 \text{Ti}_{\text{i}} + 2 \text{n}' \\
\text{O}_0 & \rightarrow \text{V}_0^{**} + 2 \text{n}' + \frac{1}{2} \text{O}_2
\end{align*}
\]  \hspace{1cm} (1.8a,b,c)
In other words, oxygen vacancies are the dominant defect. According to equation 1.7, the electron concentration is dependent on the concentration of the donor state, \( \text{Ti}_{\text{n'}} \), which is dependent on the defect equilibrium (from equation 1.8a):

\[
[\text{Ti}_{\text{n'}}][\text{Vo}^{**}]pO_{2}^{1/2} = \exp (-\Delta G/kT)
\]

(1.9)

the electroneutrality condition stipulates that

\[
2[\text{Vo}^{**}] = [\text{Ti}_{\text{n'}}]
\]

(1.10)

Combining equations 1.7, 1.9 and 1.10 gives the overall dependence of the electron concentration on the oxygen concentration:

\[
n = A pO_{2}^{-1.6}
\]

(1.11)

where \( A = 2^{1.3}\exp(\Delta G/3 + E_{a}/kT) \). Other researchers maintain that rather than oxygen vacancies as the dominant defect type, it is Ti interstitials [16]. For this case, the formation of defects can be written as:

\[
\text{Ti} + 2 \text{ O}_2 \rightarrow \text{Ti}_{\text{i}^{**}} + \text{O}_2 + 4 e'
\]

(1.12)

When Ti interstitials are the dominant defect, the electron concentration has a \( pO_{2} \) dependence of \(-1/5\).

In both of the above scenarios, only defects of pure TiO\(_2\) are taken into account when determining the dependence of the electron concentration, and thereby the conductivity, on the oxygen partial pressure. In reality, TiO\(_2\) contains impurities as well, and these make their own contribution to the electron concentration. In fact, Smyth calculates that at many operating temperatures, the concentrations of defects are such that they control the electrical behavior [17]. Odier, in models of the resistance change of titania in air, has shown that between 1000° and 1500 °C, conductivity is controlled by
impurities, not the intrinsic properties of the material [18]. The presence of an impurity in TiO₂ could be represented by the following equilibrium:

\[
Ti_{n-} + 2O_2 + 2Al_2O_3 \rightarrow 4Al_{n-}^\prime + Ti_{n-}^{****} + 4O_2
\]  

(1.13)

and to maintain electroneutrality:

\[
4[\text{Ti}_{n-}^{****}] = [\text{Al}_{n-}^\prime]
\]  

(1.14)

Combining equations 1.7, 1.9 and 1.14, the exponent of the dependence of the electron concentration on pO₂ is now -1/4.

Table 1.1 summarizes the pO₂ dependence of the conductivity of TiO₂ for a number of different defects [19]. The type of defect present in TiO₂ is temperature and pO₂ dependent according to Marucco et al. [20]. They identified three main domains where either \(V_{O}^{**}\), \(V_{O}^*\), or Ti^{****} are dominant. At temperatures above 900 °C, and at low pO₂, Ti^{****} is dominant. and as the pO₂ level increases, \(V_{O}^{**}\) starts to dominate, down to 800 °C. At even higher pO₂ above 900 °C (and at very high pO₂ at all temperatures), \(V_{O}^*\) is the dominant species [20]. The identification of the major defect species can be further complicated by the presence of impurity atoms, as well as by heat treatment of the oxide, as defects formed at high temperatures may be 'locked in' by quick cooling rates [20-23].

Under high oxygen partial pressures, Ti^{****} interstitials which had resulted from the presence of impurities, may be annihilated as follows [16]:

\[
Ti_{i}^{****} + O_2 \rightarrow Ti_{n-} + O_2 + 4 h^*
\]  

(1.15)

The presence of holes as the dominant carrier makes TiO₂ at high pO₂ concentrations a p-type semiconductor, with a pO₂ dependence of +1/4. Further discussion of the p-type behavior of TiO₂ is left to Chapter 4.
High preparation temperatures of metal oxide sensors will help create higher concentrations of defect states in the bulk of a metal oxide through the loss of oxygen to the gas phase. This equilibrium between lattice and gas phase oxygen can be used as a method of sensing. However, MOS gas sensors, especially those that are polycrystalline thick films, make use of the surface conductivity changes resulting from the adsorption/desorption of oxygen from the surface of the metal oxide particles, as discussed below.

1.2.2 Surface Conductivity Changes

Oxygen adsorbs on a metal oxide surface in either molecular form or as oxygen adatoms, with the nature of the adsorbed species controlled, in part, by temperature. For SnO$_2$, O$_2^-$ is the dominant surface species up to 160 °C, then O$^-$ is dominant up to 520 °C, when both O$^-$ and O$^{2-}$ are seen to desorb [15]. Above 500 °C, equilibration of gas phase and lattice oxygen occurs [24]. Studies on TiO$_2$ show O$_2^-$ desorption up to 250 °C [25].

The adsorption of a species at the surface of a metal oxide results in the formation of a surface state that can trap electrons from the bulk at a localized state. The result is a decrease in the charge carrier concentration in the region near the surface of the particle as pictured in Figure 1.5. This region, known as the space charge region or depletion layer, causes a potential to form between the bulk and the surface. This barrier height, $\varepsilon\Phi$,
is controlled by the concentration of surfaces states, and thereby the width of the depletion region (the Debye length, \( x_0 \)) [26]:

\[
e\Phi_s = -eN_d x_0^2 / 2\varepsilon\varepsilon_0 \tag{1.16}
\]

where \( N_d \) = number of donors in space charge region, \( \varepsilon \) = dielectric constant of the material and \( \varepsilon_0 \) is the permittivity of free space. The decreased electron concentration in the depletion layer results in a lowered surface resistance of the material. Electrons must be activated from the trapping surface state to the conduction band in order for conduction to occur.

1.2.3 Conductivity in Polycrystalline Samples

Most conductometric gas sensors are made of polycrystalline materials that have been sintered to form a pellet or a porous film. The nature of the grain boundaries in the overall sensor body, and thereby the resistance of the material and its gas sensitivity can be controlled by the degree of sintering of the sensor. Figure 1.6 is a cartoon of three different levels of sintering in a polycrystalline sample: high (a), medium (b) and low (c).

In the sample with a high amount of sintering (Figure 1.6a), open necks form between grains. Upon oxygen exposure, a depletion region will form at the surface, but the bulk interior of the grains, where the charge carrier concentration is unaffected, is connected allowing for facile conduction between grains. Changes in the surface oxygen concentration can alter the depletion layer thickness, but unless there is equilibration of
the oxygen with the bulk material, the depletion layer thickness will have little effect on
the overall conductivity. Because of this, open neck structures are not very suitable for
gas sensing applications.

For a sample that has been sintered to a lesser degree, as shown in Figure 1.6b. a
closed neck can form between two grains each with a depletion layer that overlaps the
depletion layer of the adjacent grain. Conduction can occur from one grain to the next
through the depletion region, which has a high resistance. A change in the concentration
of surface states will increase the charge carriers in this region and decrease the
resistance. If the concentration of surface states is decreased substantially, the sample will
begin to resemble an open-neck sample. Closed-neck samples are said to be surface trap
limited, and are an accepted model for thin film (<100 nm) sensors.

Polycrystalline samples with an even lower amount of sintering may form just
point contacts between grains (Figure 1.6c). In order for electrons to conduct from one
grain to the next, they must surmount the potential of the depletion region. This point
contact between grains is called a double Schottky barrier (Figure 1.7), with the
concentration of surfaces states controlling the height of the barrier, as in equation 1.16.
The conductivity from one grain to the next, across the barrier, is [26]:

\[ \sigma \propto (-e \Phi_s/kT) \]  

(1.17)

The Schottky barrier model is generally used to describe conduction changes in thick
polycrystalline film sensors [27]. Still, there is no way to insure that only one type of
neck forms between samples, and most polycrystalline sensors are a mixture of more than
one type of neck [26].
1.2.4 Sensing Other Gases

The previous three sections considered the effects of oxygen on the conductivity of a metal oxide. The interaction of other gases with the oxide surface can also affect the resistance of a metal oxide. In some cases, the resistance change is due to the adsorption of a species other than oxygen at the surface. Water vapor, for example, can adsorb on the surface of the metal oxide, and depending on the form in which it adsorbs, either increase or decrease the resistance.

\[ \text{H}_2\text{O} + \text{MO}_x \rightarrow \text{H}_2\text{O}^- + \text{e}^- \quad (1.15) \]

or

\[ \text{H}_2\text{O} + \text{O}_x^- \rightarrow 2\text{OH}^- \quad (1.16) \]

Other gases will react with the surface adsorbed oxygen species rather than adsorb themselves. CO and many hydrocarbons undergo a surface combustion reaction that decreases the concentration of surface oxygen species, thus increasing the metal oxide conductivity.

\[ \text{CO (g)} + \text{O}_x^-\text{MO}_x \rightarrow \text{CO}_2 + \text{MO}_x + \text{e}^- \quad (1.17) \]

Any gas that can oxidize on the metal oxide surface can cause a conductivity change. It is for this reason that metal oxides, though sensitive to many gases, are often not very selective.
1.3 Optimizing Metal Oxide Gas Sensors

An ideal gas sensor meets a number of different requirements. It is highly sensitive to the gas of interest at the temperature of interest and in the concentration range of interest. Secondly, it must be sensitive only to the analyte gas. that is. it must not be susceptible to interferences. Finally, the response to the gas must be quick, especially if it is to be used as means of process control.

In practice it is difficult to obtain the ideal metal oxide gas sensor. This is especially true when it comes to making sensors that are selective. Many processes in which a sensor would be of use are often complex mixtures, making it a challenge to obtain selectivity. Improving the selectivity, sensitivity and response times of gas sensors has been approached from many angles. Thin films and nanocrystalline materials have been tested as sensors, with the promise of improved sensitivity and response times. Noble metals and metal oxides have been used to enhance sensitivity and create selective sensors. Other additives serve the purpose of lowering the sensitivity to humidity, or lowering sensor drift. Finally, pattern recognition approaches, such as the algorithms used in electronic noses, have been used to extract information about specific gases in a mixture.

The next four sections detail various approaches for optimizing metal oxide gas sensors that have been reported in the recent literature. Three tables (Tables 1.2, 1.3 and 1.4), accompany the text with more details on the sensors' behavior, such as response time, sensitivity and selectivity. All the gas sensitivities are reported as relative resistance, R/R₀, both in the text and the tables.
1.3.1 Metal Oxides for Gas Sensing

Table 1.2 summarizes the response of different materials that have been investigated as CO sensors. SnO$_2$ is the most widely studied material for gas sensors, but a number of other metal oxides have shown promise as sensing elements for CO, as well as other gases. Yamaura et al. investigated 24 different metal oxides as sensor materials for CO and found that SnO$_2$, In$_2$O$_3$, and ZnO were the most promising for CO sensing [28]. The sensitivities ($R/R_n$) of these materials to 1000 ppm CO were 0.046, 0.083, and 0.044, respectively. These sensitivity values were reported for the material’s optimal sensing temperature. The In$_2$O$_3$ sensor showed the highest CO sensitivity of the three, and due to the small difference in its response to CO and H$_2$ compared to the other materials tested, various dopants were added to In$_2$O$_3$ to improve its selectivity (see next section) [28]. The sensitivity of TiO$_2$ towards CO in this study was 0.37 (to 1000 ppm CO), but the study did consider temperatures above 500 °C. Other studies have shown that TiO$_2$ is, in fact, very sensitive towards CO. In studies by Akbar and coworkers, the anatase form of TiO$_2$ had a sensitivity of 0.2 to 5000 ppm CO at 700 °C in a nitrogen containing atmosphere, better than that in wet air at a lower temperature [29, 30]. Additionally, it was noted that the sensors were able to recover to their original resistance when CO was removed, without the necessity of adding more oxygen [29].

Co$_3$O$_4$, a spinel which behaves as a p-type semiconductor, has also been investigated as a CO sensor [31]. The material was tested between 50 °C and 500 °C, but below 100 °C, changes in the resistance were not reversible, most likely because of the
inability of CO to desorb from the sample at these low temperatures [31]. Films of 
BaSnO$_3$, a perovskite, have also been examined as CO sensors [32]. The authors showed 
that the effect of humidity on the sensor was related to the concentration of oxygen in the background gas. At high concentrations of oxygen (20 vol%), the sensitivity to carbon monoxide decreased, at intermediate levels (5 vol%) there was little humidity effect, and at low O$_2$ (0.5 vol%) the CO sensitivity increased [32].

Fe$_2$O$_3$ has also been used as a CO sensitive material. Han et al. looked at Fe$_2$O$_3$ powders that had been precipitated from solutions of varying pH [33]. Those that were precipitated at a high pH (10.5) showed the greatest sensitivity in air to CO. At a lower pH (4.8), the CO sensitivity was much lower. In this study, the background gas composition had a strong effect on the baseline resistance of the high pH sensors, going from 22 MΩ in N$_2$ to 40 MΩ in Air, while the baseline resistance change between N$_2$ and air was only 1 MΩ for the pH = 4.8 sensor. The authors propose that this indicates a difference in oxygen adsorption ability and therefore a difference in the sensing mechanisms at the two different pH’s. Rather than react with surface adsorbed oxygen, CO would adsorb and ionize on the Fe$_2$O$_3$ surface in the low pH sample [33].

ZnO is another well-studied sensor material. Work by Saito et al. compared the change in the conductivity of ZnO with its efficiency in the oxidation of gases such as C$_3$H$_8$ and CO by monitoring the concentration of CO$_2$ produced as well as the resistance change [34]. ZnO showed a far greater conversion rate of CO to CO$_2$ than the C$_3$H$_8$.
oxidation rate, but the sensitivity of the sensor was greater towards C₃H₈. Another trend noted by the authors was that the resistance change increased as the number of carbon atoms in the gas increased for hydrocarbons [34].

### 1.3.2 Addition of Dopants to Metal Oxide Gas Sensors

Improvements to gas sensitivity, selectivity and response time have largely been achieved through the addition of dopants to metal oxide sensors. In some cases they are in the form of noble metals, which are either mixed with the bulk of the sensor or deposited onto the sensor surface. Mixtures of the semiconducting metal oxide with a second or third metal oxide (often one that shows some sort of catalytic response for the gas of interest) have shown improvements to the sensor response. Finally, the synthesis of mixed metal oxides, where a dopant is located at substitutional positions in a semiconducting metal oxide, show favorable sensing responses. Table 1.3 summarizes a sampling of different CO sensors that have been reported in the literature.

Pd/SnO₂ is a well-studied system for sensitive CO detection. In a study of thin films of SnO₂ with co-deposited Pd particles, the sensors had sensitivities of $S = 10^{-4}$ at 50 °C, the optimal sensing temperature, while that of pure SnO₂ films was $S = 0.33$, at 200 °C, to 300 ppm of CO in air [35]. Figure 1.8 shows how dramatic the difference in sensitivity is between the doped and un-doped SnO₂. Even at temperatures outside the optimal sensing temperature, 50 °C, the Pd-doped sample is more sensitive than the undoped sensor by a factor of 1000 or more [35]. Operating this sensor in a temperature-pulsed mode lowers the sensitivity to $S= 0.056$ at 120 °C [35].
Steiner et al. deposited Pt and Ca on the surface of SnO$_2$ sensors. The Pt addition increased the response to CO, as expected [36]. The addition of Ca caused only a slight change in the SnO$_2$ response to CO, and it was a resistance increase rather than decrease. However, by combining the two dopants on one sensor, the Ca drift helped to compensate for drift in the sensor response with time [36].

Bi$_2$O$_3$ has also been used as a dopant for SnO$_2$. Sarala Devi et al. coprecipitated Bi$_2$O$_3$ (at 10 wt %) and SnO$_2$, then tested which heat treatment resulted in the best CO sensor. In their experiments, undoped SnO$_2$ had shown the highest gas sensitivity with a heat treatment temperature of 800 °C, but the Bi$_2$O$_3$ materials had similar sensitivities, whether the heat treatment was done at 650 °C or 800 °C [37]. However, the heat treatment did affect the selectivity of the sensor. In the temperature range studied, the 800 °C Bi$_2$O$_3$:SnO$_2$ sensor showed little or no response to CH$_4$, H$_2$ and LPG, while its CO sensitivity was higher than that of the undoped SnO$_2$ [37]. The authors attribute this selectivity to the formation of Bi$_2$Sn$_2$O$_7$ during the heat treatment, and report that the Bi$_2$O$_3$:SnO$_2$ sensor has a higher concentration of oxygen species available for CO oxidation, leading to the improved sensitivity over undoped SnO$_2$ [37].

Ti-compounds have been added as dopants to metal oxides such as WO$_3$ and SnO$_2$. A study by Ferroni et al. looked at sputtered WO$_3$ films doped with titanium. Depending on the composition of the sputtering target, the films would either be WO$_3$ with interstitial Ti (Ti:W. 10:90) or WO$_3$ with a secondary TiO phase (Ti:W. 20:80) [38]. The way in which Ti was doped into the WO$_3$ affected the sensitivity to NO$_2$ and CO.
Both materials had higher sensitivities to \( \text{NO}_2 \), but in the case of the Ti-interstitial \( \text{WO}_3 \), increasing the concentration of \( \text{NO}_2 \) did not change the sensor response further. The CO response, though lower, had a dependence on concentration [38].

In some cases, the dopant is introduced substitutionally into the semiconducting metal oxide. Sberveglieri et al. investigated the response of \( \text{Sn}_{1-x}\text{Fe}_x\text{O}_3 \) thin films as CO sensors [39]. In the material, \( \text{Fe}^{3+} \) substitutes for \( \text{Sn}^{4+} \) in the \( \text{SnO}_2 \) rutile structure up to concentrations of 25 at \%. Sensing measurements showed that 1 at\% was the optimal doping level of iron. At this concentration, the sensitivity of the doped film was greater than the undoped film by a factor of 10 for 10 ppm CO at 450 \(^\circ\text{C}\). The sensor, though having an improved sensitivity to CO, does not have improved selectivity over gases such as hydrogen and ethanol [39].

In the previous section, \( \text{In}_2\text{O}_3 \) was shown to have promising sensing behavior. Yamaura et al. screened 33 three dopants in \( \text{In}_2\text{O}_3 \) to improve the sensitivity of the sensor to CO over \( \text{H}_2 \) [28]. Rb addition resulted in the greatest response difference between CO and \( \text{H}_2 \) with a sensor response ratio of 9. The next best dopants were Ca and Na, both with sensitivity ratios of 4 [28].

1.3.3 Sensitivity and Material Preparation

As mentioned in section 1.2, metal oxide sensors can be made as pellets, thick films and thin films, and composed of larger-grained or nanocrystalline materials. Some of these materials are promising because their fabrication could be done reproducibly.
others because of their low cost, and some due to their response to gases. The sample type can affect sensor sensitivity and response time. Table 1.4 lists a number of different sensor preparation methods that have been investigated.

In thin film preparation, materials are deposited onto sensing substrates by methods such as physical vapor deposition, chemical vapor deposition or by coating sol-gel materials. When films are sputtered onto substrates, a range of parameters can be controlled, such as oxygen content, deposition temperature and pressure, and film thickness, all of which influence the response of the sensing film. Di Giulio and co-workers found that reactively sputtered thin films made with 30% O\textsubscript{2} content in the deposition chamber and at temperature of 350 °C resulted in films of high CO sensitivity [40]. For these sensors, a maximum CO sensitivity was obtained at 275 °C, but even at this high temperature, the response time of the sensor was over 3 minutes. Raising the temperature further decreased the response time, but also decreased the CO sensitivity. At 325 °C, the gas sensitivity had dropped to 0.72 from 0.68 and the response time was cut in half [40].

Thin film sensor of SnO\textsubscript{2} made by spray pyrolysis, on the other hand, showed little sensitivity to CO at similar measurement temperatures. In a study by Labeau and coworkers, the sensitivity of undoped SnO\textsubscript{2} films were only about 0.10 at a measurement temperature of 400 °C, while the sensitivity to ethanol was 0.032 [41]. The authors attribute this sensitivity difference to how the two gases adsorb and react on the surface, proposing that ethanol related reactions lead to the formation of water, which when adsorbed on SnO\textsubscript{2} would donate electrons, further increasing the material’s response.
From impedance measurements, the authors also suggest that the C\textsubscript{3}H\textsubscript{7}OH may adsorb on different sites than CO [41]. Again, the addition of Pd improved the performance of the sensor in its response to both gases (see Table 1.3).

Thin film sensors have also been made by sol-gel methods. The sol contains the metal oxide as a suspended colloid, which allows for spin coating and dip coating of films. Sol-gel SnO\textsubscript{2} thin films, with crystallite sizes of 10 nm have shown a maximum sensitivity at 270 °C and a response time of about 100 seconds [42, 43]. As with the conventional SnO\textsubscript{2} powders, the addition of Pt as a dopant lowers the optimal sensing temperature and increases the gas sensitivity (See Table 1.3) [42] [43]. TiO\textsubscript{2} thin films from sol-gel materials have been made for oxygen sensing, by dip-coating sol-gel titania onto alumina [44].

M. Horrillo et al. compared the response of thick film and thin film SnO\textsubscript{2} sensors, keeping the preparation conditions as similar as possible between the two materials [45]. Their thin films were between 150 and 300 nm and the thicker of the two films was less sensitive, but had the faster response time. The thin films were also more stable than the thick films, having a more stable baseline in the background gas. The response times of the two sensors were markedly different. The thick film sensors were approximately 10 to 20 microns thick and prepared by the standard screen printing method. However, their sensitivity was low, only 0.97 to 1000 ppm CO, compared to a relative resistance value of 0.82 for the thin films to a concentration of 100 ppm CO. The addition of dopants to these thick films improved their gas sensitivity, making their response more comparable to similarly doped thin films [45].
Some authors claim that sol-gel films may form chemical bonds with the substrates, leading to well-adhered films. Through the formation Sn-O-Si bonds (when the substrate is a silica-based material). Racheva and Critchlow made spin coated thin films of sol-gel SnO₂ which were strongly bonded to the underlying substrate [46]. These films were tested as humidity sensors and were able to respond to a low relative humidity of 32%. The response and recovery times of the sensors were between 8 and 17 seconds at room temperature [46].

Free-standing films have also shown good gas sensitivity. Gouma et al. oxidized titanium foils and looked at their gas sensitivity. Foils that were oxidized at 850 °C showed sensitivities of 1.2 in 5%O₂/N₂ at 250 ppm CO, and were of a layered structure containing fine rutile grains. The behavior of these rutile sensors was p-type [47].

Nanocrystalline rutile TiO₂ has also been used for gas sensing. Lin et al. made 34 nm rutile particles and tested their sensitivity to CO and NO₂. These nanocrystalline TiO₂ sensors had an optimal working temperature of 190 °C and showed a p-type response at the temperatures and atmospheres tested [48]. At 100 ppm CO, the relative resistance was 10. The authors report that the response time of the nanocrystalline TiO₂ was 1-3 minutes [48].

Nanocrystalline materials may also be used in the form of thick films for gas sensing. Using particles produced by laser pyrolysis. Carotta and coworkers made thick films of TiO₂, with particles that were 13-28 nm in size and in the anatase phase after firing at 600 °C [49]. Extended treatments at higher temperatures, particles grew to sizes of about 120 nm. In this study, the authors were able to show a correlation between
particle size and gas sensitivity. In measurements made at 450 °C in air, the response to 100 ppm CO was highest for the smaller particles. Also, depending on the firing temperature of the material, the titania samples were insensitive to humidity and NO₂ [49].

Hayakawa and coworkers developed sensors based on nanostructured TiO₂ to obtain low temperature sensors [50]. Sol-gel TiO₂ was added to a precursor solution containing a mixture of titanium and platinum organic compounds, then coated onto sensing substrates. Maximum gas sensitivity to H₂ occurred from films where 50% of the TiO₂ came from the sol-gel source. Microstructural analysis showed that films made solely of the precursor solution contained little porosity, while the 50% sol-gel films were very porous. This porosity resulted in 50 times greater sensitivity for the sol-gel containing films [50].

1.3.4 Data Analysis Methods

Another active area of gas sensor research is in the use of pattern recognition techniques to obtain selectivity from sensors that may otherwise appear non-selective. Some of the approaches are as simple as monitoring the sensor response over a range of temperature, while others involve the use of artificial neural networks.

Takada had developed an approach for testing and extracting a selective response from a single gas sensor [51]. By looking at both the resistance change and the temperature change of a sensor when exposed to a gas, a 2-D map was developed of the sensor response to a number of gas concentrations. An example of one of these maps is
shown in Figure 1.9. Each gas has its own response curve over a range of concentrations, and the curve does not intercept the response of other gases. Using this map, the concentration and identity of an unknown gas (assuming, of course, that it is one of the gases that has been previously tested) can be determined. The method’s advantage is that if the concentration of the unknown gas changes during the course of the measurement, it will still fall on the response curve, making unique identification possible [51].

Other approaches have used dynamic temperature programming to find patterns in the response of a sensor to particular analytes [52]. Temperature pulses are applied to the sensing film, and the response of the sensor is followed with time. The conductance signature for each gas to this applied temperature pulse is unique, as shown in Figure 1.10 [52].

Pattern recognition and artificial neural network methodologies have also been utilized for making selective sensor arrays. Chambon et al. developed a pattern recognition approach using 4 different metal oxide sensors [53]. They used the response of each sensor for a number of gas concentrations, to calculate features that, though not able to determine gas quantity, could identify the gas. Two-dimensional plots of the feature vectors were used to show how the signals from the different gases clustered together. This methodology, a modification of principle component analysis, accurately identified, the two test gases, NH$_3$ and CO [53]. Hong et al. used both principle component analysis and artificial neural networks to classify and identify different flavor
compounds [54]. The principle component analysis resulted in the overlap of the signals of two of the compounds, while the artificial neural network correctly identified the flavor samples 93% of the time [54].

1.4 TiO₂ as a Gas Sensor

The initial work investigating TiO₂ as a gas sensor was done in the 1970s and 1980s. The Clean Air Act of 1970 mandated tougher restrictions on automobile emissions and the use of a sensor, which could keep the air to fuel ratio in the region of optimal combustion and minimize pollutants, was desired. Companies such as Ford and NGK spark plug investigated the rutile phase of TiO₂ for this purpose [55, 56]. Not until 1990’s was TiO₂ explored as a sensor for other gases, with Akbar and coworkers studying the anatase phase for the sensing carbon monoxide and hydrogen [30]. Since then there have been an increasing number of publications on TiO₂-based gas sensors [48, 49, 57]. As seen in the previous section, however, the amount of work done on SnO₂ as a gas sensor far exceeds that on TiO₂.

In many ways, TiO₂ and SnO₂ are alike: both are non-stoichiometric metal oxides with semiconducting behavior. Their optimal operational temperatures are different, though, with SnO₂ best below 400 °C. and TiO₂ best about 500 °C. Additionally, the influence of dopants on the sensing behavior of the two metal oxides may be different.

The following chapters discuss newly developed materials which improve upon the selectivity of gas sensors, and the mechanism by which these materials selectively detect carbon monoxide. In Chapter 2, the issue of lanthanum oxide and copper oxide
dopants on the sensitivity and selectivity of TiO₂ sensors is examined. On the basis of
infrared data, a mechanism for the sensor’s response is proposed. Chapter 3 expands upon
the infrared analysis, providing more insight into the interactions of CO and methane
with doped and undoped titania, information that may assist in the design of future
sensors. Chapter 4 details the studies on p-n composite sensors, another route for
obtaining CO selective sensors. Finally, Chapter 5 discusses sol-gel titania, and its
viability as gas sensor material.
References


### Table 1.1: Relationship between the pO\(_2\) dependence of the conductivity and the dominant defect type in TiO\(_2\). (Adapted from Reference 19)

<table>
<thead>
<tr>
<th>(m^*)</th>
<th>Predominant Defect</th>
<th>Conductivity Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>(V_{O''}, e')</td>
<td>n</td>
</tr>
<tr>
<td>4</td>
<td>(V_{O'}, e')</td>
<td>n</td>
</tr>
<tr>
<td>5</td>
<td>(Ti_{i''''}, e')</td>
<td>n</td>
</tr>
<tr>
<td>4</td>
<td>(Ti_{i''''}, e')</td>
<td>n</td>
</tr>
<tr>
<td>4</td>
<td>(A', V_{O''})</td>
<td>n and p</td>
</tr>
<tr>
<td>4</td>
<td>(V_{Ti''''}, V_{O''})</td>
<td>n and p</td>
</tr>
<tr>
<td>(\infty)</td>
<td>(A', h^+)</td>
<td>p</td>
</tr>
<tr>
<td>5</td>
<td>(V_{Ti''''}, h^+)</td>
<td>p</td>
</tr>
<tr>
<td>4</td>
<td>(V_{O'}, A')</td>
<td>n</td>
</tr>
</tbody>
</table>

* \([n] = A \ pO_2^{-1/m}\) (for n-type) and \([p] = A \ pO_2^{1/m}\) (for p-type)
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>In$_2$O$_3$</td>
<td>0.044 (1000 ppm)</td>
<td>300-600</td>
<td>350</td>
<td>Wet Air</td>
<td>1000 ppm</td>
<td>H$_2$</td>
<td>28</td>
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<tr>
<td>ZnO</td>
<td>0.083 (1000 ppm)</td>
<td>300-600</td>
<td>400</td>
<td>Wet Air</td>
<td>1000 ppm</td>
<td>H$_2$</td>
<td>28</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>0.046 (1000 ppm)</td>
<td>300-600</td>
<td>300</td>
<td>Wet Air</td>
<td>1000 ppm</td>
<td>H$_2$</td>
<td>28</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.37 (1000 ppm)</td>
<td>300-600</td>
<td>500</td>
<td>Wet Air</td>
<td>1000 ppm</td>
<td>H$_2$</td>
<td>28</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.2 (5000 ppm)</td>
<td>500-800</td>
<td>700</td>
<td>N$_2$</td>
<td>5000 ppm</td>
<td>H$_2$</td>
<td>30</td>
</tr>
<tr>
<td>Co$_3$O$_4$</td>
<td>1.22 (883 ppm)</td>
<td>50-500</td>
<td>224</td>
<td>Air</td>
<td>46 ppm</td>
<td>no</td>
<td>31</td>
</tr>
<tr>
<td>BaSnO$_4$</td>
<td>0.1 (2 vol %)</td>
<td>550-950</td>
<td>650</td>
<td>5% O$_2$/N$_2$</td>
<td>5000 ppm</td>
<td>CH$_4$/H$_2$</td>
<td>32</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.56 (400 ppm)</td>
<td>300-400</td>
<td>400</td>
<td>Air</td>
<td>400 ppm</td>
<td>C$_3$H$_8$, C$_2$H$_6$, H$_2$, n-C$<em>4$H$</em>{10}$</td>
<td>34</td>
</tr>
<tr>
<td>Fe$_2$O$_3$(pH=4.8)</td>
<td>0.028 (5000 ppm)</td>
<td>150-425</td>
<td>275</td>
<td>N$_2$</td>
<td>5000 ppm</td>
<td>no</td>
<td>33</td>
</tr>
<tr>
<td>Fe$_2$O$_3$(pH=4.8)</td>
<td>0.22 (5000 ppm)</td>
<td>150-425</td>
<td>275</td>
<td>Air</td>
<td>5000 ppm</td>
<td>no</td>
<td>33</td>
</tr>
<tr>
<td>Fe$_2$O$_3$(pH=10.5)</td>
<td>0.033 (5000 ppm)</td>
<td>150-425</td>
<td>275</td>
<td>N$_2$</td>
<td>5000 ppm</td>
<td>no</td>
<td>33</td>
</tr>
<tr>
<td>Fe$_2$O$_3$(pH=10.5)</td>
<td>0.2 (5000 ppm)</td>
<td>150-425</td>
<td>275</td>
<td>Air</td>
<td>5000 ppm</td>
<td>no</td>
<td>33</td>
</tr>
</tbody>
</table>

* Data is reported as $R_C/R_B$ where $R_C$ is the resistance with CO and $R_B$ is the resistance in the background gas. Lower numbers indicate higher sensitivity, except for p-type sensors ($R_C/R_B > 1$), where higher values indicate higher sensitivities.

** All gases tested in paper are listed, regardless of selectivity.

Table 1.2: Metal oxides that have been used for CO sensing.
<table>
<thead>
<tr>
<th>Material</th>
<th>Dopant</th>
<th>Sensitivity to Other Gases</th>
<th>Temp Range (°C)</th>
<th>Opt. Temp (°C)</th>
<th>CO Sensitivity*</th>
<th>Detect. Limit (ppm)</th>
<th>Background</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO₂</td>
<td>Bi₂O₃</td>
<td>&gt;H₂/LPG/CH₄</td>
<td>50-400</td>
<td>300</td>
<td>1.8</td>
<td>N.A.</td>
<td>N.A.</td>
<td>37</td>
</tr>
<tr>
<td>WO₃</td>
<td>Ti</td>
<td>&lt; NO₂</td>
<td>300</td>
<td>300</td>
<td>0.83</td>
<td>100</td>
<td>Wet Air</td>
<td>38</td>
</tr>
<tr>
<td>WO₃</td>
<td>TiO</td>
<td>&lt;NO₂</td>
<td>300</td>
<td>300</td>
<td>0.71</td>
<td>100</td>
<td>Wet Air</td>
<td>38</td>
</tr>
<tr>
<td>SnO₂</td>
<td>none</td>
<td>-</td>
<td>50-500</td>
<td>200</td>
<td>0.33</td>
<td>300</td>
<td>Air</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>Pd</td>
<td>-</td>
<td>50-500</td>
<td>50</td>
<td>10⁻⁴</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SnO₂</td>
<td>none</td>
<td>&gt;NO₂</td>
<td>225-575</td>
<td>575</td>
<td>0.52</td>
<td>10</td>
<td>Air</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>&lt; H₂, EtOH</td>
<td>225-575</td>
<td>450</td>
<td>0.22</td>
<td>10</td>
<td>Air</td>
<td>39</td>
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<tr>
<td>SnO₂</td>
<td>Pd</td>
<td>&lt;EtOH, MeOH</td>
<td>100-300</td>
<td>200</td>
<td>0.9</td>
<td>150</td>
<td>Air</td>
<td>42,43</td>
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<tr>
<td>SnO₂</td>
<td>Pd</td>
<td>&lt; EtOH</td>
<td>50-500</td>
<td>65</td>
<td>0.011</td>
<td>300</td>
<td>Air</td>
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<td>SnO₂</td>
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<td>&lt; NH₃</td>
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<td>270</td>
<td>.9</td>
<td>40</td>
<td>Wet Air</td>
<td>36</td>
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<tr>
<td></td>
<td>Pt + Ca</td>
<td>&lt; NH₃</td>
<td>270</td>
<td>270</td>
<td>.88</td>
<td>40</td>
<td>Wet Air</td>
<td></td>
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<tr>
<td>In₂O₃</td>
<td>none</td>
<td>&lt; H₂</td>
<td>300-600</td>
<td>350</td>
<td>0.044</td>
<td>1000</td>
<td>Wet Air</td>
<td>28</td>
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<td></td>
<td>Rb</td>
<td>&gt; H₂</td>
<td>300-600</td>
<td>300</td>
<td>0.0085</td>
<td>500</td>
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<td></td>
</tr>
</tbody>
</table>

*Data is reported as $R_C/R_B$ where $R_C$ is the resistance with CO and $R_B$ is the resistance in the background gas. Reported at the lowest measured concentration for the sample (Detect. Limit).

Table 1.3: Examples of CO sensors that use dopants to improve selectivity. When available, data for undoped sample from the same reference is included for comparison.
<table>
<thead>
<tr>
<th>Material</th>
<th>Film Type</th>
<th>Film Thickness</th>
<th>Size</th>
<th>Temp Range °C</th>
<th>Opt. Temp</th>
<th>CO Sens.*</th>
<th>Other Gases</th>
<th>Detect. Limit (ppm)</th>
<th>Response Time</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO₂</td>
<td>Thin</td>
<td>400-500 nm</td>
<td>60-100 nm</td>
<td>175-375</td>
<td>275</td>
<td>.68 (150)</td>
<td>-</td>
<td>25</td>
<td>2 min</td>
<td>40</td>
</tr>
<tr>
<td>SnO₂</td>
<td>Thin</td>
<td>N.A.</td>
<td>11-30 nm</td>
<td>50-500</td>
<td>&gt;400</td>
<td>.10 (300)</td>
<td>EtOH</td>
<td>300</td>
<td>N.A.</td>
<td>41</td>
</tr>
<tr>
<td>SnO₂</td>
<td>Thick</td>
<td>10-20 microns</td>
<td>100 nm</td>
<td>200-450</td>
<td>400</td>
<td>0.87 (1000)</td>
<td>CH₄</td>
<td>1000</td>
<td>N.A.</td>
<td>45</td>
</tr>
<tr>
<td>SnO₂</td>
<td>Thin</td>
<td>150 nm</td>
<td>5-7 nm</td>
<td>200-350</td>
<td>300</td>
<td>0.7 (50)</td>
<td>CH₄</td>
<td>50</td>
<td>N.A.</td>
<td>45</td>
</tr>
<tr>
<td>SnO₂</td>
<td>Thin</td>
<td>100 nm</td>
<td>10.6 nm</td>
<td>150-300</td>
<td>270</td>
<td>0.24 (150)</td>
<td>-</td>
<td>40</td>
<td>50 s</td>
<td>42, 43</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Thick</td>
<td>62 microns</td>
<td>500 nm</td>
<td>600</td>
<td>600</td>
<td>1.2 (250)</td>
<td>-</td>
<td>250</td>
<td>N.A.</td>
<td>47</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Thin</td>
<td>85 nm</td>
<td>10 nm</td>
<td>150-300</td>
<td>200</td>
<td>0.0333</td>
<td>CO, CH₄</td>
<td>100</td>
<td>N.A.</td>
<td>50</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Thin</td>
<td>N.A.</td>
<td>34 nm</td>
<td>50-210</td>
<td>190</td>
<td>10 (100)</td>
<td>NO₂</td>
<td>100</td>
<td>1-3 min</td>
<td>48</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Thick</td>
<td>10 microns</td>
<td>28 nm</td>
<td>400-500</td>
<td>450</td>
<td>0.45 (100)</td>
<td>NO₂</td>
<td>100</td>
<td>N.A.</td>
<td>49</td>
</tr>
</tbody>
</table>

*Data is reported as \( R_{CO}/R_{bg} \) where \( R_{CO} \) is the resistance with CO and \( R_{bg} \) is the resistance in the background gas. Numbers in parenthesis are the gas concentrations in ppm of the reported sensitivity.

Table 1.4: CO sensors made of thin films and/or nanocrystalline materials.
Figure 1.1: Schematic diagram of a potentiometric gas sensor. (Adapted from Reference 7).
Figure 1.2: Schematic Diagram of an amperometric gas sensor (Adapted from reference 13).
Figure 1.3: Schematic diagram of resistive type gas sensors. a) a heated monolith, b) 4-point measurement, c) interdigitated electrode. (Adapted from reference 13)
Figure 1.4: Band diagrams for a metal oxide semiconductor. a) defect-free insulating metal oxide b) donor impurity, n-type semiconductor; c) acceptor impurity, p-type.
Figure 1.5: Representation of oxygen adsorption on a metal oxide semiconductor. a) formation of depletion region, b) band bending as a result of surface state. (Adapted from reference 58)
Figure 1.6: Different sintering levels in polycrystalline semiconductor samples. a) open-neck, b) closed-neck, c) Schottky barrier. (Adapted from reference 15)
Figure 1.7: Formation of a Schottky barrier at the contact of two grains. (Adapted from reference 59)
Figure 1.8: Example of the effect of dopants on metal oxide gas sensors. a) SnO$_2$/Pd; b) SnO$_2$. (Adapted from reference 35)
Figure 1.9: Map of sensitivity vs. temperature change for selective detection of gases. (Adapted from reference 51)
Figure 1.10: Response of sensors to different gases with pulsed temperature operation. (Adapted from reference 52)
CHAPTER 2

ANATASE/La₂O₃/CuO SELECTIVE CARBON MONOXIDE SENSOR

Introduction

The addition of dopants to semiconducting metal oxides to improve their sensing behavior is a popular approach, as detailed in the previous chapter. Dopants are added to improve sensitivity [1], selectivity [2] and response times of sensors [3], as well as change the optimal operating temperature of the sensor [1, 2, 4]. In this chapter the influence of two dopants, La₂O₃ and CuO, on the sensing behavior of titania will be examined.

Copper oxide is well studied in the catalysis literature for its ability to oxidize CO. When supported on TiO₂, it is a more active combustion catalyst than cobalt, manganese and iron oxides on titania [5]. To a lesser extent, CuO has been used as a dopant for sensor materials. The most prevalent use of CuO as a sensor dopant is in the sensing of H₂S [6, 7]. SnO₂ is doped with CuO (a p-type semiconductor), resulting in the formation of p-n junctions between SnO₂ and CuO grains. When exposed to H₂S, the CuO reacts to form CuS, a conductor, which decreases the barrier to conduction and results in a measurable resistance decrease [6]. Dutta et al. also studied the behavior of
CuO in carbon monoxide sensing [8]. At temperatures of 400° to 600 °C, titania doped with La2O3 and CuO had a better sensitivity to CO than undoped titania when tested with a background gas of N2. In this study, the primary purpose of La2O3 was to inhibit the anatase to rutile transformation, though its presence did lower the sensitivity to CO [8]. Similar results have been observed in other studies where La2O3 has been used as a dopant. Fukui and Nakane looked at La2O3 and Au as dopants in CO sensors [9], reporting that the addition of La2O3 lowered the sensitivity of SnO2 to CO, H2, CH4 and i-C4H10 by lowering the number of active sites on SnO2 on which these gases could adsorb. The gold, however, promoted CO adsorption, but not that of the other gases, resulting in a relatively selective CO sensor. [9] Kim et al. also used La2O3 as a dopant for SnO2 sensors [10]. Their sensors, which were prepared by wet impregnation techniques, were tested for sensitivity to CO2. They found the maximum gas sensitivity after a 1000 °C heat treatment, when the sensor was tested in air at 400 °C [10].

In the Dutta et al. study, the background gas used was N2. However, in many environments where a CO sensor is needed, the environment is oxidizing [8]. The exhaust gas stream of an automobile, for example, contains up to 5% O2 [11]. This chapter focuses on the behavior of titania-based sensors that have La2O3 and CuO as dopants, and how they behave in an oxygen-containing atmosphere. In addition, the sensor was tested for the interference of hydrocarbons by using CH4 as a test gas.
2.1 Experimental

2.1a Sample Preparation

Samples of anatase (A), anatase/La$_2$O$_3$ (AL), anatase/La$_2$O$_3$/CuO (ALC) and TiO$_2$/CuO were made by ball-milling commercial grade TiO$_2$ (anatase) with the desired weight percent of La$_2$O$_3$ and/or CuO in isopropanol for 4 hours. After solvent removal by evaporation, the powders were heat treated at 800 °C for 6 hours. The anatase/CuO sample was partially rutile/CuO after this treatment. Powders were then used to make sensing samples, or for characterization by diffuse reflectance infrared spectroscopy (DRIFTS).

All sensors were prepared by depositing the mixed oxide powders on alumina substrates with screen-printed gold interdigitated electrodes (shown in Figure 2.1). Powders were sieved through a 70 micron fluorocarbon mesh, weighed to 25 mg, suspended in several drops of n-heptanol and dropped by pipette onto the sensing substrate surface. The substrate was dried in an oven at 100 °C to evaporate the solvent, leaving a compact film on the surface. The sensor was then fired at 800 °C for 6 hours in air to ensure bonding of sample film to alumina substrate.

2.1b Electrical Measurements

Sensing measurements were done at 600 °C in a background gas of 5%O$_2$ (N$_2$ balance). Figure 2.2 shows a schematic of the setup for the electrical measurements. The sensors were placed in a quartz tube placed within a tube furnace (Lindberg/Blue), which kept the sensor at a constant temperature during the measurements. The sample was exposed to different test gases, which were passed through the quartz tube. Two different
measurements were made: constant temperature with varied (0-10%) oxygen concentration. and CO/CH$_4$ tests were at a constant temperature (600 °C) and background gas (5%O$_2$/N$_2$) where CO or CH$_4$ at a concentration of 250-1000 ppm was introduced. Prior to starting sensing measurements, sensors were kept at 600 °C and 5%O$_2$/N$_2$ for 2 hours to allow for sample equilibration. Additional sensing measurements were made after the sample had been at 600 °C and 5%O$_2$ for an additional 24 and 48 hours.

2.1c Sample Characterization

Infrared spectroscopy was done with Bruker Instruments IFS-66s Fourier Transform Infrared Spectrometer, with a Spectra-Tech Collector/Environmental Chamber which allows the sample to be heated and exposed to gas phase analytes during the infrared measurement. Prior to measurements, samples were heated to a setpoint temperature of 600 °C (setting on the heater assembly of the infrared cell) for two hours under a flow of N$_2$. A background measurement was made under a flow of 5%O$_2$/N$_2$, first at 800 °C (heater setting), and then at room temperature. The sample gas (either CO, CO$_2$, or CH$_4$) was introduced at a concentration of 0.5% and measurements were made at room temperature. 800 °C setpoint and then returned to room temperature. Due to thermal conductivity losses from the sample holder and the powdered samples, actual surface temperatures were typically much lower than the temperatures set on the heater assembly. At a heater setting temperature of 600 °C, the temperature of the sample cup was measured to be 325 °C, and the top of the sample surface was between 190-312 °C. For the 800 °C heater setting, the sample cup temperature was measured at 413 °C, and the sample surface ranged from 247-412 °C. It should also be noted that the thermocouple
only measures the temperature at a single spot on the sample surface, and that the packing of the powder was loose. Because of the variation in sample temperature, throughout the text, the temperature referred to is that set on the heater assembly. Measurements were made on A. AL and ALC samples and on La₂O₃ in KBr. La₂O₃/CuO in KBr and TiO₂/CuO to clarify some aspects of the AL and ALC spectra.

All the infrared data are reported in Kubelka Munk units: $KM = (1-r)^2/2r$, where $r$ is the relative reflectance ($r_0/r_s$). The reference reflectance ($r_0$) is the single channel reflectance of a sample under a flow of 5%O₂/N₂ (at room temperature or 800 °C) and the sample reflectance, $r_s$, is that of the powder in a gas stream containing either CO or CH₄. More details on the data acquisition and analysis is given in the Appendix.

X-ray diffraction patterns were collected on a Rigaku Geigerflex diffractometer using Ni-filtered CuKα radiation at 40 kV and 25 mA between 2Θ = 20° and 80°.

Scanning Electron Micrographs were taken on either a Phillips XL30 FEG SEM or a Jeol JSM-820 electron microscope.

Results

TiO₂ can exist in several crystalline modifications, the most common forms being anatase and rutile [12]. Figure 2.3 shows the structures of the two phases. In the work by Dutta et al., the focus was on the anatase phase as a sensor material, and that will be the focus here as well [8]. First, characterization of the samples by XRD and electron microscopy is reported. This is then followed by details of the sensing behavior, and finally, infrared studies of the gas-surface reactions.
2.2 Sensor Characterization

X-ray diffraction patterns were taken of the powdered samples after heat treatment, but prior to deposition on sensing substrates. Figure 2.4 shows the X-ray diffraction pattern of single phase anatase TiO$_2$, anatase that has been heat treated with the addition of CuO, and single phase rutile, all after the 800 °C, 6 hour heat treatment. The addition of CuO results in the transformation of the anatase phase of TiO$_2$ to that of rutile (Figure 2.4 b). CuO is known to promote the transformation of anatase to rutile [13-15], lowering the transformation temperature up to 300 °C [13]. CuO also promotes the grain growth of TiO$_2$ [15]. In the literature, it has been proposed that the anatase to rutile transformation nucleates at the site of anion (O$^{2-}$) vacancies in the lattice, and that Cu$^{2+}$ substitutes onto Ti metal sites upon doping, thus increasing the concentration of vacancies and promoting the transformation [13, 15, 16].

La$_2$O$_3$ is known to inhibit the transformation of anatase to rutile, increasing the transformation temperature as much as 150 °C [17]. Figure 2.5 shows the diffraction patterns of anatase, anatase doped with La$_2$O$_3$ and anatase doped with La$_2$O$_3$ and CuO, demonstrating that the anatase to rutile transformation is suppressed. It is thought that because of its size, the La$^{3+}$ cation occupies interstitial positions in the TiO$_2$ structure. This results in a decrease in the concentration of oxygen vacancies in TiO$_2$, inhibiting the transformation [12]. Other researchers have proposed that La$_2$O$_3$ forms a surface layer on TiO$_2$, and that this surface LaO$_x$ species prevents the anatase to rutile transformation by preventing grain growth [17, 18].

X-ray diffraction measurements were also made after the sensors had been tested to assure that no further anatase to rutile conversion had occurred in the sample after
exposure to high temperatures for prolonged times. Figure 2.6 shows the XRD patterns of the ALC sample after heat treatment as a powder and after sensing measurements have been done. No transformation of anatase to rutile was observed after all of these heat treatments.

Electron microscopy was also done on the sensing samples. Figure 2.7 shows the top and side view of typical TiO₂-based sensors. The top view (Figure 2.7a) shows that the sensor is highly porous, with clusters of La₂O₃ and CuO on the surface [8]. The anatase particles are approximately 100 nm in size, while the clusters of La₂O₃ are between 300 and 600 nm, and the clusters of CuO are less than 100 nm. The cross-sectional picture was taken of an anatase sensor, and shows that the thickness of the sensing film is approximately 100 μm.

A transmission electron micrograph of an ALC sample is shown in Figure 2.8 [8]. Despite the clustering apparent in the SEM micrograph shown in Figure 2.7a, there are isolated CuO particles on the anatase. A CuO particle of approximately 9 nm is size is shown on the surface of an anatase particle in the figure. Aside from the clusters of La₂O₃, there was no evidence of individual La₂O₃ particles, or a surface layer of LaOₓ species on the TiO₂. [8]

2.3 Sensing Behavior

Figure 2.9 compares the relative resistance change (defined as R/Rₒ, where R and Rₒ are the resistances in the presence of the sensing gas and background gas, respectively) of A, AL and ALC film sensors upon exposure to CO and CH₄ in the presence of 5%O₂/N₂ at 600 °C. In the case of A and AL samples (Figures 2.9a,b), the
resistance change upon exposure to both CO and CH₄ is significant. The addition of La₂O₃ does not alter the sensing properties, except for the change in baseline resistance which increases from ~1.5 MΩ for the anatase sensor to ~2 MΩ for the AL sensor. With the addition of CuO to the sample, there is a dramatic change in the sensing behavior (Figure 2.9c). The overall sensitivity of the sample is lower than the A and AL sensors towards both CO and CH₄. However, since the ALC sensor response remains close to a R/R₀ value of 1 for CH₄ levels between 0-1000 ppm, a CO selective sensor was obtained. The baseline resistance of the ALC sensor is ~1.5 MΩ. The bars in Figure 2.9c indicate the results from three different ALC sensors, and provide information on the extent of reproducible fabrication of these sensors. The baseline resistance of the sensor, as well as the relative resistances at 250, 500, 750 and 1000 ppm of gas, are given for the three samples in Table 2.1 (CO) and Table 2.2 (CH₄).

The A, AL and ALC sensor were kept at 600 °C for a total of 48 hours, and the sensor responses were measured. Figure 2.10 shows the change in the sensing response of the three samples over time in their response to CO. A drift in the baseline resistance was noted for all samples, each of them increasing. The percent change in the relative resistance (for CO) was approximately -12% for A, +37% for AL and +12% for ALC. However, even after extended aging, the response to CH₄ for the ALC sensor remained essentially unchanged, as shown in Figure 2.11.

The recovery of the A, AL and ALC sensors is shown in Figure 2.12. The 90% recovery in resistance upon turning off the CO took about ~10 minutes for A and AL sensors, and 0.5 minutes for the ALC sensor. These times serve as a good comparison.
between the three samples, but should not be judged on an absolute basis since the dead volume of the sensing system is 350 ml.

Figure 2.13 shows the change in relative resistance for the ALC sensor at a fixed concentration of CO (500 ppm) with varying concentrations of CH₄ in the gas stream. The resistance change appears to be relatively independent of methane, confirming the CO selectivity of the ALC sensor.

Figure 2.14 shows the change in relative resistance at a fixed concentration of sensing gas (750 ppm CO or CH₄) as a function of oxygen content in the gas stream for the A and ALC sensors. On the anatase sample, both CO and CH₄ sensing data indicate an increase in sensitivity with decreasing oxygen levels. However, for the ALC sensor (Figure 2.14b), while increased sensitivity is observed for CO sensing with decreasing O₂, for CH₄, the resistance remains mostly unchanged with O₂. These data demonstrate that for the ALC sensor, CH₄ sensing is insensitive to O₂ over a wide range of O₂ concentrations.

2.4 Adsorption of CO and CH₄ on the titania surface

The infrared (IR) spectroscopic measurements in this study were done under conditions of constant gas flow at atmospheric pressures and should provide a realistic idea of what species are being produced and adsorbed under typical sensing conditions. Additionally, the background gas was always a mixture of oxygen and nitrogen, conditions similar to those used during sensing. Most of the data presented here are in-situ IR spectra obtained with a heated diffuse reflectance cell at heater settings of 800 °C (see experimental section for details on sample temperature).
The characteristic IR band of gas phase CO occurs at 2143 cm\(^{-1}\) and for CH\(_4\) at 1304 and 3016 cm\(^{-1}\), with both molecules exhibiting rotational structure [19, 20]. For all the samples, gas phase IR bands were observed upon introduction of CO or CH\(_4\) into the spectral cell. As the temperature was raised, the peaks due to the gas phase molecules decreased in intensity and were accompanied by the formation of gas phase CO\(_2\), as confirmed by the doublet around 2345 cm\(^{-1}\).

The IR spectra of the samples upon adsorption of gases at the heater setting of 800 °C were examined in order to correlate the chemistry on the solid surface with the sensing behavior. No infrared peaks characteristic of chemisorbed CO or CH\(_4\) were observed on any of the samples. The lack of chemisorbed species at the high temperatures is consistent with previous studies [19] as infrared bands due to chemisorbed CO are typically observed on anatase surfaces at room temperature and below on heavily reduced surfaces and under vacuum conditions [19, 21]. However, if the samples were exposed to CO at heater settings of 800 °C, brought back to ambient temperature and the IR spectra examined after the CO was replaced with background gas, bands due to chemisorbed species were observed. Figure 2.15 compares the IR spectra in the CO stretching region for A. TiO\(_2\)/CuO and ALC. A weak band around 2100 cm\(^{-1}\) (Figure 2.15a) is observed on anatase. Baraton reported a broad band at 2044 cm\(^{-1}\) due to CO chemisorption on titania at room temperature[19]. Tanaka and White reported that two bands at 2185 and 2115 cm\(^{-1}\) due to chemisorbed CO were formed on anatase at ambient temperatures, with evacuation resulting in loss of the 2185 cm\(^{-1}\) band. They proposed that surface reduction of anatase occurred upon exposure to CO [21]. Busca et
al. identified a band at 2100 cm\(^{-1}\) as CO chemisorbed on Ti\(^{3+}\) [22], which is comparable to the present observation and an earlier study by Dutta et al. in an anaerobic environment [8, 22].

Figures 2.15b and 2.15c show that in the presence of CuO, there is a significant increase in the intensity of the chemisorbed CO band, indicating that Cu is promoting CO adsorption. Bands were observed at 2108 cm\(^{-1}\) on CuO/TiO\(_2\) and 2090 cm\(^{-1}\) on ALC. The frequency of the CO stretch is known to vary with the copper oxidation state as follows: Cu\(^{0}\): 2105 - 2130 cm\(^{-1}\), Cu\(^{+}\): 2115 - 2130 cm\(^{-1}\) and Cu\(^{2+}\): 2140 to 2190 cm\(^{-1}\) at temperatures below 77 K [23-25]. Boccuzzi and Chiorino have reported a strong band at 2103 cm\(^{-1}\) along with shoulders at 2017 and 2128 cm\(^{-1}\) for CO on Cu/TiO\(_2\) [23]. Based on the literature, we assign the 2108 cm\(^{-1}\) band on TiO\(_2\)/CuO and the 2090 cm\(^{-1}\) on ALC to CO adsorption on Cu\(^{0}\). Inclusion of La\(_2\)O\(_3\) in the ALC sample appears to make the surface more electron-rich and leads to an 18 cm\(^{-1}\) red shift. The effect of La\(_2\)O\(_3\) on the reducibility of CuO has been noted in Temperature Programmed Desorption (TPD) studies by Jiang et al. [26]. It is also important to note that the CO is reducing the CuO to form Cu\(^{0}\) in an oxidizing environment at elevated temperatures. No CO chemisorption was noted on La\(_2\)O\(_3\) or La\(_2\)O\(_3\)/CuO samples under conditions comparable to the ALC sample. This suggests that the bulk CuO present in the ALC sample is not contributing to the IR spectrum with CO, presumably because of its low levels of concentration.

In the case of CH\(_4\), there was no evidence of chemisorption on any of the samples. Replacing the CH\(_4\) in the gas stream by O\(_2\)/N\(_2\) led to the loss of IR bands due to CH\(_4\).
2.5 Reaction Intermediates

The formation of intermediates as the gas molecules reacted on the sample surfaces was monitored via the IR spectra in the 1200 - 1800 cm$^{-1}$ region at heater settings of 800 °C. As mentioned earlier, for both CO and CH$_4$ reactions on the samples, CO$_2$ was found to be a product. In order to distinguish the reaction intermediates formed on the sample surfaces during CO and CH$_4$ oxidation from species formed via adsorption of the product gas CO$_2$, the IR spectra upon CO$_2$ reaction with La$_2$O$_3$ and ALC, also at high temperature were examined. The corresponding infrared data are shown in Figure 2.16. Strong bands were observed at 1447 and 1395 cm$^{-1}$ on La$_2$O$_3$ and weaker bands at 1515 and 1376 cm$^{-1}$ on ALC. This frequency range is typical of the asymmetric stretching vibration ($v_3$) of the carbonate ion [27]. Splitting of the $v_3$ band upon change in coordination of the carbonate ligand has been extensively studied [27]. A simple criterion for distinguishing between mono and bidentate carbonate is the extent of splitting of the $v_3$ band. ~ 100 and ~ 300 cm$^{-1}$ for mono and bidentate, respectively. La$_2$(CO)$_3$ · 8H$_2$O is reported to have strong infrared bands at 1460 and 1360 cm$^{-1}$, with a shoulder at 1330 cm$^{-1}$ and assigned to a monodentate coordinated carbonate group [28]. Thus, considering that the splitting is of the order of 52 and 139 cm$^{-1}$ on La$_2$O$_3$ and on ALC, respectively, these bands can be assigned to monodentate carbonate species coordinated to the La. It has also been reported that the value of the splitting within a fixed coordination geometry increases with the polarizing power of the coordinating cation [27, 29]. The considerably larger splitting in the ALC sample is indicative of the fact that the environment of the La in the ALC sample is quite distinct from La$_2$O$_3$. 

58
Figure 2.17 shows the data for CO reaction on A. La$_2$O$_3$. AL and ALC surfaces. The frequencies of the IR bands are distinct from those shown in Figure 2.16 formed via CO$_2$ reaction, indicating that we are not observing bands related to the adsorption of the reaction product CO$_2$. The intensity axis (y-axis) in Figure 2.17 has been kept the same in all cases to provide a quantitative picture of the extent of reaction. On the anatase surface, as well as on TiO$_2$/CuO (not shown) no bands were observed at heater settings of 800 °C. Literature reports indicate that reaction products of CO on metal oxide surfaces are only observed at low temperatures. Bands at 1420 and 1600 cm$^{-1}$ assigned to bicarbonate species have been reported on exposure of anatase to CO [21]. Bands around 1370 and 1680 cm$^{-1}$ assigned to carbonylate like species have been reported upon exposure of anatase to CO at room temperature, but these species disappear at ~ 100 °C indicating weak binding to the surface [19]. Harrison and Guest have reported the formation of bidentate, monodentate and carboxylate species upon exposure of SnO$_2$ to CO. and beyond 127 °C. the monodentate carbonates became the dominant species[30]. Harrison and Willet have examined the infrared spectra after exposure of CO to SnO$_2$. pretreated at various temperatures. These experiments were done at 56 °C and evidence was found for mono, bidentate and carbonylate species[31]. Supported CuO has been reported to exhibit infrared absorptions for bidentate and monodentate carbonates in the presence of either CO or CO$_2$, but at considerably lower temperatures [32]. The sensing data on anatase (Figure 2.9a) confirm the reactivity of the surface towards CO, and the absence of IR bands indicate that the concentration of the intermediate oxidation products of CO on the anatase surface at the elevated measurement temperatures is too small to be detected.
Upon addition of La$_2$O$_3$ to anatase, several bands were observed upon CO exposure for both AL and ALC samples, even at the heater settings of 800 °C. In order to verify that the IR signal was not arising from reactions on bulk La$_2$O$_3$ in the AL and ALC samples, pure La$_2$O$_3$ was also examined. In the case of CO reaction on La$_2$O$_3$, peaks were observed at 1540, 1474, 1375 and 1347 cm$^{-1}$ (Figure 2.17b). The intensity of these peaks were at least an order of magnitude lower than the AL and ALC samples, demonstrating that the contribution of the free La$_2$O$_3$ to the spectroscopic signal in AL and ALC sample is negligible. The two sets of bands at 1540, 1347 cm$^{-1}$ and 1474, 1375 cm$^{-1}$ on La$_2$O$_3$ are assigned to bidentate and monodentate carbonates, respectively. Rosynek and Magnuson assign monodentate carbonates at 1500 and 1390 cm$^{-1}$, with bidentate carbonates at 1565 and 1310 cm$^{-1}$ on La$_2$O$_3$ [33]. Tsyganenko et al. have reported carbonate bands formed via CO oxidation on La$_2$O$_3$ at 1559 and 1317 cm$^{-1}$ along with weaker bands at 1465, 1393 and 1330 cm$^{-1}$, which appear to be similar to the data shown in Figure 2.16b [34].

For reaction of CO on the AL sample (Figure 2.17c), intense bands at 1503 and 1356 cm$^{-1}$ are assigned to monodentate carbonates. For the ALC sample, there is a strong and broad absorption band centered at 1449 cm$^{-1}$ which cannot readily be assigned to either monodentate or bidentate carbonates. These bands are assigned to polydentate carbonates. Complicated polydentate bridged structures in which all three oxygens are bound to metal ions usually show smaller $\Delta\nu_2$ splitting [27]. Bocuzzi et al. have proposed that CO on Cu/ZnO can be held by bonding to both the Cu and Zn sites, with the bonding to Zn via a $\pi$-bond [35]. It is proposed that a similar adsorbed species exists on the ALC samples, with the carbonate bonded to the La at the Ti/Cu interface.
Figure 2.18 shows the infrared data for CH₄ reaction on A, La₂O₃, AL and ALC samples monitored at heater settings of 800 °C. No products were noted on anatase, as with the CO experiments. However, on La₂O₃, strong bands are observed with CH₄ at 1492 and 1352 cm⁻¹ (Figure 7b), indicative of monodentate carbonates. Strong bands were also observed on the AL sample at 1492, 1463, 1435 and 1382 cm⁻¹ (Figure 2.18c), and appears to be a combination of spectra of CO₂ and the CH₄ reaction on La₂O₃ (combination of Figures 2.15a and 2.18b). Thus, bulk La₂O₃ may be contributing to the infrared spectra. The difference between the CH₄ and CO oxidation on La₂O₃ may arise from the fact that CH₄ oxidation leads to formation of H₂O. La₂O₃ has been reported to form La(OH)₃ in the presence of water and such hydrated lanthanum can be readily carbonated, even under ambient conditions [36]. Moreover, thermal analysis of the hydroxycarbonate species have shown that CO₂ desorption occurs beyond 677 °C [36]. There is evidence of a band at 3499 cm⁻¹ due to the OH stretching on the La₂O₃ samples that were exposed to CH₄, strongly suggesting that hydroxycarbonates are forming on the sample.

Finally, Figure 2.18d shows that in the case of CH₄ oxidation on the ALC sample, there is no appearance of any intermediate carbonates. Clearly, the inclusion of CuO appears to be inhibiting the formation of carbonates on the sample surface.

Discussion

The two interesting aspects of this study are the discovery that ALC is a high temperature CO sensor relatively insensitive to CH₄ and that ALC exhibits reasonably rapid recovery upon turning the CO off in the gas stream, as compared to the A and AL.
samples. This discussion will focus on the role of lanthanum and copper in reducing the sensitivity of ALC towards CH₄ though keeping the response to CO at reasonable levels. Understanding the origin of the lack of sensing response of ALC towards CH₄ even at temperatures as high as 600 °C, as compared to the A and AL samples, is of importance since it will provide the framework for development of high temperature selective sensors.

2.6 Nature of ALC: Role of La₂O₃

Consistent with previous studies, La₂O₃ does inhibit the anatase to rutile transformation. From TEM analysis, there is no evidence of a surface LaO₅ species, indicating that if anything beyond the La₂O₃ clusters seen by SEM are present, it is very thin and subsurface deep [8],[18]. The infrared data, however suggests that there are LaO₅ species on the TiO₂ surface, though it does not preclude the fact that La may be penetrating into the TiO₂.

First, the intermediate carbonate species are observed on AL and ALC samples, but not on A, and the frequencies are different from that on La₂O₃ crystallites, suggesting a different form of La on the anatase surface. Second, CO chemisorption on Ti³⁺ sites occur in A but not on AL samples, indicating that the surface redox properties of A has been modified in the AL samples. Third, the frequency of the CO stretch is different for CO adsorption on TiO₂/CuO with and without La₂O₃, again suggesting that the presence of La is altering the electronic properties of the ALC surface. These observations can be explained if a layer of LaO₅ is present on the titania surface. The presence of a LaO₅ surface phase on titania has been previously noted by Nair et al. [18]. They suggest that
La$^{3+}$ wets the surface of the titania particles. Similar surface LaO$_x$ phases have been proposed on alumina [37]. LaO$_x$ species decorating the surface of Ni crystallites has also been proposed as the active catalyst in CO$_2$ reforming of CH$_4$ to synthesis gas. The role of LaO$_x$ was thought to involve storage of CO$_2$ in the form of La$_2$O$_2$CO$_3$ and release of it to appropriate Ni-based reaction sites [38].

It is proposed that the presence of lanthanum oxide on the anatase surface is providing the sites for adsorption of the reaction intermediates during CO and CH$_4$ oxidation. On the anatase surface at high temperatures, there is no way to detect these intermediate species. The stability of lanthanum carbonates at high temperatures [34] makes it possible to observe the extent of reaction on TiO$_2$. Previous studies have noted the formation of carbonates upon CO oxidation on Cu/Al$_2$O$_3$ support, with the Al$_2$O$_3$ playing a similar role to that of LaO$_x$ on the AL and ALC samples [24, 32]. However, the carbonates were not used for the type of diagnostic study that is presented here.

2.7 Sensing Mechanism

To correlate the resistance change during sensing with the infrared data, it is important to highlight the relationship between these measurements. In order for resistance changes to occur, oxidation of CO/CH$_4$ must involve reaction with O$^\circ$(ads) on the titania surface, desorption of the oxidation products from titania and the release of electrons into the bulk solid. Thus, if carbonate species remain on the anatase surface, the resistance change is not going to be manifested. No carbonate species are observed on the anatase surface in the A sample, indicating that at the temperatures at which infrared measurements are being made, most of the carbonates have desorbed. However, in the
AL and ALC samples, we do observe intermediate carbonate species that we assign as originating from the LaO$_x$ on the anatase surface. It is proposed that these lanthanum carbonates are not influencing the resistance of the sample, as they are formed by release of oxidation products from the anatase surface and immediate interaction with the LaO$_x$ because of the intimate contact of LaO$_x$ with the anatase.

Of primary interest is the difference in sensing behavior of ALC towards CO and CH$_4$. The CO results are discussed first. The studies described above indicate two forms of copper on supported catalysts. For CuO/Al$_2$O$_3$, a Cu$^{2+}$ surface phase as well as discrete CuO particles were found to be present on Al$_2$O$_3$ [39]. Jiang et al. also report that highly dispersed CuO is present on La$_2$O$_3$-CuO/$\gamma$-Al$_2$O$_3$ catalysts [26]. Larsson et al. have found that CuO/TiO$_2$ consists of well dispersed CuO$_x$ species as well as CuO crystallites [5]. The dispersed CuO$_x$ species have high catalytic activity for combustion and similar results have also been reported for Cu-Ce oxide catalysts [5]. The transmission electron microscopy of ALC indicated the presence of nanometer-sized CuO crystallites decorating the surface of anatase (Figure 2.8) [8]. No evidence was found for a distinct CuO$_x$ coating on the titania by electron microscopy indicating that such a layer, if present, must be very thin with the copper well dispersed.

The role of these two types of copper on oxidation reactions has been discussed in the literature. Cu(II)-SnO$_2$ system has been investigated for catalytic oxidation of CO and the role of Cu$^{2+}$ has been proposed to be a scavenger of electrons following reaction of CO with surface oxygen (O$^2_-$) and desorption of CO$_2$. In this case, only surface Cu$^{2+}$ was proposed to be active, and formation of CuO was predicted to kill catalytic activity [40]. Park and Ledford have examined the catalytic activity of CuO/Al$_2$O$_3$ towards CO and
CH₄ oxidation. They noted that CO oxidation is promoted on distinct CuO crystallites, but poor on the highly dispersed Cu²⁺ surface phase on Al₂O₃ [39]. Two pathways that have been proposed for CO oxidation on Cu/TiO₂ and Cu/ZnO include direct oxidation of CO adsorbed on metallic particles by gas phase oxygen or reaction of the adsorbed CO at the metal/metal oxide interface with surface lattice oxygen to form carbonate-like species that are desorbed as CO₂ [23]. The latter pathway can be written as follows:

\[
\text{CuO} \cdot O_2(O_{\text{ads}}) + CO \rightarrow \text{CuO} \cdot \text{OCO}_2(O_{\text{ads}}) \rightarrow \text{Cu} + \text{CO}_2 + O_2(O_{\text{ads}})
\]

The copper valence in the catalytic reaction was proposed to cycle between Cu(II) and Cu(0) [41]. A redox cycle mechanism involving CuO and Cu₂O has also been proposed for CO oxidation on CuO [42].

With this background on CO reactions on Cu, two interrelated issues can be discussed. First, why does the ALC sensor, even though it adsorbs more CO, have a lower sensitivity (smaller R/R₀) than the A and AL sensor (Figure 2.9). Second, why is the sensitivity of the ALC sensor reduced in the O₂ environment as compared to anaerobic environment (Figure 2.14) [8]. Based on the IR studies, it is clear that the addition of CuO to the AL sample improves the adsorption of CO via reduction of the CuO surface, thereby providing sites for CO adsorption. The resistance change that is measured upon CO sensing indicates that adsorbed oxygen species on TiO₂ (O₂⁻, O⁺, O²⁻) are involved in the CO oxidation. A possible reaction model would involve adsorption of CO on the reduced CuO on anatase and migration of CO to the Cu-TiO₂ interface where the oxidation occurs [8]. In an anaerobic environment, the oxygen species on the anatase are the main source for CO oxidation. Since the adsorption of CO on the ALC sensor is larger, the ALC sensor should have higher sensitivity than A or AL since more oxygen on
the titania surface is reacting. In the presence of O\textsubscript{2}, direct oxidation of CO on the copper species can occur, without involvement of TiO\textsubscript{2}, which would lead to decreased sensitivity, as compared to A and AL, where reaction has to occur on the anatase surface.

The other issue of importance is the insensitivity of ALC towards CH\textsubscript{4} sensing. There is no evidence for any chemisorption of CH\textsubscript{4} to the surface. This is probably not surprising, considering that the hydrogen atoms do not provide a convenient atom for chemisorption and the carbon atom is saturated. The infrared data provide clues regarding the insensitivity of ALC towards CH\textsubscript{4}. In the case of AL sample, monodentate carbonate species are evident for both CO and CH\textsubscript{4} oxidation, however in the presence of CuO, the carbonate bands have disappeared in the case of CH\textsubscript{4} reaction. The lowered reactivity of CH\textsubscript{4} directly on the anatase surface in ALC is also evident from the data shown in Figure 2.14, which shows the relative resistance changes as a function of O\textsubscript{2} in the gas stream. There is increased sensitivity towards CO when decreased amounts of oxygen are present, indicating enhanced reaction on the anatase surface. In the case of methane oxidation, the same cannot be said. While on A, the oxygen dependence is apparent, the sensitivity of methane on ALC is relatively independent of oxygen, indicating lower reactivity with the anatase surface even under low oxygen concentrations.

It is proposed that the inhibition of CH\textsubscript{4} reaction on ALC is related to the catalytic activity of the CuO. Optimal CH\textsubscript{4} oxidation has been reported for isolated Cu\textsuperscript{2+} species on Al\textsubscript{2}O\textsubscript{3} [39]. Studies where bulk CuO was dispersed in a matrix have shown a decrease in methane oxidation activity compared to samples of similar concentrations made with wet impregnation techniques [43]. The sensing temperatures of 600 °C is near the reported values of 50% oxidation (T\textsubscript{50}) for methane by CuO based catalysts. [44] and the
presence of La$_2$O$_3$ is known to lower the $T_{50}$ and $T_{99}$ of CuO, suggesting that oxidation of CH$_4$ must be occurring on ALC. Though it has been reported that in an anaerobic environment on Cu/TiO$_2$ catalysts, metal - Ti$^{n+}$ (n < 4) or metal Ti$^{n+}$ - O$^{m-}$ sites can activate CH$_4$ as well as promote the decomposition of intermediate oxidation products. the presence of oxygen may minimize the importance of this pathway [45]. La$_2$O$_3$ is also known to promote the activity of CuO/γ-Al$_2$O$_3$ towards CO and CH$_4$ oxidation by increasing the oxygen recovery rate on the CuO [26]. This would also promote oxidation on the CuO without involving titania, and is the most likely pathway for methane oxidation. So, both CO and CH$_4$ are getting oxidized on the copper species, but methane appears to have minimal interaction with the anatase surface, suggesting that the type of copper species being formed on the ALC sample is an excellent catalyst towards CH$_4$ oxidation.

A second hypothesis for why the ALC samples show no resistance change upon exposure to CH$_4$ could arise from the fact that the products and intermediates of the CH$_4$ oxidation, such as water, can adsorb onto the surface of the sensor and trap electrons. When water is adsorbed in molecular form it can have donor properties [46]:

$$\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^\ast_{(\text{ads})} + e^- $$ (2.2)

However, if water is adsorbed dissociatively as hydroxyl groups, it will behave as an acceptor [46]:

$$\text{H}_2\text{O} + \text{O}_2 \rightarrow 2 \text{OH}_{(\text{ads})} $$ (2.3a)

$$\text{OH}_{(\text{ads})} + 2e^- \rightarrow 2\text{OH}^-_{(\text{ads})} $$ (2.3.b)

At lower temperature, there would be mostly molecular adsorption, and as the temperature increases, the water would adsorb more in the form of a hydroxyl group.
Giber et al. noted that for H₂ sensing between 590-650 °C, the resistance ratio (R/R₀) decreases, whereas there is an increase in R/R₀ between 650-780 °C, consistent with the explanation that at higher temperatures, the OH from H₂O (product of H₂ oxidation) is trapping electrons. The creation of OH groups on the sample surface during methane oxidation has been noted. Even though such an electron trapping mechanism could play a role, the lack of any carbonate products on the ALC surface indicates that the modification of the chemical reactivity of CH₄ is more important.

2.8 Response Times

The increased response time for the ALC versus the AL sample can be explained based on the ease of oxygen readsortion and the role of the reduced Cu. The IR spectrum of the intermediates formed upon CO oxidation on the ALC surface have been assigned as due to polydentate carbonates partly held by the Cu. Upon turning off the CO, these Cu species can get oxidized by O₂, releasing the carbonate as CO₂ and freeing up the surface sites for oxygen readsortion. In the case of AL samples, the carbonates are bound to the surface and not influenced by redox chemistry and will be replaced by O₂ at slower rates.

2.9 Sample Aging

There are two important features in the aging of A. AL and ALC sensors. Firstly, in all three cases, the baseline resistance of the sensor increases over time. Some authors have attributed sensor aging to either an increase in the sintering between particles, or a net loss of oxygen from the sample over time [47]. Both of these scenarios would result
in a decrease in the sensor resistance, however. For this system, it seems more likely that there is an increase in the amount of oxygen in the lattice (i.e. a decrease in the number of oxygen vacancies), or an increase in the surface adsorbed oxygen, both of which would give the measured resistance increase. As this is a polycrystalline sample, and Schottky barriers between grains control the overall resistance of the sample, and therefore the surface oxygen is most important. As the sample is held at longer times in the 5% O₂ background, more O₂ adsorbs on the sensor, the increased time allowing better diffusion throughout the entire thickness of the film.

Alternatively, the presence of water could be a factor in the sensor aging. The removal of molecular water from the surface of TiO₂ over time, would cause an increase in the resistance over time according to Equation 2.2. Harkoma-Mattila et al. report that it took up to 24 hours at 500 °C for SnO₂ to fully recover from exposure to humid air [48]. However, most studies of TiO₂ show that most H₂O is removed from the surface of the sample by 400 °C [49] [50]. Furthermore, surface hydroxyl groups, not molecular water, would be dominant at the sensing temperatures and their removal would cause a resistance decrease according to equation 2.3.

A second important effect of aging is the change in the relative resistance in response to CO and CH₄. Except for the anatase sensor in its response to CO, all of the relative resistance changes are decreased (increase in sensitivity) over time. A similar result occurs on SnO₂ sensors. Ionescu and coworkers observed a decreased CH₄ sensitivity in the presence of H₂O, and proposed that CH₄ and H₂O compete for the same sites on the SnO₂ surface [51]. However, the effect of water on TiO₂ aging has been discounted above. Instead, the change in the surface oxygen concentration must also be
responsible for the change in sensor response to CO and CH$_4$. With a greater number of surface oxygen species, there is a greater number of surface sites for reaction, leading to the increased sensitivity.

In the case of CO on anatase, it is proposed that the decreased sensitivity occurs because CO on anatase can react by two different mechanisms, either reacting with surface O$_2$ from the gas phase, or by adsorbing on Ti$^{3+}$ sites, then reacting with adsorbed or gas phase oxygen species. Increases in the oxygen concentration over time may reoxidize the Ti$^{3+}$ sites, eliminating a pathway for CO oxidation on TiO$_2$.

2.10. Conclusion

An anatase based semiconducting oxide sensor was discovered to be selective for CO sensing with almost complete discrimination against CH$_4$ at operating temperatures of 600 °C. In order to maintain the anatase phase, La$_2$O$_3$ was added which inhibited the anatase to rutile transformation. The lanthanum oxide layer that formed on the anatase also served as an excellent probe for monitoring the extent of CO and CH$_4$ oxidation on the anatase by trapping the reaction products as carbonates, which could be readily detected by high temperature diffuse reflectance infrared spectroscopy. The key player in achieving selectivity towards CO versus CH$_4$ was CuO, which efficiently catalyzed CH$_4$ oxidation, thus minimizing the reaction of CH$_4$ on the anatase surface.
References


Table 2.1: Absolute and relative resistance of titania-based sensors to CO at 600 °C, 5%O₂/N₂.

<table>
<thead>
<tr>
<th>CO</th>
<th>Baseline R (MΩ)</th>
<th>R/R₀</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>250 ppm</td>
<td>500 ppm</td>
</tr>
<tr>
<td>Anatase</td>
<td>1.505</td>
<td>0.5706</td>
</tr>
<tr>
<td>Anatase/La₂O₃</td>
<td>1.839</td>
<td>0.6581</td>
</tr>
<tr>
<td>Anatase/La₂O₃/CuO</td>
<td>1.428</td>
<td>0.8361</td>
</tr>
</tbody>
</table>

Table 2.2: Absolute and relative resistances of titania-based sensors to CH₄ at 600°C, 5%O₂/N₂.

<table>
<thead>
<tr>
<th>CH₄</th>
<th>Baseline R (MΩ)</th>
<th>R/R₀</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>250 ppm</td>
<td>500 ppm</td>
</tr>
<tr>
<td>Anatase</td>
<td>1.508</td>
<td>0.7808</td>
</tr>
<tr>
<td>Anatase/La₂O₃</td>
<td>2.074</td>
<td>0.8087</td>
</tr>
<tr>
<td>Anatase/La₂O₃/CuO</td>
<td>1.553</td>
<td>1.0006</td>
</tr>
</tbody>
</table>
Figure 2.1: Scale drawing of sensing substrate. (Adapted from drawing by Laurie Dudik, Electronics Design Center, Case Western Reserve University)
Figure 2.2: Schematic of apparatus used for sensing measurements.
Figure 2.3: Unit cells of a) anatase and b) rutile. (Adapted from reference 52)
Figure 2.4: XRD patterns of the TiO$_2$ and TiO$_2$/CuO after an 800 °C heat treatment. a) anatase, b) TiO$_2$/CuO, c) rutile.
Figure 2.5: XRD patterns of doped anatase after heat treatment at 800 °C. a) anatase; b) anatase/La₂O₃; c) anatase/La₂O₃/CuO.
Figure 2.6: X-ray diffraction pattern of anatase/La$_2$O$_3$/CuO a) before preparation of sensing film and b) after sensing measurement.
Figure 2.7: SEM micrographs of titania-based sensor. a) top-view (Adapted from reference 8); b) cross-section.
Figure 2.8: TEM micrograph of CuO particle on anatase. (Adapted from reference 8)
Figure 2.9: Response of titania-based sensors to CO and CH\textsubscript{4} at 600 °C and 5\%O\textsubscript{2}/N\textsubscript{2}. a) anatase; b) anatase/La\textsubscript{2}O\textsubscript{3}; c) anatase/La\textsubscript{2}O\textsubscript{3}/CuO.
Figure 2.10: Aging of titania-based sensor over time to CO exposure. a) anatase; b) anatase/La$_2$O$_3$; c) anatase/La$_2$O$_3$/CuO.
Figure 2.11: Aging of titania-based sensor over time to CH₄ exposure. a) anatase; b) anatase/La₂O₃; c) anatase/La₂O₃/CuO.
Figure 2.12: Recovery response of titania-based sensors at 600 °C and 5%O_2/N_2. a) anatase; b) anatase/La_2O_3; c) anatase/La_2O_3/CuO
Figure 2.13: Response of anatase/La₂O₃/CuO sensor to CH₄ in a background gas of 500 ppm CO/5%O₂/N₂ at 600 °C.
Figure 2.14: Effect of oxygen on the relative resistance change of titania sensors. Measurement made at 600 °C with 5%O₂/N₂ and 750 ppm CO or CH₄. a) anatase; b) anatase, La₂O₃/CuO.
Figure 2.15: Infrared data at room temperature after exposure to CO at a heater setting of 800 °C. Measurements made under a flow of 5% O₂/N₂. a) anatase; b) TiO₂/CuO; and c) anatase/La₂O₃/CuO.
Figure 2.16: Infrared data for the CO$_2$ reaction at a heater setting of 800 °C. 
a) La$_2$O$_3$; b) anatase/La$_2$O$_3$/CuO.
Figure 2.17: Infrared data for the CO reaction at a heater setting of 800 °C. 
a) anatase; b) La$_2$O$_3$; c) anatase/La$_2$O$_3$; d) anatase/La$_2$O$_3$/CuO.
Figure 2.18: Infrared data for the CH$_4$ reaction at a heater setting of 800 °C. a) anatase; b) La$_2$O$_3$; c) anatase/La$_2$O$_3$; d) anatase/La$_2$O$_3$/CuO.
CHAPTER 3

CHARACTERIZATION OF SURFACE SPECIES ON TITANIA-BASED SAMPLES

Introduction

In Chapter 2, infrared studies were used to understand the mechanism for selective sensing of carbon monoxide by anatase/La$_2$O$_3$/CuO sensors. Due to the presence of LaO$_x$ species on the titania surface, the extent of the reactions of both CO and CH$_4$ on anatase, anatase/La$_2$O$_3$ and anatase/La$_2$O$_3$/CuO surfaces was monitored, leading to the conclusion that the presence of CuO minimized the reaction of CH$_4$ on the anatase surface, resulting in the selective behavior.

Bidentate, monodentate and polydentate carbonate species were identified as the dominant species on the doped-titania surfaces. It was noted that the positions of the bands for these different species were dependent upon both the nature of the surface, anatase/La$_2$O$_3$ vs. La$_2$O$_3$, for example, and on the gas involved in the reaction. This chapter will further investigate the nature of carbonate species formed via CO and CH$_4$ oxidation reactions by looking at the infrared spectra as a function of temperature.

There is a wealth of infrared studies in the literature regarding the nature of TiO$_2$ and supported and unsupported CuO on exposure to CO, and a slightly more limited amount
on La₂O₃ systems [1-7]. CO typically adsorbs on the surface of TiO₂ with peak positions reported between 2044 and 2200 cm⁻¹, depending on the level of oxidation and hydration of the sample [5-7]. Weak carbonate and carboxylate species have also been observed on TiO₂ after prolonged exposure to CO [5, 6]. Table 3.1 summarizes the species that have been observed on titania surfaces.

Bulk CuO and supported CuO adsorb CO at a range of sites as well, dependent on the state of reduction of the sample. Studies of bulk CuO assign bands from 2088 to 2115 cm⁻¹ to Cu⁺ sites on CuO [8], while reports of supported CuO suggest that peaks in this region are due to Cu⁰ sites [9, 10]. CO on the Cu²⁺ sites of CuO are assigned at 2172 cm⁻¹ [10]. Carbonate species have been observed on samples of titania supported CuO at room temperature, but have been attributed to titania surface species, not ones on CuO [11]. There are reports of carbonate species formed on CuO alone, as detailed in Table 3.2.

Studies on the reactivity of CO on La₂O₃ have reported the presence of carbonite, CO₂⁻, and carbonate species, the latter stable up to 700 °C [3, 4]. The carbonate species that form may be on the surface, or indicate the formation of a bulk lanthanum carbonate phase. If the atmosphere contains moisture, hydroxyl groups easily form on the La₂O₃ surface, leading to hydroxycarbonate formation. Table 3.3 summarizes the various bands that have been observed on La₂O₃ upon exposure to CO and CO₂.

Little information about the oxidation of CH₄ on various oxides is available. Primarily, the focus has been on the oxidative coupling of methane to form higher hydrocarbons as products [12]. There are some studies that have investigated the reactions of methane on La₂O₃, and shown that La₂O₃ is a good catalyst at 600 to 700 °C.
for the formation of methyl radicals [13]. These radicals then react, with a product selectivity of over 50% CO$_2$ [13]. Spectroscopically, there is less information on the surface interactions of methane. Only at low temperature (below 25 °C) has CH$_4$ adsorption been observed [14].

3.1 Experimental

Samples of Anatase, Anatase/La$_2$O$_3$, and Anatase/La$_2$O$_3$/CuO and TiO$_2$/CuO were made by ball-milling commercial grade TiO$_2$ (anatase) with the desired weight percent of La$_2$O$_3$ and/or CuO in isopropanol for 4 hours. After solvent removal by rotovap, the powders were heat treated at 800 °C for 6 hours. The anatase/CuO sample was partially Rutile/CuO after this treatment.

Infrared Spectroscopy was done with Bruker Instruments IFS-66s Fourier Transform Infrared Spectrometer, with a Spectra-Tech Collector/Environmental Chamber which allows the sample to be heated and exposed to gas phase analytes during the infrared measurement. Prior to measurements, samples were heated to a set point temperature of 600 °C for two hours under a flow of N$_2$. A background measurement was made under a flow of 5%O$_2$/N$_2$, first at 800 °C set point, followed by 400 °C setpoint and finally room temperature. The sample gas (either CO, CO$_2$ or CH$_4$) was introduced at a concentration of 0.5% and measurements were made at room temperature, then 400 °C, then 800 °C. Due to thermal conductivity losses from the sample holder and the powdered samples, actual surface temperatures were typically much lower than the set temperatures. At a setpoint of 400 °C, the base of the sample cup was 212 °C, and the
sample surface ranged from 122-208 °C; at the 600 °C setpoint these values were 325 °C and 190 -312°C; and at 800 °C, they were 413 °C and 247 – 412 °C. All the infrared data are reported in Kubelka Munk units: \( KM = \frac{(1-r)^2}{2r} \), where \( r \) is the relative reflectance \( (r_s/r_n) \). The reference reflectance \( r_n \) is the single channel reflectance of a sample under a flow of 5%O\(_2\)/N\(_2\) (at room temperature or 800 °C) and the sample reflectance, \( r_s \), is that of the powder in a gas stream containing either CO or CH\(_4\). More details about the data analysis are given in the appendix.

Results

3.2 TiO\(_2\)

Figure 3.1 shows the infrared spectra of anatase (A) when exposed to CO at room temperature, at setpoint of 400 °C and a setpoint of 800 °C. (The surface temperature is well below that of the setpoint temperature. See details in the experimental section.) The spectra are all shown on the same scale so that the relative intensities of the bands at each temperature can be compared. At room temperature there are three species present in the spectra. First, the gas phase doublet of CO is present at 2143 cm\(^{-1}\). Second, physisorbed water is present on the surface, as indicated by the broad –OH stretch between 3600 and 3000 cm\(^{-1}\), coupled with the H\(_2\)O bending mode at 1636 cm\(^{-1}\) [5, 6]. Finally, free hydroxyl groups are also present on the surface, as evidenced by the band at 3698 cm\(^{-1}\). As the temperature is increased to 400 °C and then 800 °C, the intensity of the bands related to all three species decrease in intensity, then disappear completely. At the same time, a new band grows in at 2345 cm\(^{-1}\). This doublet is attributed to gas phase CO\(_2\), indicating that the oxidation of CO has occurred.
The desorption temperature of the surface water from the sample is in agreement with various literature studies. From the above experiments, physisorbed water and free hydroxyl groups are still present at the 400 °C setpoint. (or ~160 °C) but have disappeared by the 800 °C set point (~ 300 °C. Lusvardi et al. showed that desorption of hydroxyl groups starts to occur around 150 °C. and is complete by 400 °C [15]. Yates et al. report that above 150 °C. the titania surface is completely dehydrated [16]. Finally, Morterra reports that greater than 550 °C. any remaining hydroxyl groups are undetectable by IR [7].

The lack of adsorbed CO on the sample, as well as the lack of reaction intermediates is consistent with previous studies. Only on a heavily reduced surface, or under vacuum conditions are CO adsorption bands observed, and then only at room temperature and below [5, 6]. Also, Baraton has observed carboxylate species on titania at room temperature, but only on surfaces that had undergone a reduction treatment, and these species were easily desorbed [6]. At the higher temperature, though there may be more of a reaction of CO, as indicated by the strong CO2 bands. intermediate species may be transient on the TiO2 surface and unobservable with DRIFTS.

Figure 3.2 shows the infrared spectra of TiO2 when exposed to CH4 under the same conditions as the CO experiments above. The room temperature spectrum is similar to that of the system with CO. Bands are present for both physisorbed water and free hydroxyl groups, as well as the gas phase methane that has been introduced into the sample chamber. The methane gas phase bands are centered at 3016 and 1304 cm⁻¹, each with the characteristic rotational structure. As the temperature of the sample is increased.
the bands for all three species decrease in intensity, and a weak peak for CO$_2$ appears in the spectra. This weak CO$_2$ peak indicates that the CH$_4$ is oxidizing on TiO$_2$ at this temperature to a small extent.

3.3 TiO$_2$/CuO

The addition of CuO to the anatase phase of TiO$_2$ results in the transformation of the anatase to rutile under the heat treatment used for all the titania samples as detailed in Chapter 2. Figure 3.3 shows the infrared spectrum of TiO$_2$/CuO with CO. The spectra at different temperatures are not on the same y-axis scale. At room temperature, the CO strongly adsorbs to the sample surface, showing a maximum at 2116 cm$^{-1}$. The location of this band indicates that CO is adsorbing on a Cu$^{0}$ or a Cu$^{1+}$ site. In a study of Cu$_2$ZnO$_4$ Bocuzzi identified a band at 2116 cm$^{-1}$ as CO adsorbed to a copper metal site that has also adsorbed oxygen [10]. However, Busca assigned a band at 2115 cm$^{-1}$ as CO adsorbed on a Cu$^{1+}$ species on copper (II) oxide, proposing that even on an unreduced surface, there are reduced sites due to surface defects [8]. Peaks in the range of 2100 to 2130 cm$^{-1}$ are typically assigned to Cu$^{0}$, while those between 2115 and 2130 cm$^{-1}$ are assigned to Cu$^{1+}$. Oxidation state of the adjacent sites can also influence the adsorption band of the adsorbed CO, with highly oxidizing environments increasing the frequency of the vibration [9]. Based on this previous work, Cu$^{1+}$ in a highly oxidized environment would be expected to be closer to 2130 cm$^{-1}$. The band at 2116 cm$^{-1}$ is therefore assigned as CO on Cu$^{0}$.

There is also physisorbed water and free hydroxyl groups on the surface of the sample, with the same peak positions as the water and hydroxyl groups on anatase. Once
the temperature is raised to 400 °C, the CO desorbs from the surface, and only gas phase CO is observed. At 800 °C, no surface species are observed, but there is some CO₂ present. The addition of CO appears to have raised the optimal temperature of CO oxidation on the surface.

The infrared spectra of TiO₂/CuO with CH₄, shown in Figure 3.4, are essentially the same as those of anatase with CH₄ at all temperatures. The only species present at room temperature and 400 °C are gas phase CH₄, physisorbed water and hydroxyl groups. At 800 °C, the CO₂ band appears and, qualitatively, is larger than that on the anatase sample, consistent with the role of CuO in oxidizing CH₄ proposed in Chapter 2.

3.4 La₂O₃

From the infrared spectra of the anatase and TiO₂/CuO samples described above, little information can be obtained on the formation of intermediates on TiO₂ and CuO in the presence of CO and CH₄ at different temperatures. However, as observed in the previous chapter, TiO₂ samples with added La₂O₃ are well suited for adsorbing and retaining CO₂ and carbonate-like species on its surface. These adsorbed intermediates provide valuable information regarding the reactivity of anatase and TiO₂/CuO. The interactions of CO₂, CO and CH₄ on La₂O₃ are characterized at different temperatures, in further support of the conclusion from the previous chapter, that LaOᵢ, not La₂O₃ is the dominant species in the anatase/La₂O₃ and anatase/La₂O₃/CuO samples. This is followed by a more detailed, temperature dependent study of the reactions of CO and CH₄ on the TiO₂-based samples.
3.4.1 CO$_2$ on La$_2$O$_3$

The infrared spectra of CO$_2$ treated La$_2$O$_3$ (dispersed in KBr) at room temperature and at the 800 °C set point temperature, are shown in Figure 3.5. Only the region of the spectra between 2000 and 1200 cm$^{-1}$ is shown, and the scales for the different temperature samples are not the same, so that the lower intensity bands in the room temperature spectrum can be observed. At room temperature, there are two main peaks in the infrared spectrum: a strong band at 1550 cm$^{-1}$ with shoulders at 1630 and 1406 cm$^{-1}$. There is also a band at 1330 cm$^{-1}$. These bands are due to a combination of carbonate species that have formed upon the adsorption of CO$_2$ on La$_2$O$_3$ and surface adsorbed water. The shoulder at 1630 cm$^{-1}$ is due to the water, and there are accompanying OH stretches around 3000 to 3600 cm$^{-1}$. The HOH bending mode of H$_2$O on La$_2$O$_3$ has been assigned to peaks between 1650 cm$^{-1}$ and 1630 cm$^{-1}$ [3, 17].

Free carbonate shows an absorption band at 1415 cm$^{-1}$, which splits upon adsorption on a surface [18]. The bands at 1550 and 1330 cm$^{-1}$ are likely due to the adsorption of carbonates on the La$_2$O$_3$ in a bidentate manner. Rosnyek assigned peaks at 1565 and 1310 cm$^{-1}$ as bidentate carbonates on La$_2$O$_3$ [3]. The shoulder at 1496 cm$^{-1}$ could indicate the presence of monodentate carbonates on the surface of La$_2$O$_3$. Band pairs of 1500 and 1390 cm$^{-1}$ [3] and 1460 and 1360-1330 cm$^{-1}$ [17] have been assigned to monodentate carbonates. Though the low wavenumber counterpart to this assignment is missing, but may be obscured by the band at 1330 cm$^{-1}$ which is broad and tials toward higher wavenumbers.

Upon exposure to CO$_2$ at 800 °C, there is a strong doublet with maxima at 1447 and 1395 cm$^{-1}$. These are easily assigned to a monodentate carbonate species due the
spacing between maxima and based on previous studies [17]. Also at this temperature there is a weaker band at 3566 cm⁻¹ (inset of Figure 3.5b) which indicates the presence of hydroxyl groups. La(OH)₃ shows stretching frequencies at 3610 and 3590 cm⁻¹, the latter stable up to 300 °C [3] and the bands due to the OH groups of hydroxycarbonates of lanthanum are typically assigned to lower wavenumbers, such as 3440 cm⁻¹ [2]. This suggests that the 3566 cm⁻¹ band is more likely due to the presence of surface hydroxyl groups on lanthanum oxide.

3.4.2 CO on La₂O₃

Figure 3.6 shows the infrared spectra of La₂O₃ upon exposure to CO. At room temperature there is only a weak band at 1639 cm⁻¹, which, based on the presence of bands in the hydroxyl region, is assigned to physisorbed H₂O. There is no band for adsorbed CO on La₂O₃, which would appear between 2075 and 2170 cm⁻¹ [1, 4]. At room temperature the carbonite ion CO₂⁻ has been observed on the surface of La₂O₃ after reaction with CO, its presence indicated by a band at 1390 cm⁻¹ [1, 4]. Carbonite is relatively unstable on the surface, only present at room temperature or below, and easily outgassed at room temperature [4], so the flow conditions of the experiment may be unsuitable to observe this species on the surface. Prolonged CO exposure at room temperature has also been reported to lead to the formation of carbonate species [1, 4].

At a setpoint of 400 °C, two small broad bands can be observed, with maxima at 1550 and 1395 cm⁻¹. Because these bands are poorly defined, they are likely a combination of monodentate and bidentate carbonate species on the La₂O₃ surface, based
on the assignments made above for CO$_2$ on La$_2$O$_3$. The CO$_2$ gas phase doublet is also present in the spectrum, which means that the CO is being slightly oxidized by the La$_2$O$_3$.

At the 800 °C setpoint, the intensity of the bands in the region between 2000 and 1200 cm$^{-1}$ increased in intensity and shift slightly in position. There is a maxima at 1540 cm$^{-1}$, which rides across a broader band that is from 1350 to 1550 cm$^{-1}$. The assignment is the same as that for the 400 °C setpoint, a mixture of bidentate and monodentate carbonates. No peaks appear in the hydroxyl region on this sample.

It is clear from this data, that under the various temperatures tested, little CO reacts on the surface of La$_2$O$_3$. Because the bands present are weak, there will be little interference of the bulk La$_2$O$_3$ in the study of CO oxidation on anatase and anatase CuO samples that have added La$_2$O$_3$.

### 3.4.3 CH$_4$ on La$_2$O$_3$

At room temperature, the infrared spectrum of La$_2$O$_3$ under flowing CH$_4$ looks about the same as the sample under CO, as shown in Figure 3.7. Aside from the gas phase CH$_4$ peaks, the only band that is present is that of physisorbed water at 1630 cm$^{-1}$. When the temperature is raised to 400 °C, a small broad band appears in the spectrum at about 1560 cm$^{-1}$ (Figure 3.7b). The band at 1560 cm$^{-1}$ does not have a pair, but is possibly obscured by the gas phase methane peak at 1304 cm$^{-1}$ and its rotational bands. There is a strong, sharp band at 3449 cm$^{-1}$, indicating the formation of some hydroxyl groups (Figure 3.9a). The position of the band has been identified as that of a hydroxycarbonate [2], a lamellar structure with carbonates sandwiched between layers of lanthanum hydroxide. The carbonates in hydroxycarbonates are adsorbed in a monodentate manner.
but the band observed in this spectrum has a high enough frequency that it is more likely bidentate. Instead, assignment of this band as a bicarbonate species is more reasonable. There is no evidence of gas phase CO$_2$ in the spectrum at this temperature.

By 800 °C, there is a major change in the infrared spectrum. Two sharp peaks are present in the spectrum (Figure 3.7c), one at 1492 cm$^{-1}$, the other at 1352 cm$^{-1}$. These are similar peak positions to the monodentate carbonate bands from adsorption of CO$_2$ on the La$_2$O$_3$. A band is also present at 3499 cm$^{-1}$, superimposed on a broad OH stretching band (Figure 3.8b). Here, an assignment of hydroxycarbonates species on the sample is justified. Table 3.1 summarizes the data for the La$_2$O$_3$ sample.

3.5 Anatase/ La$_2$O$_3$

Now that there is an understanding of the reactivity and adsorption properties of La$_2$O$_3$ in the presence of CO, CH$_4$ and CO$_2$, anatase/La$_2$O$_3$ (AL) samples can be examined. Again, the different spectra are not on the same scale so that the lower intensity bands can be observed. As the adsorption of CO$_2$ to form carbonates was the dominant interaction observed above, CO$_2$ on AL will be discussed first.

3.5.1 CO$_2$ on Anatase/La$_2$O$_3$

Figure 3.9 shows the infrared spectrum of the AL sample under flowing CO$_2$ at different temperatures. The carbonate region of the infrared spectrum at room temperature has a strong band at 1665 cm$^{-1}$, with shoulders at 1695, 1641 and 1570 cm$^{-1}$. There are also weak bands at 1480, 1330 and 1277 cm$^{-1}$. There is some absorption in the region between 3000 and 3600 cm$^{-1}$ of the spectrum, so the shoulder at 1641 cm$^{-1}$ is
probably due to physisorbed water. The bands at 1480 and 1277 cm$^{-1}$ are assigned as bicarbonate species, HCO$_3^-$, on La$_2$O$_3$. On alumina, peak positions at 1650, 1450 and 1230 cm$^{-1}$ were assigned to bicarbonate species [19]. The shoulder at 1570 and weak band at 1330 cm$^{-1}$ suggest the presence of bidentate carbonate species on the surface as well [3].

The source of the strongest peak in the spectrum at this temperature, 1665 cm$^{-1}$, and its shoulder at 1691 cm$^{-1}$, are not easily identified. The hydroxyl region bands are weak in comparison, and there are not any other significant carbonate region bands to make an assignment as a carbonate species plausible. The position of the band suggests the formation of a carboxylate species on the surface. These carboxylate species appear to be unique to the LaO$_x$ species on TiO$_2$, as they are not observed on the La$_2$O$_3$ samples.

The intensity of the bands in the carbonate region at room temperature is much higher than CO$_2$ on La$_2$O$_3$. The La$_2$O$_3$ on TiO$_2$, because of the ball-milling and heat treatment procedure, is probably better dispersed than La$_2$O$_3$ that has only been mixed with KBr, the latter having fewer adsorption sites.

When the temperature is raised to 400 °C (Figure 3.10b), with CO$_2$, the band at 1663 cm$^{-1}$, attributed to carboxylate, has disappeared. There are now 3 main bands at 1548, 1438 and 1372 cm$^{-1}$, with the band at 1548 cm$^{-1}$ having two shoulders. The bands in this region are assigned as a mixture of carbonate species at these two temperatures. At 400 °C, the bands at 1438 and 1372 cm$^{-1}$ are assigned as a monodentate carbonate species, with a separation distance of 66 cm$^{-1}$, while the band at 1548 cm$^{-1}$ is assigned to
a bidentate carbonate species. The expected band around 1330 cm⁻¹ is missing, however, based on the relative intensities of the 1551 to 1330 cm⁻¹ peaks observed on the La₂O₃ sample (Figure 3.5a), it is likely that it is not present in the spectrum.

A further increase in temperature to 800 °C increases the intensity of the bands at 1438 and 1372 cm⁻¹, and the band at 1548 cm⁻¹ shifts to a lower wavenumber, 1497 cm⁻¹, and a more distinct shoulder appears at 1470 cm⁻¹. At this temperature there appears to be three different types of monodentate carbonates, with high wavenumber vibrations at 1497, 1470 and 1438 cm⁻¹, and the low wavenumber vibrations, which would be expected between 1350 and 1370 cm⁻¹, observed as only one band at 1372 cm⁻¹. Also at 800 °C, a band appears at 3566 cm⁻¹ and a shoulder at 3350 cm⁻¹ (see inset of Figure 3.10c). Both free hydroxyl groups and hydroxycarbonates are present on this sample as well.

### 3.5.2 CO on Anatase/La₂O₃

Figure 3.11 shows the region of the infrared spectra between 2000 and 1200 cm⁻¹ of the AL sample upon exposure to CO at room temperature, at 400 °C setpoint and an 800 °C setpoint. At room temperature, there is a strong band present at 1640 cm⁻¹ with shoulders at 1658 cm⁻¹ and 1687 cm⁻¹. A weaker band is also present at 1292 cm⁻¹. The band at 1640 cm⁻¹ is assigned to the presence of water on the sample surface, as observed in the CO₂ exposed sample. The bands at 1687, 1648 and 1292 cm⁻¹ suggests the presence of a carboxylate on the surface.

As the temperature is raised to 400 °C, there is a broad band centered at 1558 cm⁻¹ (Figure 3.10b). It is more intense than the bands present at the lower temperature. There
is also a weak band present at 3143 cm$^{-1}$. This band is attributed to a bicarbonate species, similar to that observed at 400 °C from CO$_2$ exposure. Also present on this sample (not shown) is a strong CO$_2$ gas phase doublet at 2345 cm$^{-1}$.

Two strong bands at 1503 and 1356 cm$^{-1}$ appear when the temperature is raised to 800 °C, as shown in Figure 3.11c. There are also weak shoulders on both of these bands between 1450 and 1380 cm$^{-1}$. The two strong bands are assigned to a monodentate carbonate species, and there is a slightly larger separation (147 cm$^{-1}$) between the peaks compared to the monodentate carbonates on La$_2$O$_3$ at this temperature. The shoulders at 1434 and 1387 cm$^{-1}$ are also due to a monodentate carbonate. At this temperature there is also a band in the hydroxyl region of the spectrum at 3566 cm$^{-1}$ with a shoulder at 3450 cm$^{-1}$, shown as the inset to Figure 3.11c, which suggests that both lanthanum hydroxide and hydroxycarbonates are present. Table 3.5 summarizes the assignments for CO species on anatase/La$_2$O$_3$.

3.5.2 CH$_4$ on Anatase/La$_2$O$_3$

The infrared spectra of AL with methane are shown in Figure 3.13. At room temperature, the spectrum is similar to the room temperature spectra of anatase/La$_2$O$_3$, with a strong band at 1640 cm$^{-1}$. There are shoulders on both the low frequency and high frequency sides. The only other band in the spectrum at this temperature is the gas phase methane band at 1304 cm$^{-1}$. Due to the presence of broad bands between 3600 and 3000 cm$^{-1}$ in the hydroxyl region, the band at 1640 cm$^{-1}$ is assigned as the bending mode of physisorbed water.
At 400 °C (Figure 3.13b), the spectrum appears very similar to that of CO₂ on AL, with bands at 1548, 1484 (sh), 1434 and 1372 cm⁻¹. As in the case of CH₄ on La₂O₃, this indicates that the product of CH₄ oxidation, CO₂, is readsorbing on the surface. It is necessary to point out that these bands are much lower in intensity than the direct reaction of CO₂ on AL. In other words, methane is not forming very much CO₂ at this temperature.

With the temperature raised to 800 °C, the intensity of bands in the carbonate region increases, and there is clearly a distinct doublet at this temperature with peaks at 1438 and 1383 cm⁻¹. There are also shoulders at 1497 and 1470 cm⁻¹, and a band at 3566 cm⁻¹ (see inset of Figure 3.13c). As with the exposure to CO₂, these bands both represent a mixture of monodentate carbonate and hydroxyl groups on the surface.

### 3.6 Anatase/La₂O₃/CuO

In Chapter 2, anatase/La₂O₃/CuO (ALC) samples were shown to be selective CO sensors. Preliminary results showed that this was due to the ability of CuO to oxidize both the CO and CH₄ oxidation reactions without interaction with the TiO₂. La₂O₃ was added to prevent an anatase to rutile transition, but due to the formation of a LaOₓ surface layer on TiO₂, carbonates and other intermediate species were trapped on the surface by the LaOₓ layer allowing for infrared observation of the high temperature reactions. Little beyond linearly adsorbed CO is present on the TiO₂/CuO surface at all the temperatures studied in Section 3.3. Here, the addition of La₂O₃ is used to provide more insight into the CO and CH₄ reactivity at a number of temperatures. This data are summarized in Table 3.6.
3.6.1 CO$_2$ on Anatase/La$_2$O$_3$/CuO

The CO$_2$ interaction with ALC at different temperatures is shown in Figure 3.14. At room temperature, the strongest band is at 1665 cm$^{-1}$ as was the case with the AL sample. There are shoulders on the band at 1695, 1641, 1570 cm$^{-1}$. A weaker band is also present at 1277 cm$^{-1}$ with a shoulder at 1330 cm$^{-1}$. The band at 1640 cm$^{-1}$ is assigned to physisorbed water and the bands at 1695, 1665 and 1277 cm$^{-1}$ assigned to carboxylates as on previous samples. The remaining bands are also assigned to similar features of CO$_2$ on ALC, bidentate carbonates (1570,1330 cm$^{-1}$).

As the temperature of the sample is raised to 400 °C, only a single broad band is present with a maximum of 1548 cm$^{-1}$. There is no low wavenumber band to be assigned as the second band of a carbonate pair, but based on the peak’s low intensity, this band may not be observed. This band is assigned to a bidentate carbonate, similar to that observed on the AL sample, but at a much lower intensity.

At 800 °C there is a broad feature that is made up of at least two bands, one at 1514 cm$^{-1}$ and the other at 1377 cm$^{-1}$. These are assigned as a monodentate carbonate species, with a separation between the peaks of 137 cm$^{-1}$. The peak positions do not match any found on either La$_2$O$_3$ or AL samples. It is possible that more than one type of monodentate species is present at this temperature, as the two peaks are not completely resolved from one another. A small band is also present at 3566 cm$^{-1}$ and shows that there are free hydroxyl groups on the surface.
3.6.2 CO on Anatase/La₂O₃/CuO

Figure 3.13 shows the infrared spectra of ALC with CO. The carbonate region of the spectrum at room temperature looks similar to that of CO₂ on ALC. There is a maximum at 1640 cm⁻¹, with shoulders at 1687 and 1658 cm⁻¹, and a small band at 1292 cm⁻¹, making this spectrum nearly identical to that of the room temperature spectrum of the AL sample upon exposure to CO. The species are assigned as physisorbed water (1640 cm⁻¹), and carboxylates (1687, 1658, 1292 cm⁻¹), as in the anatase-La₂O₃ sample. In addition to these species in the carbonate region of the spectrum, there is also a band at 2090 cm⁻¹ superimposed on the gas phase CO doublet (see inset of Figure 3.15a). This absorption band is characteristic of CO adsorbed onto a Cu⁰ site [9, 11]. For our samples, this indicates that even in an oxidizing environment, the CO is reducing the CuO enough to form a significant amount of Cu⁰ species. Adsorption of CO on Cu²⁺, the species that has been added to this sample, would show an adsorption between 2140 to 2190 cm⁻¹ [9, 20].

When the ALC sample is at a setpoint of 400 °C, there are only weak species present on the surface of the sample at 1550 and 1361 cm⁻¹. Bands belonging to gas phase CO₂ are also present. There are no bands in this region in the hydroxyl region, suggesting that these bands are due to a bidentate carbonate species. At 800 °C, there is a large broad band centered at 1449 cm⁻¹ and stretching between 1600 and 1300 cm⁻¹. This band is attributed to the presence of either a mixture of monodentate and bidentate species that cannot be resolved, and possibly polydentate species on the surface.
3.6.3 \( \text{CH}_4 \) on Anatase/\( \text{La}_2\text{O}_3/\text{CuO} \)

All of the bands present on the ALC sample after exposure to \( \text{CH}_4 \) are weak compared to previous samples examined under flowing \( \text{CH}_4 \). Figure 3.17 shows the infrared spectra of ALC with \( \text{CH}_4 \) at room temperature, 400 °C setpoint, and 800 °C setpoint. The room temperature infrared spectrum is, except for intensity, the same as that of the anatase/\( \text{La}_2\text{O}_3 \) sample, with a strong band at 1640 cm\(^{-1} \) (with an accompanying hydroxyl region OH stretches), some high and low wavenumber shoulders on the 1640 cm\(^{-1} \) band and the gas phase methane band at 1304 cm\(^{-1} \). This indicates that at room temperature only physisorbed water is on the surface.

At 400 °C, some gas phase \( \text{CH}_4 \) is still observed, as well as a broad band centered at 1545 cm\(^{-1} \), which could be the beginning of bidentate species forming on the surface. By 800 °C, the band at 1545 cm\(^{-1} \) is no longer apparent, and only a weaker band centered at 1460 cm\(^{-1} \) that is assigned as a monodentate carbonate.

**Discussion**

3.7 Chemistry of Surface Carbonates

The adsorbed species resulting from the interaction of CO and \( \text{CH}_4 \) on the samples are similar to those of \( \text{CO}_2 \) adsorbed on the same sample. It is likely that CO and \( \text{CH}_4 \) react on the surface with the formation of carbonates as intermediate species. Carbon monoxide should be able to adsorb as a carbonate on adjacent surface oxygen atoms, but as seen by the interaction of CO on \( \text{La}_2\text{O}_3 \), this is not a dominant mechanism under the reaction conditions studied here. This result contrasts with the work of other researchers. Bailes et al. and Tsyganeko et al. both observed CO adsorbing on the surface as a
carbonite species, then forming carbonate species with prolonged exposure [1, 4]. On these samples, however, the introduction of O₂ to the sample was done after CO was introduced, allowing for preliminary adsorption of CO on La³⁺ sites on the surface [1, 4]. This same behavior does not occur on the La₂O₃ samples, as the presence of oxygen in the ambient gas from the beginning of the experiment saturates these Lewis acid sites.

There are several types of surface carbonate species present on the samples. There are bicarbonate species (hydroxyl group bound to carbonate), monodentate and bidentate carbonates, and some of these are hydroxycarbonates (hydroxyl groups bound to surface). The nature of the surface, whether it is La₂O₃, AL or ALC, also has an effect on the adsorption of the carbonate species. The carbonate ion has an adsorption at 1415 cm⁻¹ due to the asymmetric stretch of the molecule. When adsorbed on a surface, the vibration, which was originally doubly degenerate, splits into two bands, the lower wavenumber due to the C-O stretch associated with the dangling oxygen and the high wavenumber band due to the C-O stretch involving the surface oxygen [21]. Bidentate carbonates show a higher degree of splitting as compared to the monodentate species. Additionally, the polarizing power of the cation can affect the splitting of the carbonate band. For the samples studied in this thesis, this means that the polarizing ability of La³⁺ is affected by its local coordination and, possibly, whether it is dispersed in KBr or doped onto TiO₂.

The surface of La₂O₃ is known to be complex, in part due to its sevenfold coordination of La³⁺. The surface heterogeneity results in carbonate adsorption sites with varying polarizability, and therefore different splitting. This is evident in the variability in the positions of the monodentate carbonate bands on La₂O₃, which show a Δν₃ that ranges from 53 to 132 cm⁻¹. The carbonate bands that form on AL show an even greater
degree of variability in the positions of the carbonate bands. As discussed in the previous chapter, La$_2$O$_3$ can form a LaO$_x$ layer on the surface of the TiO$_2$. which will have different polarizing properties than La$_2$O$_3$.

With the addition of CuO, the $\Delta v_3$ of the carbonate peaks is unresolved on ALc. compared to carbonates on the surface of AL. This smaller distance between the monodentate peaks may be due to the influence of CuO on the polarizability of La$_2$O$_3$ and as suggested earlier, the presence of polycarbonate species that are partially adsorbed on CuO.

There is a general trend in the type of carbonate species adsorbed on the titania-based samples. At room temperature, carboxylate bands are present on the surface. As the temperature is raised, these bands desorb from the surface and are replaced by bicarbonate and bidentate species on the surface, and eventually they are replaced by monodentate carbonate and hydroxycarbonate species. These different species are all adsorbed on a surface coating of LaO$_x$ on the titania surface, as noted by the contrast in their peak positions when compared to La$_2$O$_3$ samples. In addition, the La$_2$O$_3$ samples do not appear to form carboxylate species at low temperatures, and it is instead unique to the LaO$_x$-titania sample.

Temperature plays a role in which type of carbonate is present on the surface, giving an indication of the relative stability of the different species. This temperature related stability is best observed in the CH$_4$ reaction over ALc (Figure 3.17), as only low concentrations of carbonates are observed, eliminating the concentration effect that was discussed above. At room temperature, the bicarbonate species are most stable, but at higher temperatures they are replaced by bidentate species, which have a greater stability.
as they have two points of attachment on the surface. On Ni/Al₂O₃, bicarbonate species decomposed above 100 °C, and on these samples replaced by formate species [22]. Further increases in the temperature result in the formation of monodentate species. Other studies have observed an influence of temperature on surface species on La₂O₃, but were mostly focused on lower temperature. Tsyganenko showed that carbonite species are present on La₂O₃ at -173 to 25 °C [4]. Rosnyek showed a transformation of monodentate species to bicarbonate species upon heat treatment at 275 °C, but this was attributed to a decrease in surface carbonate concentration, as the heat treatment is done under vacuum [3]. However, they did report that on samples with a large number of hydroxide groups, conversion to bidentate species did not occur, possibly due to the formation of layered carbonate structures [3]. As there are hydroxyl groups present on samples that show small amounts of carbonate formation, such as CH₄ on anatase/La₂O₃:CuO, it is likely that these structures are stabilized over bicarbonate formation, superceding the expected concentration effects.

### 3.8 Reactivity of CO/CH₄ on Anatase

CO is oxidized on the surface of the anatase phase of titania, as observed in Figure 3.1. A significant amount of CO₂ is formed on the surface, starting at the 400 °C setpoint, but is not accompanied by the formation of any intermediate surface species. In the case of CH₄, there is a small amount of oxidation to CO₂, but this does not occur until the 800 °C setpoint, suggesting that it is more difficult to oxidize CH₄ on the TiO₂ surface.
There are two oxidation mechanisms that are possible. In the first, the gas phase reactant, either CO or CH$_4$, reacts with surface adsorbed O$_2$ to form CO$_2$. No other reaction products are observed. The reduction of the titania surface creates a secondary reaction pathway. In this case, a reducing gas adsorbs on a Ti$^{3+}$ surface site. The adsorbed gas can either react with an adjacent surface adsorbed O$^-$, or with gas phase O$_2$, the latter having no effect on the titania conductivity. This secondary mechanism is only possible for CO, as it adsorbs readily on a reduced TiO$_2$ surface (see Figure 2.15) while CH$_4$ does not.

3.9 Reactivity of CO/CH$_4$ on TiO$_2$/CuO

TiO$_2$/CuO shows the presence of a band at 2116 cm$^{-1}$ at room temperature, assigned to the CO adsorption on a Cu$^{1+}$ site in a highly oxidized environment. As shown in Chapter 2, if TiO$_2$/CuO is exposed to CO at a high temperature, then cooled to room temperature, the band for CO adsorption is at 2108 cm$^{-1}$, an 8 cm$^{-1}$ shift. The change in the position of the CO band on TiO$_2$/CuO before and after heat treatment with CO is due to changes in the environment of the surface species. At high temperatures, more Cu$^{2+}$ is reduced to Cu$^0$, making sites adjacent to adsorbed CO more likely to be reduced copper than the oxidized form. Padley et al. showed similar behavior in Cu/Al$_2$O$_3$ samples that were exposed to CO, with shifts in the position of CO on the surface dependent on the concentrations of Cu$^{1+}$ and Cu$^{2+}$ species [9].

In comparison to the anatase sample, little CO$_2$ is observed at 400 $^\circ$C after the TiO$_2$/CuO sample has been exposed to CO. Only at 800 $^\circ$C are CO$_2$ peaks observed, the presence of CuO raising the oxidation temperature of the CO. At the lower temperatures.
the CO preferentially adsorbs on the surface of the copper oxide at the expense of the oxidation reaction on TiO$_2$. Once the 800 °C setpoint is reached, the CuO oxidation of the CO starts to occur, and gas phase CO$_2$ is observed.

Because the CuO does not adsorb CH$_4$, a change in the oxidation temperature is not observed when CuO is added to the TiO$_2$. Instead, there is an increased amount of CO$_2$ observed in the spectra, indicating that CuO is promoting the CH$_4$ oxidation at the 800 °C setpoint temperature.

3.10 Reaction of CO$_2$ with La$_2$O$_3$, Anatase/La$_2$O$_3$ and Anatase/La$_2$O$_3$/CuO

On the AL and ALC samples, treatment with CO$_2$ results in the formation of carboxylate and bicarbonate species on the sample at room temperature. In contrast, the CO$_2$ on La$_2$O$_3$ forms bidentate carbonates at this temperature. This difference is a result of the nature of the surface, since the AL and ALC contain LaO$_x$. These carbonate region bands are also much more intense on the AL and ALC samples vs the La$_2$O$_3$ sample. This is probably because of better dispersion of the LaO$_x$ on the titania surface as opposed to the mixing of the bulk La$_2$O$_3$ sample with KBr.

The intensity of the species on the sample at the 400 °C setpoint is much lower than at room temperature, indicating that the low temperature species have desorbed. There are three bands on the AL sample, assigned to a mixture of monodentate and bidentate carbonate species, but only one band is present on the ALC sample. The position of this band on ALC is similar to that of the highest intensity band on AL, suggesting that the same species is present, but that it is at a much lower concentration.
At the 800 °C sample, the intensity of the species on the La₂O₃ sample far exceed that of either the AL or the ALC sample. The greater intensity for the carbonate region bands on the La₂O₃ sample could be due to the formation of a lanthanum carbonate phase, as opposed to just surface adsorbed species. This may not be possible for the LaO₇ species, as it is a surface layer. The carbonate bands on the AL and ALC samples are much higher at 800 °C vs 400 °C, indicating that there is a temperature dependence to surface carbonate formation on LaO₇.

3.11 Reaction of CO with Anatase/La₂O₃ and Anatase/La₂O₃/CuO

At low temperatures, CO shows the same reactivity on the AL and ALC surface, and small amounts of carboxylates are formed on the surface. When the temperature is raised to 400 °C, the spectra of the two samples differ slightly with bicarbonate present on AL and bidentate carbonates present on ALC. Gas phase CO₂ is observed in both spectra. The low intensity of the carbonates is not surprising, as carbonate adsorption from CO₂ treatment was not very strong at this temperature. The high amount of gas phase CO₂ on the ALC sample is unexpected at 400 °C, however, as CO oxidation on TiO₂/CuO did not start to occur until the 800 °C setpoint. At this temperature, most of the oxidation of CO must be coming from the anatase phase.

At 800 °C, the carbonate regions of the AL and ALC samples now appear much different than each other. It is at this temperature that the CuO becomes active for the CO oxidation reaction, resulting in the production of the polydentate carbonate species on the ALC sample, while the reactivity on the AL sample does not change substantially.
Figure 3.16 illustrates the reactions taking place on the AL and ALC surfaces after exposure to CO at the different setpoint temperatures. As discussed above, the reactivity of CO on AL and ALC is similar at room temperature and the 400 °C setpoint, but at 800 °C, CuO begins to influence the ALC reactivity.

3.12 Reaction of CH\textsubscript{4} on anatase/La\textsubscript{2}O\textsubscript{3} and anatase/La\textsubscript{2}O\textsubscript{3}/CuO

Little gas phase CO\textsubscript{2} is observed on the anatase/La\textsubscript{2}O\textsubscript{3} or anatase/La\textsubscript{2}O\textsubscript{3}/CuO samples in either of the temperature studies. From sensing measurements at higher temperatures discussed in Chapter 2, it is clear that CH\textsubscript{4} can react on AL to form CO\textsubscript{2}. The temperature of the sensing measurement is significantly higher (600 °C) compared to the infrared measurements, which could account for this discrepancy. While studies have shown that CH\textsubscript{4} oxidation on bulk CuO is 50% complete at 600 °C (T\textsubscript{50}), and while reports have shown that the addition of La\textsubscript{2}O\textsubscript{3} to catalysts lowers the T\textsubscript{50} and T\textsubscript{90} of CH\textsubscript{4}, the sample temperatures obtained in the infrared sample chamber may be too low for significant amount of oxidation to occur [23]. Other analytical methods, such as GC-MS may be more suitable for correlating CO\textsubscript{2} production from CH\textsubscript{4} oxidation with data from both infrared spectroscopy and the sensing measurements to develop a more complete picture of AL and ALC reactivity.

3.13 Conclusion

Infrared spectroscopy was used to observe the formation of surface species on titania based samples during interaction with CO, CH\textsubscript{4} and CO\textsubscript{2}. Examination of the TiO\textsubscript{2} and TiO\textsubscript{2}/CuO samples gave little information regarding the reactivity of the gases on
these surfaces. However, on the TiO$_2$/CuO sample there was evidence that CO had adsorbed on the surface and was oxidized. By adding La$_2$O$_3$ to these samples, more information was obtained regarding the nature of surface species resulting from the reactions of the three gases. The presence of an LaO$_x$ surface layer on TiO$_2$ proposed in Chapter 2 was confirmed, showing that peak positions of specific surface carbonates is dependent on the nature of the sample and not the gas to which it was exposed.

Temperature studies showed that monodentate carbonates are the most stable at higher temperatures, possibly due to the presence of surface hydroxyl groups observed on the samples. Finally, two different types of monodentate carbonates were identified on the samples, with the frequency difference between the carbonate bands influenced by the presence of hydroxyl groups on the sample surface.
References


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<th>Reference</th>
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</tr>
<tr>
<td>1577. 1520. 1440. 1337. 1220</td>
<td>carbonate-like</td>
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</tr>
<tr>
<td>1485 - 1325</td>
<td>bidentate carbonate</td>
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</tr>
<tr>
<td>1580-1320</td>
<td>bidentate</td>
<td>18</td>
</tr>
<tr>
<td>1577. 1460</td>
<td>monodentate</td>
<td>6</td>
</tr>
<tr>
<td>1590-1575. 1370-1320</td>
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<td>formate</td>
<td>18</td>
</tr>
<tr>
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</tr>
<tr>
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<tr>
<td>1650-1600</td>
<td>water deformation</td>
<td>28</td>
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Table 3.1: Literature assignments of species adsorbed on TiO₂.
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<th>Wavenumber (cm⁻¹)</th>
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</thead>
<tbody>
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<td>1470, 1400, 1370</td>
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<td>1460, 1360, 1330, 1075</td>
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<td>3440, 1600-1200</td>
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<td>3660, 3580</td>
<td>-OH (methoxy?)</td>
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<td>1367, 1372, 1245, 1140, 1062</td>
<td>(CₖOₖ)⁻² oligomers</td>
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<td>monodentate and bidentate carbonates</td>
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<tr>
<td>1565, 1310</td>
<td>bidentate</td>
<td>3</td>
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<tr>
<td>1500, 1390</td>
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</tr>
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<td>3605, 3580, 3452, 3443 (200 C)</td>
<td>La(OH)₃</td>
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</tr>
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<td>La(OH)₃</td>
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<td>1834, 1754, 1550, 1464, 1088</td>
<td>La₂O₂CO₃</td>
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Table 3.2: Literature assignments for species adsorbed on La₂O₃.
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<td>Cu(OH)₂CO₃</td>
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Table 3.3: Literature assignments for species adsorbed on CuO and Cu.
Table 3.4: Summary of infrared data for $\text{La}_2\text{O}_3$ dispersed in KBr.

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<td></td>
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<td>1477, 1395</td>
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<td>CO</td>
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<td>400</td>
<td>1550, 1395</td>
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<td>800</td>
<td>1550 -1350</td>
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<td>CH$_4$</td>
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<td>hydroxycarbonate</td>
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Table 3.5: Summary of infrared data for anatase/La₂O₃.
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<td></td>
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<td>bidentate carbonate</td>
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<td>1514, 1377</td>
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Table 3.6: Summary of infrared data for anatase/La₂O₃/CuO.
Figure 3.1: Infrared spectra of anatase upon exposure to CO. a) room temperature; b) 400 °C setpoint; c) 800 °C setpoint.
Figure 3.2: Infrared spectra of anatase upon exposure to CH₄. a) room temperature; b) 400 °C setpoint; c) 800 °C setpoint.
Figure 3.3: Infrared spectra of TiO$_2$/CuO upon exposure to CO. a) room temperature; b) 400 °C setpoint; c) 800 °C setpoint.
Figure 3.4: Infrared spectra of TiO\textsubscript{2}/CuO upon exposure to CH\textsubscript{4}. a) room temperature; b) 400 °C setpoint; c) 800 °C setpoint.
Figure 3.5: Infrared spectra of La₂O₃ upon exposure to CO₂. a) room temperature; b) 800 °C setpoint.
Figure 3.6: Infrared spectra of La$_2$O$_3$ upon exposure to CO. a) room temperature; b) 400 °C setpoint; c) 800 °C setpoint.
Figure 3.7: Infrared spectra of La$_2$O$_3$ upon exposure to CH$_4$. a) room temperature; b) 400 °C setpoint; c) 800 °C setpoint.
Figure 3.8: Infrared spectra of La$_2$O$_3$ with CH$_4$ showing the hydroxyl region. a) 400 °C; b) 800 °C.
Figure 3.9: Infrared spectra of anatase/La$_2$O$_3$ upon exposure to CO$_2$. a) room temperature; b) 400 °C setpoint; c) 800 °C setpoint.
Figure 3.10: Infrared spectra of anatase/La$_2$O$_3$ upon exposure to CO. a) room temperature; b) 400 °C setpoint; c) 800 °C setpoint.
Figure 3.11: Infrared spectra of anatase/La$_2$O$_3$ upon exposure to CH$_4$. a) room temperature, b) 400 °C setpoint; c) 800 °C setpoint.
Figure 3.12: Infrared spectra of anatase/La$_2$O$_3$/CuO upon exposure to CO$_2$. a) room temperature; b) 400 °C; c) 800 °C.
Figure 3.13: Infrared spectra of anatase/La$_2$O$_3$/CuO upon exposure to CO. a) room temperature; b) 400 °C; c) 800 °C.
Figure 3.14: Infrared spectra of anatase/La$_2$O$_3$/CuO upon exposure to CH$_4$. a) room temperature; b) 400 °C setpoint; c) 800 °C setpoint.
Mechanism 1

\[
\begin{array}{c}
O^- \quad O^- \quad O^- \quad O^- \quad TiO_2 \\
\text{CO + CH}_4 \quad \rightarrow \quad O^- \quad O^- \quad O^- \quad + \text{CO}_2 \\
\end{array}
\]

Mechanism 2

\[
\begin{array}{c}
O^- \quad O^- \quad O^- \quad O^- \quad TiO_2 \\
\text{CO} \quad \rightarrow \quad O^- \quad O^- \quad CO \quad O^- \\
\text{or} \quad \rightarrow \quad O_2 \\
\text{or} \quad \rightarrow \quad O^- \quad O^- \quad + \text{CO}_2 \\
\text{or} \quad \rightarrow \quad O^- \quad O^- \quad + \text{CO}_2 \\
\end{array}
\]

Figure 3.15: Mechanism of CO and CH₄ oxidation on anatase.
Figure 3.16: Illustration of adsorbed species on anatase/La$_2$O$_3$ and anatase/La$_2$O$_3$/CuO following reaction with CO.
CHAPTER 4

ANATASE AND RUTILE COMPOSITE SENSORS

Introduction

The addition of dopant metal oxides is the most common route for obtaining selective gas sensors, but other routes have been investigated. One such route is to use both p-type and n-type semiconductors in various architectures, to make use of each semiconductor's unique electrical and chemical response. These p-n sensors include heterocontacts, p-n transition sensors, and composites.

Heterocontact gas sensors are essentially p-n diodes made of two pellets, one of a p-type semiconductor, the other n-type, that are placed in mechanical contact [1, 2]. Typically, the I-V characteristics of the heterocontact are measured under a bias voltage, both in the absence of and the presence of the test gas. Heterocontact structures have largely been made of ZnO (n-type) and CuO (p-type), but other materials, such as heterocontacts of ZnO and LaCuO₄ or other lanthanide cuprates have been examined [1, 3]. It is believed that CO preferentially adsorbs on the CuO, and reacts with oxygen
adsorbed on the ZnO. The reaction at the interface of the p-type and n-type material alters the barrier to charge carrier transport, increasing the forward bias current [1].

Other studies have investigated materials that can transition between n-type and p-type regimes as chemical sensors. Solis et al. studied the sensing behavior of α-SnWO₄[4]. At 200 °C, the resistance decreased upon exposure to CO, but at 300 °C, the resistance increases. Additionally, increasing the CO concentration at constant temperature also resulted in a transition from n-type to p-type behavior [4].

Composite sensors have also been made from p-type and n-type materials. Choi and coworkers made ZnO-CuO ceramic composites and tested their sensitivity to CO and H₂. The composites contain ZnO-ZnO (n-n), ZnO-CuO (n-p and p-n) and CuO-CuO (p-p) junctions, the relative concentrations of which were determined by impedance spectroscopy of samples of different ZnO: CuO ratios [5]. There was a higher CO sensitivity for the mixed oxide sensor as compared to either oxide in the pure form, which the authors reason is a result of p-n junctions in the composite [6]. The presence of CO lowers the concentration of holes, increasing the current flow across the ZnO-CuO junctions [6].

In chapter 1, the ability of TiO₂ to act as both a p-type and an n-type semiconductor was briefly discussed. Several metal oxides, such as SnO₂, Ta₂O₅ and BaTiO₃, have transitions between n-type and p-type behavior that are dependent on temperature, oxygen partial pressure and impurity concentrations [7]. In TiO₂, it appears that only the rutile phase shows this transition, as there are no known reports of p-type behavior in anatase. This means that under certain sensing conditions, it is possible to
make composite mixtures that are composed solely of TiO$_2$, but are p-type/n-type mixtures. The sensing behavior of these composite sensors is studied in this chapter.

4.1 Experimental

TiO$_2$ (anatase) was obtained from Aldrich and heat treated for 6 hours at 800 °C. The rutile phase is made by heat treating the anatase for 24 hours at 1000 °C. The anatase-rutile mixtures were made by stirring the previously heat treated powders in isopropanol in the desired weight ratios. Samples were dried by rotovap, then heat treated at 800 °C for 6 hours. Powders were sieved through a 70 micron fluorocarbon mesh and approximately 25 mg was suspended in heptanol and dropped by pipette onto 1.5 cm by 1.5 cm alumina substrates with gold-printed interdigitated electrodes. These TiO$_2$ on alumina was heat treated at 800 °C for 6 hours.

Electrical measurements were performed as described in Section 2.2b. Gas concentrations of 250 to 1000 ppm CO and CH$_4$ were tested at 5%O$_2$/N$_2$. Additionally, measurements of the pO$_2$ dependence of the resistance were made at 600 °C for some of the samples.

X-ray diffraction patterns were collected on a Rigaku Geigertflex diffractometer using Ni-filtered CuK$_\alpha$ radiation at 40 kV and 25 mA between $2\Theta = 20^\circ$ and 80°. Using the relation derived by Spurr and Myers [8], the weight fraction of anatase ($f$) can be determined from XRD patterns from:

$$ f = \frac{1}{(1 + 1.265 I_R/I_A)} \quad (4.1) $$
where $I_R$ is the integrated intensity of the strongest peak of rutile ($2\theta = 25.36^\circ$) and $I_A$ is the integrated intensity of the strongest diffraction peak of anatase ($2\theta = 27.46^\circ$).

Scanning Electron Micrographs were taken on either a Phillips XL30 FEG SEM or a Jeol JSM-820 electron microscope.

**Results**

**4.2 Sensing Behavior of Pure Anatase and Rutile**

As detailed in Chapter 1, TiO$_2$ behaves as an n-type semiconductor, but under certain conditions of temperature and oxygen partial pressure, can act as a p-type semiconductor. Figure 4.1 shows how oxygen affects the resistance of both the anatase and rutile phases of TiO$_2$ at 600 °C. The resistance of the anatase phase increases with $pO_2$, making it an n-type semiconductor. Under the same changes in the $pO_2$ concentration, the rutile phase responds to increased oxygen with a resistance decrease, making it a p-type semiconductor.

As would be expected, the different electrical behavior of anatase and rutile to oxygen results in differences in the electrical response to reducing gases. Figure 4.2 shows the response of anatase (Figure 4.2a) and rutile (Figure 4.2b) to carbon monoxide and methane. As the direction of the response of anatase and rutile to the reducing gases was opposite, it was of interest to see what would happen if composite sensors of anatase and rutile were fabricated. Different composition mixtures (1:3, 1:1, 3:1) of anatase and rutile were made, characterized and tested for their sensing behavior as detailed below.
4.3 Mixing of p-n Composites

Prior to testing the composite sensors, characterization of the samples was done to evaluate how homogeneous the mixtures of anatase and rutile were, and how reproducibly the mixtures could be deposited on sensing substrates. X-ray Diffraction and Scanning Electron Microscopy were used to examine the materials.

4.3.1 X-ray Diffraction

Figure 4.3 shows the XRD patterns of anatase (Figure 4.3a), rutile (Figure 4.3e) and mixtures containing 25%, 50% and 75% Rutile. After an 800 °C heat treatment, the anatase to rutile composition was calculated using equation 4.1 using the integrated peak areas. The percentage of rutile calculated from the diffraction patterns was 22%, 50% and 75% rutile for the nominal 25%, 50% and 75% rutile samples, respectively.

XRD patterns were also taken of samples after they had been deposited on the alumina sensing substrates to examine how uniformly the original sample powder was deposited on substrates during the fabrication of the sensor. When films on sensing substrates are examined, it is important to check the pattern for diffraction peaks from the underlying alumina substrate. The diffraction peak of alumina at 2θ = 25.8 may overlap with the 25.36° peak of anatase, skewing the calculated anatase to rutile ratio. The strongest alumina reflection is at 35.5°, and its presence is noted below when there is concern that the anatase to rutile ratio may contain some error.

Figure 4.4 shows the XRD patterns for the 25% rutile sample as a powder (Figure 4.4a) and on two different sensing substrates (Figures 4.4b and c). In Figure 4.4.b, there is a small peak present at 35.5°, but its intensity is apparently too small to compromise
the anatase to rutile ratio. Sensor 25-1 (Figure 4.4b) shows 20% rutile in the sensing film, but sensor 25-2 (Figure 4.4c) does not show the presence of any rutile. Using a razor blade, powder was removed from the sensing surface and the remaining material was examined by XRD to see if the rutile had settled to the bottom of the sensing film during sample preparation. Figure 4.5 shows the XRD patterns of sensor 25-2 with no. 3 and 5 and 6 layers removed from the film. With three layers of film removed, the XRD pattern indicates only the presence of the anatase phase. After 5 layers are removed, peaks belonging to the underlying alumina substrate and gold electrodes start to appear in the XRD pattern, and by the time 6 layers are removed only peaks belonging to the alumina and gold are present in the diffraction pattern, even though there is still titania on the substrate. If rutile is present in the lower layers of the film, it is not detected due to interference from the alumina substrate because the titania layer is too thin.

Figure 4.6 compares the 50% rutile powder with two different sensors. Both sensor 50-1 and 50-2 have rutile concentrations comparable to the original powder, with sensor 50-1 at 42% rutile and sensor 50-2 at 43%. There are small peaks due to the alumina substrate apparent at $2\theta = 35.5$ in both of the diffraction patterns. This indicates that the percentage of rutile in the sensor may be slightly higher than calculated. The XRD patterns of two 75% rutile sensors are compared with the original sample powder in Figure 4.7. The calculated rutile concentration for sensor 75-1 is 74% rutile and that of sensor 72-1 is 73% rutile.
4.3.2 Scanning Electron Microscopy

In Figure 4.8, the electron micrographs of 100% anatase powder (after an 800 °C heat treatment) and 100% rutile powder (after 800 °C heat treatment) are pictured. The anatase particles (Figure 4.8a) are spherical and range in size from 100 to 200 nm (check), while the rutile particles (Figure 4.8b) are much larger in size, and have a different morphology. While there are some spherical particles, the powder is composed mostly of elongated particles.

SEM micrographs of the different composite sensors were also taken. Figure 4.9 shows the pattern of the two 25% rutile sensors examined by XRD (Figure 4.4 and 4.5). In the sensor 25-1, several rutile particles, identified by their particle size and shape compared to Figure 4.5. However, in sensor 25-2, only one rutile particle could be identified, after examination of several different regions of the sensor.

A micrograph of a 50% rutile sample is shown in Figure 4.10. The image shows the presence of both the larger rutile particles among numerous smaller anatase particles. The presence of the rutile appears to have increased the porosity of the sample somewhat, as compared to the 25% rutile sample.

Two different images of a 75% rutile sample are shown in Figure 4.11. The top figure is of the same magnification as that of one of the 25% rutiles samples (Figure 4.9b) and the 50% rutile sample (Figure 4.10), while the other is of a lower magification. As with the 50% rutile sample, there are rutile particles amongst the smaller anatase particles, though their concentration is larger, as expected. The porosity of the sample is also greater than the other two samples. In Figure 4.11b, a lower magnification image of the 75% rutile sample, it appears that there is a high degree of connectivity between rutile
particles, with which it is possible to make a complete connection across the entire image. The connectivity between anatase particles, though lower than in the other two samples, is still significant in the 75% rutile sample as well.

4.3.3 Sample reproducibility

From the XRD analysis, the 25% rutile sample is the most difficult to reproduce from sample to sample, with some sensors that are 25% rutile not showing any rutile at all by XRD. The 50% and 75% samples appear to be more reproducible. One hypothesis is that the rutile particles preferentially settle to the bottom of the sensing substrate during sample preparation, making an anatase-rich surface, and a rutile-rich area near the sensing substrate and electrodes. As there is far more rutile in the other two composite mixtures, any settling effects are not pronounced.

4.4 Sensing Behavior of p-n Composites

The results of the sensing measurements for CO at 5%O₂ and 600 °C are shown in Figure 4.12. The error bars on the graphs indicate the degree of reproducibility of a particular composition upon subsequent measurements of three different freshly prepared samples. The anatase, 25% rutile and 50% rutile samples all show similar responses within the error bars. For the sample that was composed of 75% rutile, however, the response changes with the sensitivity dropping. A similar trend occurs when these same samples are exposed to CH₄ (Figure 4.13), with the response of the 75% rutile sample midway between the response of the pure anatase and pure rutile sensors. Clearly, in the
75% sample, the added rutile begins to have an effect on the gas response of the sensor. A summary of the different responses of the composite sensors to CO and CH₄ appears in Table 4.1 (CO) and Table 4.2 (CH₄).

Also listed in the tables are the 90% recovery times of the composite sensors. In general, the trend is for the recovery time to decrease as the percentage of rutile increases. The only exception is the 25% rutile sample, which has a shorter recovery time than any of the other samples.

Discussion

In Chapter 1, the ability of TiO₂ to behave as both an n-type and p-type semiconductor was discussed briefly. This behavior has only been noted in the rutile phase of TiO₂, not the anatase phase. Logothetis showed that rutile TiO₂ switched from an n-type behavior, with resistance increasing when the oxygen concentration increased, until between 1x10⁻⁶ and 1x10⁻² atm (dependent on temperature), the behavior was p-type, where increases in oxygen concentration resulted in a decrease in resistance. [9] In our work, the lowest concentration of oxygen tested (0.02 atm) shows a resistance decrease relative to nitrogen and is well within the p-type conductivity range reported by Logothetis.

There are many examples of metal oxides that show a transition from n-type to p-type behavior, from binary compounds such as Ta₂O₅ and SnO₂, to perovskite structures such as BaTiO₃ and KTaO₃ [7]. The p-type behavior of all these materials has been
attributed to the presence of impurities in the structure [7]. For example, if TiO₂ has an
impurity such as alumina, the Al³⁺ can substitute onto titanium sites, moving titanium to
an interstitial position.

\[ 2 \text{Al}_2\text{O}_3 + \text{Ti}_\text{Ti} \rightarrow 4 \text{Al'}_{\text{Ti}} + \text{Ti}_{
\text{II}'}^{\text{III}'} + 3 \text{O}_2 \]  

(4.2)

According to equation 1.12, the interstitial titanium defects provide a source of
electrons for conduction in TiO₂. The concentration of this intrinsic defect decreases
with \(\text{pO}_2\) (and increases with temperature) [10] so that in a certain range of temperature
and pressure, the effects of both intrinsic defects and extrinsic defects (such as Al³⁺) are
apparent on the electrical conductivity [11]. Further increases in the oxygen concentration
results in the annihilation of more interstitial titanium according to [12]:

\[ \text{O}_2 + \text{Ti}_{
\text{II}'}^{\text{III}'} \rightarrow 2 \text{O}_\text{O} + \text{Ti}_\text{Ti} + 4 \text{h}^{'} \]  

(4.3)

The behavior of TiO₂ is now p-type due to the excess of holes in the material. Generally,
p-type behavior only occurs in metal oxides with cations that are capable of being
oxidized such as FeO and MnO, but the presence of acceptor impurities in rutile TiO₂
allows it to have oxygen excess. The ease of this process is such that the enthalpy of
oxidation is actually lower than the enthalpy of reduction (2.2 eV as compared to 10.6
eV) in TiO₂ [7].

Since the electrical responses of anatase and rutile in the presence of \(\text{O}_2\) are
different, so are their responses upon the reaction of the surface adsorbed oxygen on
TiO₂. In the case of anatase, CO reacts with the surface adsorbed species, releasing the
trapped electron back into the grain, increasing its conductivity. On rutile, this same surface reaction occurs. However, as the majority carriers in the material are holes, the injected electron recombines with the hole, resulting in a conductivity decrease.

4.5 Differences in Semiconducting Properties of Anatase and Rutile.

It is shown in Figure 4.1 that, at least in the temperature and pO$_2$ range examined, the anatase phase of TiO$_2$ remains n-type. There are also no known reports of a p-type response of anatase in the literature. The reason for the difference between anatase and rutile has not been thoroughly investigated, but there are several factors that could cause this difference, such as the electronic or crystallographic structure, the relative impurity concentrations of the two phases, difference is grain size, or differences in the interaction of the two samples with oxygen. Each of these points is addressed below.

The unit cells of anatase and rutile were shown in Chapter 1. Both phases of TiO$_2$ have octahedral symmetry with the Ti coordinated to 6 oxygen atoms and the oxygen coordinated to 3 titanium atoms. The two crystal structures are assigned to the same point groups (D4h), but they are each distorted in a different manner from a typical octahedral arrangement (anatase is designated as I4$_1$/amd and rutile as P4$_2$/mnm using space group notation). Because these differences in the anatase and rutile structures are slight, their electronic structures are similar. The band gap of anatase is slightly larger, at 3.2 eV and indirect [13], compared to the 3.0 eV direct gap of rutile [14]. Anatase also has a shallow donor level which leads to a metallic transition at low temperatures [13]. However, it is unlikely that these small differences in electrical structure will affect the n-type vs. p-type behavior of TiO$_2$. Smyth maintains that the impurity concentrations in semiconducting
metal oxides are so much greater than that of the intrinsic \(V_{O}^{\cdot -}\) and \(Ti_{i}\) defects, that the electronic behavior is completely controlled by the presence of these extrinsic defects [7]. Odier et al. state that impurities control the semiconducting behavior above 1000 °C based on fits of the log conductivity vs. log pO2 curves [15].

The anatase and rutile samples used in this study come from the same source material, so it can be assumed that the impurity levels of the samples are the same. These impurities include Fe, Al, Ca, Cr and Zr. Both anatase and rutile go through similar processing conditions, so it seems likely that any additional impurities acquired during preparation would be similar as well. So, the overall amount of impurities can be ruled out as a cause for this p-type behavior. This does not exclude the possibility that the location of impurities in the anatase is different from that in rutile.

If all the impurities in anatase exist as a separate phase (\(Al_{2}O_{3}, Fe_{2}O_{3}\)) or are entirely at interstitial positions, there would be little effect on the electrical response of the material. Commercial anatase was heat treated to obtain the rutile phase. The density of the rutile phase is 4.13 g/cm³, while that of anatase is 3.79 g/cm³ [16], so it is possible that cations which easily fit in the interstitial sites of anatase must move to substitutional positions in the rutile structure.

Most studies of the p-type behavior of rutile consider \(Al^{3+}\) as the model impurity, but there are problems with using this cation as an example when trying to develop a rationale for a lack of p-type behavior in anatase. The ionic radius of \(Al^{3+}\) cation is 0.55 Å, while that of \(Ti^{4+}\) is 0.61 Å [17], so it will easily fit substitutionally on in TiO₂, consistent with models of its electrical behavior [11],[7, 10, 12]. Computer models predict a substitutional doping at low concentrations and interstitial doping at higher \(Al^{3+}\).
concentrations [18]. However, most studies on solid state solutions of Al₂O₃ and rutile report that the solubility is low and that, when it does enter the TiO₂ lattice, it does so interstitially [19, 20]. Furthermore, Al₂O₃ inhibits the anatase to rutile transformation and some reports indicate that it does so by substituting onto a Ti⁴⁺ site [21]. The Al³⁺ cation is then expelled from the TiO₂, forming Al₂O₃ during the transformation. Granted, the concentrations of Al³⁺ considered in studies of electrical behavior are small (<200 ppm) compared to the concentrations used in studies of solid solutions and transformation temperatures, so it is probable that there is Al³⁺ on Ti⁴⁺ sites in small amounts [18, 20]. However, not enough is known about the role of Al³⁺ in anatase for any conclusions to be drawn about the lack of p-type behavior in that structure.

TiO₂ also contains numerous other impurities, some of which are both trivalent and substitutional dopants. One of these is the chromium cation, Cr³⁺. It has an ionic radius of 0.62 Å [17] and has been shown to substitute for titanium in TiO₂. Carpentier et al. showed that doping rutile TiO₂ with chromium lowered the pO₂ level at which the transition from n-type to p-type behavior occurs at 1000 °C [22]. However, the behavior is complicated by equilibrium between Cr⁵⁺ and Cr⁶⁺, which can decrease the concentration of holes [22]. Cr³⁺ is also known to promote the transition of anatase to rutile in a mechanism similar to that described in Chapter 2 for copper [23]. It substitutes onto TiTi⁴⁺ sites, increasing oxygen vacancy concentrations where the transformation nucleates. Venezia et al. show that Cr³⁺ does substitute for Ti⁴⁺ in anatase, but as the temperature is raised, these cations leave their substitutional sites coincident with a transformation of anatase to rutile [24]. The Cr³⁺ then become substitutional impurities in rutile [18, 24]. It is therefore proposed that the high temperatures required for the sensing
sample pretreatment. Substitutional impurities such as Cr\(^{3-}\) are expelled from the Ti\(^{4-}\) lattice sites in anatase and cannot cause p-type behavior in that phase. Based on the Al\(^{3-}\) cation expulsion model that has been proposed for the anatase to rutile transformation [21], it is possible that this same mechanism applies for Al\(^{3-}\) impurities if they are indeed on substitutional sites [18, 20] in anatase.

It has also been proposed that the size of the TiO\(_2\) grains can influence the anatase to rutile transformation. As shown in Figure 4.8 the anatase particles are spherical and have a particle size of approximately 100-200 nm, while the rutile particles are much larger and are more rod-like in shape. Some authors have attributed particle size differences to the p-type and n-type behavior of the material. Knauth and Tuller observed that nanocrystalline anatase grains (35 nm) showed an n-type to ionic conductivity transition, while the coarse-grained rutile shows the n-type to p-type transition [12]. In this work the same source of material was used for both the anatase and rutile, making the impurity concentrations similar. The authors explain that in the nanocrystalline sample, the high density of grain boundaries (as compared to coarse-grained material) allows for ionic conduction along these boundaries. In addition to the ionic transition, there is also a pO\(_2\)^{-1/2} dependence of the conductivity of the nanocrystalline anatase particles [12], which the authors attribute to doubly ionized Ti interstitials. From the limited amount of conductivity data obtained in this study as a function of oxygen, the dependence is somewhere between pO\(_2\)^{-1/4} to pO\(_2\)^{-1/5}. The anatase particles in this study are also larger (100-200 nm as compared to 35 nm), so it appears that the suggested
mechanisms controlling the lack of p-type behavior in the Knauth study do not apply here. Instead, differences in the location of impurities in the anatase and rutile structures, as outlined above, are more plausible for the samples in this study.

4.6 Percolation in p-n Composites

From the data, it is clear that the sensor responds with n-type behavior at certain anatase to rutile compositions, then switches to p-type conduction. The transition between these two behaviors can be described by a percolation phenomena. The behavior of the n-type material is fairly constant until the behavior switches to n-type. Figure 4.14 shows this transition more clearly at one gas concentration.

An example of a percolating system is shown in Figure 4.15. Two different types of spheres, one conducting and one insulating, are contained within a 2-D box. At low concentrations of the conducting spheres, a continuous pathway from one end of the box to the other is not possible (Figure 4.15a), and the system is insulating. However, once a critical concentration is reached, a continuous path is possible (Figure 4.15b). This critical concentration is called the percolation threshold, and occurs at 16% for a 3-d system of monosized spheres [25]. Because the difference between the conductivities of the two particles is large, the transition between insulating and conducting behavior is sharp.

In the p-n composite, a similar behavior occurs, but the transition is between the p-type and n-type behavior, and so percolation of both n-type and p-type grains must be considered. The percolation threshold of each of the grain types will be dependent on the relative particle sizes and shapes of anatase and rutile, and the conductivities of these
particles. and the porosity of the matrix. The anatase particles are much smaller than the rutile particles. which should allow them to easily form a continuous pathway through the matrix. even at low concentration. which explains why the n-type behavior is dominant down to less than 25% rutile. It is still not as low as that of a 3-D monosized sample. but due to the presence of porosity in the sample. not all of the n-type grains will be in contact. Ineffective contact between particles will increase the percolation threshold [25].

The effect of the resistances of the two different particles is much more complex. In the case of the insulator conductor composites. once the conducting spheres percolate. the material easily conducts. and the insulating phase is really just a matrix. In the anatase-rutile composite both particles are semiconductive. with similar baseline resistances. In a polycrystalline sample. the contacts between the grains. which are much more resistive than the bulk. control the behavior of the sample. Instead of just n-n contacts. as would be present in a pure anatase sample. composite sensors also have p-p contacts. and forward and reverse biased p-n contacts. Complicating things further is the fact that the resistance of each of these boundaries is influenced by the presence of reducing gases. So. though there is an abrupt change in which type of conductivity (p-type or n-type) is dominant in the sensor matrix. there are differences in the behavior of the sensors depending on their compositions. As the anatase to rutile ratio changes. the response to the reducing gas changes.

4.6.1 25% Rutile

The sensors made with 25% rutile are well below the percolation threshold based on the SEM micrographs. so the response of the sensor is expected to be similar to that of
a sensors made of purely anatase. For the response to CO, the average response of the 25% rutile sensor is very similar to that of the average anatase response. However, in the case of CH₄, the average sensor response is lower than that of the 50% sample.

Of the three composite mixtures, the 25% rutile has the largest deviation in behavior between sensors. This is most likely due to the ineffective mixing of the anatase and rutile in the 25% rutile sample. Based on the XRD data, the 25% rutile samples are not homogeneously mixed, and this poor mixing, possibly with rutile particles preferentially at the bottom of the film, affects the sensor behavior. In this layered sample, the smaller anatase particles will penetrate the pores of the rutile layer, resulting in a rutile-rich layer near the electrodes and if the electrodes mostly sample the film nearest the electrode, then the response of the sensor will more closely resemble that of a high rutile concentration sensor, such as the one that is 75% rutile.

4.6.2 50% Rutile

As with the 25% sample, the SEM indicates that the 50% rutile sample is well below the percolation threshold. The sensing behavior resembles that of the pure anatase. The deviation between the different 50% sensors made is smaller than that of the 25% rutile sensor, which can be explained by the more homogeneous nature of the sensing films, as evidenced by XRD. All the sensors tested showed similar rutile concentrations to that of the original mixture.
4.6.3 75% Rutile

In the 75% rutile sample, the SEM micrographs show significant contact between rutile grains, suggesting that this is a composition where both the anatase and rutile particles percolate. These two pathways for conduction can be considered as two parallel resistors, with the overall resistance, $R_{\text{eff}}$, based on contributions from both pathways:

$$\frac{1}{R_{\text{eff}}} = \frac{1}{<R_{\text{nn}}>} + \frac{1}{<R_{\text{pp}}>} \quad (4.4)$$

where $<R_{\text{nn}}>$ is the resistance of an n-type chain divided by the number of n-type chains, and $<R_{\text{pp}}>$ is the resistance of a p-type chain divided by the number of p-type chains. Clearly, as the behavior of the sensor is n-type, there are more n-type chains than p-type chains in the composite.

Another possibility is with the greater number of p-type grains, there are more p-n junctions in the film and that they are now controlling the response of the sensor. Yoon et al. used this reasoning to explain the behavior of their CuO-ZnO composites [6]. They reasoned that gas exposure lowered the saturation current for the reverse bias electron transport across the p-n junction, increasing the resistance of the p-n pathway, and leading to diminished sensitivities [6]. However, in a 3-D matrix, it seems more likely that an electron would find an alternate pathway, in other words, a more conductive p-p path, and this p-n effect would not be important. The micrographs of the 75% sample, which show a high degree of contact between rutile particles, support a parallel pathway, rather than p-n junctions, for the decreased gas response.

While the mixture of anatase and rutile near the percolation threshold diminishes the gas sensitivity of CO and CH₄, the result is sensor selectivity. Figure 4.16 compares
the response of CO and CH$_4$ of the 75% rutile sensor. Throughout the concentrations studied, the CH$_4$ response remains negligible, similar to that achieved through doping of anatase with CuO in Chapter 2. In this case, however, an electrical rather than chemical difference is the mechanism for the selectivity.

4.7 Modeling of p-n Composite Sensors

In collaboration with researchers in the Department of Physics at The Ohio State University, a model has been developed to describe the behavior of the p-n composite. Using Generalized Effective Medium Theory, Brian Chwieroth and Professor Bruce Patton have calculated the percolation threshold for the anatase-rutile system and can model where surface connectivity of the different grain type occurs as a function of volume fraction of these grains.

Chwieroth and Patton considered five types of grain contacts to be contained within the composite sensing film: n-n, n-p, p-n, p-p and grain-void. Whether the behavior of the composite is n-type or p-type depends on which pathway is the least resistive. Of the five possible pathways, the grain-void, and the p-n (reverse bias) pathways are considered highly resistive and therefore not likely to control the p-n transition. The n-p contact is the least resistive, but once an electron has reached a p-type grain, it has to have a continuous chain of p-type grains in order to conduct to another grain. In other words, the path must be nnnnnppppp in order to be a least resistive path. The probability of this path occurring, and influencing the transition is unlikely.

Only two possible pathways remain of the original 5, the n-n and the p-p. Therefore, in order for the composite to be p-type, the rutile particles must percolate.
for the response to be n-type, the anatase particles must percolate. Chwieroth and Patton calculated first the percolation threshold, the relative amount of surface contact necessary to have a continuous chain for one type of particle. Then developed a model for the amount of surface contact present in the composite for one type of grain as a function of particle size (of both anatase and rutile) and porosity. The fractional value of the n-n surface contact ($f_{nn}$) is:

$$f_{nn} = \frac{(1 - f_p) \left( (1 - f_p) + f_p \left( \frac{r_p}{r_n} + \frac{1}{0.789 \left( \frac{1 - f_n}{1 - f_p} \right)} \right) \right)^2}{(1 - f_p) + f_p \left( \frac{r_p}{r_n} + \frac{1}{0.789 \left( \frac{1 - f_n}{1 - f_p} \right)} \right) \left( \frac{r_p}{r_n} + \frac{1}{0.789 \left( \frac{1 - f_n}{1 - f_p} \right)} \right)^2} \quad (4.4)$$

where $f_p$ is the weight fraction of the p-type material, $r_p$ is the radius of the p-type grain, $r_n$ is the radius of the n-type particle and $f_n$ is the porosity of the composite. Figure 4.17 shows the result of their model. The results show that the n-type grains stop percolating at the same time that the p-type grains start percolating, at a concentration of 82% rutile, a reasonable match to the experimental data. This means that in the n-type regime, only n-type particles contribute to the overall conductivity, and in the p-type regime only the p-type particles contribute to the overall conductivity. However, the experimental data, particularly the 75% rutile sample, shows that both pathways may be contributing to the measured response. The model only considers the differences in the sizes of the anatase and rutile particles, and not differences in the shapes (it assumes that they are both spheres), which may account for this difference between experiment and model. The
addition of further detail to the model, such as the distribution and shapes of the rutile particles to more closely match those shown by SEM, is expected to compare better with the experimental results.

4.8 Conclusion

Mixture of anatase (n-type) and rutile (p-type) behave as percolating system, with n-type behavior below 80% rutile and p-type behavior above this concentration. The percolation threshold is governed by both the relative conductivities of the two phases of TiO₂, and by their relative particles sizes. Calculations using Effective Medium Theory support the transition concentration, and based on a model that considers only n-n or p-p pathways, predicts that only one of the two types of chain are percolating. SEM micrographs indicate that there may actually be two percolative paths in the 75% sample and that the overall resistance change of the sample is a sum of both their behaviors. The diminished sensitivity to CO and CH₄ of the 75% sample leads to selective CO sensing in the concentration range evaluated.
References


### Table 4.1: Summary of sensing behavior of anatase-rutile composite to carbon monoxide at 600 °C, 5%O₂/N₂.

<table>
<thead>
<tr>
<th>Sample</th>
<th>R₀ (MΩ)</th>
<th>250 ppm</th>
<th>500 ppm</th>
<th>750 ppm</th>
<th>1000 ppm</th>
<th>Recovery (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>anatase*</td>
<td>1.11</td>
<td>0.500</td>
<td>0.413</td>
<td>0.372</td>
<td>0.338</td>
<td>830</td>
</tr>
<tr>
<td>25% rutile*</td>
<td>2.43</td>
<td>0.653</td>
<td>0.548</td>
<td>0.500</td>
<td>0.424</td>
<td>40</td>
</tr>
<tr>
<td>50% rutile*</td>
<td>2.25</td>
<td>0.556</td>
<td>0.478</td>
<td>0.438</td>
<td>0.404</td>
<td>500</td>
</tr>
<tr>
<td>75% rutile*</td>
<td>1.94</td>
<td>0.782</td>
<td>0.720</td>
<td>0.684</td>
<td>0.654</td>
<td>380</td>
</tr>
<tr>
<td>rutile</td>
<td>1.38</td>
<td>1.67</td>
<td>1.856</td>
<td>1.92</td>
<td>1.956</td>
<td>230</td>
</tr>
</tbody>
</table>

*average results of three different sensors

### Table 4.2: Summary of sensing behavior of anatase-rutile composite to methane at 600 °C, 5%O₂/N₂.

<table>
<thead>
<tr>
<th>Sample</th>
<th>R₀ (MΩ)</th>
<th>250 ppm</th>
<th>500 ppm</th>
<th>750 ppm</th>
<th>1000 ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>anatase*</td>
<td>1.11</td>
<td>0.746</td>
<td>0.695</td>
<td>0.662</td>
<td>0.653</td>
</tr>
<tr>
<td>25% rutile*</td>
<td>2.43</td>
<td>0.968</td>
<td>0.939</td>
<td>0.914</td>
<td>0.891</td>
</tr>
<tr>
<td>50% rutile*</td>
<td>2.25</td>
<td>0.869</td>
<td>0.824</td>
<td>0.790</td>
<td>0.768</td>
</tr>
<tr>
<td>75% rutile*</td>
<td>1.94</td>
<td>0.981</td>
<td>0.971</td>
<td>0.966</td>
<td>0.960</td>
</tr>
<tr>
<td>rutile</td>
<td>1.38</td>
<td>1.08</td>
<td>1.121</td>
<td>1.16</td>
<td>1.21</td>
</tr>
</tbody>
</table>

*average results of three different sensors
Figure 4.1: Effect of oxygen on the resistance of titania sensors. a) anatase, b) rutile.
Figure 4.2: Response of TiO$_2$ sensors to CO and CH$_4$ at 600 °C and 5%O$_2$/N$_2$. a) anatase; b) rutile.
Figure 4.3: XRD of anatase-rutile composite mixtures after 800 °C heat treatment. a) 100% anatase; b) 25% rutile; c) 50% rutile; d) 75% rutile; e) 100% rutile.
Figure 4.4: XRD patterns of 25% rutile composite. a) powder; b) sensor 1; c) sensor 2.
Figure 4.5: X-ray diffraction patterns of 25% rutile sensor with layers of sensing film removed. * alumina, ^ gold.
Figure 4.6: X-ray diffraction pattern of 50% rutile sensors. a) powder; b) sensor 50-1; c) sensor 50-2.
Figure 4.7: X-ray diffraction patterns of 75% rutile sensor. a) powder; b) sensor 75-1; c) sensor 75-2.
Figure 4.8: SEM micrographs of TiO$_2$ that has been heat treated at 800 $^\circ$C. a) anatase; b) rutile. (Micrographs by Ms. Hyunjung Lee)
Figure 4.9: SEM micrographs of 25% Rutile composite sensors. a) sensor 1, b) sensor 2. (Micrographs by Dr. Perena Gouma and Ms. Hyunjung Lee)
Figure 4.10: SEM micrograph of 50% rutile composite sensor. (Micrograph by Ms. Hyunjung Lee)
Figure 4.11: SEM Micrographs of 75% rutile sample at two different magnifications. (Micrographs by Ms. Hyunjung Lee)
Figure 4.12: Response of p-n composite sensors to CO at 5%O₂/N₂, 600 °C. a) 100% anatase; b) 25% rutile; c) 50% rutile; d) 75% rutile; e) 100% rutile.
Figure 4.13: Response of p-n composite sensors to CH$_4$ at 5%O$_2$/N$_2$, 600 °C. a) 100% anatase; b) 25% rutile; c) 50% rutile; d) 75% rutile; e) 100% rutile.
Figure 4.14: Bar graph representation of percolation in anatase-rutile composite at 750 ppm CO (in 5%O₂/N₂) at 600 °C.
Figure 4.15: Schematic drawing of insulator-conductor composites. a) below percolation threshold; b) above percolation threshold.
Figure 4.16: Sensing response of 75% rutile sensor at 5%O₂/N₂, 600 °C. a) CO; b) CH₄.
Figure 4.17: Results of model of composite. (Data courtesy of Mr. Brian Chwieroth).
CHAPTER 5

SOL-GEL TITANIA SENSORS

Introduction

There are a number of different methods for making materials for sensor applications. As we saw in Chapter 2, one method is to ball-mill, or solution mix the semiconducting metal oxide with dopants for making thick film sensors. Alternatively, wet-impregnation techniques can be used for adding dopants to sensing powders either before or after deposition on a sensing substrate. For thin film sensors, materials are either sputtered [1] or deposited through chemical vapor deposition, methods which generally result in low porosity films with small particles sizes [1]. Finally, there is the sol-gel route to making sensor materials, which can be used for making either thick or thin films [2, 3].

In the sol-gel synthesis of metal oxides, a metal alkoxide is hydrolyzed, then suspended in a solution (usually water and/or alcohol based) called a sol. This sol can be evaporated to a powder, allowing for the preparation of thick films, or coated in sol form onto the sensing substrate, resulting in thin film sensor materials.
The use of sol-gel methodology offers several potential advantages to sensor development. Firstly, dopants can be added directly to the sol prior to any drying or deposition steps, resulting in a homogeneous dispersion of the dopants in the final film [2]. Sol-gel synthesis also produces materials with small initial particle sizes. Though these particles will grow substantially with heat treatments, the final particle sizes are often smaller than those of commercial grade powders, giving a much higher surface area and presumably, higher sensitivity and faster responses to gases [4]. It has also been proposed that the use of a wet synthesis and sensor fabrication method, such as sol-gel, may produce films that exceed the stability of films made by dry synthesis methods such as sputtering [5]. Lastly, because both thick and thin films can be made from materials from the same synthesis method, comparisons between thick and thin film sensor performance can be made and not be encumbered by the material’s history (i.e. heat treatments, starting materials and impurities).

A number of authors have explored sol-gel materials for sensor applications [6-9]. Primarily, the focus has been on thin film SnO2 sensors, which show differences in sensitivity and selectivity based on sol-gel synthesis conditions and sample heat treatment and testing temperatures [4. 6. 7]. Reports on sol-gel sensors generally show good sensitivity to analyte gases, though the rationale for this sensitivity is a subject of debate. Though it is agreed upon that differences in the sensor microstructure are important in gas sensitivity, which aspect of the microstructure, such as porosity, particle size or film thickness, is responsible for changes in gas sensitivity [2. 7. 8. 10] is not agreed upon. Most research is focused on the comparison of preparation conditions of the
sol-gel sensor, but a few compare the sol-gel sensor performance with that of conventional sensor types. Chung et al. report higher gas sensitivities for their In$_2$O$_3$ thin film sensors as compared to the pellet-type sensors [11].

Only a few researchers have investigated sol-gel derived TiO$_2$ as a sensing material. Li and Chen have studied sol-gel TiO$_2$ as an oxygen sensor at temperatures of 600 to 1000 °C [3]. They found that the sensors showed the expected linear change of log R vs log pO$_2$, with the slope changing with temperature, indicating that the dominant defect type varied with temperature. Their sensors had response times below 1 second [3]. Hayakawa et al. studied TiO$_2$ sol-gel films doped with Pt as sensors for H$_2$ that discriminated against CO and CH$_4$ [2]. By adding a sol-gel with a confirmed particle size of 7 nm to a 'precursor' TiO$_2$ sol containing 2 wt.% Pt, the sensitivity to H$_2$ at low temperatures was altered. Depending on the concentration of the 7 nm sol added, the final porosity and microstructure of the sensing films was affected, influencing the behavior [2].

5.1 Sol-Gel Chemistry

Figure 5.1 shows a flow chart for the process for preparing sol-gel materials. Typically, the starting material in the synthesis of transition metal oxides is a metal alkoxide [12], MOR, where M is the metal atom and R is an alkyl group. In the presence of water, metal alkoxides easily react to form metal hydroxides:

\[ \text{M-OR} + \text{H}_2\text{O} \rightarrow \text{M-OH} + \text{R-OH} \]  

(5.1)
Following the hydrolysis step, a number of different condensation reactions occur which result in the formation of metal-oxygen-metal bonds, the eventual result being an extended metal oxide network [12, 13]. Two examples of condensation reactions are given below.

Alkoxolation:

\[ \text{M-OH} + \text{M-OR} \rightarrow \text{M-O-M} + \text{R-OH} \]  \hspace{1cm} (5.2)

Oxolation:

\[ \text{M-OH} + \text{M-OH} \rightarrow \text{M-O-M} + \text{H}_2\text{O} \]  \hspace{1cm} (5.3)

In the synthesis of some metal oxides, an acid catalyst is added to the reaction mixture which protonates the alkoxy group and makes it a better leaving group. The ends of the chains (with 3 -OR ligands) are more easily protonated, so the addition of the acid promotes hydrolysis reactions that lead to longer chain lengths rather than a highly branched metal oxide network [12].

The metal oxide networks that form from the above reactions often coagulate, and sometimes precipitate, from the solution. However, the particles can be redispersed through a process called peptization. The presence of an acid can help in the peptization process by (re)establishing a double layer on the particles [12].

Once the sol has formed, it can be used directly for coating processes, or can be dried. During the removal of the solvent the colloidal sol first forms a gel, and upon further solvent evaporation, a powder.
A number of parameters can be used to alter the final properties of the metal oxide derived from the sol-gel process. A high water:alkoxide ratio has been shown to reduce the crystallite size of calcined titania by favoring nucleation (hydrolysis) rather than crystal growth (condensation) [13]. The type of acid used in the synthesis has been shown to affect particle growth, and in the case of titania, influence the temperature of the anatase to rutile transformation [14]. Oxalic acid, for example, shows little rutile formation after a 900 °C heat treatment compared to similar pH sols made with different acids [14]. The pH itself can also be a factor, affecting the surface area and porosity of titania films [15]. The number of parameters which effect sol-gel derived materials is limitless, with peptization temperatures, the addition of co-solvents, and alkoxide group also playing a role.

In this chapter the use of sol-gel titania as the active material for gas sensing is explored. The influence of various synthesis and preparation parameters on sol-gel titania is studied. The pH, temperature and dopants are the parameters that are varied, and their influence on both the structure of titania (both crystallographic and morphological) as well as their influence on the sensing behavior is compared. In addition, a preliminary study of the viability of thin films of titania (< 1 micron thick) made from sol-gel materials is presented.
5.2 Experimental

The sol-gel titania was synthesized based on a procedure by Xu and Anderson for making highly porous titania membranes [15]. Titanium isopropoxide was added to a solution of HNO₃ in water so that the ratio of Ti : H₂O : H⁺ was 1:140:0.3. A white precipitate formed immediately upon the addition of the titanium isopropoxide to the acid solution. The solutions was stirred at room temperature for 3 days allowing this white precipitate to peptize ('re-dissolve') in the solution, resulting in a clear sol with a TiO₂ concentration of 0.3 M. The pH of the sol was adjusted to a desired level by dialysis with a Spectra Por cellulose membrane with a molecular weight cutoff of 35,000.

A Headway Research Inc. photo-resist spinner was used to spin coat the thin film sensors. The sensing substrate was placed on the rotating post of a spin coater, and a few drops of the sol dropped on the surface. The post was then rotated at 2000 rpm for 40 s. At this point a dry film was present on the surface. The film was heated at 450 °C for one hour between layers. A final 700 °C heat treatment was done on all the films.

A portion of the sol would be dried at room temperature in a petri dish until all of the water had evaporated and a powder remained. This titania powder could be deposited on the sensing substrates in the same method as the commercial powder sources (see sections 2.2 and 4.2).

Doping with La³⁺ was done by adding the desired volume of a 0.3 M La(NO₃)₃ solution to the sol. Copper doping was done in a similar manner with a 2.2 x 10⁻⁴ M
Cu(NO$_3$)$_2$ solution. A portion of the sol would be dried at room temperature in a petri dish until all of the water had evaporated and a powder remained.

X-ray diffraction patterns were collected on a Rigaku Geigerflex diffractometer using Ni-filtered CuK$_a$ radiation at 40 kV and 25 mA between 2$\theta$ = 20$^\circ$ and 80$^\circ$.

Scanning Electron Micrographs were taken on either a Phillips XL30 FEG SEM or a Jeol JSM-820 electron microscope. Raman spectra were taken with a Dilor XY Raman microscope using the 514.5 nm line of an Innova Coherent 300 Ar$^+$ ion laser. A 200 cm$^{-1}$ cutoff filter was used to remove the Raleigh line.

**Results**

**5.3 Effect of Heat Treatment on Sol-Gel Derived TiO$_2$ Powders**

The sol-gel materials for this study were synthesized at room temperature, but since the sensing measurements were made at much higher temperatures, it is important to understand how high temperatures affect these materials. Metal oxide particles suspended in a sol are typically of the order of 3-5 nm. Studies of TiO$_2$ sols agree with these results. Figure 5.2 shows a TEM micrograph of particles of TiO$_2$ that have been deposited directly from the sol on copper grids. The particles are 5-8 nm in size and made up of anatase and amorphous material. N$_2$ BET measurements of an as-dried sol-gel sample showed that the initial surface area was 190 m$^2$/g. Elemental analysis of the sol-gel samples was also done. The results showing that the sol-gel TiO$_2$ (after ball-milling and heat treatment) had the following impurities: 403 ppm Ca, 300 ppm Fe, 44 ppm Cr, 37 ppm Ni, 11763 ppm Zr, and <60 ppm Al. The high zirconia impurity likely comes from
the zirconia balls used for milling. For comparison, the commercial anatase (used for Chapter 4) had these same impurities in the following concentrations: 115 ppm Ca, 115 ppm Fe, 485 ppm Al, 16 ppm Cr, 9 ppm Ni and 582 ppm Zr.

5.3.1 X-ray Diffraction Analysis

Figure 5.3 shows the XRD pattern of sol-gel derived TiO$_2$ (sol pH = 2.58) as synthesized (Figure 5.3a) and as it is heated at 500 and 700 °C for 1 hour (Figures 5.3b and 5.3c, respectively). As can be seen in the figures, increasing the temperature results in the transformation of anatase to rutile, in addition to particle size growth (as evidenced by line narrowing). Table 5.1 summarizes the effect of temperature on this sample. The amount of rutile was quantified using equation 4.1, and shows that at 500 °C, the sample is 69 % rutile, and by 700 °C, is 100 % rutile.

Particles sizes ($t$) for the untreated, 500 °C and 700 °C heat treated samples were estimated using the Scherrer equation:

$$t = \frac{0.9 \lambda}{B \cos \Theta_B}$$  \hspace{1cm} (5.4)

where $\lambda$ is the wavelength of the x-ray (1.5418 Å for Cu), $B$ is the full width at half maximum in radians, and $\Theta_B$ is the diffraction angle of the peak. Line broadening shows that, initially, the anatase particles are about 14 nm in size and do not change much in size as the temperature increases. The rutile particles are slightly larger in size, about 20 nm at 500 °C, and grow to 25 nm by 700 °C.

Heat treatment studies were also done on sol-gel powders from different pH sols. After peptization, the pH of the sol is typically between 1.2 and 1.5, but by using dialysis.
the pH of the sol can be raised, as was the case for the sample discussed above. Figures 5.4 and 5.5 show the XRD patterns of samples that had sol pH's of 1.72 and 1.44, respectively. In each of these two samples the amount of rutile formed was slightly less than that of the higher pH sol (see Table 5.1). After a 500 °C heat treatment, the pH 1.72 sol has 68% rutile, close to that of the pH = 2.56 sample, while the pH 1.44 sol has 46% rutile.

The change in pH also has an effect on the particle growth of the titania. The anatase particles from the pH = 2.56, 1.72 and 1.44 samples have similar sizes (14-15 nm) at 500 °C, but at 700 °C, the particles are larger, 33 nm for pH 1.72 and 23 nm for pH 1.44. The rutile particles do not seem to have as dramatic a change in size as the anatase particles. After the 700 °C heat treatment the particle sizes are 21 nm for the pH = 1.72 sample and 24 nm for the pH = 1.44 sample.

Allowing the low pH samples to age over a period of months does not appear to significantly affect the anatase to rutile transformation or the particle size growth, as summarized in Table 5.1. This indicates that the sols are quite stable and that a time constraint on their use is not crucial. Heat treatments of these aged samples at 800 °C showed the expected result: that the TiO₂ is completely in the rutile phase at this temperature. The rutile particles are larger than those after lower temperature treatments, 32 and 51 nm for pH's of 1.72 and 1.44, respectively.
5.3.2 Electron Microscopy

Electron microscopic techniques were used to obtain supporting information about the particle sizes and morphologies of anatase and rutile. The studies of the anatase to rutile transformation were by collaborators P. I. Gouma and Professor M. J. Mills using in situ TEM [16]. Figure 5.6 shows the transmission electron micrograph of titania films at room temperature, and the accompanying diffraction pattern. This initial particle size is estimated at 8 nm, and the diffraction rings correspond to the anatase phase. Figure 5.6b shows the evolution of the titania upon in situ heating of the sample to 400 °C. Some of the anatase particles have grown in size to about 20 to 30 nm, but the majority of the matrix is still about 8 nm. Upon further heating, to 500 °C, the larger anatase particle begins to transform into rutile, and consume the neighboring nanocrystalline anatase as they grow. By 600 °C, the rutile particles are much larger, about 200 to 300 nm, and the remaining anatase particles are about 20 nm.

Interestingly, TEM micrographs of titania particles that were transformed from anatase to rutile ex situ show a strikingly different rutile morphology. Figure 5.7 shows the TEM micrographs of the same sol gel sample if transformed directly to rutile by a 2 hour heat treatment at 600 °C. These rutile particles are elongated, not spherical, and most are 300 nm or more in length.

SEM micrographs were taken of some of the samples described in section 5.3.1. Figure 5.8 shows the scanning electron micrographs of the pH=2.56 and pH=1.72 samples after heat treatment for 1 hour at 700 °C. Both had shown mostly rutile by the X-ray diffraction patterns. Here both samples have similar micrographs. Each shows a
mixture of 80-100 nm particles, spherical in shape and highly agglomerated. Within each mixture, however, there are larger crystals that appear as 'chunks' of approximately 1-3 microns in size. Increasing the temperature of the heat treatment does not appear to affect this distribution of spherical particles to larger 'chunks'. Figure 5.9 shows an SEM micrograph of the particles upon heat treatment at 800 °C for 1 hour (pH = 1.72). Again, the sample shows an abundance of the 80-100 nm particles.

To summarize, the heat treatment applied to the undoped sol-gel materials cause both grain growth and a transformation of the anatase phase to the rutile phase. This transformation occurs at a temperature well below that of the commercial anatase powders studied in earlier chapters. Changing the pH of the sol-gel had a small effect on the final sol-gel powder. TEM analysis supports the phase transformation and grain growth behavior observed by XRD.

5.4 Effect of Heat Treatment on Doped Sol-Gel Titania

In Chapter 2, it was discussed how the addition of dopants can either inhibit or promote the anatase to rutile transformation. Doping TiO₂ sols with La(NO₃)₃ solutions has been demonstrated as an effective means of inhibiting the anatase to rutile transformation at temperatures up to 900 °C [17]. As the method of preparing the sols can influence the transition, studies of the effect on La addition by solution phase doping have been done for the sol-gel samples discussed in section 5.3. Copper addition to
anatase is known to promote the transformation to the rutile phase. However, there are examples in the literature of copper stabilizing the anatase phase when prepared by the sol-gel method.

5.4.1 X-ray Diffraction Studies

The concentration of La can affect the transformation of the TiO$_2$ from the anatase to rutile phase. At a pH of 2.58, even a small addition of La (0.5 mol\%$)$ can influence the transformation, with a 500 °C treatment resulting in a 30% transformation, and a second hour at 700 °C results in 85% transformation as shown in Figure 5.11a and 5.12a. Increasing the concentration of La suppresses the transformation further. At 7 mol \% La, there is no transformation after 1 hr at 500 °C, and a second hour at 700 °C increases the amount of rutile to only 23% (Figures 5.11b and 5.12b). The 10\% La sample shows no transformation after exposure to either temperature. Temperatures of 800 °C are required to make a significant transformation for these higher La content samples. Figure 5.13 shows the XRD patterns of the 7% La and 10% La samples after an additional hour at 800 °C. The 7 mol \% sample shows 78% transformation, while the 10% sample is 100% transformed to rutile. The XRD pattern for the 10% La doped sample shows the presence of La$_2$O$_3$ as a separate phase. The diffraction peak for La$_2$O$_3$ at $2\Theta = 27.0$ is only observed on this sample.

By changing the pH of the La-doped sols, further inhibition of the anatase to rutile transformation is possible. Figure 5.14 shows the XRD patterns of pH = 1.44, 1.72 and 2.58 sols that have been heated to 500 °C, then 700 °C and finally 800 °C, each
temperature for one hour. The lower pH samples show much lower degrees of transformation. The pH = 1.44 sample shows almost no transformation until 700 °C, and is only 32% rutile at 800 °C, while the pH = 2.58 sample is 23% rutile at 700 °C and 78% rutile at 800 °C.

Table 5.2 summarizes the anatase to rutile transformation data, and includes the estimated average particle size from XRD lineshape broadening. The La-doped samples show no significant particle size changes with temperature. The anatase particles are generally 10-15 nm, and the rutile particles are always 20-30 nm.

The effect of added copper on the sol-gel titania was also investigated. Figure 5.15 shows the XRD patterns of sol-gel titania doped with 2 mol\% Cu(NO₃)₂ that has been heat treated at either 500 °C or 700 °C for one hour. Following the 500 °C heat treatment, the sample is over 50% rutile, the same as the non-doped sample. At 700 °C, however, the sample is 100% rutile, exceeding the concentration of the undoped counterpart (pH = 1.72). The addition of Cu²⁺ also increases the rutile particle size. After the 700 °C heat treatment, the XRD lineshape broadening estimates the rutile particle size as 59 nm.

5.4.2 Electron Microscopy

SEM micrographs of the doped samples after the high temperature treatments of both the 7 and 10 mol% La samples are shown in Figure 5.16. The estimated particle size of the TiO₂ particles after heat treatment at 800 °C are 100 nm, and the particles are
highly agglomerated, in clusters of up to 2 microns. Analysis of these same samples by Energy Dispersive X-rays (EDX) did not show any peaks that could be attributed to La. Only those due to Ti were present.

An electron micrograph of the Cu-doped sol-gel is pictured in Figure 5.17. The micrograph shows particles that are as small as 100 nm in size, which by XRD are known to be entirely rutile. The particles are highly sintered, making it difficult to estimate a maximum particle size. EDX analysis of the sample had peaks that could be attributed to Cu. However, specific particles in the sample could not be clearly identified as CuO. This suggests that copper is highly dispersed.

The addition of La\(^{3+}\) to the sol-gel titania raises the temperature at which the anatase to rutile transformation occurs as well as inhibiting the growth of the particles. This effect is more pronounced in samples that are at a lower pH. If Cu\(^{2+}\) is added instead of La\(^{3+}\), the transformation is more comparable to the undoped samples. Final rutile particle sizes with added Cu\(^{2+}\) are larger than those from undoped and La\(^{3+}\)-doped titania.

5.5 Thick Film Sensors

The powders described in the previous three sections were investigated for their sensing behaviors, with the results summarized in Tables 5.3 and 5.4. The effect of pH, heat-treatment temperature and dopants was studied. Two heat treatments were done on each sample. Heat treatment 1 (HT1) refers to the heat treatment of the sol-gel derived powder prior to deposition on the sensing substrate (either 500\(^\circ\)C, 700\(^\circ\)C or 800\(^\circ\)C for 1...
hour), and heat treatment 2 (HT2) refers to the heat treatment after the sensor was deposited onto the sensing substrate (either 700° or 800°C). HT2 was always greater than or equal to HT1. Figure 5.19 shows the effect of pH on the sensing behavior of the sol-gel sensor, where HT1 was 500 °C and HT2 was 700 °C, with the measurement made at 600 °C, 5%O2/N2. The trend in the response to CO is pH = 2.58 > 1.44 = 1.72, all n-type behavior. The trend for the response to methane is reversed, with pH = 2.58 the least sensitive. The baseline resistances also show a trend, with pH = 2.58 having the lowest $R_\infty$, 2.95 MΩ, and the pH = 1.72 and 1.44 having $R_\infty$'s of 11.8 and 12.8 MΩ, respectively. The pH appears to have a greater effect on the baseline resistance of the sensor than on the gas sensitivity. The recovery times of the sensors do not follow a trend; the pH=1.44 sensor recovers the fastest, and the pH=1.72, the slowest.

Changing either the powder (HT1) or on-substrate (HT2) heat treatment temperature of the materials does not appear to affect the gas sensitivity of the sensors. Figure 5.20 shows the response of the pH=1.72 sensor at two different HT1 temperatures, 700° and 800 °C, while HT2 is 800 °C for both sensors. There is little difference in the behavior of the two materials. When the HT1 temperature is the same for the powders, but HT2 is varied (either 700° or 800 °C), there is a more noticeable difference in the sensing behavior as seen in Figure 5.21. The response to CO is greater when the HT2 temperature is 800 °C, but that to CH4 decreases. The recovery time of the sensors subjected to different heat treatment conditions are similar to one another.

Table 5.4 summarizes the response of the doped sol-gel samples to CO and CH4. After the heat treatments, HT1 and HT2, the sensors, whether doped with La³⁺ or Cu²⁺ are
mostly rutile. The addition of La$^{3+}$ to the samples only affects the gas sensitivity slightly. Figure 5.22 shows the response of pH 2.58 sol-gel titania doped with 7 mol% La and 10 mol% La. compared with the undoped sample. The addition of La$^{3+}$ decreases the response to CO and increases the response to CH$_4$, but there is little difference in the gas sensitivity between the two concentrations of La$^{3+}$. The baseline resistance of the samples with 7 and 10 mol% La are 11 and 14 MΩ, respectively, while that of the undoped is 3 MΩ. A difference in the first heat treatment, HT1, also causes small changes in the sensor response, as shown in Figure 5.23. Increasing HT1 from 700° to 800 °C improves the response to both CO and CH$_4$. This temperature change also greatly affects the baseline resistance of the sensor, dropping it from 64 to 11 MΩ.

The effect of Cu$^{2+}$ doping is shown in Figure 5.24 and 5.25. The response of the sensors to CO and CH$_4$ is still n-type, but the sensitivity has dropped to both gases. The response to CH$_4$ is nearly baseline, while that to CO is greatly reduced when compared to the undoped titania. The heat treatment temperature also has an effect on the gas sensitivity. Figure 5.25 shows the response of the Cu$^{2+}$ doped sensor after a HT1 of 700° and 800 °C. The sensitivity to both CH$_4$ and CO drops when the heat treatment temperature is increased. The copper doping also reduces the baseline resistance of the sensors to 2-3 MΩ. The recovery times of the two Cu-doped sensors are similar.

For the thick film sensors, the addition of Cu$^{2+}$ as a dopant has the largest effect on the gas sensitivity, decreasing the sensitivity to both CO and CH$_4$. The changes to the other parameters result in only minor effects to the gas sensitivity. Despite these small changes, it is interesting to note that whenever the CO sensitivity increases for the non-
doped sensors, the sensitivity to CH₄ drops. However, for the doped sensors, either the sensitivity to both gases increases (or decreases) as a condition is changed.

5.6 Thin Film Sensors

The thin film sensors were made by spin coating the TiO₂ from the sol onto the sensing substrate, then heat treating the films prior to sensing measurements as done in the thick film samples. The effect of sample thickness and heat treatment time on the sensing response was studied to provide preliminary information into the feasibility of sol-gel thin films as high temperature gas sensors. To characterize these films, a combination of SEM and Raman spectroscopy were used to obtain information about particles sizes, titania polymorphs and film thickness.

5.6.1 Characterization of Thin Films

For the thick film sol-gel based sensors, characterization results of the bulk powders were assumed to apply to the powders on sensing substrates. In part, this is because most of the heat treatments were done on the powder prior to deposition on the substrate. Furthermore, the film thickness is such that the small amount of sample in contact with the substrate is a small percent of the total sample. For the thin film samples this same assumption cannot be made. These films are optically clear, so the assumption is that alumina-titania and gold-titania interfaces could be important in the nature of the sensing film. The thinness of these films, while presenting the possibility of different behavior than the thicker films, are difficult to analyze, as the penetration depth of many
5.6.1a Raman Spectroscopy

The anatase and rutile phases of TiO$_2$ have different Raman spectra, making it possible to determine the presence of either of the two phases. Using the microprobe, a small section of the coated alumina substrate could be brought into focus, but the film itself could not be resolved. Still, the film was thick enough to detect the presence of TiO$_2$ on the surface using Raman. Figure 5.26 shows the spectra of two different sensors, the first (a) with 1 layer of titania, and the other (b and c) with 20 layers of titania. The raman spectra for the anatase phase of TiO$_2$ has peaks at 143 (vvs), 194 (w), 326 (vw), 393 (m), 512 (m), 635 (m) and 794 (vw) cm$^{-1}$, while rutile has peaks at 143 (w), 236 (m), 442 (s), 607 (s), 695 (vw) and 825 (vw) cm$^{-1}$ [18]. Typically, the relative intensity of the strongest bands of anatase (143 cm$^{-1}$) and rutile (607 cm$^{-1}$) are used to determine the relative amount of anatase and rutile of titania [18], but because of the 200 cm$^{-1}$ cutoff filter in place the 143 cm$^{-1}$ was not present in the spectra, and the region between 200 cm$^{-1}$ and 400 cm$^{-1}$ shows some spectral artifacts from the presence of the filter. Instead, the spectra were monitored for the presence 635 and 512 cm$^{-1}$ bands of anatase. Qualitatively, it is apparent that in both the 1 layer and 20 layer films there is anatase present.
Figure 5.26b and 5.26c show two different regions of the same 20 layer sensor, separated from one another by a distance of 50 μm. The two different regions give two different spectra. One, Figure 5.26b, a mixture of anatase and rutile, and the second, Figure 5.26c, completely rutile. This suggests that the film is not converting to rutile homogeneously.

5.6.1b Scanning Electron Microscopy

Figure 5.27 shows the scanning electron micrographs of thin film TiO₂ sensor with 3 layers. Looking at the film from the top view, there is slight evidence that a film is present, though it appears to be highly cracked. A cross-sectional view of the same sensor, however, does not give any indication of a film. The film is too thin for its thickness to be resolved by SEM. A 20 layer film was also examined by SEM. Its cross section is shown in Figure 5.28. The thickness of the film is approximately 1 μm, making each layer about 50 nm thick.

5.6.2 Sensing Measurements

Preliminary experiments with thin film sensors were done to establish whether there was an effect of film thickness on the sensitivity of the sensor to CO and CH₄. Figure 5.29 shows the response of sensors of 1, 3, 5, 10, 15 and 20 layers to CO and CH₄ at 600 °C and 5%O₂/N₂. There are a number of trends in the data. Firstly, the response of the sensors to both CO and CH₄ increases as the number of layers increases, then stabilizes above 10 layers. Secondly, the baseline resistance of the sensors decreases with
an increase in the number of layers. The 1 layer sample has a starting resistance value of 400 MΩ and has a noisy background, while the 20 layer sample has a resistance response of 18 MΩ. Figure 5.30 shows the trend in the resistance decrease. All of the results for these sensors are summarized in Table 5.5. The recovery times of the sensors are also dependent on the number of layers, with the thinner films recovering more quickly.

Additionally, measurements on sensors with increased heat treatment times were performed. Figure 5.31 shows the sensing behavior of two different three-layer sensors, each with an on-substrate heat treatment temperature of 700 °C, but one heated for 1 hour and the other for 6 hours. Increasing the heat treatment time increases the gas sensitivity of the sensor to both CO and CH₄. This sensitivity increase is larger in response to the CO.

5.7 Sensitivity Difference between Sol-Gel and commercial TiO₂

Sensors of the sol-gel synthesized titania were made using similar preparation conditions as the sensors from the thick films of TiO₂ from commercial materials discussed in Chapters 2 and 4. Two preparation methods were explored. One was the heat treatment procedure used for anatase-phase TiO₂ sensors, a 6 hour, 800 °C heat treatment of the powder (HT1) followed by a 6 hour, 800 °C heat treatment on the sensing substrate (HT2). The second method was similar to that used for the rutile sensors, where HT1 was 6 hours at 1000 °C. As shown in section 5.3, these materials are in the rutile phase.
Figure 5.32 compares the sensing results of the sol-gel derived thick films with the n-type anatase sensor from Chapter 4. The response of the sensor prepared with HT1 of 800 °C for 6 hours shows n-type behavior and its response is compared to that of an anatase sensor in Figure 5.32. The sol-gel sensor is more sensitive to CO and less sensitive towards CH₄ than both the commercial anatase-phase TiO₂ sensor and the sol-gel sensor discussed in section 5.5 that was heated for a shorter period of time.

When HT1 is 1000 °C for 6 hours, the behavior of the sol-gel sensor is more p-type than n-type. Figure 5.33 compares the response of this sensor with that of a rutile sensor made from commercial material. Upon exposure to 250 ppm CO, the sensor shows a p-type response, but as the concentration of CO is increased, the relative resistance change becomes negative. When exposed to CH₄, the response is always p-type. The sensor that was made from the commercial TiO₂ is more sensitive than the sol-gel in this case. If the sensor is doped with Cu and heated to 1000 °C, the behavior is p-type to all concentrations of CO and CH₄. The sensitivity is similar to that of the commercial rutile sensor.

Figure 5.34 compares the 10-layer spin-coated sample with the commercial anatase sensor. The thin film is much more sensitive to CO than the commercial anatase sensor. However, the sensitivity to CH₄ is the same for both sensors.

The recovery response of three sensors: the thick film commercial material sensor, the thick film sol-gel sensor, and the thin film-sol gel sensor, are compared in Figure 5.35. Of the three sensors, the recovery of the thick film sol-gel sensor is the fastest, followed by the thin film sol-gel sensor and finally the commercial anatase sensor.
thin film sensor may be less porous than the thick film sensor made from the sol-gel titania which would account for the difference in recovery times.

Discussion

In sections 5.3 and 5.4, the effect of pH, heat treatment temperature and dopant on the phase transformation and grain growth of sol-gel titania was demonstrated. Not only do these parameters influence microstructural properties of titania, but they also influence, in varying degrees, the sensing behavior of sol-gel titania. Below, the mechanisms for both the microstructural and electrical changes which result from the different parameters are discussed. In addition, the behavior of thin films is explained and compared to both the thick films made of sol-gel and commercial titania.

5.8 Phase Transformation and Grain Growth of TiO₂

In Chapter 2, it was shown that commercial anatase does not transform to rutile until 1000 °C. With addition of Cu⁺, this transformation temperature decreased to 800 °C. and the addition of La⁺ was necessary to prevent the transformation. However, in the sol-gel titania, the transformation temperature is much lower, starting as low as 500 °C. The difference in the transformation temperatures has to do, in part, with the difference in the starting particle sizes of the anatase. The commercial anatase was initially 100-150 nm in size, while that of the sol-gel is under 10 nm. It is generally believed that the transformation of anatase to rutile nucleates at surface defect sites, then the rest of the particle transforms. Smaller particles mean higher surface areas, and more defects.
leading to transformation at lower temperatures. The results suggest, as rutile particles are not observed below 17 nm in size, that anatase must reach a critical size before the transformation can occur. Several studies have shown that the anatase to rutile transformation occurs once the anatase particles have reached a critical size (somewhere between 13 nm and 30 nm) [19] [16].

Because of the critical transformation size of anatase particles, mixtures of anatase and rutile typically show two different average particle sizes, a smaller one for anatase and larger for rutile. The different particle sizes for anatase and rutile are confirmed by the XRD lineshape analysis and TEM studies. The TEM analysis by Gouma et al. which showed that anatase particles are typically about ten times smaller than the rutile particles produced by heating the samples [16]. The anatase particles are estimated at about 15 nm by XRD and 20 to 30 nm (at their largest) by TEM. This difference can be attributed to the fact that the XRD is giving an average picture of the particle size, while the TEM looks at individual particles. For the rutile particles, there is a greater disparity between the XRD and TEM particle sizes. From the XRD, the estimated particle size is 25 to 30 nm, and even larger (up to 50 nm) after 800 °C heat treatments, but the TEM gives particles that are 10 times that size. XRD lineshape analysis often underestimates the particle size, so the TEM results are considered to be more accurate. Other studies have noted differences in particle size between anatase and rutile. Gribb and Banfield showed that anatase particles were 27 nm and rutile particles were 45 nm after a 425 °C heat treatment. They also noted that the rutile particles coarsened much faster than the anatase particles, and were 70 nm after 800 hours at 465 °C, while anatase particles remained
about 30 nm [19]. Kumar also saw a size difference between the anatase and rutile particles. after a 500 °C heat treatment they were 25 and 51 nm, respectively. As the heat treatment temperature increased, Kumar saw much faster growth of the anatase particles, narrowing the size difference to 50 nm for anatase and 55 nm for rutile [20].

The SEM micrographs taken of the non-doped sol-gel samples at higher temperatures show two different particle sizes, 100 nm spherical particles and larger, micron-sized ‘chunks’. The XRD of all three samples shown in the SEM micrographs showed that the materials are mostly rutile, suggesting that both particle morphologies belong to the rutile phase. The TEM studies also showed different morphologies for rutile particles, spheroidal for the in situ heat treatments, and plate-like for the ex situ. The particle sizes observed in the La⁺⁺ doped samples was the same as the non-doped samples, consistent with the trend from the XRD measurements. However, the rutile particles in the Cu⁺⁺ doped samples are predicted to be larger than the undoped and La⁺⁺ samples, but all three samples have the same particle size according to the SEM micrographs. The Cu⁺⁺ doped samples are well sintered based on the SEM micrographs, which may account for the higher particle size estimate by XRD.

5.8.1 Effect of pH

A change in the pH of the peptized sol can affect the transformation of the sample. The effect of the pH on the anatase to rutile transformation is small, with just a difference of 10% transformation between the pH = 2.56 and pH = 1.72 at 700 °C. As only a small pH range was examined, this small effect is not unexpected. Studies of the effect of pH
on the transformation typically look at a much broader pH range[14, 15]. Furthermore, the high temperature of the heat treatment may minimize these effects. Studies of porosity and surface area vs. pH see diminished trends at higher temperatures [15].

The effect of decreasing pH in this study is to decrease the rate of the transformation of anatase to rutile. This inhibitive effect is due to the way the protons surround the small titania particles produced from the sol-gel process. It is generally accepted that when an acid is added during synthesis, hydrolysis (leading to chain growth) is favored over condensation (branching), and that when added during peptization, it reduces particle agglomeration by altering the attractive/repulsive forces between particles [12, 13]. In the work by Xu and Anderson, dynamic light scattering shows that particles at lower pH’s are agglomerated to a lesser extent (20 nm clusters) than the higher pH’s (20 – 80 nm clusters) [15]. So the particles from the pH = 2.56 sol are more agglomerated than those in the pH = 1.44 sol and these agglomerates are the initial stages of the titania crystallites. It is therefore proposed that the smaller agglomerates are below this critical particle size, and must grow in size prior to transforming, but the larger agglomerates that form at the higher pH are already at or above the critical particle size, and transform more readily.

However, studies of the anatase to rutile transformation as a function of pH that are discussed in the literature do not clearly support this mechanism. The results of Giannelis and Berglund agree with those reported above, finding that the addition of acid produces anatase particles that are stable up to 650 °C, while a neutral synthesis produces a mixture of anatase and rutile at the same heat treatment temperature [21]. They added
the acid during the hydrolysis step, but if acid is added during the peptization step, an
opposite trend results. In work by Biscoff and Anderson, the addition of acid during the
peptization step resulted in mixtures of anatase and rutile when the peptization occurred
at room temperature, but was a mixture of anatase and brookite if the sol was heated
during peptization [22]. Meanwhile, Bokhimi et al. report that pH is unimportant in the
control of the anatase to rutile transformation, and that instead, the type of acid used is
more important. In their case, the use of oxalic acid during the hydrolysis step at a pH of
5 was more successful at preventing the anatase to rutile transformation than either low
pH or high pH experiments with other catalysts [14].

In this chapter, acid was present during the hydrolysis step, and the pH changed
after peptization. Furthermore, the samples were ball-milled in isopropanol prior to heat
treatment, essentially, unpeptizing the sample. Other researchers have noted the effects of
ball-milling on nanocrystalline metal oxide materials, the procedure breaking up the size
of the hydrated agglomerates [6].

Both the presence of acid after peptization and the ball-milling step help maintain
smaller particle and/or agglomerates of the initial anatase phase of TiO$_2$. These smaller
particles/agglomerates then transform more slowly because they are below a critical
particle size.

5.8.2 Effect of La$^{3+}$ dopant

Previously, a number of different mechanisms were proposed for the effect of La
on the anatase to rutile transformation (Chapter 2). In one case, the presence of the La$^{3+}$
on interstitial sites of the TiO₂ lattice prevents the transformation by decreasing the concentration of oxygen vacancies [23]. Others have proposed the formation of a surface layer of LaO₃ species that can inhibit the transformation by inhibiting grain growth. Lin et al. suggest that the La₂O₃ coats the TiO₂ grains and due to differences in the sintering rate of the La₂O₃ compared to the titania, prevents grain growth and transformation [24]. The La³⁺ doped sol-gel samples provide evidence for both arguments. On one hand, the XRD analysis does not show a range of anatase particle sizes, suggesting that there is a layer of LaO₃ on the surface preventing the grain growth. If La₂O₃ forms a surface monolayer, as has been proposed by other researchers [24], it may be difficult to detect. Studies with the inhibition of the anatase to rutile transformation using alumina have also suggested that the dopant is acting at the surface[25]. Since the transformation process is surface nucleated in these small anatase particles, it is proposed that the La₂O₃ forms either a surface monolayer, or is highly concentrated near the surface of the particles, where it will decrease the number of oxygen vacancies, and inhibit the surface nucleated transformation. The addition of 7 mol % La almost completely suppresses the transformation of anatase to rutile, especially in samples with a low pH.

For the 10 mol% La sample, the transformation is not as effective as the 7 mol%.

and in the XRD, evidence of La₂O₃ as a separate phase is apparent. This critical concentration coincides with work by Gopalan and Lin, where the concentration for monolayer coverage was 12.7 mol%, and above that concentration either La₂O₃, as a separate phase, or lanthanum titanates were observed by XRD [17].
5.8.3 Effect of Cu\textsuperscript{2+} dopant

It is expected that the CuO will promote the anatase to rutile transformation by substituting onto Ti\textsuperscript{4+} lattice sites and increasing the concentration of oxygen vacancies, the nucleation site for the transformation [26-28]. This means that a higher degree of transformation compared to undoped titania of a similar pH should be observed, but at 500 °C, the percent of rutile is close to that of the undoped sample of similar pH (Table 5.1 and 5.2). At 700 °C, however, the copper doped sample is fully transformed, while the non-doped sample is still 10% anatase. This suggests that at 500 °C, the copper has not substituted into the lattice enough to cause a transformation. Mackenzie showed through kinetic studies that the ability of transformation promoting dopants decreased as the temperature was lowered [29]. In this study, with commercial titania, the anatase was less than 10% transformed after 1 hour at 845 °C [29]. In work by Iida and Ozaki, the transformation of anatase to rutile was less than 3% at 700 °C for coarse-grained titania doped with copper [28].

5.9 Effect of Sample Preparation on Thick Film Sensor Response

The effects of pH, temperature and dopants are not limited to microstructural characteristics of sol-gel titania. All three of these parameters, to different extents, affect the sensing behavior of the sol-gel titania thick film sensors. First, the non-doped sensors change sensitivity with both pH and heat treatment temperature, with the CO response decreasing, but that of the CH\textsubscript{4} increasing under the testing conditions of 600 °C and 5%O\textsubscript{2}/N\textsubscript{2}. When doped with La\textsuperscript{3+}, the sensor response is similar to that of the non-doped
sol-gel titania, but when doped with Cu$^{2+}$ it has lost most of its sensitivity to CH$_4$. Finally, under the sensor preparation conditions, most of the materials examined should be in the rutile phase, but none of them show p-type behavior that the transformed commercial material showed in Chapter 4. These points are elaborated below.

5.9.1 Effect of pH and Heat Treatment on Pure Sol-Gel Titania Sensors.

The trend in the sensing behavior as a function of both pH and temperature are similar to those shown in the aging study in Chapter 2. At higher heating temperatures, the baseline resistance of the sensor shows no specific trend, decreasing in some cases, such as when HT1 is increased, but the baseline increases in other cases, as when the HT2 temperature is raised (see Table 5.3). Williams and Coles have proposed in SnO$_2$ sensors that two competing processes occur when the metal oxides are heated [30]. One is sintering which would decrease the resistance because of better contacts between grains. Secondly, it is possible that oxygen vacancies present in the sample will be eliminated upon heating in air [30]. In the sol-gel sensors, these same two processes are likely to be occurring, the pH and heat treatment temperature both having effects, but variations in the samples themselves, such as intergranular contact, pore structure and film thickness may vary enough from sample to sample to cause these small changes as well.

As in the case of the aged samples shown in Chapter 2, when the response to CO decreases, the response to CH$_4$ increases, suggesting that the same mechanism is occurring here. Basically, CH$_4$ and CO have different sites on titania on the sample for reaction, so changes in the particle surfaces as a result of temperature, etc., result in
differing response changes to the two gases. However, as the variation in the sensor to sensor behavior of commercial titania sensors can be large (as demonstrated in Chapter 4) the differences observed here may not have a great amount of importance compared to those resulting from sample preparation differences.

5.9.2 Effect of Dopants on Thick Film Sensors

In the commercial powders, La$_2$O$_3$ was added at 10 wt%, and had little effect on the gas sensitivity of titania sensors (see Figure 2.9). In sol gel samples in which La has been added, it is added as a La(NO$_3$)$_3$ solution at a concentration of 7 mol %, equivalent to 14 wt % La$_2$O$_3$. This small increase in the amount of lanthanum oxide has a little effect on the sensitivity behavior of the sol-gel sensors, as was the case in the commercial powders.

The strong decrease in gas sensitivity in the presence of copper dopant is attributed to the same mechanism described in Chapter 2. CO and CH$_3$ are oxidized directly on CuO in the oxidizing atmosphere, without electronic interaction with the titania support, resulting in the lower sensitivity.

5.9.3 n-Type Response of Sol-Gel Rutile

Despite the inhibitory effects of pH and La$^{3+}$ on the anatase to rutile transformation, once the sensing samples have been prepared (which requires at least two 1 hour, high temperature heat treatments) they are mostly rutile. From the results in Chapter 4, it is expected that the rutile phase will behave as a p-type semiconductor.
However, it is not until the heat treatment temperatures of the sensor (HT1) reach 1000°C that any p-type behavior is observed. Instead, most of the sensors examined show an n-type response despite the fact that they are in the rutile phase.

A few different explanations for the p-type response of the rutile films were discussed in Chapter 1 and Chapter 4. It is thought that the presence of trivalent impurities in TiO₂ result in, under certain conditions of temperature and pO₂, the formation of holes in the material which become the dominant charge carrier. The relative amount of impurities of the sol-gel TiO₂ compared with that of the commercial powders could be an explanation for their n-type response. However, elemental analysis results show that with the exception of Al, the sol-gel sample has the same level of impurities or commercial anatase. Al as a trivalent dopant responsible for the p-type behavior of rutile is well studied, so this difference in concentration would be a plausible explanation for the difference between the samples. When elemental analysis of commercial rutile is examined, however, the amount of Al is similar to that of the sol-gel samples, yet it still shows p-type behavior. Even with the addition of Cu⁺⁺⁺, which is reported to substitute onto Ti⁺⁺⁺ sites [26], and therefore be an acceptor dopant, the sol-gel sensors are still n-type when the heat treatment temperatures are below 1000°C.

If it is not the concentration of impurities that influences the behavior of the sensor, the distribution of these impurities in the TiO₂ framework are a more likely explanation for the sensing behavior of the sol-gel TiO₂. At the lower temperatures, trivalent impurities are mostly at interstitial positions, but as the heat treatment temperature is raised, these impurities migrate to substitutional positions and p-type
behavior can be observed. For the non-doped sensors, after 6 hours at 1000 °C, this p-type behavior is observed, but at high CO gas concentrations looks n-type again. When the sensor is doped with Cu, the behavior is p-type for all concentrations of CO and CH, that were tested.

5.10 Effect of Thickness on Thin Film Sensors

The decrease in the resistance of the thin film titania sample with increased thickness can be explained by the increase in the number of pathways current can travel through the sample. Bae et al. showed similar effects in their studies of CuO-ZnO sol-gel sensors [10], and attribute the resistance decrease to that of increased density of the film upon additional coatings. Once a sufficient film density is achieved, no further change in the film resistance is observed [10]. Chung et al. observed similar decreases in the film resistance as the number of coatings increased [5]. They also noted that the underlying substrate influenced the resistance of the film. Using alumina, with its rough surface texture (∼45 nm), resulted in a more porous film, allowing gases to better penetrate. This meant that gas phase oxygen, which causes a resistance increase, would have more of an effect on a less dense film [5]. Chung et al. reported a linear change in the baseline resistance with increasing layers, however they only measured up to 7 layers (200 – 250 nm thick)[11]. Yoo et al. also observed a decreased resistance with increased film thickness, but did not observe a linear change. Instead the resistance change was steep below a thickness of 100 nm, then changed more gradually as the film thickness was increased [4]. Figure 5.30 does not show a linear change in resistance with increased
thickness of the sol-gel titania films, however, the films are examined up to a much larger thickness. As the film thickness increases, adding more layers has a less pronounced effect.

The increase in the film sensitivity as the thickness increases is opposite to the trend observed by other researchers [10, 11]. In one reported system, a noticeable difference in grain size was observed between the films with a small number and large number of layers [10]. Increasing the number of layers in this case does not increase the surface area and thereby sites for sensing. In$_2$O$_3$ thin films showed a maximum in gas sensitivity for 160 nm thickness, and decreased above that thickness[11]. It was suggested that gas penetration decreased as the thickness increased, resulting in an overall decrease in sensitivity. This can only be true if the film density is such that the gases cannot easily penetrate the film. If the film is porous, or cracked as the titania films are, this same trend may not apply. As the titania films are heat treated if they crack, or the particles grow, the surface area should be larger than just the surface (as would be the case in one layer) and gas sensitivity should increase as is the trend observed.

The recovery times of the thin film sensors also show a trend. As the film gets thicker, the recovery time increases. This is because the thicker the film, the further the gases must diffuse in order to effect a change.

5.11 Comparison of Commercial Titania and Sol-Gel Sensors

The response of the thick film sensors made of sol-gel titania did not show a significant sensitivity improvement over the sensors made from commercial powders.
Based on the similarities of the particle sizes of the two materials, this is not surprising. While there is no advantage in terms of sensitivity, sol-gel derived materials may have an advantage over the commercial materials when it comes to the addition of dopants. Individual La$_2$O$_3$ or CuO particles were not observed in the doped sol-gel samples, indicating that the dopants are well dispersed, a factor that has the potential to improve sensor to sensor reproducibility.

The thin films with the greater number of layers had gas sensitivities that were similar to those of both the commercial and sol-gel thick films, offering no possible advantage except for the sensor fabrication method, which is a means of producing multiple sensors of the same thickness. The thin films that are only a few layers thick, while not being as sensitive to CO, recovered much faster than the thicker films. Unfortunately, their baseline resistances were very high, presenting a potential problem in their use.

As shown in Figure 5.35, the recovery times of the sol-gel prepared films were faster than the recovery measured for the commercial-titania sample. This faster recovery is another advantage of sol-gel sensors.

### 5.12 Conclusion

The interest in the anatase phase of TiO$_2$ as a sensor material developed, in part, because of its smaller particle size compared to rutile. It is also more common to find n-type materials used for sensing, and at the conditions of interest (oxidizing atmosphere), the anatase phase is n-type while the rutile phase is p-type. Sol-gel titania was explored as
a sensor material in this chapter because it is a method of making smaller anatase particles, which could mean higher gas sensitivities are possible. The pH and dopant concentration, by affecting the surface properties of the titania, were shown to control the anatase to rutile transformation. However, these smaller anatase particles are not very stable at the temperatures of interest for sensing (above 600 °C). Even with the addition of La\(^{3+}\), the anatase converts to rutile and the particle sizes increase with a brief heat treatment at 800 °C. However, the rutile particles produced by this method are mostly 100 to 300 nm in size, similar to that of the commercial anatase used in Chapter 2, and show n-type behavior, making the material a viable candidate for selective gas sensing. Because they are already in the rutile phase, the addition of La\(^{3+}\) is now unnecessary, and with the added Cu\(^{2+}\), a CO selective material is obtained which is similar to those detailed in Chapter 2. It is only at a heat treatment temperature of 1000 °C that the sol-gel sensors show p-type behavior.

Additionally, thin film titania sensors can be made by spin-coating the sol onto sensing substrates. This method of sensor preparation will offer greater control in the sensing behavior as shown by just the variation of one parameter, film thickness. The thickness, which can be controlled by the number of layers of film applied by spin coating, affected by both the gas sensitivity and response time of the TiO\(_2\) sensors.
References


Table 5.1: Effect of pH, temperature and aging on sol-gel titania.

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<tr>
<th>pH</th>
<th>Temp (°C)</th>
<th>Age</th>
<th>% Rutile</th>
<th>Particle Size (nm)*</th>
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<tbody>
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<td></td>
<td></td>
<td></td>
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</tr>
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</tr>
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<td>-</td>
</tr>
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<td>23</td>
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<td>19 months</td>
<td>65</td>
<td>14</td>
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<tr>
<td>1.44</td>
<td>800</td>
<td>19 months</td>
<td>100</td>
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* particle size by X-ray diffraction
Table 5.2: Effect of Dopants on sol-gel TiO$_2$. 

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<tr>
<th>pH</th>
<th>Temp (°C)</th>
<th>Dopant</th>
<th>%Rutile</th>
<th>Particle Size (anatase)*</th>
<th>Particle Size (rutile)*</th>
</tr>
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<td>2.58</td>
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<td>0.5% La</td>
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<td>10</td>
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<td>-</td>
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<td>-</td>
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<tr>
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<td>7% La</td>
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<td>10</td>
<td>-</td>
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<td>20</td>
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<td>700</td>
<td>0.2% Cu</td>
<td>100</td>
<td>-</td>
<td>59</td>
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</table>

* particle size by X-ray Diffraction
<table>
<thead>
<tr>
<th>pH</th>
<th>HT(1) °C*</th>
<th>HT(2) °C**</th>
<th>$R_0$ $\Omega$</th>
<th>$R/R_0$</th>
<th>250 ppm CO</th>
<th>1000 ppm CO</th>
<th>250 ppm CH$_4$</th>
<th>1000 ppm CH$_4$</th>
<th>Recovery Time (s)</th>
</tr>
</thead>
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<td>1.44</td>
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<td>700</td>
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<td>-</td>
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<td>700</td>
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<td>700</td>
<td>5.25</td>
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<td>800</td>
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<td>0.718</td>
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* Heat treatment temperature of powder
** Heat treatment on substrate

Table 5.3: Summary of sensing behavior of undoped sol-gel titania at 600 °C and 5%O$_2$/N$_2$. 
<table>
<thead>
<tr>
<th>Dopant</th>
<th>HT-1 °C</th>
<th>HT-1 °C</th>
<th>$R_0$ MΩ</th>
<th>250 ppm CO</th>
<th>1000 ppm CO</th>
<th>250 ppm CH₄</th>
<th>1000 ppm CH₄</th>
<th>Recovery Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 mol% La</td>
<td>800</td>
<td>800</td>
<td>14.2</td>
<td>0.460</td>
<td>0.275</td>
<td>0.769</td>
<td>0.556</td>
<td>550</td>
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<tr>
<td>7 mol% La</td>
<td>800</td>
<td>800</td>
<td>11.1</td>
<td>0.513</td>
<td>0.281</td>
<td>0.771</td>
<td>0.575</td>
<td>690</td>
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<tr>
<td>7 mol% La</td>
<td>700</td>
<td>800</td>
<td>64.6</td>
<td>0.591</td>
<td>0.374</td>
<td>0.841</td>
<td>0.703</td>
<td>700</td>
</tr>
<tr>
<td>7 mol% La</td>
<td>500</td>
<td>700</td>
<td>43.2</td>
<td>0.624</td>
<td>-</td>
<td>0.855</td>
<td>-</td>
<td>480</td>
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<tr>
<td>2 mol% Cu</td>
<td>700</td>
<td>700</td>
<td>2.93</td>
<td>0.915</td>
<td>0.783</td>
<td>0.995</td>
<td>1.001</td>
<td>700</td>
</tr>
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<td>2 mol% Cu</td>
<td>700</td>
<td>800</td>
<td>2.70</td>
<td>0.951</td>
<td>0.814</td>
<td>1.000</td>
<td>1.012</td>
<td>770</td>
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Figure 5.4: Summary of the effect of dopants and heat treatment temperatures on the sensing response of sol-gel titania sensors at 600 °C and 5%O₂/N₂.
<table>
<thead>
<tr>
<th># of Layers</th>
<th>$R_0$</th>
<th>$R/R_0$ 1000 ppm CO</th>
<th>$R/R_0$ 1000 ppm CH$_4$</th>
<th>Recovery Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>0.595</td>
<td>1.076</td>
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<td>3</td>
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</tr>
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<td>28.3</td>
<td>0.166</td>
<td>0.569</td>
<td>2030</td>
</tr>
<tr>
<td>20</td>
<td>18.3</td>
<td>0.167</td>
<td>0.578</td>
<td>2300</td>
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</table>

Table 5.5: Summary of thin film sol-gel sensor response to CO and CH$_4$. 
Figure 5.1: Procedure for making sol-gel materials. (Adapted from reference 12)
Figure 5.2: TEM micrographs of as-dried sol-gel TiO$_2$. (Adapted from reference 16)
Figure 5.3: The effect of heat treatment temperature on sol-gel TiO$_2$. a) as-dried, b) after 1 hr at 500 °C, c) after 1 hr at 700 °C.
Figure 5.4: The effect of heat treatment on sol-gel TiO$_2$ of pH sensor. a) 1 hr at 500 °C; b) 1 hr at 700 °C.
Figure 5.5: XRD of pH=1.44 sol-gel after heat treatment. a) 500 °C; b) 700 °C.
Figure 5.6: TEM micrographs of sol-gel TiO$_2$ taken during *in situ* experiments. a) 400 °C; b) 500 °C; c) 600 °C. (Adapted from reference 16)
Figure 5.7: TEM micrographs of sol-gel TiO$_2$ that has been heat treated to 600 °C \textit{ex situ.} (Adapted from reference 16)
Figure 5.8 SEM micrographs of pH = 2.56 sol-gel TiO$_2$ after 700 °C heat treatment. Magnification: a) 50,000X; b) 9500X. (Micrographs by Ms. Hyunjung Lee)
Figure 5.9: SEM micrographs of pH=1.44 sol-gel TiO$_2$ after 700 °C heat treatment. Magnification: a) 85,000X; b) 9500X. (Micrographs by Ms. Hyunjung Lee)
Figure 5.10: SEM micrograph of pH=1.44 sol-gel TiO$_2$ after 800 °C heat treatment. (Micrograph by Ms. Hyunjung Lee)
Figure 5.11: The effect of La doping on sol-gel TiO$_2$ after a 1 hr, 500 °C heat treatment. a) 0.5 mol%; b) 7 mol%; c) 10 mol%.
Figure 5.12: The effect of La doping on sol-gel TiO₂ after 1 hr at 700 °C heat treatment. a) 0.5 mol%; b) 7 mol%; c) 10 mol%.
Figure 5.13: The effect of La doping on sol-gel TiO$_2$ after 1 hr at 800 °C heat treatment. a) 7 mol%; b) 10 mol%.
Figure 5.14: The effect of pH on La-doped sol-gel TiO₂. a,c, and e) 500 °C; b,d, and f) 700 °C.
Figure 5.15: Effect of pH and $\text{La}^{3+}$ doping on sol-gel TiO$_2$ at 800 °C. a) pH = 2.56; b) pH = 1.44.
Figure 5.16: Effect of Cu$^{2+}$ doping on sol-gel titania after a) 500 °C and b) 700 °C heat treatments for 1 hour.
Figure 5.17: SEM micrographs of La-doped sol-gel TiO$_2$ after 800 °C heat treatment. a) 7 mol %; b) 10 mol %. (Micrographs by Ms. Hyunjung Lee)
Figure 5.18: SEM micrograph of Cu-doped sol-gel TiO$_2$ after 700 °C heat treatment. (Micrograph by Ms. Hyunjung Lee)
Figure 5.19: Sol-gel TiO$_2$ sensor response with heat treatment at 700 °C for 1 hour. Measurement made at 600 °C, 5%O$_2$/N$_2$. a) pH=1.44; b) pH=1.72; c) pH = 2.56.
Figure 5.20: Effect of sol-gel powder heat treatment temperature on the sensing response at 600 °C and 5% O₂/N₂. Samples were heat treated on substrate at 800 °C (HT2). HT1: a) 700 °C, b) 800 °C.
Figure 5.21: Effect of on-substrate heat treatment on the sensing response at 600 °C and 5%O₂/N₂. HT2: a) 700 °C; b) 800 °C.
Figure 5.22: Effect of La-doping on gas sensitivity of sol-gel titania sensors at 600 °C and 5%O₂/N₂. a) no dopant; b) 7 mol% La; c) 10 mol% La.
Figure 5.23: Effect of powder heat treatment temperature on gas sensitivity of La-doped sol-gel titania sensors. a) 700 °C; b) 800 °C.
Figure 5.24: Effect of Cu-doping on the gas sensitivity of sol-gel titania sensors at 600 °C and 5%O₂/N₂. a) no dopant; b) 2 mol% Cu.
Figure 5.25 Effect of on-substrate heat treatment temperature on the gas sensitivity of Cu-doped sol-gel titania sensors. a) 700 °C; b) 800 °C.
Figure 5.26: Raman spectra of sol-gel TiO$_2$ films. a) 1 layer film; b & c) two areas of 20 layer film. (*) indicates peaks belonging to the anatase phase.
Figure 5.27: SEM micrograph of top view of sol-gel TiO$_2$ sensing film. (Micrograph by Dr. Perena Gouma)
Figure 5.28: SEM micrograph of cross-section of sol-gel TiO₂ film. (Micrograph by Ms. Hyunjung Lee)
Figure 5.29: Effect of film thickness sensor response at 600 °C and 5% O₂/N₂. Top: CO, Bottom: CH₄. Note that the responses of the 15 layer and 20 layer sensors to CO overlap one another.
Figure 5.30: Change in baseline sensor resistance as a function of sensor thickness at 600 °C and 5%O_2/N_2.
Figure 5.31: The effect of increased heat treatment time on thin film sensor response. Measurements made at 600 °C and 5%O₂/N₂. a) 1 hr, 700 °C; b) 6 hr, 700 °C.
Figure 5.32: Comparison of sensor response of thick film sol-gel and commercial anatase at 600 °C, 5%O₂/N₂. a) commercial anatase response to CO; b) commercial anatase response to CH₄; c) sol-gel TiO₂ response to CO; c) sol-gel TiO₂ response to CH₄.
Figure 5.33: Comparison of sensor response of thick films of sol-gel and commercial rutile at 600 °C, 5%O₂/N₂. a) sol-gel TiO₂ response to CO; b) sol-gel TiO₂ response to CH₄; c) commercial rutile response to CO; d) commercial rutile response to CH₄; e) Cu-doped sol-gel TiO₂ response to CO; f) Cu-doped sol-gel response to CH₄.
Figure 5.34: Comparison of thin film sol-gel TiO$_2$ response with commercial anatase sensor response at 600 °C, 5%O$_2$/N$_2$. a) commercial anatase to CO, b) commercial Anatase to CH$_4$, c) thin film response to CO, d) thin film response to CH$_4$. 

263
Figure 5.35: Comparison of recovery response of different TiO$_2$ sensors. a) commercial anatase; b) thick film sol-gel TiO$_2$; c) thin film sol-gel TiO$_2$. 
CHAPTER 6

CONCLUSION

In the preceding chapters, the viability of TiO$_2$ as a gas sensing material was demonstrated. Different strategies for obtaining selective carbon monoxide sensors as well as different materials preparation techniques were studied. Not only were CO selective sensors developed, they were also characterized in order to obtain information regarding the mechanism by which selectivity was obtained.

The two methods for obtaining selective CO sensors, p-n composites and metal oxide doping, both have advantages. Selectivity of the p-n composite sensors results from electrical cancellation. At a certain concentration of rutile, 75\%, the p-type rutile and n-type anatase responses to CH$_4$ are equal in opposite, resulting in no resistance change when the sensor is exposed to CH$_4$. This cancellation mechanism is potentially gas concentration independent, meaning there would be no interference from CH$_4$ no matter what its concentration.

Sensors made by doping the anatase phase of TiO$_2$ with La$_2$O$_3$ and CuO (ALC) also show substantial selectivity for CO over CH$_4$. The recovery and response times of
the ALC sensor are much faster than those of non-doped sensors, of which the p-n sensors can be categorized. The CO sensitivity of these sensors is also greater than that of the p-n composite sensors. Based on the infrared data, the ALC sensor is selective because the CH₄ is oxidized on the CuO, not on the TiO₂. This makes it unclear whether the ALC sensor will be able to maintain CH₄ insensitivity up to high CH₄ concentrations, as would the p-n composite sensor.

The dopant method was easily applied to sensors that were made from sol-gel synthesized materials. The addition of Cu²⁺ in the solution phase to sol-gel TiO₂ also resulted in the same selective CO sensing made by ball-milling techniques. Furthermore, the effects of heat-treatment temperature on the semiconducting behavior of TiO₂ (whether it is p-type or n-type) support a mechanism of impurity migration to substitutional positions as the reason for why rutile shows p-type or n-type semiconducting behavior, but anatase only shows n-type behavior. Other results from the sol-gel experiments such as the effect of film thickness, heat-treatment and dopants on sensor response, though preliminary, show that sol-gel TiO₂ has a promising future as a sensing material.

Finally, it is with characterization methods such as infrared spectroscopy, electron microscopy and X-ray diffraction that detailed information about the sensors and what gives them the desired selectivity is obtained. It is with a good understanding of sensor behavior that future work in developing highly sensitive and selective sensors can be made.
APPENDIX

DATA ANALYSIS FOR \textit{in situ} DRIFTS

The study of powdered samples by infrared spectroscopy often utilizes the technique of diffuse reflectance. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) offers a number of advantages over transmission measurements. Sample preparation is often minimal, eliminating the necessity for preparing nujol muls or pressing self-supporting pellets. The detection limits are also good, with quantities as low as 200 ng of a moderately absorbing sample or 2 ng of a strongly absorbing sample detectable [1]. Additionally, it has been observed that $10^{-5}$ monolayer of CO can be detected on supported catalysts by DRIFTS [2].

As we have seen in the preceding document, DRIFTS can be useful for the study of gas-surface reactions. Here it has been used as a means of understanding gas sensor mechanisms, but this sort of analysis has also proven to be useful for the study of catalysts as well [2, 3].

In diffuse reflectance spectroscopies, it is critical that the sample surface, and hence the intensity of light reflected from it, does not vary significantly between background and the sample except, of course, where the absorption bands occur. In
reality, variations in the overall reflection are common, either because the background and sample are two different powders (one KBr, the other an inorganic or organic suspended in KBr) and similar surface roughness is impossible to obtain, or to changes in the surface due to disturbances of a gas passing across the surface or the heating or cooling of a sample, causing the powders to expand or settle.

Various approaches have been taken in the literature to correct for these reflection differences. Brimmer and Griffiths proposed a method in which the relative reflectance is multiplied by a factor to bring it below 1 [4]. Other researchers have simply multiplied relative reflectance by a large number such as 20 [3], and still others simply choose to represent the data as relative reflectance or absorbance. Van Every briefly mention a method where the background reflectance is multiplied by a factor to bring the baseline of the sample (in a region where there is no absorption bands) to 100%. There is merit to some of these methods, but rarely is there a detailed explanation of such correction factors, and what the effects may be on the peak intensities and positions. Here, different methods for correcting data are detailed and compared in an effort to find the best method for gas-surface studies. Furthermore, criteria for data collection and manipulation for this type of system is outlined.

A.1 Review of Diffuse Reflectance and Kubelka Munk

In absorbance spectroscopy, light passes through a sample, and the change in the intensity of the light at a specific wavelength gives information on the nature of the sample (Figure A.1a). This change in the light intensity is the transmittance of the sample:
\[ T = \frac{I}{I_0} \quad \text{(A.1)} \]

\( I_0 \) is the intensity of the incident light, and \( I \) is the intensity of the transmitted light. More often, data is reported as the absorbance (\( A \)):

\[ \log \% T = A = a b c \quad \text{(A.2)} \]

where \( a \) is the molar absorptivity of the sample at a given wavelength, \( b \) is the sample pathlength and \( c \) is the concentration of the analyte. Equation A.2, known as Beer's Law, is useful for the quantitative analysis of samples due to its linearity.

In diffuse reflectance spectroscopy, rather than measure changes in transmitted light, changes in reflected light are measured. On a smooth surface, such as a mirror, light hits the surface and is reflected off at an angle equal to the angle of incidence. This reflection, as pictured in Figure A.2a, is called specular reflection. On a matte surface, such as that of a powder, there is not only specular reflection, but also diffuse reflection (Figure A.2b). This diffusely reflected light occurs because the sample surface is made up not only of one plane, that of the mirror surface, but of a number of different planar surfaces, the faces of the different crystals, all at a different orientation. Some of the incident light may also be absorbed by the sample, and it is the relationship between light being absorbed and scattered by a sample that is measured in diffuse reflectance spectroscopy.

Beer's Law does not hold for diffuse reflectance spectroscopy, as it does not account for sample scattering. Instead Kubelka Munk Theory is routinely used to describe light that has been both adsorbed and diffusely reflected by a sample, and how these processes are related to sample concentration. The theory was derived based on the radiant flux of monochromatic light in a polycrystalline sample. Restricting the light to
path that is perpendicular to the sample surface (Figure A.3) there are two main fluxes.
light coming from the top surface in the +x direction, I, and light coming from the bottom
surface in the -x direction, J. The change in the light intensity as a function of depth can
be written as [5. 6]:
\[
dl = -(k+s) I \, dx + s J \, dx \quad (A.3a)
\]
and
\[
dJ = +(k+s) J \, dx - s I \, dx \quad (A.3b)
\]
where \( k = 2 \epsilon \) (\( \epsilon \) = amount of light absorbed per unit path length) and \( s = 2 \sigma \) (\( \sigma \) =
amount of light scattered per unit path length.) So basically, the intensity of the light in
the -x direction is decreased by any absorbance and scattering of this light, but can be
increased due to light scatter from the opposing flux. A similar relationship holds for the
-x direction.

Integrating equations A.3a and b gives:
\[
I = A(1-\beta)e^{\kappa x} + B(1+\beta)e^{-\kappa x} \quad (A.4a)
\]
and
\[
J = A(1+\beta)e^{\kappa x} - B(1-\beta)e^{-\kappa x} \quad (A.4b)
\]
Where \( \kappa = [k(k+2s)]^{1/2} \), \( b = \kappa/(k+2s) \), and A and B are constants depending on the
boundary conditions. When a sample transmits light [5. 6]:
\[
T = \frac{I_{\text{transmitted}}}{I_0} = \frac{4\beta}{(1+\beta)^2e^{\kappa d}-(1-\beta)^2e^{-\kappa d}} \quad (A.5)
\]
If there is no scattering from the sample, equation A.5 simplifies to:
\[
T = e^{-kd} = e^{-2.3ee} \quad (A.6)
\]
in other words, Beer's Law.
The reflectance, \( r \), of a sample is the ratio of the reflected to incident light flux [5, 6]:

\[
\frac{r}{I_\infty} = \frac{(1 - \beta^2) \sinh kd}{(1 + \beta^2) \sinh kd + 2 \beta \cosh kd}
\] (A.7)

At an infinite thickness, \( x = x_\infty \), the transmission of the sample is zero, and the reflectance reduces to [5, 6]:

\[
r_e = \frac{1 - \beta}{1 + \beta} = \frac{1 - (k/(k + 2s)^{1/2})}{1 + (k/(k + 2s)^{1/2})}
\] (A.8)

When expressed as a function of \( r_e \), this relationship is known as the Kubelka Munk equation [5, 6]:

\[
F(r_e) = \frac{k}{s} = \frac{(1 - r_e)^2}{2r_e}
\] (A.9)

the expression commonly used to describe diffuse reflectance data. To obtain quantitative information from the Kubelka Munk expression, log-log plots are made of \( \log F(r_e) \) vs \( \log k \) (i.e. log concentration) at a certain wavelength in order to obtain a calibration curve. Since:

\[
\log F(r_e) = \log k - \log s
\] (A.10)

when the scattering coefficient is constant (an assumption at low concentrations of analyte [7]) the log-log plot is equivalent to the calibration curves made for solution analysis with Beer's Law [5, 6].

\[\text{A.2 Experimental}\]

All measurements were made in a Bruker IFS 66 spectrometer using a DTGS detector and a globar source. The spectrometer was equipped with a Spectratech
environmental diffuse reflectance accessory (The Collector). Figure A.4 shows schematic diagram of the Collector. Light is focused, then collected from the sample surface using a system of seven mirrors. Mirror 3 and mirror 5 are curved in order to maximize the light collected from the sample surface (Figure A.4a). In order to control the atmosphere the sample is exposed to, a gas-tight dome is fitted over the sample holder. Light enters and exits through KBr windows that are sealed with o-rings, and gas is allowed to enter and exit the dome through 2 different ports. The base of the sample holder serves as the heating unit, with feedback control through use of a thermocouple under the sample. There is also a thermocouple in the dome that can be used to monitor the surface temperature.

All samples were pretreated at a setpoint temperature of 600 °C, under a flow of 100 %N₂. Measurements were made on gas exposed samples using a step profile. Figure A.5 is a diagram of the temperature step method. A background measurement is made at a setpoint of 800 °C in 5%O₂/N₂, then at a constant atmosphere, the temperature is lowered to 600, 400, 200 and 25 °C, a measurement made at each temperature. After the room temperature measurement, the analyte gas is introduced at 0.5% in the presence of 5%O₂/N₂, and the temperature is stepped from 25 to 800 °C, with a measurement every 200 °C.

Due to thermal conductivity losses of the sample post and powdered sample, the temperature of the sample is well below that of the setpoint. The setpoint temperatures, along with the sample post temperatures and surface temperatures are listed in Table A.1.
A.3 Single Channel Spectra

Single channel data was collected at wavelengths between 4000 and 1000 cm\(^{-1}\). Figure A.6a shows the single channel reflectance of a powdered KBr sample at room temperature, giving a profile of the source after going through the diffuse reflectance accessory. It is similar to that of the light passing through an empty chamber, as shown in Figure A.6b. The signal is a factor of 100 less after the light passes through the diffuse reflectance chamber, indicating that there is a substantial loss of light intensity from the chamber and the powdered sample.

Figure A.7a shows the single channel reflection of a sample of anatase/La\(_2\)O\(_3\)/CuO (ALC) upon exposure to N\(_2\) and CH\(_4\)/O\(_2\)/N\(_2\) at room temperature. The profile of the sample is different than that of KBr, with less intensity in the region below 1500 cm\(^{-1}\). This indicates two things, that KBr is more reflective (though this may be due to differences in particle size, as reflectance increases with decreased particle size [1]) and that the ALC sample is absorbing in the region below 1500 cm\(^{-1}\).

As the temperature changes, so does the reflectance of the sample. Figure A.7b shows the single channel reflectance of the same sample at the 800 °C setting under both N\(_2\) and CH\(_4\)/O\(_2\)/N\(_2\). At this higher temperature, the reflected light intensity is less than that of the lower temperature measurement. Second, unlike the 25 °C spectra, the single channel spectra of the N\(_2\) exposed sample is different than that of the CH\(_4\)/O\(_2\)/N\(_2\) exposed sample, the latter being more reflective. This difference in the reflection could be due to changes in the sample resulting from the reaction with the sample gas. It is also likely that the method used to collect the data is a factor. By acquiring the data in a stepwise manner, the amount of time between the N\(_2\) and CH\(_4\)/O\(_2\)/N\(_2\) spectra was a couple of
hours, and the sample had gone through a cooling/heating cycle. However, the 25 °C samples were taken one after the other, with no intermediate heating or cooling.

A.4 Kubelka Munk Spectra

Obtaining the Kubelka Munk spectra of a sample requires the single channel reflectance of the sample of interest (in this case a powder that has been exposed to a gas) to be referenced against a background to get $r'$. An important requirement for Kubelka Munk is that $r'$ is < 1. In other words, the background is always more reflective.

Traditionally, KBr is used as a background in the infrared, due to its high reflectance, and the sample is a mixture of KBr and analyte powder [7]. This insures that the scattering properties of the sample and the background are the same over a range of concentrations.

For gas adsorption measurements, it is not suitable for KBr and the solid sample to be mixed (due to potential influence on the catalytic properties [2]), so the sample can be used alone for the measurement, with KBr still used as the background. Alternatively, the sample in the presence of N$_2$ can be used for the background, and the sample with the analyte gas used as $r_s$. These different approaches to presenting diffuse reflectance data are compared below, with ALC as the powder, and CH$_4$ as the analyte gas.

A.4.1 KBr as background

When KBr is used as the background, $r_B$, two different Kubelka Munk spectra are needed in order to gain information regarding the gas surface interactions. One uses ALC under N$_2$ as $r_S$ and the other uses ALC under CH$_4$/O$_2$/N$_2$ as $r_S$. The two Kubelka Munk spectra are then subtracted, as $K_{M_{CH_4}} - K_{M_{N_2}}$, to give the final corrected spectra. Figure
A.8 shows the Kubelka Munk spectra of N2 and of CH4 exposed ALC before (A.8a) and after (A.8b) subtraction at 25 °C. and Figure A.9 show the results obtained by applying the same method at 800 °C. At both temperatures, the baseline is very close to zero after the subtraction for almost the entire range of each spectrum. For the 25 °C spectrum, (Figure A.8b) the baseline begins to slope below zero at wavenumbers below 1700 cm⁻¹. This sloping baseline is much more pronounced in the 800 °C sample. Additionally, the spectra are quite noisy, especially between 4000 and 3500 cm⁻¹, and around 1500 cm⁻¹. Increasing the number of scans does not improve the signal to noise, indicating that this may not be noise, but could be an artifact of the instrument. This is further confirmed by the single channel spectrum of the empty chamber shown in Figure A.6b, where there is a great deal of this 'noise' in the spectrum. The exact source of this artifact has not been pinpointed, but it must come from either the source, the detector, the beamsplitter, or gas in the empty chamber. Most likely, the presence of moisture in the chamber could be causing this artifact. Ideally, the background and sample reflectance should be almost identical, and the artifact would be cancelled out by the relative reflectance calculation. Due to the difference between the intensity of rKBr and rALC, coupled with the difference between rALC-N2 and rALC-CH4, it does not.

A.4.2 Sample Powder as Background

An alternative to using KBr as rB, is to use ALC under O2/N2 as the background, and ALC under CH4/O2/N2 flow as rB in the relative reflectance calculation. This eliminates the need for the subsequent subtraction step used with KBr. Figure A.10 shows the Kubelka Munk spectra calculated with ALC as the background at 25 °C.
(Figure A.10a) and 800 °C (Figure A.10b). For the 25 °C spectra, the baseline is at zero, and it does not slope as it did with KBr as the background. For the 800 °C data, the baseline does slope in the negative direction as it did when KBr was used as the background, but because the sample and background are similar, a broad peak is observed due to carbonate adsorption on the sample.

A.4.3 Comparison of Background Methods

It is clear that the more alike the reflectance profiles of the sample and background, the better the Kubelka Munk spectra appears. KBr and TiO₂ are too dissimilar, as shown by the sloping baseline. This results in peaks being obscured in the region below 1700 cm⁻¹ that are clearly present when ALC-N₂ is used as the background. However, even with the use of ALC-N₂ as the background, there are still problems with the Kubelka Munk spectra as when the sample goes through a temperature cycle the reflectance changes. Van Every and Griffiths noted similar changes in the reflectance of the sample as a result of changes in the gas flow rate affecting the packing of the sample powder [2]. Here temperature, rather than gas flow, appears to cause this reflectance change. The cooling and heating cycles changing the packing. Ideally, measurements should be made by the constant temperature method to minimize these effects, but it is not always the most suitable method depending on the sample or the information required for the analysis, and even with the constant temperature approach, there are still reflectance differences that appear. It is therefore desirable to have a suitable method to correct diffuse reflectance data.
A.5 Data Correction

Previously, Brimmer et al. have described a method of correcting the relative reflectance of powder samples in the infrared to compensate for differences in the reflective intensity of the sample and background. This method is outlined below and compared with a similar method, based on the correction of the single channel rather than relative reflectance data.

A.5.1 Correction of Relative Reflectance

Of the methods outlined in the literature for the correction of diffuse reflectance data, the Brimmer and Griffiths method is among the most reasonable [4]. It is based on the argument that the relative reflectance, \( r_r \), must be less than 1 in order for the Kubelka Munk expression to apply. Any relative reflectance spectrum that is greater than 1 is multiplied by a factor so that the highest point in the spectrum is brought below one. Figure A.11 shows the uncorrected and corrected relative reflectance spectrum of the 25°C sample, as well as the corresponding Kubelka Munk spectrum. Both the corrected and uncorrected data have relatively flat baselines, and have the same peak positions. The only significant difference between the two spectra is the intensities of the peaks. Clearly, the use of a correction factor causes an increase in the absorption band intensities. There is also a change in the relative ratio of different absorption bands. The ratio of the band at 3016 cm\(^{-1}\) to the band at 1640 cm\(^{-1}\) is 4.3 for the uncorrected spectrum, and reduces to 3.4 in the corrected spectrum.

When the measurements are made at 800 °C (Figure A.12) the uncorrected spectra do not make a significant difference in the quality of the spectra. In both cases the
baseline is not flat, and due to the requirement of making the highest point in the relative reflectance less than 1, the baseline is not a zero. In addition, the relative peak intensity between the bands at 3016 cm\(^{-1}\) and 1447 cm\(^{-1}\) are more pronounced, with the uncorrected having a ratio of 0.39, while the corrected data has a ratio of 1.9.

**A.5.2 Correction of Single Channel Spectra**

An alternative to correcting the data as relative reflectance is to correct the single channel spectra. A protocol was developed to minimize the amount of user judgement in the correction process. A region of the single channel spectrum, where it is assumed that there is no absorption by adsorbed gas and surface species, is selected. A macro was then written using SigmaPlot which computes the multiplicative factor necessary to make the selected point on the sample spectrum 0.0001 less than the same point on the background spectrum. This factor is then multiplied by the entire sample reflectance so it is slightly less in reflective intensity than the background spectrum. In other words, the relative reflectance will be less than 1. This same method is briefly noted in a paper by Van Every and Griffiths without much elaboration [2].

Figure A.13 shows the uncorrected and corrected single channel spectra and corresponding Kubelka Munk spectra for the 25 °C sample. The results are similar to those obtained by correcting the relative reflectance as discussed above. The baselines for both the corrected and uncorrected data are similar, but there are differences in the relative intensity of peaks in the spectra. The ratio of the intensity of bands at 3016 cm\(^{-1}\) and 1640 cm\(^{-1}\) is 4.3 for the uncorrected data and 2.8 for the corrected data.
When the correction is made to measurements made at 800 °C using this method, the results are much different than those obtained using the relative reflectance method. Figure A.14 shows both corrected and uncorrected single channel and Kubelka Munk spectra. The spectrum that has been corrected now has a flat baseline that is near zero. There is also still a difference in the relative intensity of the 3016 cm⁻¹ and 1447 cm⁻¹ bands, as was seen in the relative reflectance spectrum correction, but now 2.9. The final difference is the band around 1300 cm⁻¹. In the Kubelka Munk spectra from the uncorrected data and the relative reflectance correction, it is difficult to determine whether there is a band present, or if the baseline is just sloping severely in this region. From the single channel correction, it is clear that a band is present, and the baseline is relatively flat.

A.5.3 Selecting a correction method

Figure A.15 compares the uncorrected Kubelka Munk spectra with those corrected by the two different methods described above. In many cases, the factor obtained by the single channel correction and the relative reflectance spectra are very similar, which is not surprising, as the two methods are similar in approach. Occasionally, the relative reflectance correction and the single channel correction require correction factors that are very different from one another. This is most prominently seen in samples where there are negative peaks. In other words, a species disappears upon gas exposure. Because the relative reflectance method considers the highest point in the spectrum, the baseline upon the conversion to Kubelka Munk is often well above zero. In addition, the factor used is often much greater for these spectra, resulting in a greater
distortion of the relative intensities of the different peaks in the spectra. The single channel correction is not without problems in this case either. Because \( R_\text{r} \) needs to be less than 1, peaks that are negative in the relative reflectance spectra become positive in the Kubelka Munk spectra due to the \((1-R_\text{r})^2\) term of the function.

### A.6 Criteria For Data Collection

Using both the above experiments and the assumptions of the Kubelka Munk expression, it is possible to outline criteria for studying gas-surface reactions of powdered samples using diffuse reflectance spectroscopy.

1. The sample and background reflectance should be as similar as possible. As demonstrated in section A.3, differences in the reflectance that occur when using KBr for the background result in sloping baselines, and in some cases, absorbance bands may be obscured.

2. The temperature at which the background reflectance and sample reflectance are taken should be similar since the reflective properties of the sample change with temperature. This is in part due to the vibrations of the base material, such as TiO\(_2\), that may become more intense (leading to lower reflectance) at increased temperatures.

3. The single channel spectra must be equal to (or slightly greater than) the sample spectra. Ideally, the relative reflectance would be 1 everywhere there is no adsorbed or gas species.

4. Correction factors are best applied to single channel spectra. With negative peaks, larger correction factors are needed to correct the data, meaning greater...
distortion of the peak intensities when using the relative reflectance data. It is preferable to note, from the appearance of the relative reflectance spectrum, which species in the Kubelka Munk Spectra are due to a decrease of a species.

5. The correction factor can alter the relative intensity of peaks in the infrared spectra. In cases where large correction factors are necessary, only qualitative information should be extracted from the calculated Kubelka Munk spectra.
A.8 References


Table A.1: Summary of measured temperature of infrared chamber as compared to the setpoint temperature.

<table>
<thead>
<tr>
<th>Setpoint (°C)</th>
<th>Bottom of Sample Cup (°C)</th>
<th>Sample Surface (°C)</th>
<th>Specifications* (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>25</td>
<td>25</td>
<td>-</td>
</tr>
<tr>
<td>200</td>
<td>108</td>
<td>65-109</td>
<td>-</td>
</tr>
<tr>
<td>400</td>
<td>212</td>
<td>122-208</td>
<td>248</td>
</tr>
<tr>
<td>600</td>
<td>325</td>
<td>190-312</td>
<td>372</td>
</tr>
<tr>
<td>800</td>
<td>413</td>
<td>247-412</td>
<td>489 (at 771 °C)</td>
</tr>
</tbody>
</table>

* From Spectra-Tech. Inc. Measurement at sample cup under N₂ flow of 40 mL min
Figure A.1: Schematic of Transmission Spectroscopy.
Figure A.2: Reflection of light from a surface. a) specular reflection from a mirror surface; b) diffuse reflection from a matte surface.
Figure A.3: Depiction of light flux used for derivation of Kubelka Munk expression.
Figure A.4: Schematic diagram of environmental DFIFTS chamber. a) diffuse reflectance collector; b) close-up of sample holder.
Figure A.5: Temperature profile for DRIFTs step experiment.
Figure A.6: Single channel reflectance of KBr. a) in The Collector; b) compared with empty chamber source profile.
Figure A.7: Single Channel Spectra of Anatase/La$_2$O$_3$/CuO upon exposure to CH$_4$ and N$_2$. a) 25 °C; b) 800 °C. The spectra taken at 800 °C show a greater difference in reflective intensities of the N$_2$ and CH$_4$ spectra compared to the room temperature spectra.
Figure A.8: Correction of data using KBr as background at 25 °C. a) Kubelka Munk Spectra vs KBr; b) $K_{\text{MC}}{\text{H}_4}$-$K_{\text{MN}_2}$, showing the infrared absorption bands that result from the reaction of $\text{CH}_4$ on ALC.
Figure A.9: Correction of data using KBr as background at 800 °C. a) Kubelka Munk Spectra vs KBr; b) $\text{KM}_{\text{CH}_4}$-$\text{KM}_{\text{N}_2}$. Shows infrared absorption bands that result from $\text{CH}_4$ reaction on ALC at 800 °C.
Figure A.10: Kubelka Munk spectra obtained by using ALC under N₂ as rₐ, a) 25 °C; b) 800 °C. The baseline for the 800 °C sample is below zero and not flat.
Figure A.11: Correction of 25 °C Diffuse Reflection Data by relative reflectance method. a) corrected and uncorrected relative reflectance; b) Kubelka Munk spectrum of uncorrected and corrected data. Correction of spectra results in a flat baseline and decreases the intensity of the absorption bands.
Figure A.12: Correction of 800 °C diffuse reflection data by relative reflectance method. a) corrected and uncorrected relative reflectance; b) Kubelka Munk spectrum of uncorrected and corrected data. Before correction spectrum baseline is greater than zero, after it is above zero.
Figure A.13: Correction of 25 °C DRIFTS data by single channel method. a) corrected and uncorrected single channel reflectance; b) Kubelka Munk spectra of uncorrected and corrected data. Baseline of corrected data is flat compared to the uncorrected data.
Figure A.14: Correction of 800 °C DRIFTS data by single channel method. 
a) corrected and uncorrected single channel reflectance; b) Kubelka Munk spectra of uncorrected and corrected data. Baseline of corrected sample is flat and close to zero.
Figure A.15: Comparison of diffuse reflectance spectra corrected by different methods. a) no correction factor; b) relative reflectance correction; c) single channel correction.


