Monitoring CO Concentration in Fuel Cells Using Microcantilever Sensors

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MONITORING CARBON MONOXIDE CONCENTRATION IN FUEL CELLS USING MICROMECHANICAL CANTILEVER SENSORS

A Thesis
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
Mechanical Engineering

by
Tugba Demir
December, 2009

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ABSTRACT

Estimating the concentration of gases including carbon monoxide (CO) in the hydrogen fuel exiting the reformer and entering the fuel cell is imperative. A high concentration of CO can cause fuel-cell catalyst poisoning, which permanently destroys the cell. Current practices call for utilizing expensive and bulky spectral analyzers to achieve this task. In addition to their high cost, these methodologies, undoubtedly, hinder the portability and self-containment of the cell. To overcome these problems and achieve the desired objectives of a portable, self-contained, and real-time measurement module, this thesis presents and experimentally investigates a new enabling technology based on utilizing an array of microcantilever sensors to detect minute concentrations of CO in the fuel cell. Results of this study indicate that microcantilevers can be spin coated with homogenous layers of copper-exchanged Y zeolite (CuY). This zeolite is capable of adsorbing CO over a range pressures and fuel cell operating temperatures. As a result of this adsorption, the sensor experiences a shift in its resonance frequency, which can be measured and related to the concentration of CO. It is determined that maximum adsorption capacity of the sensor occurs at 40 °C using CuY zeolite that is loaded with 10 wt% Cu. Furthermore, experimental findings indicate that the sensitivity of the sensor increases as the number of zeolite layers is increased up to a certain threshold (4 layers). Beyond this threshold, adding more layers will only result in a less sensitive sensor. In the experiments described in this thesis, a maximum repeatable shift of 275 Hz in the first modal frequency of the microcantilevers is measured. Ultimately, such frequency shifts can be
related to the concentration of CO in the gas mixture, allowing closed-loop, real-time control and diagnosis of the flow of gases into and out of the fuel cell. This can help avoid fuel-cell starvation and prevent catastrophic deactivation of the necessary fuel cell catalyst.
DEDICATION

I would like to dedicate this thesis to my family, especially my aunts for their continuous love and support.
ACKNOWLEDGMENTS

I would like to thank my advisor, Professor Mohammed Daqaq, for his guidance, encouragement, advice, and discussion during my research at Clemson. His technical insight has made my graduate research meaningful and enjoyable. I also would like to thank Professor David Bruce, my co-advisor, for his support and allowing me to use his laboratory for the experimental work. I also thank Professor Pierluigi Pisu for his continuous guidance and support. Special thanks are also due to Professor Igor Luzinov, Professor Tanju Karanfil and their research groups for their help and friendship while conducting some experiments in their laboratories.

I would also like to express my appreciation to my research group with whom I have studied and worked: Yousef Qaroush, Thiago Seuacius, Clodoaldo DaSilva, Amin Bibo, Chris Stabler, Ravendra Masana, Gregory Batt, Abdouf Abuson and Keyur Shah. I also thank all my friends whom I consider as family: Fehime Vatansever, Atiye Seker, Fatma Ozkayalar, Onur Ozcalik, Durukan Kuzu, Sule Bekaroglu, Ayse Tascan, Nuray Ates, Prince Anyaba, Tugba Boztas, Selcen Koseler, Hatice Tokpunar, Sine Kontbay, Levent Tekinalp, Meric Selbes, Alaa Qattawi, Ayse Korucu and Nguyen Hai Ha.

Finally, I would like to express my deepest gratitude to my mother, Umran; my father, Kadri; my brother, Erkan; and my sisters, Asuman and Busra for their love and support throughout my life. I could not have come this far without them. Special thanks also go to my aunts, Humeyra, Semran, Sukran, Aynisah and my cousin Yavuz for their continuous encouragement.
Last, but not least, I would like to thank God for all the gifts He has bestowed on me.
TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>TITLE PAGE</td>
<td>i</td>
</tr>
<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>LIST OF TABLES</td>
<td>ix</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>x</td>
</tr>
<tr>
<td>CHAPTER 1</td>
<td></td>
</tr>
<tr>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Motivations</td>
<td>1</td>
</tr>
<tr>
<td>1.1.1 Production Of Carbon Monoxide (CO) In The Fuel Cell</td>
<td>3</td>
</tr>
<tr>
<td>1.2 Monitoring CO Concentration</td>
<td>11</td>
</tr>
<tr>
<td>1.2.1 Proposed Approach For Monitoring CO Concentration In Fuel Cells</td>
<td>14</td>
</tr>
<tr>
<td>1.3 Thesis Contributions</td>
<td>17</td>
</tr>
<tr>
<td>1.4 Thesis Organization</td>
<td>18</td>
</tr>
<tr>
<td>CHAPTER 2</td>
<td></td>
</tr>
<tr>
<td>Recent Advances And Applications Of Microcantilever Sensors</td>
<td>19</td>
</tr>
<tr>
<td>2.1 Brief Overview</td>
<td>19</td>
</tr>
<tr>
<td>2.2 Detection Methods</td>
<td>21</td>
</tr>
</tbody>
</table>
2.2.1 Optical Lever Method ................................................................. 22
2.2.2 The Piezoresistive Method ......................................................... 23
2.2.3 Capacitive Methods ................................................................. 23
2.2.4 Piezoelectric Methods .............................................................. 24
2.2.5 Comparison Of Detection Methods .......................................... 25

2.3 Applications Of Microcantilever Sensors ................................. 26
2.3.1 Gas Detection ........................................................................... 26
2.3.2 Biotechnology .......................................................................... 26

CHAPTER 3

Coating Of Microcantilevers With Zeolite ........................................ 30

3.1 Brief Literature Review ............................................................... 29
3.1.1 Natural Zeolite ........................................................................ 32
3.1.2 Synthetic Zeolites ................................................................. 33
3.1.3 Applications Of Zeolite .......................................................... 36

3.2 Preparation Of Copper-Y (Cuy) Zeolite ...................................... 38
3.2.1 Methodology And Results ...................................................... 39

3.3 Coating Microcantilevers With Cuy Zeolite .............................. 49
3.3.1 Methodology And Results ...................................................... 49
3.3.2 Effect Of Cuy Zeolite Coating On Microcantilevers’ Resonance Frequency .................................................................................................................. 52

CHAPTER 4
Detection Of Carbon Monoxide Using Microcantilever Sensors ............................................. 59

4.1 Brief Overview ................................................................................................... 57

4.2 CO Adsorption Capacity Of Cuy Zeolite ........................................................... 59

4.2.1 Effect Of Cu Content .................................................................................. 61

4.2.2 Effect Of Temperature On CO Adsorption..................................................... 65

4.3 Monitoring Resonance Frequency Shift Of Microcantilevers Due To CO Adsorption ..................................................................................................................... 66

4.3.1 Methodology ............................................................................................... 67

4.3.2 Results And Discussions............................................................................. 68

CHAPTER 5
Conclusions And Recommendations For Future Work....................................................... 76

APPENDICES.............................................................................................................77

A: Adsorption isotherms of N₂ on CuY zeolite at 77 K.............................................78

B: Adsorption isotherms of CO on CuY zeolites at 40°C..........................................79

C: Adsorption isotherms of CO adsorbed on CuY(10%) zeolites at 40, 50 and 60°C .............................................................83

REFERENCES........................................................................................................86
<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 2. 1. Advantages and disadvantages of detection methods</td>
<td>25</td>
</tr>
<tr>
<td>Table 3. 1. Y-Zeolites used in this study</td>
<td>39</td>
</tr>
<tr>
<td>Table 3. 2. BET results of CuY zeolite</td>
<td>42</td>
</tr>
<tr>
<td>Table 3. 3. Geometric and material properties of the MicroMash microcantilever beams</td>
<td>49</td>
</tr>
<tr>
<td>Table 3. 4. Material properties of microcantilever and CuY zeolite</td>
<td>56</td>
</tr>
<tr>
<td>Table 4. 1. Run conditions of CO adsorption process</td>
<td>60</td>
</tr>
<tr>
<td>Table 4. 2. Quantitative data on the adsorption of CO on CuY zeolites</td>
<td>65</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1. 1. A schematic of a PEMFC fuel cell operation.</td>
<td>2</td>
</tr>
<tr>
<td>Figure 1. 2. General scheme of Steam Reforming Process.</td>
<td>4</td>
</tr>
<tr>
<td>Figure 1. 3. General scheme for the partial oxidation process.</td>
<td>5</td>
</tr>
<tr>
<td>Figure 1. 4. Schematic of CO poisoning the Pt catalyst.</td>
<td>7</td>
</tr>
<tr>
<td>Figure 1. 5. Simulation of 2% O$_2$ bleeding to mitigate CO poisoning.</td>
<td>10</td>
</tr>
<tr>
<td>Figure 1. 6. Schematic of microcantilever-based DNA hybridization.</td>
<td>13</td>
</tr>
<tr>
<td>Figure 1. 7. The general process for the monitoring CO in the fuel cell.</td>
<td>15</td>
</tr>
<tr>
<td>Figure 2. 1. Sensors with optical lever readout.</td>
<td>19</td>
</tr>
<tr>
<td>Figure 2. 2. (a) Cantilever vibrating at its natural resonant frequency and (b) the resonant frequency shift due to the added.</td>
<td>21</td>
</tr>
<tr>
<td>Figure 2. 3. Optical lever method for cantilever deflection measurements.</td>
<td>23</td>
</tr>
<tr>
<td>Figure 3. 1. Framework Structure of zeolites.</td>
<td>30</td>
</tr>
<tr>
<td>Figure 3. 2. A typical zeolite structure. [<a href="http://www.lenntech.com/zeolites">www.lenntech.com/zeolites</a>]</td>
<td>32</td>
</tr>
<tr>
<td>Figure 3. 3. Structure of Synthetic Linde Type-A Zeolite.</td>
<td>33</td>
</tr>
<tr>
<td>Figure 3. 4. Structure of Faujasite Zeolite.</td>
<td>34</td>
</tr>
<tr>
<td>Figure 3. 5. Diagram of the FAU zeolite structure, illustrating.</td>
<td>35</td>
</tr>
<tr>
<td>Figure 3. 6. Adsorption isotherms of N$_2$ on CuY-zeolites at 77 K.</td>
<td>41</td>
</tr>
<tr>
<td>Figure 3. 7. X-Ray Diffractometer [Sintag, 1999].</td>
<td>44</td>
</tr>
<tr>
<td>Figure 3. 8. XRD spectra of Cu-loaded Y zeolites. a) HY, b) CuY(10wt%),</td>
<td>45</td>
</tr>
<tr>
<td>Figure 3. 9. Scanning Electron Microscope (SEM).</td>
<td>47</td>
</tr>
</tbody>
</table>
List of Figures (Continued)

Figure                                                                 Page

Figure 3. 10. SEM image of CuY zeolite................................................................. 48
Figure 3. 11. Schematic drawing of MicroMasch microcantilever ....................... 49
Figure 3. 12. a) Scheme of spin coating process,

b) Spin coater used in the experiments. ............................................................... 51
Figure 3. 13. SEM images of coated micromicocantilever surface using .......... 52
Figure 3. 14. Experimental setup for the monitoring resonance frequency.......... 53
Figure 3. 15. Schematic of the microcantilever after CuY zeolite coating .......... 53
Figure 3. 16. Resonance frequency of 350 $\mu m$ microcantilevers...................... 53
Figure 3. 17. Resonance frequency shift of 300 $\mu m$ microcantilevers............. 58
Figure 3. 18. Resonance frequency shift of 250 $\mu m$ microcantilevers

a) Experimental results, b) theoretical results....................................................... 58
Figure 4. 1. Schematic of multilayer adsorption showing................................. 58
Figure 4. 2. Micromeritics ASAP 2010 apparatus............................................. 62
Figure 4. 3. Adsorption isotherms of CO adsorbed at 40$^\circ$C on the CuY zeolites with
different Cu content. ....................................................................................... 63
Figure 4. 4. Schematic of CO adsorption.............................................................. 64
Figure 4. 5. CO adsorption isotherms of CuY (10%) zeolite at different temperatures. 66
Figure 4. 6. Setup for CO detection................................................................. 67
Figure 4. 7. Microcantilever and its holder......................................................... 68

List of Figures (Continued)
Figure 4. 8. Frequency response curves of the beam with 350 µm microcantilever with 3 layers during CO adsorption. .................................................. 69

Figure 4. 9. The resonance frequency shift of the 250 µm microcantilevers coated with 1, 2 and 4 CuY(10%) layers. ................................................................. 71

Figure 4. 10. The resonance frequency shift of 250 µm microcantilevers coated with 4, 8, 10 and 12 CuY(10%) layers. ................................................................. 72

Figure 4. 11. Sensitivity of 250 µm microcantilevers coated with different zeolite layers during CO adsorption. ................................................................. 72

Figure 4. 12. Resonance frequency shift of 250 µm microcantilevers coated with 4 layers and exposed to different amount of CO........................................ 73

Figure 4. 13. Resonance frequency of the microcantilever samples coated with +1 layer, ♦2 layers, ▲4 layers, ■8 layers, ◡10 layers, ●12 layers...................... 74
Chapter 1

Introduction

1.1 Motivations

Due to the current energy crisis and our critical need for clean and sustainable power sources, fuel cell technology has flourished over the last two decades, becoming one of the major thrusts of energy research. In principle, fuel cells produce electric energy using hydrogen (H₂) or hydrogen-containing fuels, and therefore, have the capability to provide an environmentally friendly supply of energy. Furthermore, since they are more efficient than internal combustion engines, they could prove useful for a broad-range of applications in transportation, military, and as a portable or stationary power supply for building sites, utilities, and factories.

One of the most widely utilized fuel cell technologies is the polymer electrolyte membrane fuel cell (PEMFC), also called the proton exchange membrane fuel cell. PEMFC is commonly used in transportation applications and consists of i) a polymer
electrolyte membrane (PEM) that conducts only hydrogen protons; \( ii \) anode and cathode catalysts, typically platinum; \( iii \) electrically-conductive porous backing layers; and \( iv \) plates that deliver the fuel and oxidant to the reactive sites. The operating principle of a PEMFC is illustrated in Figure 1.1.

The process of generating electricity starts by passing \( \text{H}_2 \) or a \( \text{H}_2 \)-rich fuel gas through the plates to the anode side, where a catalyst, usually platinum (Pt), oxidizes the hydrogen to give electrons and protons. A Polymer Electrolyte Membrane (PEM) allows the protons to pass directly to the cathode; whereas, the negatively charged electrons can only flow through a conductor to the cathode, creating an electric current as shown in

![Figure 1.1. A schematic of a PEMFC fuel cell operation [www.fueleconomy.gov].](image-url)
Figure 1.1. At the cathode, the electrons and protons combine with oxygen \( (O_2) \) to form water, which flows out of the cell.

### 1.1.1 Production of Carbon Monoxide (CO) in the Fuel Cell

The hydrogen needed for fuel cells is routinely produced by reforming hydrocarbon fuels, a process which results in a product mixture of hydrogen, carbon dioxide, and a small amount of carbon monoxide (CO). Although the CO concentration can be reduced to approximately 100 ppm, fuel cell potential and its energy conversion efficiency can still be compromised by the presence of even a minute amount of CO in the fuel mixture entering the cell. This stems from CO reacting with the Pt catalyst adversely affecting its oxidation capability.

In general, two processes are often utilized to produce \( H_2 \) for use in a fuel cell, namely Steam Methane Reforming (SMR) and Partial Oxidation (POX). Here, we present an overview of these techniques.

#### 1.1.1.1 Steam Reforming

Steam reforming has been one of the most effective hydrogen production methods for several decades. Tessie du Motay and Marechal first described a process for the conversion of hydrocarbons into hydrogen in the presence of steam in 1868 [Adris, 1996]. The steam reforming process consists of three steps for producing hydrogen as shown in Figure 1.2. Methane \( (CH_4) \) is first catalytically reformed at an elevated temperature (750-800°C) and pressure to produce a synthesis gas (syngas) mixture of \( H_2 \) and CO.
A catalytic shift reaction occurring at 180-350°C subsequently combines CO and H\textsubscript{2}O to produce the H\textsubscript{2} product, which is purified through adsorption. The reforming is initiated via the endothermic reaction:

$$\text{CH}_4 + \text{H}_2\text{O} \rightarrow 3 \text{H}_2 + \text{CO} \quad \Delta H = + 206 \text{ kJ/mol} \quad (1.1)$$

In the previous reaction, CH\textsubscript{4} is treated with high-temperature steam to produce a mixture of H\textsubscript{2} and CO. Excess steam is then used to enhance conversion and to prevent thermal cracking and coking according to:

$$2 \text{CO} \rightarrow \text{CO}_2 + \text{C} \quad \Delta H = -172 \text{ kJ/mol} \quad (1.2)$$

Excess steam is then used to promote the second step in the process associated with the conversion of syngas to the desired H\textsubscript{2} product, following the reaction:

$$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H = -41 \text{ kJ/mol} \quad (1.3)$$

The preceding water-gas shift is conventionally carried out at a lower temperature than the reforming reaction. At this step, most of the CO reacts with H\textsubscript{2}O to produce hydrogen. Once the third reaction is complete, pressure swing adsorption (PSA) is utilized to remove the water, CO\textsubscript{2}, N\textsubscript{2}, and CO from the gas mixture, producing a pure hydrogen product.
1.1.1.2 Partial Oxidation

While steam reforming is very efficient for raw materials containing little petroleum, partial oxidation (POX) is preferred when there is a higher amount of oil. One of the advantages of POX is that it works with all kinds of hydrocarbons, including natural gas, petroleum residue, and petroleum coke, even solid feeds such as coal or metallurgical coke can be utilized. Other advantages are a short start up time, simplicity, and reliability. Also compared to the steam reforming process, the POX reactor is less expensive than the steam reformer [Demir, 2006]. In the POX process, which can be carried out non-catalytically as shown in Figure 1.3, or catalytically, air is used as an oxidant. As such, nitrogen is mixed with the hydrogen produced, which reduces the partial pressure of the latter and consequently, lowers the fuel cell output [Abaci, 2006].

![Figure 1.3. General scheme for the partial oxidation process](adopted from Adams et al., 2006).

The partial oxidation of methane produces a syngas mixture of CO and H₂, according to

\[
\text{CH}_4 + \frac{1}{2} \text{O}_2 \rightarrow \text{CO} + 2\text{H}_2 \quad \Delta \text{H} = -36 \text{ kJ/mol} \quad (1.4)
\]
This process also includes a water-gas shift, where CO reacts with H₂O to produce hydrogen according to:

$$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$$  \[\Delta H = -41 \text{ kJ/mol}\]  (1.5)

At this stage, a carbon slurry separator is used to recover carbon, thereby decreasing the amount of CO or CO₂ in the resulting gas mixture.

### 1.1.1.3 Fuel Cell Poisoning

Although the availability of pure H₂ makes the process very efficient, its generation in transportation applications is not always viable because of lack of high pressure. To overcome this problem, the on-board generation of H₂-rich reformate generated through steam reforming, partial oxidation of hydrocarbons, such as methanol, gasoline or natural gas, is used instead of pure H₂ [Jiang, R., 2006]. As a result, small concentration of CO gas can remain in the gas mixture. In the PEMFC, the presence of small amounts of CO in the reformate poisons the Pt catalyst used at the anode, shown in Figure.1.4. Oetjen et al. [1996] explained that such poisoning is caused by the adsorption of CO on the Pt catalyst, which blocks the adsorption of H₂, according to the reactions:

$$2\text{Pt} + \text{H}_2 \rightarrow 2\text{Pt-H}_{\text{ads}}$$  (1.6)

$$\text{Pt} + \text{CO} \rightarrow \text{Pt-CO}_{\text{ads}}$$  (1.7)
As a result of the previous reactions, a large number of Pt sites for hydrogen adsorption are blocked during CO adsorption. This happens because the H$_2$ – Pt bond is much weaker than the CO-Pt bond. As such, the sticking probability of H$_2$ on Pt is 15 times lower than that of CO [Baschuk and Li, 2001]. Over the long run, this phenomenon decreases fuel cell performance until ultimately no reaction or power generation occurs.
1.1.1.4 Techniques to Reduce CO Poisoning

To avoid detrimental problems associated with CO adsorption/poisoning, several techniques have been developed to reduce CO. Three of these techniques include i) using a CO tolerant Pt alloy catalyst, ii) raising the operating temperature, and iii) feeding oxygen.

Initial studies examining the use of Pt alloy catalysts began in the early 1990’s with the first study conducted by Schmidt et al. [1995]. Oetjen et al. [1996] also investigated the use of different Pt-Ru alloys, such as Pt, Pt\textsubscript{0.7} Ru\textsubscript{0.3} and Pt\textsubscript{0.5} Ru\textsubscript{0.5}, at the anode side of the cell to determine their effects on PEMFC performance. In these experiments, the two mechanisms described in Equations 1.8 and 1.9 were used. Results indicated that as a result of the formation of Ru-OH, due to Ru being activated with water, some of the adsorbed CO on neighboring Pt sites is oxidized by the adjacent Ru-OH to create CO\textsubscript{2}. Consequently, the amount of CO is reduced, effectively increasing the number of active sites for hydrogen adsorption. Oetjen et al. concluded that the Pt\textsubscript{0.5} Ru\textsubscript{0.5} catalyst was the most CO tolerant.

\begin{equation}
\text{Ru} + \text{H}_2\text{O} \rightarrow \text{Ru-OH}_{\text{ads}} + \text{H}^+ + e^- 
\end{equation}

\begin{equation}
\text{Pt-CO} + \text{Ru-OH} \rightarrow \text{Pt-Ru} + \text{CO}_2 + \text{H}^+ + e^- 
\end{equation}

Using the previous reactions, Giorgi et al. [2001] also investigated the oxidation kinetics of H\textsubscript{2} and O\textsubscript{2} with 100\text{ppm} CO using Pt, Pt\textsubscript{0.66}Ru\textsubscript{0.33}, and Pt\textsubscript{0.5}Ru\textsubscript{0.5} catalysts. The
compared the performance of fuel cells incorporating the three different catalysts. Corroborating the results of Oetjen et al. [1996], they determined that best all performance was observed with the Pt$_{0.5}$Ru$_{0.5}$ catalyst.

In addition to the Pt-Ru alloy, other Pt-alloys have also been examined to determine their ability to reduce CO poisoning. For example, Watanabe et al. [2003] used a Pt-Fe alloy on a Mordenite support as a preferential oxidation (PROX) catalyst, oxidizing CO with an addition of O$_2$ to form CO$_2$. They found that this catalyst is very selective, and has high activity for CO oxidation reactions, and can be used to remove CO completely from a hydrogen fuel consisting of 1% CO, 25% CO$_2$, 20% H$_2$O and 54% H$_2$. In another demonstration, Gasteiger et al. [1995] investigated the use of a Pt-Sn alloy to reduce CO poisoning, but they concluded that Sn was not as effective as Ru.

Another technique for reducing CO poisoning is operating the fuel cell at elevated temperatures. Generally, the operating temperature of the fuel cell varies from 50 to 80 °C depending on the type of fuel cell. In an attempt to improve CO tolerance, Zawodzinski et al. [1997] used a 100ppm CO fuel and varied the operating temperature of the PEMFC’s from 80 to 120 °C. They concluded that a minimum temperature of 100 °C is necessary to prevent CO from reacting with the catalyst. In a similar experiment, Xu et al. [2006] varied the operating temperature from 120 to 150 °C. However, they discovered that the cell internal resistance increases as the temperature increases. To address this issue, the humidity was increased using a pressurization process. This, however, resulted in a decrease of the PEMFC efficiency. Another investigation of the effect of fuel cell temperature was conducted by Jiang et al. [2006]. They used Nafion®–
Teflon®–Zr(HPO$_4$)$_2$ (NTZP) composite membranes at 80, 105 and 120 °C under 1atm with 0, 10, 100, 200 and 500 ppm CO in the hydrogen fuel. They observed an improved CO tolerance at 120 °C for higher CO concentrations (>100ppm).

The last technique, known as O$_2$ bleeding, uses oxygen on the anode side of the cell to reduce CO poisoning. In 1988, Gottesfeld et al. [1988] introduced 1-4% O$_2$ into the anode gas stream, obtaining CO tolerance at concentrations up to 500 ppm. Subsequently, Zawodzinski et al. [1997] achieved effective CO tolerance at concentrations greater than 100ppm. Another study conducted by Baschuk et al. [2003] modeled CO poisoning with O$_2$ bleeding in a PEM fuel cell. Comparing concentration levels of CO before and after O$_2$ bleeding, their results, illustrated in Figure 1.5, indicated that the performance of the fuel cell decreases as the presence of CO increased to 100ppm causing an anode overpotential of about 0.5 Volts at moderate current densities. However, by introducing 2% O$_2$ to the anode side of the fuel cell, results were improved significantly.

![Figure 1.5. Simulation of 2% O$_2$ bleeding to mitigate CO poisoning. [Baschuk et al., 2003].](image-url)
1.2 Monitoring CO Concentration

In addition to the previous techniques used to reduce CO concentration in the fuel cell, monitoring the concentration of CO in the gas mixture entering the cell or near the anode can be very beneficial as it allows for fuel cell diagnostics and for precise control of inlet gas concentration. This helps avoid fuel cell starvation and localized catastrophic phenomena within the cell. As of today, such critical measurements of gas concentration are attained through spectral analyzers that are, generally, expensive and bulky limiting the self-containment of the cell.

One potential solution to this problem lies in utilizing micro- and nano-scale sensors that are both small in size and ultra-sensitive. In particular, microcantilever sensors, shown in Figure 1.5, have attracted significant attention in the area of gas sensing. As specifically illustrated in Figure 1.6, chemical reactions occurring on one side of the sensor result in surface stress changes that cause the cantilever to deflect and shift its resonance-frequency [Gupta et al., 2004; Yang et al., 2003]. These chemically-induced mechanical forces can be estimated by measuring the cantilever deflection (static mode) and/or its resonance-frequency shift (dynamic mode) [Chen et al., 1995; Dareing and Thundat, 2005].

Indeed, these types of measurements permit an investigation of the interactions between individual molecules in a host of various media at high sensitivity down to forces of a few pN [Su et al., 2003]. In addition to the previous techniques used to reduce CO concentration in the fuel cell, monitoring the concentration of CO in the gas mixture entering the cell or near the anode can be very beneficial as it allows for fuel cell
diagnostics and for precise control of inlet gas concentration. This helps avoid fuel cell starvation and localized catastrophic phenomena within the cell. As of today, such critical measurements of gas concentration are attained through spectral analyzers that are, generally, expensive and bulky limiting the self-containment of the cell.

One potential solution to this problem lies in utilizing micro- and nano-scale sensors that are both small in size and ultra-sensitive. In particular, microcantilever sensors have attracted significant attention in the area of gas sensing. As specifically illustrated in Figure 1.6, chemical reactions occurring on one side of the sensor result in surface stress changes that cause the cantilever to deflect and shift its resonance-frequency [Gupta et al., 2004; Yang et al., 2003]. These chemically-induced mechanical forces can be estimated by measuring the cantilever deflection (static mode) and/or its resonance-frequency shift (dynamic mode) [Chen et al., 1995; Dareing and Thundat, 2005].

Indeed, these types of measurements permit an investigation of the interactions between individual molecules in a host of various media at high sensitivity down to forces of a few pN [Su et al., 2003]. It had been documented that microcantilever sensors are capable of detecting vapors [Baller et al., 2000], bacterial cells, proteins, and antibodies [Illic et al., 2004; Zhang et al., 2004; Savran et al., 2003], and can provide a mechanism for DNA hybridization [Hansen et al., 2001].
Figure 1.6. Schematic of microcantilever-based DNA hybridization [Spaniak et al., 1998].

Microcantilever sensors have also impacted healthcare by providing a mechanism to measure blood glucose levels for diabetes diagnoses [Pei et al., 2004] as well as identifying important cardiac muscle proteins indicative of myocardial infarction [Arntz et al., 2003] and detecting antigens specifically used to monitor prostate cancer [Lee et al., 2005].

With proven potential for label-free detection of complex biomolecular organisms and molecules, chemical applications for these sensors have also evolved. Dangerous chemical agents such as toxic vapors [Dareing and Thundat, 2005] and chemical nerve weapons [Yang et al., 2003] have been precisely and accurately identified. Industrial utilization, such as swelling of polymer brushes [Bumbu et al., 2004] and pH changes [Zhang et al., 2004b], has also been demonstrated. Physical applications are also growing and may include, for example, thermal detection and measurement [Corbeil et al., 2002; Berger et al., 1996], micro-scale investigations of solid electrode-electrolyte
interfaces [Tian et al., 2004], phase transitions [Berger et al., 1996; Nagakawa et al., 1998], and detecting infrared radiation [Thundat et al., 1995].

1.2.1 Proposed Approach for Monitoring CO Concentration in Fuel Cells

With all the previously mentioned applications of microcantilever sensors, we propose to utilize these sensors to monitor the concentration of CO in fuel cells. The process of monitoring CO concentration in fuel cell applications using of microcantilevers is envisioned as depicted in Figure 1.6. The monitoring process starts as follows: The H₂-rich reformate gas produced by hydrocarbons or natural gas, consisting of H₂, CO, CO₂ and H₂O enters the fuel cell. This gas mixture passes by microcantilevers, which can be installed at the entrance and/or different locations within the cell.
In general, when these cantilevers are functionalized with a proper coating that can selectively adsorbs CO, their natural frequency changes due to the additional mass of adsorbed CO. If these cantilevers are sufficiently sensitive, which they are, the change in their natural vibrational frequency can be measured in real time using a piezoelectric patch or a capacitive mechanism (see Chapter 2 for details). These frequency changes can be further related to the CO concentration in the gas mixture through a calibration curve, or other means. With that, if the adsorbed CO concentration becomes higher than a
critical value defined by the end user, a diagnosis signal can be sent subsequently to correct the situation by either shutting down the cell or feeding O$_2$ to oxidize the excess CO.

Each of the previously mentioned monitoring steps is a challenging objective that requires in-depth analysis and study; however, the first and essential step is to develop a selective sensor for CO gas. Therefore, the focus of this thesis is on finding a suitable adsorbent that can be used to coat the surface of the microcantilever and selectively adsorb CO gas from the fuel mixture. The material sought should have the following properties:

1) It should have a high adsorption capacity and should be capable of selectively adsorbing CO from a gas mixture for the range of possible fuel cell operating temperatures [40-100°C].

2) The adsorption process should not include a chemical reaction that changes the property of the adsorbent or exhausts it over time.

3) It should be capable of desorbing CO at elevated temperature. This allows us to desorb CO from the microcantilevers when needed, so as to avoid an accumulation of CO on the surface of the sensor, which would limit the long term accuracy of the sensor. Such elevated temperatures can be realized by passing an electric current through a nano-wire embedded within the sensor.
1.3 Thesis Contributions

The main purpose of this research is to use microcantilever sensors as portable, accurate, ultra-sensitive, and self-contained sensors for the real-time monitoring of CO concentration in fuel cells. The operation concept of these sensors is based on coating the cantilevers with an adsorbent that can selectively adsorb CO. As a result of this adsorption, the sensor experiences a shift in its natural frequency which can be measured and related to the concentration of CO in the gas mixture. The specific objectives can be summarized as follows:

- **Identification of a suitable CO adsorbent**

  In this study, Cu doped Y zeolite (CuY) is identified as a suitable CO adsorbent. In addition to satisfying the previously mentioned requirements, this material has enough surface area and a porous structure, with pores large enough to allow CO adsorption to occur. The material was synthesized and subsequently characterized using X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES), and N$_2$ adsorption analysis. The CO adsorption capacity of the CuY zeolites was also studied for different Cu loading and under varying pressures and temperatures.

- **Devising a suitable approach for coating the microcantilevers with CuY zeolite.**

  Although published literature contains many techniques for preparing zeolite coatings, most of them are not very suitable for use at the micro-scale because of the small size and fragility of microcantilevers. In this thesis, two methods, namely spin and dip coating, are
devised and compared. In these tests, silicon wafers, instead of microcantilevers, were first coated with zeolite in order to determine the most suitable technique that leads to a homogenous zeolite layer. These wafers were used for initial testing because of they exhibited similar surface features to the microcantilevers but were much less lower in cost. Subsequently, the more suitable technique was used to coat the microcantilevers.

Detection of carbon monoxide using CuY-coated Microcantilevers

Using the state-of-the-art Microsystem Analyzer (MSA-400), we studied the time variation of the resonant frequency of CuY coated microcantilevers as a function of the adsorption of CO at different pressures. A specially-designed pressure- and temperature-controlled chamber was constructed for this purpose. The sensitivity of the microcantilevers were determined as using the number of CuY zeolite coatings. The ability of the cantilevers to desorb CO was also tested and confirmed.
1.4 Thesis Organization

The rest of this thesis is organized as follows: In Chapter 2, we present the latest advances, detection methodologies, and applications of microcantilever sensors. In Chapter 3, we present an overview of zeolites, their structure, and applications. Subsequently, we describe the procedure and characterization techniques used to synthesize CuY zeolites for our experimental purposes. We present and compare two techniques for coating microcantilevers. Additionally, we use the MSA-400 to find a correlation between the microcantilever’s frequency shift and the number of CuY zeolite coatings. In Chapter 4, we study the effect of Cu content on the CO adsorption capacity of CuY zeolites. We then study the effect of CO adsorption on the frequency shift of the microcantilevers and confirm the ability of the microcantilevers to desorb CO at elevated temperatures. Finally, in Chapter 5, we present our conclusions and recommendations for future work.
Chapter 2

Recent Advances and Applications of Microcantilever Sensors

2.1. Brief Overview

When Atomic Force Microscopy (AFM) introduced microcantilever sensors as a tool for characterizing surface structure and stresses in solids, scientists soon discovered that molecular adsorption occurring on one side of these cantilevers generates enough surface stress energy that culminates in measurable deformations. With cost-effective fabrication means in place, microcantilever sensors, shown in Figure 2.1, were readily available for further experimental studies transducing chemical and biological processes into static deflections (static operation mode) that can be measured and used to detect the presence of a certain agent. Soon, they were realized to be the ideal choice for detecting the most infinitesimal mechanical responses generated by molecular interactions.
Figure 2.1. Sensors with optical lever readout for different applications [Fritz et al., 2008].

It was also observed that detection of a certain species on a microcantilever surface can also be achieved by measuring the shift in the cantilevers’ natural frequency as shown in 2.2. This mode of operation, also known as the *dynamic mode*, has been used extensively in the literature especially for mass sensing applications.

Specifically, as shown in Figure 2.2, the amount of adsorbed mass can be obtained by measuring the natural frequency of the cantilever before and after the addition of the mass according to:

$$
\Delta m = \frac{k}{4\pi} \left( \frac{1}{f_1^2} - \frac{1}{f_0^2} \right)
$$  \hspace{1cm} (2.1)

where \(f_0\) is the natural frequency of the cantilever before the addition of the mass and is given by
\[ f_0 = \frac{1}{2\pi} \sqrt{\frac{k}{ml^2}} \]  

(2.2)

where \( k = 3EI/ml^2 \), is the spring constant. Here \( I \) is the cantilever’s mass moment of inertia, \( E \) is its Young’s modulus, \( l \) is the length, and \( m \) is the effective mass of the cantilever beam. After mass loading, and assuming that \( k \) does not change, the resonance frequency of the cantilever can be obtained using

\[ f_1 = \frac{1}{2\pi} \sqrt{\frac{k}{m+\Delta m}} \]  

(2.3)

**Figure 2.2.** (a) Cantilever vibrating at its natural resonant frequency and (b) the resonant frequency shift due to the added mass [Kadam, 2006].

### 2.2. Detection Methods

For real-time and accurate measurements of the frequency shift and/or deflection of the microcantilevers, various methods have been proposed and implemented in the open
Some microcantilever sensors have optical levers or piezoresistive materials embedded to measure the deflection [Fritz, 2008; Meyer and Amer, 1998; Sone et al., 2004]. Others measure variation in the capacitance between the beam and an electrode to detect deflections as well as frequency variations [Vashist, 2007; Fragakis et al., 2005; Furukawa et al., 1979; Gaucher et al., 1998]. Variations in the voltage across a piezoelectric layer attached to the surface of the beam has also been used as a self-sensing mechanism. Laboratory experiments often employ laser-based optical components, similar to the Micro-System Analyze (MSA-400) used in this work, to measure the frequency shift of the cantilevers. In what follows, we review the principle operating mechanism for these approaches.

2.2.1. Optical Lever Method

With the optical lever method, which is depicted in Figure 2.3, the deflection of the cantilever beam is measured by pointing a laser beam unto the end of the cantilever. The beam surface, which is usually made of a reflective material, reflects the laser beam onto a photo sensing diode (PSD). When the cantilever bends, the reflected laser beam moves on the PSD’s surface changing its output, which can be related to the deflection of the cantilever.
The main advantage of the optical lever method, which was first introduced by Meyer and Amer [1998], is the sub-nanometer resolution with which it can measure the deflection of the beam. In addition, it is simple, reliable, and also has a linear response. Its main drawbacks are the bulk of the optical components required for measurements. This defeats the main purpose of designing compact and self-contained measurement methodology. Further, this method requires two complex and time-consuming alignment steps: first, the laser beam must be aligned to focus on the end of the cantilever, and second, the photosensitive detector must be aligned to detect the reflected laser beam from the cantilever.

2.2.2. The Piezoresistive Method

Piezoresistivity is an electromechanical phenomenon in which the bulk resistance of a material changes with its stress state. Some materials change their length with applied load, resulting in a change of their resistance. In this method, the deformation of a resistive material attached to the microcantilever is measured using a Wheatstone bridge.
that monitors variations in the resistance, $R$, of the material. This can be realized by measuring variations of the bridge output voltage due to variations in $R$.

The piezoresistive method has some advantages over the optical lever method. For instance, there are no bulky optical components, which permits its use for \textit{in vivo} applications. In addition, measurements within an opaque liquid media are possible since no laser is required for measurements. Further, the piezoresistive method requires no alignment steps because the deflection can be directly related to changes in the resistance. A drawback of this method is that it only has less than one nanometer deflection resolution, which is not even comparable to the one angstrom deflection resolution, attained using the optical lever method. Also, heat from the working current can causes deviations in the measurements. Specifically, temperature fluctuation in the cantilever, due to resistive heating effects that vary with the extent of cantilever deflection, make the measurements less accurate.

2.2.3. \textbf{Capacitive Methods}

Another detection method is based on measuring the capacitance between two conductive electrodes, which is proportional to the displacement between them. One of the electrodes is attached to the lower surface of the cantilever while the other is a fixed conductor on a substrate. When the cantilever deflects, the displacement between the two electrodes changes and causes a change in the measured capacitance.

The capacitive method is used in both the static and the dynamic mode of sensing. The advantage of this method is its sensitivity. Two major drawbacks, however, are that it can only measure very small deflections and that it is not suitable for use in an
electrolyte solution due to the Faradic currents that develop between the two electrodes [Vashist, 2007].

2.2.4. Piezoelectric Methods

The piezoelectric method uses a piezoelectric (PZT) layer attached to the surface of the microcantilever to measure its deflection and frequency shift. In PZTs, there is a relationship between the mechanical stress of the material and its electric potential. When the beam deflects, it produces a strain in the PZT layer, which produces a voltage difference that can be measured and related to the deflection of the beam. Two types of PZT materials were used in microcantilever sensors: Furukawa et al. [1979] and Gaucher et al. [1998] used lead zirconium titanate. Xu et al. [2003] used crystalline zinc oxide. The advantage of this method is that PZT materials can be used as both actuators and sensors. In other words, there is no need for external actuators or optics for measurement purposes. A major disadvantage stems from the need for a thick PZT layer to get a measurable voltage output. The thick PZT layer can stiffen the microcantilever beam making it unsuitable for operations at lower frequencies.

2.2.5. Comparison of Detection Methods

As mentioned in the previous subsections, selection of a certain detection method over another depends on the applications and the detected sample features. Table 2.1 summarizes the major advantages and disadvantages of each of the detection methodologies.
Table 2.1. Advantages and disadvantages of detection methods.

<table>
<thead>
<tr>
<th>Detection Methods</th>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Optical Lever Method</strong></td>
<td>Sensitive&lt;br&gt;Reliable&lt;br&gt;Sub-nanometer Resolution</td>
<td>Cannot be used in vivo</td>
</tr>
<tr>
<td><strong>Piezoresistive Method</strong></td>
<td>Use in vivo&lt;br&gt;Use in non-opaque liquid media&lt;br&gt;No alignment steps</td>
<td>Nanometer resolution&lt;br&gt;Affected by heat</td>
</tr>
<tr>
<td><strong>Capacitive Method</strong></td>
<td>Sensitive&lt;br&gt;Measures absolute displacement&lt;br&gt;No alignment steps</td>
<td>Small displacement&lt;br&gt;Cannot be used in electrolyte solution</td>
</tr>
<tr>
<td><strong>Piezoelectric Method</strong></td>
<td>Sensitive&lt;br&gt;Used as both actuator and sensor&lt;br&gt;No alignment steps</td>
<td>Thick PZT layer</td>
</tr>
</tbody>
</table>

2.3. Applications of Microcantilever Sensors

2.3.1. Gas Detection

Numerous studies utilizing microcantilever sensors for gas detection have been conducted. For instance, Thundat et al. [1995b] examined the detection of mercury vapor in air using silicon nitride microcantilevers coated with a 50 nm gold film. They considered both the resonant frequency and deflection changes due to adsorption of mercury vapor on the gold surface. Their results indicated a 0.7 pg/Hz sensitivity of the cantilever. In a similar study, Lang et al. [1998] used Pt-coated and Polymethylmethacrylate-coated (PMMA) cantilevers to identify H₂ gas and alcohol.
vapors, respectively. According to their findings, a maximum surface stress change of 
0.4±0.1 $Nm^{-1}$ due to $H_2$ gas adsorption was recorded. Furthermore, a maximum resonant 
frequency shift of 52.120 $Hz$ due to alcohol vapor absorption was measured.

Maute et al. [1999] used SiN cantilevers coated with polydimethylsiloxane
(PDMS) to detect volatile organic compounds, such as $n$-octane, toluene, and $n$-butanole.
They compared sensitivities of microcantilevers both with and without the polymer
coating for $n$-octane vapor detection. They found that microcantilevers coated with
polymers were much more sensitive to the presence of volatile organic compounds.
Specifically, their results indicated a 13% $Hz/ppm$ sensitivity for the microcantilevers
with coating and 0.25 % $Hz/ppm$ of microcantilevers without it. In further research,
Pinnaduwage et al. [2004] used the optical lever method to detect 2,4-dinitrotoluene
(DNT) gas by measuring the deflection of SXFA-[poly(1-(4-hydroxy-4-trifluoromethyl
-5,5,5-trifluoro) pent-1-enyl) methylsiloxane] - polymer-coated microcantilevers. They
detected 300 $ppt$ of DNT gas in 5s. Another demonstration involved the detection of
2-mercaptopethanol (HS—CH2–CH2–OH) vapors. In this study, Datskos and Sauers [1999]
used gold-coated silicon nitride micromachined cantilevers to measure the adsorption-
induced deflection of 2-mercaptopethanol, detecting a minimum of 50 $ppb$ mercaptan
vapor. They also concluded that the sensitivity of adsorption-induced deflection was an
order of magnitude larger than the resonance frequency sensitivity.

2.3.2. Biotechnology

During the past twenty years, biotechnology and biosensing have grown exponentially
worldwide. Biosensors are currently being used to monitor substances for medical
diagnostics, drug and environmental screening, as well as in military applications. In such applications, an ideal biosensor should not only detect the specific molecules at increasingly low concentrations but also identify the composition of the samples in real time. In addition, it should be small, portable, reliable and inexpensive. Although, surface plasmon resonance (SPR) or quartz crystal oscillation (QCO) can be used as biosensors, they are not convenient because the former is too complex and expensive, and the latter is not sensitive enough. Microcantilever sensors can provide a viable solution due to their high sensitivity and selectivity in detecting a small amount of the desired biomaterial in an acceptable amount of time.

In 1996, Baselt et al. [1996] first used a single cantilever as a transducer in biological systems, detecting the presence of receptor-coated magnetic beads on the cantilever surface by measuring cantilever deflection as they applied a magnetic field to the beads. Four years later, Fritz et al. [2000] conducted the first biosensing experiments using cantilevers for DNA detection, demonstrating the transduction of DNA hybridization and receptor-ligand binding into the direct nanomechanical response of a microfabricated cantilever. In this study, cantilevers were coated with a thin gold layer on which thiol-modified oligonucleotide was immobilized. The surface stress changes due to DNA hybridization between two parallel cantilevers were monitored.

Baselt’s investigations prompted additional research on cantilevers, mostly investigating their utilization to analyze endocrine-disrupting chemicals, DNA–DNA hybridization, and antigen-antibody reactions among others [Sone et al., 2004b]. Ramos et al. [2007] measured the Escherichia coli (E. coli) bacteria mass by monitoring
resonance frequency of microcantilevers. In addition, Ilic et al. [2000] monitored *E. coli* O157:H7 by fabricating bulk microcantilevers rather than using commercial microcantilevers as Ramos et al. did. Ilic et al. [2000] immobilized an antibody layer on a silicon nitride surface and then measured the frequency shift as a function of additional cell loading. They detected $14.7 \times 10^{-15} \text{g}$ *E. coli* O157:H7 cells at a sensitivity of 6.81 Hz/pg.

Research has also been conducted on the use of cantilever sensors in antigen–antibody applications, in both dynamic and static modes. Hwang et al. [2006] investigated the relationship between the resonance frequency shift and the surface stress induced through myoglobin antigen-antibody interactions with antigen concentrations of 1, 10, and 100 ng/ml. They obtained a 1 Hz resonance frequency shift for the first mode and a range from 100 to 600 Hz shift in the second modal frequency for the same antigen concentration. They reported serious degradation of the microcantilever’s sensitivity because of a reduction in the system resonant frequency resulting from the damping effect of viscous fluids.
Chapter 3

Coating of Microcantilevers with Zeolite

3.1. Brief Literature Review

Zeolites are a group of hydrated aluminosilicates of alkali or alkaline earth metals such as sodium, potassium, magnesium and calcium. Aluminosilicates consist of silicon and aluminum atoms that are tetrahedrally coordinated with one another through shared oxygen atoms to form three-dimensional frameworks containing pores and channels filled with adsorbed molecules or cations of discrete size, [Houssin, 2003], as shown in Figure 3.1.

Zeolites have attracted considerable research attention in the last 50 years because of their ability to act as catalysts, adsorbents, and chemical sensors. This stems from their uniform pore structure, small pore size, strong solid acidities, high adsorption capacity, high internal surface area, and controlled chemistry [Okada et al., 2004; Tao et al., 2006].
Based on their pore size, which is determined by the number of oxygen atoms surrounding the smaller central atoms of the tetrahedral, zeolites are classified into three categories: small-pore, medium-pore, and large-pore zeolites. Small-pore zeolites consist of 8 oxygen atoms and have pores with radii that are smaller or equal to 5 Å. Medium-pore zeolites are surrounded by 10 oxygen atoms and have a pore size that ranges between 5 and 6 Å, and, finally, large-pore zeolites have 12 oxygen atoms and pore sizes ranging between 7-8 Å [Scherzer, 1990]. Zeolites can be represented by the empirical formula

\[ \text{M}_{\frac{x}{m}} \cdot \text{Al}_x \text{Si}_{2-x} \text{O}_4 \cdot z \text{H}_2\text{O} \]

where \( m \) is the valence of \( M \) which can be \( \text{Na, K, Li, Ca, Mg, or Ba} \) cations and \( 0 \leq x \leq 1 \).
Due to the flexibility of Si-O-Si bonds, more than 200 zeolite structures have been constructed. These zeolite structures have many structural and compositional elements. For instance, depending on framework type shown in Figure 3.2, the channel network may be 1, 2 or 3 dimensional; therefore, the pore sizes vary significantly.

![Figure 3.2. A typical zeolite structure.](www.lenntech.com/zeolites-structure-types]

### 3.1.1. Natural Zeolite

Zeolites are separated into natural and synthetic zeolites. Natural zeolites form in low temperature geologic environments such as, volcanic environments, salt lakes, and sediment layers [Tabatabaei and Liaghat, 2005]. More than fifty natural zeolites with varying physical and chemical properties are published by the Hewin International Research Service. Particle density, cation selectivity, molecular pore size, and strength are only some of the properties that can differ depending on the type of zeolite [www.chemistryexplained.com/zeolites].

The most widely used natural zeolites are Clinoptilolite, Mordenite, Dachiardite, Analsim, Phillipsite, and Heulandite [Tabatabaei and Liaghat, 2005]. Clinoptilolite, for
example, is formed by the alteration of fine-grained volcanic deposits with underground water [Jegg, 2009].

3.1.2. Synthetic Zeolites

Synthetic zeolites, which have a wider range of properties and larger cavities than their natural counterparts, are obtained by heating aqueous alkali mixtures that contain water, alkali, SiO$_2$, and Al$_2$O$_3$ as essential components. The first of such zeolites, known as small-port Mordenite, was created in 1948 [Barrer, 1948]. Because of the high temperatures involved in creating Mordenite, pure crystalline phases could not be realized [Zhdanov, 1981]. Milton and Breck [1981] synthesized the commercially significant A, X and Y zeolites at lower temperature and pressure. In 1953, the first utilized zeolite, Linde type-A (LTA) zeolite, shown in Figure 3.3, was synthesized to act as an adsorbent for the removal of oxygen impurities from argon at a Union Carbide plant [Milton, 1968].

![Figure 3.3. Structure of Synthetic Linde Type-A Zeolite [Meier, 2008].](image)

Figure 3.3. Structure of Synthetic Linde Type-A Zeolite [Meier, 2008].
In addition to LTA synthetic zeolite, Faujasite type (FAU) zeolites, whose structure is shown in Figure 3.4, represent another important type. It occurs in natural form and can also be synthesized industrially [Meier, 2008]. FAU zeolite structures are formed by alternating silicon-oxygen and aluminum-oxygen tetrahedrons, which are compensated with cations. In the skeleton of the FAU, cations are not fixed, so that they are capable of interchanging. Because of this feature, many cation exchanged FAU zeolites can be synthesized.

![Figure 3.4. Structure of Faujasite Zeolite](image)

[Meier, 2008].

The FAU framework is cubic with a Fd-3m symmetry [Houssin, 2003] consisting of 24 tetrahedracuboctahedral units called sodalite cages, which combine to form hexagonal prisms (double-6 rings), as shown in Figure 3.5. The supercage forming the center of the prism is 12 Å in diameter [Scherzer, 1990]. These large supercages, which
are an indication of the zeolite adsorption capacity, suggest that FAU zeolites can adsorb larger molecules.

![Diagram of the FAU zeolite structure, illustrating the oxygen positions and cation site designations [Klein et al.1994].](image)

**Figure 3.5.** Diagram of the FAU zeolite structure, illustrating the oxygen positions and cation site designations [Klein et al.1994].

The most common FAU zeolites are the X and Y zeolites. These differ in the amount of aluminum present in the cage (Y zeolite have less aluminum than X zeolite). Of interest to our research are the Y zeolites, which consist of three-dimensional frameworks of SiO$_4$ and AlO$_4$ tetrahedra that are combined to create sodalite cages. These cages have a diameter of 7.4 Å. Together, twelve of these cages form a ring that creates a cavity with a diameter of 12 Å [Scherzer, 1990]. The unit cell is cubic in shape having a height of 24.7 Å [Klein *et al.*, 1994]. Zeolite Y is usually synthesized in the Na form; cations are usually exchanged with Na using ion exchange method.
3.1.3. Applications of Zeolite

Both natural and synthetic zeolites are gaining more interests in industrial applications. Natural zeolites, especially Clinoptilolite, is used in many industries and have several agricultural and medical applications [Rivera et al., 2003; Pavelic et al., 2001]. This stems from its physical structure and its stability under extreme pressures. Furthermore, Clinoptilolite structure can be changed only under caustic or acidic conditions [Nguyen et al., 2004; Zeolite Structure, 2009]. Generally, natural zeolites are also known to be good natural filters for water providing improved performance over sand and carbon filters. Besides, they are used in industrial gas separation, odor control, and heat storage.

Synthetic zeolites have many commercial applications spanning different fields. Most of these applications stem from their ability to separate and adsorb. Because of their unique structure, zeolites act as effective sieves that can screen based on molecular size, shape, and polarity [Cui et al., 2003]. As such, they act as effective membranes in separation devices, chemical sensors, and purification applications. They have also been used commercially for gas sensing [Burggraaf et al., 1998; Mintova and Bein., 2001; Mann et al., 2007; Labhsetvar et al., 2008,], and for the catalytic cracking of hydrocarbons in the production of transportation fuels from crude oil [Katikaneni et al.,1995; Twaiq et al.,2003].

Many transition metals exchanged Y zeolites, such as Na-, Cu-, Ni-, Cr-, Mn-, Zn- and Cd-Y zeolites, have been investigated for such applications. Mann et al. [2007] synthesized Cr-Y and Mn-Y zeolites through the solid state method and applied them to
improve the selectivity of metal oxide detection of heptane, octane, and nonane gases. Labhsetvar et al. [2008] investigated the catalytic activity of Ruthenium-exchanged H and Na forms of ultra-stable Y zeolite in the NO-CO reaction. Elzey et al. [2007] used NaY and nanocrystalline CuY zeolites to examine the selective catalytic reduction of NO$_2$ with ammonia to N$_2$ and O$_2$ at room temperature.

Synthetic zeolites are also frequently used in purification applications, specifically as adsorbents. Because of their low cost and their ion-exchange capability, they are one of the primary adsorbents for waste water treatment. In particular, they are used to remove heavy metals from water [Curkovic et al., 1997; Labhsetvar et al., 2008].

One of the most important areas of research and the focus of our study is the use of zeolites for gas sensing purposes. Mintova and Bein [2001] investigated fabrication of a zeolite-based piezoelectric sensor for vapor sensing. Using a seeding method to synthesize LTA and beta (BEA) zeolite films with thickness of 250 and 450 nm, respectively; they compared the sensitivity of these zeolite films to detection of different organic and water vapors. They found that BEA-based sensors have a higher adsorption capacity. In another demonstration, Salama et al. [2006] investigated the catalytic efficiency of Copper (Cu-II) complex of salysilidine benzene-sulphonylhydrazone (SBSH) encapsulated in Y zeolites for CO adsorption. They compared the CO adsorption efficiency of Cu-II-Y and Cu-II- SBSH/Y zeolite samples, finding that the latter is more active than the former in CO adsorption because it contains higher density of positive charges.
Rakic et al. [1999] also investigated the interaction of CO with cation-exchanged (Fe²⁺, Co²⁺, Ni²⁺ and Cu²⁺) X and Y zeolites, synthesizing them using the ion exchange method. The CO adsorption ability of these zeolites was investigated, and according to their results, Cu-Y zeolite was found to have the best adsorption capacity of CO at room temperature.

3.2. Preparation of Copper-Y (CuY) Zeolite

A main objective of this study is to find a suitable adsorbent with support material that can be used to coat the microcantilevers for CO detection. Based on previous literature review, and our experiments carried out next, we decided that Y zeolite with Cu support (CuY) is the best material for our purposes. This stems from i) the large adsorption capacity of CuY zeolite because of its large surface area and big enough pores that can be used to adsorb CO [Salama et al., 2006], ii) the ability of CuY to selectively adsorb CO in a gas mixture for the range of operating temperatures in a PEMFC fuel Cells [80-100 °C] [Baschuk and Li, 2001], iii) the adsorption process does not change the properties of CO or CuY which could exhaust the zeolite over time, and finally iv) adsorption of CO on CuY zeolite is a reversible process under elevated temperature, i.e., CO can be desorbed from zeolite if the temperature of the sensor is elevated [Rakic et al., 1999].

To achieve this objective, CuY zeolite with different Cu content was prepared using impregnation method. The resulting structure was then characterized using different techniques to identify the most suitable Cu content for the experiment and to investigate the homogeneity and adsorption capacity of CuY and different pressures and
temperatures. The characterization techniques included i) Inductively-Coupled Plasma Atomic Emission Spectroscopy (ICP) which was used to determine the content and weight percentage of Cu in the resulting zeolite; ii) N\textsubscript{2} adsorption isotherms which was implemented to determine the pore size and the surface areas of zeolite after Cu loading. This is essential to give us an indication of the capacity of CuY zeolite; iii) X-Ray Diffraction (XRD) which was utilized to characterize the zeolite structure crystallinity after loading; and, finally, iv) Scanning Electron Microscopy (SEM) which was used to determine the morphology of formed zeolites and the homogeneity of the resulting coatings.

3.2.1. Methodology and Results

A commercial Y-type zeolite in the H form (Zeolyst Co., CBV780) and copper nitrate hemipentahydrate [Cu (NO\textsubscript{3})\textsubscript{2}•2.5H\textsubscript{2}O] (Fisher Co.) were used to synthesize CuY zeolite. In the experiment, 25 g HY zeolite was weighed using Denver XL-410 balance and dried at 100°C in oven (Fisher Scientific, isotemp oven). Afterwards, an impregnation method was used to prepare CuY zeolite. In this method, 1 M Cu nitrate solutions were used to achieve a complete wetness of the 5 g dried zeolite powder which was then dried at room temperature. This process was repeated to synthesize 10, 13, 19 and 24 wt % Cu loaded zeolite samples. All samples were then calcined at 450 °C for 2 h to remove nitrate from the sample structure.

After preparation of CuY zeolite samples, ICP, N\textsubscript{2} isotherms, XRD and SEM analyses were performed to characterize the resulting CuY zeolites.
3.2.1.1. ICP and \( N_2 \) isotherms analysis:

ICP is an experimental technique used to determine the content and concentration of atomic and molecular species in various media. In this technique, inductively coupled plasma is used to excite the atoms and ions. The wavelength of the resulting electron magnetic radiation is then measured to determine the identity and composition. In our experiment, we used ICP to determine the concentration of Cu, Al, and Si in the CuY zeolite. Each sample was digested in \( H_2SO_4 \) and \( NH_4NO_3 \) to make zeolite dissolve into solutions.

CuY zeolites with different Cu\(^{2+} \) contents were prepared as listed in Table 3.1. The Cu\(^{2+} \) content was controlled by regulating the amount of Cu nitrate solution. After preparation of the samples according to our theoretical calculations, ICP analysis was conducted to determine the actual experimental composition. Results shown in table 3.1 indicate that weight percentage of Cu in the samples as measured experimentally is in excellent agreement with our theoretical calculations. As such, CuY zeolite with the proper CuY content is now readily available for further experimentations.

<table>
<thead>
<tr>
<th>Zeolites</th>
<th>Composition</th>
<th>Cu Content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HY ( H_{56}(AlO)<em>{56}(SiO2)</em>{136} )</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CuY(10) ( Cu_{21}H_{14}(AlO)<em>{56}(SiO2)</em>{136} )</td>
<td>10.40</td>
<td>10.47</td>
</tr>
<tr>
<td>CuY(13) ( Cu_{28}(AlO)<em>{56}(SiO2)</em>{136} )</td>
<td>13.40</td>
<td>12.80</td>
</tr>
<tr>
<td>CuY(19) ( Cu_{42}(AlO)<em>{56}(SiO2)</em>{136} )</td>
<td>18.90</td>
<td>18.97</td>
</tr>
<tr>
<td>CuY(24) ( Cu_{56}(AlO)<em>{56}(SiO2)</em>{136} )</td>
<td>23.70</td>
<td>24.06</td>
</tr>
</tbody>
</table>
The porosity of Y zeolite with varying Cu\(^{2+}\) content was determined using N\(_2\) adsorption isotherms (data shown in Appendix A). In this process, the N\(_2\) adsorption capacity of zeolites is measured by filling the pores with N\(_2\) gas. Variation of the volume of the adsorbed N\(_2\) gas at different pressures is shown in Figure 3.6. As the figure demonstrates, N\(_2\) adsorption decreases as constant pressure as the Cu content increases. Based on these results, it is concluded that the original zeolite, HY, has the highest N\(_2\) adsorption capacity at the lowest pressure. This does not imply that the HY zeolite or the lower Cu content has a larger adsorption capacity of CO because CO adsorption is dependent on the reaction with Cu which, in turn, depends on the amount of Cu present in the zeolite.

**Figure 3.6.** Adsorption isotherms of N\(_2\) on CuY-zeolites at 77 K.
To further explain these results, we use the BET theory which describes the physical adsorption of gas molecules on a solid. (“BET” consists of the first initials of Stephen Brunauer, Paul Hugh Emmett, and Edward Teller who published an article about the BET theory [wikipedia]). The BET plot is used to measure the specific surface area and pore volume of the CuY zeolite samples. Results listed in Table 3.2 indicate that the surface area and pore volume decrease from 765 to 544 m$^2$/g and 0.22 to 0.16 cm$^3$/g, respectively, as the Cu$^{2+}$ content increases from 0 to 24 w%.

<table>
<thead>
<tr>
<th>Zeolites</th>
<th>CuY</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S(m$^2$/g)</td>
</tr>
<tr>
<td>HY</td>
<td>765</td>
</tr>
<tr>
<td>CuY(10)</td>
<td>669</td>
</tr>
<tr>
<td>CuY(13)</td>
<td>631</td>
</tr>
<tr>
<td>CuY(19)</td>
<td>583</td>
</tr>
<tr>
<td>CuY(24)</td>
<td>544</td>
</tr>
</tbody>
</table>

* t-plot micropore volume

Surface area changes were also observed in previous studies conducted by Richter [2007] and Matsumoto et al. [1999] who synthesized CuY zeolites with varying Cu content. The former researcher found that the surface area decreased from 793 to 711 m$^2$/g, and the latter that it decreased from 730 to 620 m$^2$/g. Although they used almost the same wt% Cu as in the study reported here, their surface areas are different. Probably because one used a NaY zeolite and the other used a HY zeolite of a different composition. However, the results reported here, as well as, those from previous studies suggest that the surface area decreases as the amount of Cu increases, partially because the Cu starts filling some of the zeolite pores during impregnation.
3.2.1.2. **XRD analysis:**

X-Ray Diffractometry (XRD) is an efficient, non-destructive technique used to obtain information about the structure of a crystalline material based on their atomic arrangement. When X-rays interact with the crystalline phase, a diffraction pattern is obtained [Sintag, 1999]. These patterns are the fingerprints of the substrate. Using XRD technique, the atomic positions, the chemical bonds, the bond lengths, and angles can be determined.

As shown in Figure 3.7, an X-Ray Diffractometer consists of an X-ray tube, a sample holder and a detector. Crystalline samples are mounted on the sample holder, so that it remains stationary. X-ray beams are generated using the X-ray tube and directed to this sample. When they interact with sample, some of the beams are transmitted, some are refracted, and some others are diffracted [Sintag, 1999]. The detector detects these signals and represents them as peaks on a monitor [Dutrow and Clark, 2009].

In XRD analysis, Bragg’s Law below is used to determine the distance (d-spacing) between the adjacent planes of the atoms;

\[
 n \lambda = 2d \sin \theta \tag{3.1}
\]

where \( n \) is the order of the diffracted beam, \( \lambda \) the wavelength of the X-ray beam, \( d \) the distance between the adjacent planes of the atoms, \( \theta \) is the angle of the X-ray beam. According to Bragg’s Law, d-spacing is calculated by measuring \( \theta \) and knowing \( \lambda \). Based on measurements and standard references of d-spacing, unknown samples can be characterized and then identified.
Crystal structures of synthesized CuY zeolites as well as the original HY zeolite were analyzed using a Scintag XDS 2000 X-Ray. X-Ray diffraction analysis was conducted at 2θ values of 10-45° with a step size of 0.03 and time per step of 10 seconds. CuKα radiation at 45 kV and 40 mA was used in this analysis. After calcination of the CuY zeolite samples at 450°C, the XRD patterns shown in Figure 3.8 were obtained. First, the XRD pattern of HY (Figure 3.8- a) was compared with the reference spectrum in the database to confirm the formation of HY zeolite.
Figure 3.8. XRD spectra of Cu-loaded Y zeolites. a) HY, b) CuY (10 wt%), c) CuY (13 wt%), d) CuY (19 wt%) and e) CuY (24 wt%).

The peak positions and the intensity of peaks were also compared. As Figure 3.8 illustrates, the original and the Cu-loaded Y zeolites all have similar XRD patterns, suggesting no significant changes in the zeolite structure during copper loading. For example, the principal features of the XRD peaks of CuY (10%) are the same as those of HY in the 2θ range of 10-42°. In the former sample, no shift in the peak position and no significant diffraction lines assigned to any new phase are observed. However, peaks associated with Y zeolites with 13, 19 and 24 wt% Cu occur to the right of the original
peaks, indicating that some small structural changes have occurred. This change suggests that the supercages of the CuY zeolites have become smaller, but not significantly.

In addition, high intensity peaks appeared during the Cu loading, suggesting that crystallinity occurred on the zeolite surface. It is assumed that the reason for this crystallinity is the effect of CuO forming on the zeolite surface. This assumption is supported by the fact that these new peaks appear at the same angle where the CuO appears which is indicated by the red line in Figure 3.8. The CuO does not perform any peaks in the XRD over 36° as seen in Fig.3.8-b. This is because the amount of Cu is not large enough to allow the excess to form CuO on the surface. In addition, the peaks associated with CuY zeolites shown in Fig.3.8-e appear to the right of the original peaks. This indicates that some structural changes have occurred.

The effects of CuO similar to these were also observed in previous studies. For example, Gu et al. [2008] found the CuO peaks start to appear when the Cu content exceeds a threshold of 5%, but in our results, no CuO peaks appeared until Cu content exceeded 13wt%. The reason for such differences is perhaps the type of Y zeolite used in their experiment. Gu et al. [2008] used the Na form which is heavier than the HY zeolite used here.

3.2.1.3. SEM analysis:

Scanning Electron Microscopy (SEM) shown in Figure 3.9 is used to image the sample’s surface of CuY zeolites to determine its morphology and the resulting particle size. This was achieved using a SEM- Hitachi H4800 Scanning Electron Microscope. SEM provides images with three-dimensional effects up to a magnification of approximately
5000X for flat polished specimens and up to 200000X with a depth of focus [www.unl.edu/CMRAcfem/semoptic.htm]. Because of these features, it is used in numerous fields such as chemistry, material science, biology, and electronics.

![Diagram of Scanning Electron Microscope (SEM)](image)

**Figure 3.9.** Scanning Electron Microscope (SEM)

[Adapted from Delpiere and Sewel, 1992]

In the SEM, an electron gun creates electron beams having a diameter of few micrometers. Lenses are then used to demagnify the diameter of the beams and focus it onto the sample. As the electron beam interacts with the sample, electrically-charged signals are generated. Secondary electrons knocked out of their orbital by the electron
beam are detected by the secondary electron detector [Smith, 1992]. As a result, images based on elemental composition, topography, and density of the sample can be formed.

The analysis shown in Figure 3.10 illustrates the morphology of the CuY zeolite particles. Hexagonal structures were obtained for both the original and the coated zeolites, suggesting that copper does not modify the HY zeolite morphology. Although modest structural changes in the CuY zeolite were observed, the particle size remained largely unchanged. Since Cu appears not to play a significant role in modifying the morphology of zeolite, it is likely present on the surface and, as a result, possibly plays an active role in the CO adsorption process.

![SEM image of CuY zeolite.](image)

**Figure 3.10.** SEM image of CuY zeolite.
3.3. Coating Microcantilevers with CuY Zeolite

3.3.1. Methodology and Results

3.3.1.1. Preparation of microcantilevers and binder:

For the purpose of monitoring CO gas concentration, MikroMasch (NSC12) microcantilevers with three beams of varying lengths on each side of the tipples were used, see Figure 3.11. The microcantilevers were fabricated using silicon dioxide, SiO$_2$, which plays an important role in supporting the structure. The geometric properties are listed in Table 3.3.

**Table 3.3.** Geometric and material properties of the MicroMash microcantilever beams.

<table>
<thead>
<tr>
<th>t: thickness of the beam (µm)</th>
<th>w: width of the beam (µm)</th>
<th>L: length of the beam (µm)</th>
<th>Spring constant (N/m)</th>
<th>$f_0$: natural frequency (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>35</td>
<td>350</td>
<td>0.3</td>
<td>23</td>
</tr>
<tr>
<td>2</td>
<td>35</td>
<td>300</td>
<td>0.35</td>
<td>32</td>
</tr>
<tr>
<td>2</td>
<td>35</td>
<td>250</td>
<td>0.65</td>
<td>45</td>
</tr>
</tbody>
</table>

*Figure 3.11. Schematic drawing of MicroMasch microcantilever [spmtips.com].*
For coating purposes, a binder is necessary because CuY zeolite is not a naturally sticky material. Therefore, a suitable binder consisting of pseudoboehmite (BASF Catalyst, H406A11-1) and HNO₃ solution (Fluka, v %> 69) was used to bind zeolite to the microcantilever surface, thereby preventing the zeolite from detaching from the surface during microcantilevers’ oscillations. To prepare the binder, pseudoboehmite and zeolites were first crushed by Wiggle-bug for 10 minutes to avoid agglomeration in solution. Subsequently, 5 gr zeolite was mixed with 10 ml distilled water and stirred for an hour. The resulting solution was then mixed with a second solution obtained by mixing 0.5g pseudoboehmite with 1 ml HNO₃ solution (v%>69) and 10 ml distilled water. Both solutions were filtered using a micro sieve, and then stirred together for an hour.

Before coating, all impurities were removed from the surface of the microcantilevers by soaking them in piranha solution composed of 70% H₂SO₄ and 30% H₂O₂ at 90 °C for 45 minutes. The purified cantilevers were then stored in deionized water.

3.3.1.2. Coating the microcantilevers:

To coat the microcantilevers with CuY zeolite, two techniques, namely, spin and dip coating were considered. To determine the best approach, silicon wafers were used initially instead of the microcantilevers. As such, they were cleaned using the piranha solution and stored in de-ionized water. Before being coated, the wafers were dried using N₂ gas.
In the spin coating technique, silicon wafers were mounted on a spin coater as shown in Figure 3.12. A micropipette was then used to cover the surface of the wafers with 100 $\mu l$ of CuY-binder solution. The excess water was removed using a spinner set at 2000 rpm for 1 min. This process was repeated until appropriate thickness of zeolite layer was obtained. Subsequently, all samples were calcined at 450 °C for 2 h. In the dip coating method, the silicon wafers were soaked in CuY-binder solution for 2 min; then they were removed and calcined at 450 °C for 2 h.

![Spin coating process](image)

**Figure 3.12.** a) Scheme of spin coating process, b) Spin coater used in the experiments.

SEM images of dip and spin coated silicon wafers shown in Figure 3.13 illustrate the distribution of zeolite particles on the wafer surfaces. It is evident that the zeolite layer obtained using the spin coating method is homogeneous and uniformly distributed over the entire silicon surface; whereas, the dip coating method yields sporadic regions of zeolite-coated surface. This probably stems from the use of non-homogeneous zeolite–binder solution. An important requirement for the dip coating method to be successful is
that the zeolite particle dispersions must be stable in the dispersed state. Pre-mature agglomeration due to colloidal instability leads to inhomogeneous coverage. This makes uniform zeolite particle distribution difficult by dip coating method when compared to spin coating.

To overcome this problem, there are some ways to improve colloidal stability. One approach is based on adjusting the pH of the aqueous dispersion medium to achieve charge-stabilization [Gu et al., 2008].

3.3.2. Effect of CuY zeolite coating on microcantilevers’ resonance frequency

After coating microcantilevers with CuY zeolite, a series of experiments were conducted to investigate the influence of coating the microcantilever surface with zeolite on its resonance frequency. The experimental setup consisted of a Polytec MSA-400 Micro System Analyzer, and a Micromash microcantilever as shown in Figure 3.14.

![Figure 3.13. SEM images of coated micromicrocantilever surface using a) Dip coating method, and b) spin coating method.](image)

To overcome this problem, there are some ways to improve colloidal stability. One approach is based on adjusting the pH of the aqueous dispersion medium to achieve charge-stabilization [Gu et al., 2008].

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In these experiments, the first fundamental (resonance) frequency of uncoated microcantilevers was determined experimentally. Subsequently, the resonance frequency of the microcantilevers was monitored as the number of zeolite coating layers is increased.

**Figure 3.14.** Experimental setup for the monitoring resonance frequency of microcantilever.

**Figure 3.15.** Schematic of the microcantilever after CuY zeolite coating.
The shift between the frequencies of the coated and uncoated microcantilevers is then used to establish a correlation between the CuY zeolite layers and resonance frequency of the micromicrocantilevers. The resonance frequency of microcantilevers coated with 1 to 12 zeolite layers was measured experimentally as shown in Figure 3.16 and then compared to the fundamental frequency of the original microcantilever.

Figure 3.17-a depicts variation of the 350 µm-cantilever resonance frequency shift as the number of zeolite layers is increased. It is evident that, as the number of layers is increased, the resonance frequency decreases initially due to mass loading which causes
the effective resonance frequency of the microcantilever to decrease as per Equation (2.4). It is also noted that, increasing the number of layers beyond a certain threshold causes the resonance to increase again. This can be counterintuitive if one was to neglect variation of the stiffness due to the addition of zeolite into the microcantilever. However, the overall thickness of zeolite increases by adding more zeolite layers to the microcantilever surface. As such, the beam starts to behave more like a composite structure of two layers, namely silicon (Si) and CuY zeolite. Depending on the modulus of elasticity of the zeolite layer and its thickness, the overall stiffness of the cantilever can increase significantly overcoming the increase in mass associated with addition of CuY zeolite.

![Figure 3.17. Resonance frequency shift of 350 μm microcantilevers](image)

- **a)** Experimental results, **b)** theoretical results.
These findings can be further confirmed by studying the stiffness of a composite beam which is governed by the following Equation:

$$k_{\text{eff}} = \frac{E_z I_z + E_b I_b}{l^3}$$  \hspace{1cm} (3.2)

where \( E_z \) and \( E_b \) are the Young’s Modulii of zeolite and silicon, respectively; \( I_z \) and \( I_b \) are the moments of inertia of zeolite layer and beam, respectively, and \( l \) is length of the beam. Material properties are listed in Table 3.4.

**Table 3.4.** Material properties of microcantilever and CuY zeolite.

<table>
<thead>
<tr>
<th></th>
<th>Microcantilever</th>
<th>CuY Zeolite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s Modulus (GPa)</td>
<td>1290</td>
<td>71.7</td>
</tr>
<tr>
<td>Density (kg/m(^3))</td>
<td>2330</td>
<td>1290</td>
</tr>
</tbody>
</table>

$$I_z = \frac{1}{12} w_z t_z^3$$ \hspace{1cm} (3.3)

$$I_b = \frac{1}{12} w_b t_b^3$$ \hspace{1cm} (3.4)

where \( w_z \) is the width of the zeolite layer, \( t_z \) is thickness of the zeolite layer, \( w_b \) is width of the beam and \( t_b \) is thickness of the beam.

With that, the resonance frequency of the microcantilever with the CuY zeolite coating can be obtained using

$$f_1 = \frac{1}{2\pi} \sqrt{\frac{k_{\text{eff}}}{m_b + m_z}}$$ \hspace{1cm} (3.5)

where \( m_b \) is the mass of the beam and \( m_z \) is mass of the zeolite layer. Finally, the resonance-frequency shift is calculated as

$$\Delta f = f_1 - f_0$$ \hspace{1cm} (3.6)

where \( f_0 \) is the resonance frequency of the microcantilever before coating.
Using Equation (3.6), the resonance-frequency shift of the 350 $\mu m$ microcantilever is calculated as the thickness of zeolite layer is increased. The results are depicted in Figure 3.16-b. It can be clearly seen that the resonance frequency shift increases initially as the thickness of the zeolite layer is increased. However, as the thickness is increased beyond 0.9 $\mu m$, the shift in the natural frequency decreases again. These theoretical trends corroborate our experimental findings that have similar frequency variations with the number of zeolite layers.

It is also noted that the maximum resonance frequency shift obtained experimentally, is lower than that obtained theoretically. One reason for such deviations stems from the homogeneity and uniform distribution of the zeolite layer. In the theoretical analysis carried here, it was assumed that the layer is homogeneous and that the thickness of the layers is uniform which obviously is not the case. This creates some deviations between the theoretical and experimental data. Similar experimental trends were also obtained for the smaller cantilevers, see Figures 3.18 and 3.19.
Figure 3. 18. Resonance frequency shift of 300 \( \mu m \) microcantilevers
Experimental results, b) theoretical results.

Figure 3. 19. Resonance frequency shift of 250 \( \mu m \) microcantilevers
a) Experimental results, b) theoretical results
Chapter 4

Detection of Carbon Monoxide Using Microcantilever Sensors

4.1. Brief Overview

When carbon monoxide reaches a concentration higher than 10 ppm in the gas mixture entering a fuel cell, it acts as a poison that decreases the fuel cell efficiency. To address this issue, reliable CO sensors with high sensitivity and selectivity are required to monitor the concentration of CO gas in the fuel cell. In this chapter, we present some experimental findings on the utilization of microcantilever sensors as means to monitor...
the concentration of CO gas. For that purpose, and for the reasons explained in the previous chapter, CuY zeolite was chosen as the microcantilever’s coating material for CO adsorption.

As shown in Figure 4.1, adsorption is an exothermic process that occurs when a gas solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (adsorbate). Zeolites are among the most suitable adsorbents because of their porous structure and large surface area.

![Figure 4.1. Schematic of multilayer adsorption showing random distribution of molecules on the material surface.](image)

Past research efforts have concluded that FAU(Y) zeolites modified with transition metals exhibit a high CO adsorption capability which is influenced by the framework composition and the charge-balancing cations [Jacobs, 1977; Sachtler, 1993; Rakic et al, 1999]. Specifically, a transition metal such as copper (Cu) acts as an active site in Y zeolites, thereby increasing CO adsorption capacity.

Many studies have focused on CO adsorption using FAU(Y) zeolites [Borovkov and Karge, 1995; Rakic et al., 1999; Huber and Knozinger, 1999; Datka, and Kozyra, 2005]. In one demonstration, Rakic et al. [1999] compared the interactions of CO with transition materials such as Cu, Fe, Co, Ni loaded into X and Y zeolites. They determined
that the CuY zeolites were more selective for CO adsorption than zeolites modified with other metals. In another demonstration, Huber and Knozinger [1999] investigated CO interaction with NaY and NaX zeolites. They concluded that only the supercages in NaX and NaY zeolites can interact with CO emphasizing the importance of transition metals in CO adsorption.

Various researchers have also investigated the influence of temperature on CO adsorption. Rakic et al. [1999] found that CuY zeolites can adsorb CO at room temperature and reported that maximum desorption occurs at 200 °C. Datka and Kozyra [2005] have also determined that adsorption occurs at room temperature but noted that CO desorption on CuY zeolites can start to occur at temperatures as low as 77 °C.

4.2. CO Adsorption Capacity of CuY Zeolite

4.2.1. Effect of Cu Content

In the previous chapter, we analyzed many of the characteristics of CuY zeolite. One important property that remains to be determined, however, is the effect of Cu loading on the CO adsorption capacity of CuY zeolite. As such, we carried out an experiment to analyze the effect of CuY loading on CO adsorption. In this experiment, 1g zeolite from four samples having different Cu contents (10, 13, 19 and 24 wt% Cu content) was placed into the Micromeritics ASAP 2010 apparatus shown in Figure 4.2. The samples were first exposed to N₂ gas at 420°C to activate the CuY zeolites for 2 h. Subsequently, the samples were cooled down to about 27°C and the N₂ gas was vacuumed from the tube for 1 h. Timeline of the experimental procedure is listed in Table 4.1.
Table 4.1. Run conditions of CO adsorption process

<table>
<thead>
<tr>
<th>Task Name</th>
<th>Gas</th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evacuation</td>
<td>-</td>
<td>27</td>
<td>30</td>
</tr>
<tr>
<td>Flow</td>
<td>N₂</td>
<td>420</td>
<td>120</td>
</tr>
<tr>
<td>Flow</td>
<td>N₂</td>
<td>27</td>
<td>30</td>
</tr>
<tr>
<td>Evacuation</td>
<td>-</td>
<td>26</td>
<td>60</td>
</tr>
<tr>
<td>Analysis</td>
<td>CO</td>
<td>40</td>
<td>136</td>
</tr>
</tbody>
</table>

Figure 4.2. Micromeritics ASAP 2010 apparatus.
Once the N\textsubscript{2} gas was vacuumed, zeolite was exposed to CO and the volume of adsorbed CO was measured under different pressures. Figure 4.3 depicts variation of the total volume of adsorbed CO per one gram of zeolite (first primary isotherms) with the pressure for different Cu loading at a temperature of 40°C. The total volume shown in the Fig.4.3 represents the volume both of the physically and chemically adsorbed CO.

![Figure 4.3](image)

**Figure 4.3.** Adsorption isotherms of CO adsorbed at 40°C on the CuY zeolites with different Cu content.

To determine the irreversible volume of the adsorbed CO (chemically bonded), CO was vacuumed from zeolite as shown in Figure 4.4. Subsequently, secondary isotherms shown in Appendix B were measured at different pressures and subtracted from the primary isotherms.
Table 4.2 lists the surface area and pore volume of zeolite as well as the total and irreversible volume of the adsorbed CO at a pressure of 900 mmHg. First, it can be noted that total volume of adsorbed CO decreases as the Cu content is increased from 10% to 24%. This can be attributed to the reduction of both the zeolites surface area and pore size due to the CuY loading as shown in Table 4.2. Additionally, it was observed that, except for the sample with the 19% Cu content, the irreversible volume of CO also decreases with the Cu loading. For instance, the irreversible volume reduces by 43% when the Cu loading is increased from 10 to 24 wt%. This can be attributed to the fact that, during impregnation, Cu fills the pores and does not leave enough space for CO to enter. We also believe that the 19% Cu result which opposes this trend can be a result of an experimental error. As such, it is concluded that, for the samples considered herein, the 10wt% Cu had the highest adsorption capacity.
Table 4.2. Quantitative data on the adsorption of CO on CuY zeolites with different Cu content.

<table>
<thead>
<tr>
<th>Zeolites</th>
<th>CuY</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$S^a (m^2 g^{-1})$</td>
</tr>
<tr>
<td>HY</td>
<td>765</td>
</tr>
<tr>
<td>CuY(10)</td>
<td>669</td>
</tr>
<tr>
<td>CuY(13)</td>
<td>631</td>
</tr>
<tr>
<td>CuY(19)</td>
<td>583</td>
</tr>
<tr>
<td>CuY(24)</td>
<td>544</td>
</tr>
</tbody>
</table>

$^a$: BET surface area, $^b$: t-plot micropore volume, $^c$: total volume of adsorbed CO, $^d$: irreversible volume

4.2.2. Effect of Temperature on CO Adsorption

To determine the effect of temperature on CO adsorption capacity, samples of 10wt% CuY zeolites were placed in the ASAP 2010 apparatus at 40, 50 and 60 °C (data shown in Appendix C). The volume of adsorbed CO was then measured at these temperatures and pressures varying from 0 to 900 mmHg in increment of 100 mmHg. The results of this experiment are depicted in Figure 4.5.
Figure 4.5. CO adsorption isotherms of CuY (10%) zeolite at different temperatures.

As the figure indicates, the amount of adsorbed CO decreases with temperature, the highest CO adsorption occurred at the lowest temperature. These results support the findings of Zheng and Gu [1998] who compared CO adsorption capacity of CuY zeolites at 30, 50 and 70 °C and found that highest adsorption of CO occurs at 30°C. As a result, it was decided that all subsequent experiments will be carried at 40 °C to maximize the adsorption efficiency and hence the sensitivity of the sensor.

4.3. Microcantilevers due to CO adsorption

In the previous chapter, we described the process necessary for coating the microcantilever sensors. We also successfully used the MSA-400 to measure the
frequency shift of the sensor due to the multiple layers of CuY coating. As a result of these coating, we noted that the resonance frequency of the sensor drops initially due to the additional weight of zeolite and then increases again due to the stiffening effect resulting from the thick zeolite layer. Next, we study the effect of CO adsorption on the frequency shift.

4.3.1. Methodology

To achieve this goal, an aluminum chamber was designed and constructed to imitate the process carried out earlier in Micromeritics ASAP 2010. The aluminum chamber shown in Figure 4.6 consists of a pressure gauge, heater, and thermometer. The pressure gauge is used to monitor the pressure in the chamber. The heater and thermometer are used to control the temperature inside the chamber. To allow the laser beam of the MS-400 to get through the chamber and onto the top surface of the microcantilever, a glass window was incorporated into the upper side of the chamber.

![Image of the setup for CO detection](image.png)

**Figure 4.6.** Setup for CO detection.
Because the microcantilever holder shown in Figure 4.7 used in our experiment cannot withstand temperatures exceeding 60°C, the first process of the experiment which involves exposing zeolites to N₂ gas at 420°C was carried out separately in an oven. After cooling the cantilevers to below 60°C, they were placed in the chamber, which was then filled with N₂ gas at 50°C to remove moisture from zeolites. Next, it was cooled again and exposed to CO at 40°C. Finally, the resonance frequency of the microcantilevers during the CO adsorption was measured using MSA 400 Polytech apparatus shown in Figure 3.13.

![Microcantilever and its holder.](image)

**Figure 4.7.** Microcantilever and its holder.

### 4.3.2. Results and Discussions

#### 4.3.2.1. Monitoring Resonance Frequency during CO Adsorption

The resonance frequency of the microcantilevers was measured in real time during the experimental procedure. It was found that the resonance frequency did not change significantly during N₂ exposure. Further it was observed that the resonance frequency returned to its original value when the N₂ gas was removed from the chamber. The slight
variation of the resonance frequency, during N\(_2\) gas exposure can be attributed to the additional damping exerted on the cantilever during N\(_2\) gas circulation. After N\(_2\) gas was removed, the microcantilever was exposed to CO until the pressure inside the chamber increased to 571 mmHg at 40°C. During CO adsorption, the resonance frequency of the microcantilever was measured at discrete intervals of time for about 45 minutes as illustrated in Figure 4.8.

![Figure 4.8](image.png)

**Figure 4.8.** Frequency response curves of the beam with 350 \(\mu\)m of microcantilever with 3 layers during CO adsorption.

Figure 4.8 depicts the frequency-response curves at different instants of time during CO adsorption. The peak in the resonance frequency curves drops and shifts to the left during CO adsorption. This implies that the resonance frequency decreases due to mass loading and that CO adsorption has minimal effect on the stiffness of the cantilever. For this experimental run, it was also observed that the frequency did not shift
significantly during the first 10 minutes and then there was a significant shift after 20 and 30 min. This indicates that most of CO adsorption occurred after the first 20 minutes of exposure. Beyond the first 30 minutes, zeolite became saturated with CO, and no additional shift in the resonance frequency was detected.

We also observed a change in the sensitivity of the microcantilevers as the number of CuY coating layers is increased. Figure 4.9 depicts variation of the cantilever resonance frequency with time for three different cantilevers coated with 1, 2, and 4 layers, respectively. It is observed as that the number of layers is increased, the frequency shift increases significantly. For instance, a measurement taken after 45 minutes indicates that the frequency shift increases from 0.05 kHz using 1 layer to about 0.25 kHz using 4 CuY layers. This constitutes about 5 times sensitivity enhancement and can be attributed to the fact that more CO can be absorbed on cantilevers that have more zeolite. One other interesting observation is that, when the number of layers is increased, the frequency shift reaches its steady (saturation) value in a much shorter time.
Figure 4.9. The resonance frequency shift of the 250 µm microcantilevers coated with 1, 2 and 4 CuY(10%) layers.

Figure 4.10 illustrates that increasing the number of layers does not necessarily yield a more sensitive sensor. Indeed, by increasing the number of layers to 8, the frequency shift drops to about 0.225 kHz after 45 minutes. Increasing the number of layers further will only result in a less sensitive sensor. This can be explained by knowing that when the number of zeolite layers increases, both the initial mass and stiffness of the sensor increase making it less sensitive to variations in any additional mass resulting from CO adsorption.
Figure 4.10. The resonance frequency shift of 250 µm microcantilevers coated with 4, 8, 10 and 12 CuY(10%) layers.

Figure 4.11. Sensitivity of 250 µm microcantilevers coated with different zeolite layers during CO adsorption.
Figure 4.11 depicts the sensitivity of microcantilevers coated with different number of CuY zeolite layers under the same pressure and temperature conditions. Here, the difference in the natural frequency before and after CO adsorption divided by the original frequency before CO adsorption is used as a sensitivity measure. It can be clearly seen that the cantilever with 4 CuY zeolite layers is the most sensitive to the presence of CO yielding a sensitivity of about 0.76%.

Figure 4.12. Resonance frequency shift of 250 \( \mu \text{m} \) microcantilevers coated with 4 layers and exposed to different amount of CO.

Figure 4.12 depicts that the resonance frequency shift of microcantilever coated with 4 layers when exposed to different amounts of CO. It is observed that the frequency shift increases with the number of moles of CO. This can be explained by the obvious fact that, the larger the amounts of CO present in the chamber, the higher the probability
that CO would enter and fill the zeolite pores. This increases the microcantilever’s mass resulting in higher frequency shifts.

### 4.3.2.2. Desorption of Carbon Monoxide

For successful implementation of the sensor in a fuel cell, the sensor should be capable of CO desorption when necessary. Otherwise, CO will accumulate on the sensor and real time information about CO concentration cannot be obtained. Since desorption of CO can occur at elevated temperatures [Rakic et al., 1999], it is possible to pass an electric current through a nanowire embedded on the surface of the sensor to elevate its temperature. Since we do not have such microcantilevers available at our disposal, the cantilevers were placed in an oven and heated up to 200°C for an hour. Subsequently, their resonance frequency was measured and recorded. Results are depicted in Figure 4.13.

![Figure 4.13](image)

**Figure 4.13.** Resonance frequency of the microcantilever samples coated with +1 layer, ♦ 2 layers, ▲ 4 layers, ■ 8 layers, ◊ 10 layers, ● 12 layers.
Figure 4.13 indicates that the resonance frequency, which decreases after CO adsorption, increases again after heating. This indicates that some desorption actually occurs. However, as shown in the figure, the resonance frequency does not return back to its original value meaning that the adsorption process is not completely reversible and some CO remains trapped in the pores.
Chapter 5

Conclusions and Recommendations for Future Work

This thesis detailed the development, synthesis, and testing of a microcantilever sensor suitable for monitoring the concentration of Carbon Monoxide (CO) in a fuel cell. For that purpose, we initially identified a suitable high-capacity CO adsorbent that can be used to coat the microcantilevers to selectively adsorb CO in a gas mixture for the range of fuel cell operation temperatures. It was determined that CuY zeolite can act as a proper adsorbent for CO. As such, CuY zeolites with 10, 13, 19 and 24 wt% Cu content were synthesized using the impregnation method then characterized using ICP, XRD, and SEM analyses to determine their composition, structure, and morphology.

Following these analyses, CuY zeolite samples were exposed to CO for a range of pressures to determine their adsorption capacity, including the effects of copper loading. Experimental results indicated that CuY zeolite samples with 10 wt% Cu content exhibit the highest adsorption capacity. To investigate the effect of temperature on the adsorption
capacity, the same experiment was repeated at different temperatures, namely, 40, 50 and 60 °C. Results indicated that a temperature of 40 °C yields the highest CO adsorption capacity. As such, all subsequent experiments were carried at that temperature.

To identify a suitable microcantilevers’ coating method, two techniques, namely, spin and dip coating were utilized and compared. Based on SEM analysis, it was determined that the spin coating method is more effective because it yields a homogeneous zeolite coating layer. Using the spin coating method, all microcantilevers were then coated with different number of CuY (10%) zeolite layers ranging from 1 to 12 layers per cantilever.

Using the microsystem analyzer, MSA-400, the resonance frequency before and after coating with zeolite was experimentally measured. It was determined that 8 layers of CuY(10%) zeolite causes the largest frequency shift (decrease). Beyond the 8 layers, any additional layer will cause the frequency shift to start increasing again. This was attributed to the fact that, when the number of zeolite layers increases beyond a certain threshold, the microcantilevers start to act like a composite beam with the thickness of the zeolite layer increasing the stiffness of the cantilever. The increase in stiffness causes the frequency to increase, which offsets the frequency decrease, caused by the additional mass.

To investigate the ability of the microcantilevers to detect CO, the microcantilevers were mounted in a temperature- and pressure-controlled gas chamber. Microcantilevers with different number of zeolite layers were then exposed to CO gas at different pressures. The first resonance frequency of the cantilevers was monitored and
recorded at different time intervals. Results indicate that the number of zeolite layers have a great influence on the ability of the cantilevers to adsorb and detect CO. Specifically, it was determined that the resonance frequency shift of the microcantilevers increases with the number of layers up to 4 coating layers. Beyond that point, the resonance frequency, and hence, sensitivity starts to decrease with the addition of any more coating layers. The reduction in the sensitivity is attributed to the large mass and additional stiffness that the additional zeolite layers add to the microcantilever making it less sensitive to variations in small CO mass. During the experiments, a maximum resonance frequency shift of $275 \text{ Hz}$ was recorded using 4 CuY(10%) zeolite layers. The maximum sensitivity of the microcantilever was determined to be 0.76%. With that, this thesis demonstrates that microcantilever sensors are capable of detecting CO using their resonance frequency shift. This implies that they can be effectively utilized to monitor CO gas concentration in fuel cells.

While this thesis has focused on finding a proper CO adsorbent and proving the feasibility of CO detection using microcantilever sensors; a large number of research studies should be carried out before the actual implementation of these sensors in fuel cells becomes feasible. Following, we present some of our recommendations for future work:

1) Due to experimental difficulties that are beyond our control, we only carried the experiments in environments that contain pure CO. In other words, the ability of the sensors to detect CO in a gas mixture has not yet been verified. Future studies should investigate the sensitivity of the sensor in detecting
different concentrations of CO within a mixture of gases. The resulting frequency shift can be further related to CO concentration in the gas mixture using calibration curves or other means.

2) We used a bulky optical lever method, namely MSA-400 microsystem analyzer as a measurement methodology to detect the frequency shift during CO adsorption. Obviously, it is not feasible to use such methodology for actual fuel cell operations. Other types of microcantilevers that employ a self-sensing detection approach, e.g., piezoelectric or piezoresistive, see Chapter 2, should be employed and tested in the future.

3) Since the microcantilevers used in this experiment are passive. In other words, they cannot be heated or actuated unless an external heating or actuation source is employed; the desorption experiments presented were carried by heating the cantilevers in an oven. A more realistic study should contain microcantilevers that can be internally heated by passing a current through a nanowire embedded within the sensor.

4) After the previous three issues are carefully and comprehensively treated, future studies should aim to implement these sensors in an actual fuel cell. With that, new unseen challenges can appear which might require further theoretical and experimental studies.

In summary, this thesis provides some preliminary findings proving the feasibility of using microcantilevers as a means for monitoring CO concentration in a gas mixture.
This is only a first step in a journey that will involve many more challenges before their actual implementation in a fuel cell.
Appendix A
Adsorption isotherms of N$_2$ on CuY-zeolites at 77 K.

Table A-1. Adsorption isotherms of N$_2$ on HY, CuY zeolites with 10 and 13wt% Cu content at 77 K.

<table>
<thead>
<tr>
<th>HY Zeolite</th>
<th>CuY (10%) Zeolite</th>
<th>CuY (13%) Zeolite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of adsorbed N$_2$/ zeolite (cm$^2$/g)</td>
<td>Pressure (mmHg)</td>
<td>Volume of adsorbed N$_2$/ zeolite (cm$^2$/g)</td>
</tr>
<tr>
<td>0.06</td>
<td>204.38</td>
<td>0.06</td>
</tr>
<tr>
<td>0.08</td>
<td>208.78</td>
<td>0.08</td>
</tr>
<tr>
<td>0.12</td>
<td>215.62</td>
<td>0.12</td>
</tr>
<tr>
<td>0.17</td>
<td>220.96</td>
<td>0.16</td>
</tr>
<tr>
<td>0.21</td>
<td>225.94</td>
<td>0.21</td>
</tr>
</tbody>
</table>

Table A-2. Adsorption isotherms of N$_2$ on CuY-zeolites with 19 and 24wt% at 77 K.

<table>
<thead>
<tr>
<th>CuY (19%) Zeolite</th>
<th>CuY (24%) Zeolite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of adsorbed N$_2$/ zeolite (cm$^2$/g)</td>
<td>Pressure (mmHg)</td>
</tr>
<tr>
<td>0.06</td>
<td>152.69</td>
</tr>
<tr>
<td>0.08</td>
<td>155.89</td>
</tr>
<tr>
<td>0.12</td>
<td>160.12</td>
</tr>
<tr>
<td>0.16</td>
<td>163.53</td>
</tr>
<tr>
<td>0.21</td>
<td>166.26</td>
</tr>
</tbody>
</table>
Appendix B
Adsorption isotherms of CO adsorbed on the CuY Zeolite with different Cu contents at 40°C

**Table B.1.** Adsorption isotherms of CO adsorbed on the CuY Zeolite with 10wt%Cu contents at 40°C

<table>
<thead>
<tr>
<th>CuY(10%)</th>
<th>Primary Isotherms</th>
<th>Secondary Isotherms</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Volume of adsorbed N₂/zeolite (cm²/g)</td>
<td>Pressure (mmHg)</td>
</tr>
<tr>
<td>----------</td>
<td>----------------------------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>0.982</td>
<td>0.933</td>
<td>0.970</td>
</tr>
<tr>
<td>9.985</td>
<td>1.319</td>
<td>9.994</td>
</tr>
<tr>
<td>25.709</td>
<td>1.682</td>
<td>23.761</td>
</tr>
<tr>
<td>49.544</td>
<td>2.043</td>
<td>49.751</td>
</tr>
<tr>
<td>98.214</td>
<td>2.576</td>
<td>98.270</td>
</tr>
<tr>
<td>197.209</td>
<td>3.451</td>
<td>197.630</td>
</tr>
<tr>
<td>297.804</td>
<td>4.269</td>
<td>298.853</td>
</tr>
<tr>
<td>399.382</td>
<td>5.060</td>
<td>399.492</td>
</tr>
<tr>
<td>499.276</td>
<td>5.822</td>
<td>499.285</td>
</tr>
<tr>
<td>599.288</td>
<td>6.568</td>
<td>599.240</td>
</tr>
<tr>
<td>799.288</td>
<td>8.038</td>
<td>799.199</td>
</tr>
</tbody>
</table>
Table B.2. Adsorption isotherms of CO adsorbed on the CuY Zeolite with 13wt%Cu contents at 40°C.

<table>
<thead>
<tr>
<th></th>
<th>ZPrimary Isotherms</th>
<th></th>
<th>Secondary Isotherms</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pressure (mmHg)</td>
<td>Volume of adsorbed N\textsubscript{2}/zeolite (cm\textsuperscript{2}/g)</td>
<td>Pressure (mmHg)</td>
</tr>
<tr>
<td>CuY(13%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.181</td>
<td>0.130</td>
<td>1.236</td>
</tr>
<tr>
<td></td>
<td>9.788</td>
<td>0.953</td>
<td>10.531</td>
</tr>
<tr>
<td></td>
<td>28.827</td>
<td>1.361</td>
<td>25.369</td>
</tr>
<tr>
<td></td>
<td>49.788</td>
<td>1.653</td>
<td>48.994</td>
</tr>
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<td>498.317</td>
<td>5.408</td>
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<td></td>
<td>798.078</td>
<td>7.692</td>
<td>798.037</td>
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</table>
Table B.3. Adsorption isotherms of CO adsorbed on the CuY Zeolite with 19wt%Cu contents at 40°C.

<table>
<thead>
<tr>
<th>Pressure (mmHg)</th>
<th>Volume of adsorbed N₂/zeolite (cm²/g)</th>
<th>Pressure (mmHg)</th>
<th>Volume of adsorbed N₂/zeolite (cm²/g)</th>
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<tr>
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<td>4.810</td>
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<td>12.096</td>
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<td>27.756</td>
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</tr>
<tr>
<td>49.925</td>
<td>1.400</td>
<td>49.254</td>
<td>0.973</td>
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<tr>
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<td>1.868</td>
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</tr>
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</table>
Table B.4. Adsorption isotherms of CO adsorbed on the CuY Zeolite with 24wt%Cu contents at 40°C.

<table>
<thead>
<tr>
<th></th>
<th>Primary Isotherms</th>
<th>Secondary Isotherms</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pressure (mmHg)</td>
<td>Volume of adsorbed N₂/zeolite (cm²/g)</td>
</tr>
<tr>
<td></td>
<td>0.994</td>
<td>0.220</td>
</tr>
<tr>
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<td>9.736</td>
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<tr>
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<td>50.235</td>
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</tr>
<tr>
<td></td>
<td>98.635</td>
<td>1.660</td>
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<td>197.824</td>
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<tr>
<td></td>
<td>799.492</td>
<td>6.781</td>
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</table>
Appendix C

Adsorption isotherms of CO adsorbed on the CuY (10\%) Zeolite at different temperatures

Table C.1. Adsorption isotherms of CO adsorbed on the CuY (10\%) Zeolite at 40°C.

<table>
<thead>
<tr>
<th>Pressure (mmHg)</th>
<th>Volume of adsorbed N\textsubscript{2} \hspace{1mm}/ zeolite (cm\textsuperscript{2}/g)</th>
<th>Pressure (mmHg)</th>
<th>Volume of adsorbed N\textsubscript{2} \hspace{1mm}/ zeolite (cm\textsuperscript{2}/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.982</td>
<td>0.933</td>
<td>0.970</td>
<td>0.216</td>
</tr>
<tr>
<td>9.985</td>
<td>1.319</td>
<td>9.994</td>
<td>0.592</td>
</tr>
<tr>
<td>25.709</td>
<td>1.682</td>
<td>23.761</td>
<td>0.898</td>
</tr>
<tr>
<td>49.544</td>
<td>2.043</td>
<td>49.751</td>
<td>1.271</td>
</tr>
<tr>
<td>98.214</td>
<td>2.576</td>
<td>98.270</td>
<td>1.773</td>
</tr>
<tr>
<td>197.209</td>
<td>3.451</td>
<td>197.630</td>
<td>2.612</td>
</tr>
<tr>
<td>297.804</td>
<td>4.269</td>
<td>298.853</td>
<td>3.399</td>
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<tr>
<td>399.382</td>
<td>5.060</td>
<td>399.492</td>
<td>4.152</td>
</tr>
<tr>
<td>499.276</td>
<td>5.822</td>
<td>499.285</td>
<td>4.889</td>
</tr>
<tr>
<td>599.288</td>
<td>6.568</td>
<td>599.240</td>
<td>5.613</td>
</tr>
<tr>
<td>799.288</td>
<td>8.038</td>
<td>799.199</td>
<td>7.047</td>
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</table>
Table C.2. Adsorption isotherms of CO adsorbed on the CuY (10%) Zeolite at 50°C.

<table>
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<th>50°C</th>
<th>Primary isotherms</th>
<th>Secondary isotherms</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pressure (mmHg)</td>
<td>Volume of adsorbed N₂/zeolite (cm²/g)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.395</td>
<td>0.031</td>
</tr>
<tr>
<td></td>
<td>10.476</td>
<td>0.165</td>
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### Table C.3. Adsorption isotherms of CO adsorbed on the CuY (10%) Zeolite at 60°C

<table>
<thead>
<tr>
<th>Pressure (mmHg)</th>
<th>Volume of adsorbed N₂/zeolite (cm²/g)</th>
<th>Pressure (mmHg)</th>
<th>Volume of adsorbed N₂/zeolite (cm²/g)</th>
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<td>797.857</td>
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REFERENCES


Matsumoto, A., T. Kitajima, and K., Tsutsumi, 1999. Adsorption Characteristics and


www.unl.edu/CMRAcfem/semoptic.htm.