Electrodeposited Cu-based Catalysts for Alcohols from CO Hydrogenation and Electrodeposition of CuNiW/CuNi Multilayered Alloys

Mayank Gupta
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ELECTRODEPOSITED Cu-BASED CATALYSTS FOR ALCOHOLS FROM CO HYDROGENATION AND ELECTRODEPOSITION OF CuNiW/CuNi MULTILAYERED ALLOYS

A Dissertation
Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Gordon A. and Mary Cain Department of Chemical Engineering

by
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May 2010
Om Namah Shivaya

“Om Namah Shivaya”

Dedicated to the memory of my grandparents and sister Pinky
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ABSTRACT

Ethanol and higher alcohols can be used as a fuel or fuel additive in gasoline engines as well as a hydrogen carrier. One of the promising methods to synthesize these alcohols is based on thermochemical conversion of CO and H₂ (CO hydrogenation). Conventional catalysts used for the conversion CO and H₂ (syngas) to ethanol typically give yields less than 20% with the balance resulting mostly in the formation of the thermodynamically favored products CH₄ and CO₂. New catalysts with compositions designed to kinetically favor the formation of ethanol and higher alcohols are needed. Electrodeposition of nanowires offers a means to control the surface properties of multimetallic catalysts in a way that is not possible with conventional catalyst preparation methods such as co-precipitation and impregnation. A principle advantage of electrodeposition over conventional methods centers on its ability to control the active metal environment at the atomic level.

In this work, Cu-ZnO and Mn-Cu-ZnO novel nanowire/tube catalysts have been prepared by electrodeposition using a template synthesis technique. To the best of our knowledge, electrodeposited Cu-based nanowires have never been used as heterogeneous catalysts. Different current and pulsed current schemes were used to control composition and morphology of the resulting nanowire/tube catalysts. Pulse waveforms with suitable on-time (cathodic current) and off-times (no current) were used to tailor the atomic environment of the nanowire catalysts.

A fixed bed tubular reactor was used to synthesize alcohols from CO and H₂ (syngas). In addition to C₂-C₄ alcohols products of interest, methanol, methane, propylene, and CO₂ were the main side products at various reaction conditions. The reaction was performed at varying
temperature (250°C-310°C), pressure (10-20 bar), H₂/CO ratio (1-3), and GHSV (7,500-33,000 scc/h-gcat). The addition of Mn to the Cu-ZnO catalyst increased the selectivity toward ethanol and higher alcohols by reducing methanation. Schulz-Flory distributions of the products suggest that the synthesis of alcohols and hydrocarbons require different sites.
CHAPTER 1: INTRODUCTION

1.1 Alternative Fuel/Additives: Ethanol and Higher Alcohols

There is a need for alternative fuels because of limited oil supply [1], increased oil demand [1], and persistent increase in oil prices [2]. According to the Hubbert peak theory oil production has already peaked in non-Organization of the Petroleum Exporting Countries (OPEC) and non-Former Soviet Union (FSU) countries and is declining (Figure 1.1). The situation is worsened by the increased demand for oil. According to U.S. Energy Information Agency, world demand for crude oil (including natural gas liquids) is projected to increase from 77.1 million barrels/day in 2001 to 89.7 million barrels/day in 2010, an increase of about 16% in just 9 years [3]. Similarly, world liquids consumption is projected to increase from 85 million barrels/day in 2006 to 107 million barrels/day in 2030 [4], an increase of more than 25%. In the United States, demand for oil is growing, however, domestic production is projected to decline [1]. By 2025, U.S. demand of oil and oil products is expected to reach 29.2 million barrels/day, which will require the import of nearly 19.8 million barrels/day [1].

The oil prices are increasing; which is evident from Figure 1.2 [2]. In the reference case, the average world oil price increased from $61/barrel in 2009 to $110/barrel in 2015 and $130/barrel in 2030. This will have an adverse impact on economy and social infrastructure of the world if the production of alternative fuels is not increased significantly.

One of the promising way to avoid this impact is the exploration and production of alternative fuel and additives. One such fuel/additive is ethanol or a mixture of ethanol and higher alcohols [5-7]. Ethanol is already in use as fuel additive in the US and many other
countries such as Canada, Brazil, and Sweden. Developing countries like India and China have also started promoting ethanol as fuel additive on a pilot basis.

Figure 1.1 Oil Production of non-OPEC and non-FSU countries [1].

Figure 1.2 World oil prices, 1980-2030 [2].
Ethanol and higher alcohols are good fuel additives because they provide oxygen directly to the fuel. Benefits of adding alcohol mixtures to gasoline include increase in gasoline volume, enhanced octane rating, and less pollution [6] by reducing emissions of NOx, CO₂ and, unburnt hydrocarbons [8]. However, there are some disadvantages; such as increased fuel cost and less overall energy efficiency [6]. Another important application of ethanol is that it can be used for transporting hydrogen. For example, fuel cells (an efficient source of energy) require hydrogen as energy carrier and can be supplied with hydrogen in the form of ethanol. Ethanol can then be steam reformed or partially oxidized to produce hydrogen [5, 9, 10].

Ethanol is the most attractive alcohol because it can be produced from renewable energy sources [11] such as biomass. Ethanol is produced commercially in two ways – 1) hydration of ethene, and 2) fermentation of sugars. The first method does not solve our problem of dependency on oil because it requires ethene, a petroleum product. The second one interferes with our food supplies as sugars come from biomass feedstocks such as corn/maize, sugar cane, and sugar beets. For instance, in the US, corn-based ethanol has caused a sudden rise in price of corn when the demand for corn exceeded its supply [12]. Hence, there is a drive to explore new methods that can supplement these resources to meet the increasing fuel demand in the future. One potential method is thermochemical conversion of biomass or coal derived-syngas (CO and H₂) to ethanol and higher alcohols. One of the main merits of this method over fermentation is that it does not require any specific type of biomass feedstock. Another advantage is that it does not require separation of biomass components such as cellulosic material and lignin [13].
1.2 CO Hydrogenation (Syngas Conversion) to Ethanol and Higher Alcohols

Research on the production of alcohols from syngas has been going on for over 90 years [7]. Syngas conversion to ethanol seems to be a promising renewable alternative source of energy due to its environmental friendliness and cost due to easily accessible raw materials. Figure 1.3 is a schematic of production of alcohols from syngas. Syngas is primarily a mixture of CO and H₂ with some CO₂ and H₂O. It is produced via gasification of biomass [14] or coal [15]. Syngas is fed to a chemical reactor over a dry catalyst to produce alcohols and other side products. In general, the presence of CO₂ in syngas has detrimental effects on higher alcohol synthesis [5, 7], but it can be captured using CaO [16]. A comprehensive overview of syngas production can be found in these articles [15, 17].

![Diagram](image_url)

Figure 1.3 Generic schematic of biomass/coal derived syngas to alcohols.

Ethanol and higher alcohol synthesis from syngas is being explored by many researchers using different types of catalysts [5, 18-21]. It is worth mentioning that the conversion of syngas to methanol over Cu/ZnO supported with Al₂O₃ or Cr₂O₃ catalysts is a very efficient industrial process with over 99% yield [7, 22]. Nevertheless, the yields of ethanol and higher alcohols are generally below 15% from CO hydrogenation even though ethanol is thermodynamically
favored compared to methanol. Therefore the problem is one of kinetic control [18]. However, an appropriate selection of catalysts and operating conditions should increase the ethanol and higher alcohol yield.

1.2.1 Thermodynamic Aspects

Ethanol can be produced via CO hydrogenation (eq 1) [5, 21].

\[ 2 \text{CO} + 4 \text{H}_2 \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O} \quad (1) \]

\[ \Delta H_r^\circ = -61.2 \text{kcal/mol of ethanol} \]
\[ \Delta G_r^\circ = -29.3 \text{kcal/mol of ethanol} \]

Above reaction is thermodynamically favorable and highly exothermic. Figure 1.4 shows the equilibrium composition of various reactants and allowed products during direct CO hydrogenation. Formation of ethanol and water decreases with temperature while that of CO and H\(_2\) increases. Thermodynamics suggests that CO hydrogenation should be done below 350\(\circ\)C. Another important point to be noted here is that methanol is less thermodynamically favorable than ethanol, yet it is one of the main products of this reaction. Therefore, the kinetics should be controlled in such a way that can enhance ethanol and higher alcohol synthesis.

Ethanol can also be produced via homologation of methanol (eq 2). The reaction involves reductive carbonylation of methanol over a redox catalyst to form a C-C bond and thus ethanol [21].

\[ \text{CH}_3\text{OH} + \text{CO} + 2\text{H}_2 \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O} \quad (2) \]

\[ \Delta H_r^\circ = -39.5 \text{kcal/mol of ethanol} \]
\[ \Delta G_r^\circ = -23.2 \text{kcal/mol of ethanol} \]
Both of the above reactions are accompanied by several side reactions to produce many products such as methanol, i-propanol, n-propanol, n-butanol, i-butanol, acetone, acetaldehyde, i-butane, n-butane, hexane, methane, CO₂, ethane, propadiene, propylene, and propane. The most undesirable side reaction is methanation (eq 3). Methanation is a highly exothermic reaction. It should be avoided because heat dissipation is a big problem at industrial level during higher alcohols synthesis [7]. Methane is most thermodynamically favored product of CO hydrogenation reaction, as shown in Figure 1.5.

\[
\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O} \quad (3)
\]

\[\Delta H_r^\circ = -49.3 \text{ kcal/mol of ethanol}\]

\[\Delta G_r^\circ = -33.9 \text{ kcal/mol of ethanol}\]

Figure 1.4 Equilibrium composition for the hydrogenation of CO to ethanol (H₂/CO=2, 10 bar).
Another important side reaction is the water gas shift (WGS) reaction (eq 4) because it can affect the H₂/CO ratio as it produces H₂ along with CO₂. It is favorable for feeds containing lower H₂/CO ratio but undesirable for feed with a high H₂/CO ratio [21]. Figure 1.6 shows that CO₂ is favored in the temperature range where ethanol is also a favored product. However, its amount is less than ethanol and this can further be decreased if the reaction is carried out below 300°C.

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad (4)
\]

\[
\Delta H^0_r = -9.8 \text{ kcal/mol of ethanol}
\]

\[
\Delta G^0_r = -6.8 \text{ kcal/mol of ethanol}
\]

Figure 1.5 Equilibrium composition for the hydrogenation of CO to ethanol when methane was allowed as a product (H₂/CO = 2.0, 10 bar).
1.2.2 Cu-based Catalysts

To date, rhodium-based catalysts have been the most promising but their prohibitive cost and limited supply hinder their ability to be used as industrial catalysts [21]. Thus, much less expensive copper-based catalysts [23, 24] are an attractive option. These catalysts are alkali-promoted Cu/ZnO/Al₂O₃ or Cu/ZnO/Cr₂O₃ [19, 23, 25-28], non-alkali promoted Cu-ZnO-Al₂O₃ [23], Cu-Mn-ZrO₂ [29-31], and alkali-promoted/unpromoted different combinations of all or some of these components: Cu, Co, Zn, Al [32-35]. Promoters are added to Cu-based catalysts because they have been shown to enhance ethanol and higher alcohol synthesis [5, 21, 28]. An optimum promoter concentration is necessary because too much of it decreases selectivity [26-28, 36] and activity of a catalyst [37-39]. In general, Cu-based catalysts have widely been used and produced promising results in the temperature range of 280-310 [23, 24, 26, 29, 30, 34, 35, 38, 40-43]. The average range for pressure is about 40-100 bar [25, 27, 29, 31, 32, 35, 38, 41, 42, 44-48]. H₂/CO ratio is another important parameter and reported to be in between 0.45 and 2.33 by various researchers [24, 26, 27, 29-31, 38, 41, 42, 44, 48, 49].

1.2.3 Novel Catalysts: Electrodeposited Nanowires/tubes

Generally, heterogeneous catalysts are prepared by conventional methods such as co-precipitation and impregnation. To further increase the performance of these catalysts, a control over the atomic level morphology (a critical property of a catalyst) is essential. Therefore, it has become necessary to explore novel catalyst preparation methods that can provide some control over the morphology and structure of these catalysts that cannot be achieved with conventional methods. Novel catalyst preparation methods have been used by some workers and found promising results [50-52].
A potential promising alternative is electrodeposited nanowires/tubes because it offers a means to control the surface properties of multimetallic catalysts in a way not possible with conventional catalyst preparation techniques. A principle advantage of electrodeposition over conventional methods centers on its ability to control the active metal environment at the atomic level.

Figure 1.6 Equilibrium composition for the hydrogenation of CO to ethanol with CO₂ allowed as a product (H₂/CO = 2.0, 10 bar).

Nanowires and tubes can be synthesized via diverse techniques including lithographic patterning [53, 54], vapor transport techniques [55-60], and many more [61-65]. Most of these techniques are either slow, and/or fabrication cost is high. However, template based synthesis involving electrodeposition is promising owing to the low cost and control over the nanowire properties by changing the electrolyte composition, pH, temperature and applied current or
Template synthesis is relatively simple, inexpensive, and is a high throughput method [67, 68]. Electrodeposition can be carried out via direct current (DC) or pulsed deposition. During DC deposition, an appropriate current or potential is applied for some time. Whereas during pulse deposition an off-time (no current) is given between short deposition times and the cycle is repeated several times. Different types of pulse schemes are discussed in detail elsewhere [69].

1.3 Outline of Dissertation

Chapter 1 discusses the urgency for ethanol and higher alcohols as alternative fuel/fuel additives and current method of their production. It also discusses about an alternative method to produce alcohols that can help in meeting the increasing demand of ethanol.

Chapter 2 covers a thorough literature survey of Cu-based catalysts, effect of promoter, effect of reaction conditions, and reaction mechanisms for the synthesis of ethanol and higher alcohols from syngas. It also discusses novel catalyst preparation method viz. electrodeposition of nanowires/tubes using template based synthesis technique.

Chapter 3 covers experimental sections of each chapter in more detail.

Chapter 4 is a published paper from Catalysis Today. It reports fabrication, characterization, and syngas conversion (at varying reaction conditions) of electrodeposited nanowires/tubes of Cu-ZnO (both DC and pulsed) and Mn-Cu-ZnO (only DC). This is the first paper that reports on the use of electrodeposited nanowires as heterogeneous catalysts. It reports some promising results at mild reaction conditions. The effect of rest/off-time and Mn addition on the properties of nanowires is also discussed.
**Chapter 5** is another manuscript that has been submitted to *Journal of Electrochemical Society*. It discusses the pulse electrodeposition of Cu-ZnO and Mn-Cu-ZnO in more detail than the paper presented in Chapter 4. One of the main differences is the pulse off and on-time. Pulse times are much shorter (50-600 ms) than in Chapter 4 (20-120 s). Specifically, it discusses probable electrochemical and chemical reactions during electrodeposition of these nanowires. Also, the effect of deposition conditions and electrolyte composition on nanowire properties are explained and discussed.

**Chapter 6** reports the fabrication, characterization, and catalytic performance of Mn-Cu-ZnO nanowire catalysts and it will be submitted to *Catalysis Communications*. It covers the effects of various reaction conditions on product selectivity. Based on the product distribution and literature, it proposes a reaction pathway for the formation of ethanol and other major products.

**Chapter 7** reports the electrodeposition of multilayered copper-nickel-tungsten films and nanowires. The deposit composition and current efficiency were characterized using rotating cylinder electrodes with and without a Hull configuration. This manuscript is an accepted paper to be published in *Journal of Applied Electrochemistry*.

**Chapter 8** covers the conclusions derived from all the chapters in this dissertation. Based on the results obtained, future path forward has also been suggested.

**1.4 References**


CHAPTER 2: LITERATURE REVIEW

Numerous research papers are available on the conversion of syngas to ethanol and higher alcohols [1-5]. This chapter covers the catalysts types, possible reaction mechanisms, role of promoter(s), and effect of reaction conditions, and novel catalysts.

The catalysts to produce ethanol and higher alcohols from CO hydrogenation can be divided mainly into the following categories.

1. Cu-based catalysts
2. Rh-based catalysts
3. Modified Fischer-Tropsch catalysts
4. Mo-based catalysts

Only the first category i.e. Cu-based catalysts are discussed here because the main focus of this work was to develop novel Cu-based catalyst. A comprehensive review of other types of catalysts can be found elsewhere [1-4].

2.1 CO Hydrogenation on Cu-based Catalysts

During methanol synthesis on Cu-based catalysts, small amounts of higher alcohols were noted on catalysts with trace amount of alkali. This led researchers to explore the addition of alkali to these catalysts to produce higher alcohols [6]. As early as 1923-24, that these types of catalysts started attracting attention due to their ability to produce higher alcohols along with methanol [1]. Most of the catalysts in this category are Cu/ZnO/Al₂O₃ or Cu/ZnO/Cr₂O₃ modified/promoted with one or more alkali [2, 3]. Others are non-alkali promoted Cu-ZnO-Al₂O₃ [7], Cu-Mn-ZrO₂ [8-10], and different alkali promoted/unpromoted combinations of all or some of these components (Cu, Co, Zn, Al) [11-14].
Cu-based catalysts should be modified in such a way that they increase the formation of higher alcohols and at the same time reduce the formation of unwanted products such as methane and other hydrocarbons [15]. The main products on these catalysts are methanol, ethanol, methane, CO$_2$, 1-propanol, acetaldehyde and iso-butanol.

Selectivity to ethanol and higher alcohols depends on many parameters such as type and amount of promoter(s), feed composition, pressure, temperature, space velocity (contact time). The effect of all these variables and some plausible reaction mechanisms found in literature are discussed in the following sections.

2.1.1 Role of Promoters

Alkali promoters have been found to enhance the selectivity toward higher alcohols. They follow the general trend - Li<Na<K<Rb<Cs in their ability to enhance higher alcohol production [16]. Basic promoters such as alkalis, neutralize acidity of catalysts and thus suppress the undesired reactions such as dehydration, isomerization, coke formation [3], and methanation. For example, on a Cu-Cr$_2$O$_3$-Al$_2$O$_3$-ZnO catalyst, it has been reported that alkali (K and/or Na) promotion was always necessary to suppress methanation below 290°C [17].

In general, promoters such as Cs or K on Cu/ZnO, Cu/ZnO/Al$_2$O$_3$, and Cu/ZnO/Cr$_2$O$_3$ show maxima in selectivity toward ethanol and higher alcohols [6, 13, 16, 18-20] with alkali loading. This is due to the bifunctional nature of alkali-promoted Cu-based catalysts. Cu/ZnO part of the catalyst provides sites for hydrogenation and Cs and its counter ion provide basic sites that carry out various C-C and C-O bond-forming reaction. Higher Cs content inhibits the alcohol synthesis by blocking the hydrogenation sites [21]. Higher alkali content also suppresses the
activity of the catalyst [21-23]. Stiles et al. [15] reported that alkali (K/Cs/Rb) loading even as low as 1% reduced the activity of their Cu/ZnO/Al₂O₃ catalyst drastically.

However, ethanol yield seems to follow a different trend with Cs loading on some catalysts. For example, it was reported that ethanol yield on Cu/ZnO first increased up to 1.5 mol% Cs and then became constant thereafter as shown in Figure 2.1 [19]. In another study [24], the same workers reported for a similar catalyst (Cu/ZnO) that Cs loading had an adverse effect on ethanol yield as can be seen Table 2.1. The reason could be the different reactions conditions used in these studies. However, other higher alcohol yields improved significantly up to 0.34 mol% alkali loading and then decreased. Higher levels of Cs loading reduced the catalytic activity significantly. Nevertheless, methanol and CO₂ remained the dominant product at any Cs-loading [24].

![Figure 2.1 Yield of methyl formate and ethanol as a function of cesium loading over the calcined-doped Cu/ZnO catalyst. Experimental conditions: T= 250 C, P=76 bar, H₂/CO=2.33 [19]. (Reproduced with permission from ref [19]. Copyright © 1988, Elsevier.)](image-url)
There seems to be no effect on ethanol yield on a Cs/Cu/Zn/Cr catalysts reported by Nunan et al. [21]. However, cesium doping enhanced the yields of higher alcohols such as 1-propanol, 2-methyl-1-propanol, and 2-methyl-1-butanol. Later, Hilmen et al. [25] reported that the addition of Cs on a Cu/ZnO/Al$_2$O$_3$ catalyst enhances selectivity to ethanol, 1-propanol, 2-methyl-1-propanol. However, in their study only two levels of dopings were used.

Table 2.1 Product Yields over the Cu/ZnO = 30/70 Catalyst and the Cesium-Doped Cu/ZnO Catalysis Obtained with a H$_2$/CO = 0.45 Synthesis Gas at 585 K and 7.6 MPa with GHSV = 3260 Liters (STP)/kg cat/hr [24].

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CO$_2$</th>
<th>Alkanes</th>
<th>Methanol</th>
<th>Ethanol</th>
<th>1-Propanol</th>
<th>2-Methyl-1-propanol</th>
<th>1-Butanol</th>
<th>2-Methyl-1-butanol</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped Cu/ZnO</td>
<td>367</td>
<td>16.8</td>
<td>204</td>
<td>22.6</td>
<td>10.1</td>
<td>20.7</td>
<td>3.4</td>
<td>8.6</td>
<td>34.1</td>
</tr>
<tr>
<td>0.25 mol% Cs/Cu/ZnO</td>
<td>412</td>
<td>16.2</td>
<td>181</td>
<td>22.7</td>
<td>29.6</td>
<td>28.9</td>
<td>8.6</td>
<td>11.5</td>
<td>53.8</td>
</tr>
<tr>
<td>0.34 mol% Cs/Cu/ZnO</td>
<td>403</td>
<td>13.4</td>
<td>157</td>
<td>17.0</td>
<td>38.1</td>
<td>48.6</td>
<td>8.2</td>
<td>15.5</td>
<td>82.3</td>
</tr>
<tr>
<td>0.43 mol% Cs/Cu/ZnO</td>
<td>340</td>
<td>4.3</td>
<td>213</td>
<td>8.1</td>
<td>18.0</td>
<td>4.8</td>
<td>-</td>
<td>-</td>
<td>10.9</td>
</tr>
</tbody>
</table>

*a* Alkanes = methane, ethane and propane  
*b* Others = methyl esters, aldehydes, ketones, C$_4^+$ linear primary and secondary alcohols, C$_4^+$ branched primary and secondary alcohols, and methyl formate

Another promising alkali promoter reported in the literature is potassium. K$_2$CO$_3$ was used by Smith et al. [6] to promote Cu/ZnO/Al$_2$O$_3$ catalysts. They reported that the addition of K$_2$CO$_3$ enhanced selectivity toward higher alcohols, particularly isobutanol. Maximum selectivity for higher alcohols was obtained at 0.5 wt% K$_2$CO$_3$ loading. Similarly, Boz et al. [13] used a commercial CuO/ZnO/Al$_2$O$_3$ catalyst and promoted it with potassium. Methanol selectivity increased and hydrocarbons decreased with K$_2$O loading. Higher alcohols and aldehyde had
highest selectivity at 0.5 wt%. Maximum yield for propanol, n-butanol, and isobutanol occurred at low K₂O loading but for methanol and ethanol, maxima occurred at a higher loading (1.0 wt%). The effect of K₂O loading was in agreement with Smith et al.’s work [6]. On a Cu/ZnO/Cr₂O₃ Calverley et al. [20] reported that promotion with K showed a maxima toward methanol and higher alcohol yield with K-loading. It was also reported that 0.5% K₂CO₃ loading shows more activity than 4% loading toward higher alcohols as well as methanol. Similarly, on a Co-Cu-ZnO catalyst, Boz et al. [12] reported a maxima in ethanol and higher alcohols selectivity at 5% K-loading. Similar effects were observed with Cs addition by others and were attributed to the blockage of the active sites of the catalyst at higher alkali loadings [21-24].

It seems that the role of alkali promoters is different on some catalysts. For examples, on an unpromoted Cu-Al catalyst, the ethanol yield was zero but Li increased the ethanol yield as well as methanol yield and almost had no effect on methanation [23]. Cs increased ethanol and methanol yields (much more than Li) and decreased methanation. Higher methanol yield from the promoted catalyst may be due to direct interaction of alkali and CO adsorbed on Cu, favoring the hydrogenation of CO through a larger coverage of catalytic sites by CO. However, on Al-Co-Cu-M catalysts, where, M is one of the alkali (Li, Na, K, Cs), Cs found to be the worst alkali due to the lack of its direct interaction with CO, because Cs is the weakest Lewis acid among the alkalis studied [23]. The reason behind the different effect of Cs on these catalysts was not explained, which could be due to the support (Al₂O₃) or the addition of cobalt.

Another group of promoters is the non-alkali promoters [7]. Most promising non-alkali promoter was found to be manganese [15, 26]. However, manganese also showed a deactivating effect [15]. Slaa et al. [26] reported that the addition of Mn increased higher
alcohol production only at 300°C, and at lower temperatures, it enhanced methanol selectivity and decreased higher alcohol selectivity. Addition of K to this catalyst decreased selectivity to higher alcohols, CO₂, and methane but increased methanol selectivity.

Ce is another non-alkali promoter found to enhance selectivity toward higher alcohols particularly iso-butanol [26, 27]. Small amounts of Ce (2 wt%) were reported to enhance selectivity toward iso-butanol and had no effect on ethanol, methane and CO₂ formation. Higher amount (4 wt% Ce) had an adverse effect on higher alcohol formation and increased undesired reactions such as methanation and CO₂ formation [26].

Mixture of both alkali and non-alkali promoters can also be promising [7]. For example, Hofstadt et al. [28] used non-alkali promoters such as MnO, Cr₂O₃ and ThO₂ with methanol synthesizing catalysts (CuO-ZnO-Al₂O₃-K) to increase the selectivity toward higher alcohols. MnO was particularly found to improve the selectivity toward ethanol. Cr₂O₃ and ThO₂-promoted catalysts favored the formation of propanol and butanol, respectively.

Other promoters such as Fe and Ni have been used on CuMnZrO₂ catalysts [8-10]. Xu et al. [8, 9] reported that the Fe addition increased the selectivity to C₂⁺ alcohols, CO₂ and hydrocarbon, and decreased the selectivity to methanol with overall reduction in catalytic activity. Similar results were reported for a Cu/Mn/ZrO₂ catalyst when it was promoted with Ni, but in this case catalytic activity improved [10]. Addition of Co was similar to Ni with regard to catalytic activity; however, more higher alcohols were produced. This was ascribed to the stronger chain growth ability of Co than Ni. However, the addition of Fe produced much less higher alcohols than the Ni and Co modified catalysts and more hydrocarbons.
The ability of a promoter to modify a catalyst also depends on how it has been added to the catalyst [9, 27]. For example, Slaa et al. [27] reported that the addition of Mn to Cu/ZnO by coprecipitation (added ions were present throughout the catalyst) increased methanol and methane, and slightly increased iso-butanol but decreased ethanol formation. However, Mn addition by impregnation (added ions were present at the surface) had no effect on ethanol and methane formation, and increased the selectivity toward CO$_2$ and iso-butanol.

It can be inferred from the above findings that the role of a promoter is dependent on reaction conditions and catalyst composition and support. Nevertheless, promoters do play an important role in enhancing ethanol and higher alcohol selectivity. An optimum amount is always necessary to achieve this goal.

**2.1.2 Effect of H$_2$/CO Ratio**

The H$_2$/CO feed ratio is very important for higher alcohol selectivity [6]. H$_2$/CO ratios ranging from 0.45 to 3 [6, 8-10, 13, 19, 21, 24, 26, 27, 29-31] have been reported in the literature. Unless the experiments are carried out at differential conversions, this ratio can change with reactor position because of the water-gas-shift reaction (WGS) [4]. In general, low H$_2$/CO ratios favor the coke formation and C-C chain growth, and therefore selectivity toward higher alcohol. Higher H$_2$/CO ratios favor methanol synthesis [4, 6, 32, 33].

In an effort to understand the effect of feed composition on higher alcohol synthesis, Boz et al. [13] varied the H$_2$/CO ratio (0.5, 2, 3) using a K-promoted Cu/ZnO/Al$_2$O$_3$ catalyst. Selectivity to higher alcohols, hydrocarbons and aldehydes was highest at the lowest H$_2$/CO ratio and while greater H$_2$/CO ratios favored methanol (Figure 2.2). Similar trends were found by other researchers [4, 16, 34].
2.1.3 Effect of Pressure

Higher alcohol synthesis is thermodynamically favored at higher pressures [4]. Pressures as low as 20 bar [31] and as high as 400 bar [13] have been reported in the literature. In general, the average range is about 40-100 bar [8, 10, 11, 14, 17, 19-21, 24, 26-29, 35].

Figure 2.2 Effect of H₂/CO ratio on product selectivities on a K/Cu/ZnO/Al₂O₃ catalyst [13].

Unfortunately, there are few studies on the effect of pressure on higher alcohol synthesis. Stiles et al. [15] studied the effect of pressure in a range of 82-310 bar. The optimum operating pressure was 172 bar based on high productivity ((mL alcohol/mL catalyst)/h), suppressed methanation, and controlled distribution of higher alcohols for the purpose of directly adding it to gasoline as a fuel additive. It was also found that as the pressure increased,
the productivity of higher alcohols increased only to a lesser extent than methanol. Similar results were found on a Cu-Co2O3-ZnO-Al2O3 catalyst by Mahdavi et al. [36]. They reported that increasing pressure (range: 40-70 bar), enhanced total alcohol selectivity and decreased methane selectivity. It also increased the overall yield and CO conversion.

2.1.4 Effect of Temperature

Higher alcohol synthesis is favorable only in a narrow range of temperatures 280-310°C [6-9, 12-14, 21, 24, 27, 30, 31, 33, 36]. However, temperatures as high as 350°C [28] and 375°C [15] were found to be suitable for some catalysts. The main problems associated with the higher temperatures are:

1. Instability of some oxygenates at temperatures above 450°C [4],
2. Formation of CO2 and methane at temperatures above 280°C [7, 10, 15],
3. Deactivation of the catalyst due to sintering [20, 29, 33].

In general, higher temperature resulted in enhanced selectivity toward higher alcohols [6, 13, 15, 20, 29, 33] however, opposite was true for methanol [6, 13, 29, 33]. Majocchi et al. [33] reported that all the alcohols go through a maximum (Figure 2.3) because at higher temperatures CO2 formation dominates. A similar maxima in higher alcohol selectivity was reported by others [7, 10, 12, 26].

It can be concluded that the reaction temperature is a critical variable. Careful investigation of literature reveals that the best temperature range for higher alcohol synthesis on most of the Cu-based catalysts is 280-300°C. Also, good temperature control is required during an actual operation because main and side reactions during CO hydrogenation are highly exothermic ($\Delta H^0 = -90$ to $-200$ KJ/mol) [37].
2.1.5 Effect of Space Velocity

In general, low space velocities or higher contact times were found to be favorable for higher alcohol synthesis [7, 28, 36] which indicates that higher alcohols are formed at a slower rate than methanol [12, 13]. Low space velocities are also favorable for high conversion [13, 36].

Figure 2.4 shows the effect of decreasing space velocity (6000-1000 h⁻¹), represented by increasing conversion. It is evident from the figure that a decrease in space velocity increased higher alcohols, methane, and CO₂ selectivities and decreased methanol selectivity. Interestingly, the selectivity toward aldehydes goes through a maximum at about CO conversion of 6.4% [13].
2.1.6 Effect of CO₂

Syngas generated from biomass contains up to 25% of CO₂. Therefore it would be preferred in an industrial setting to synthesize catalysts that can covert CO₂ to higher alcohols because this would eliminate the CO₂ removal step in upstream [3]. Unfortunately, CO₂ typically has a negative impact on higher alcohol synthesis, but has a promoting effect on methanol formation [2, 15]. However, in some cases it is reported that CO₂ inhibits the formation of both methanol and higher alcohols [12, 25], or only of higher alcohols [11]. Another drawback of CO₂ addition is that it enhances methanation [12, 15]. Hilmen et al. [25] ascribed this to high oxygen coverage and therefore reduction in the number of reduced Cu atoms available for methanol and higher alcohol synthesis. Higher alcohol productivity (g/kg/h) is also decreased by
neutralization of basic sites (responsible for chain growth) by CO₂. Another possible explanation could be the blockage of active sites by reversible preferential adsorption of CO₂ [12].

However, on some catalysts low levels of CO₂ (2-6%) were found to increase higher alcohol productivity (mol/l/h) [13], yield [20], and rate of formation (mg/g/h) [30]. For example, Calverley [20] reported that CO₂ is directly involved in the synthesis of higher alcohols. Addition of CO₂ enhanced higher alcohols yield when the loading was 0.5% K₂CO₃ but was not beneficial at higher K-loading (4%). Higher alcohol yield passes through a maximum (4% CO₂) for both unpromoted and promoted catalysts, similar behavior was observed for methanol. Because of these similarities it can be said that CO₂ also participates in higher alcohol synthesis since CO₂ was already believed to participate in methanol synthesis [38, 39]. It appears that copper/alkali interface sites convert CO to methanol and higher alcohols and Cu site convert CO₂ to methanol and higher alcohols [20].

2.1.7 Role of Support

Interaction of support and active components can significantly alter selectivity to ethanol and higher alcohols. For example, Nunan et al. [21] showed that ethanol yield remained almost constant Cs loading over Cu/Zn/Cr catalysts, however it decreased [21] on Cu/Zn/Al. They also reported that a much higher level of Cs was needed for Cu/Zn/Cr catalyst than Cu/Zn because of Cr is acidic in nature and therefore more Cs is needed to neutralize this catalyst. Cu/ZnO/Cr₂O₃ produced more C₂⁺ alcohols and hydrocarbons than Cu/ZnO/Al₂O₃ but the latter produced more total alcohols. However, at the reaction conditions used, both catalysts gave almost identical products.
2.1.8 Reaction Pathways

There can be several reactions occurring in parallel during CO hydrogenation. Table 2.2 shows some of the main reaction occurring [37]. Reaction a shows that a specific stochiometric combination of CO and H\textsubscript{2} produces alcohols and also the side product H\textsubscript{2}O. Reaction b and c shows another stoichiometry produces alcohol and the side product CO\textsubscript{2}. Reaction c is the water-gas shift reaction. Reaction d and e produce hydrocarbons. Reaction f produces aldehydes. Third type of reaction so called ‘consecutive reactions’ g, h, and i produce ester, ketones and β alkyl oxygenated compounds. These consecutive reactions are favored at low H\textsubscript{2}/CO ratios. All these main and side reactions are not thermodynamically limited in the operating temperature range (250-350 °C) other than methanol and water-gas shift reaction.

Several mechanisms for the formation of ethanol have been suggested in the literature [1-4] and some of the main reaction mechanisms are discussed here. The mechanisms discussed here are only for the formation of ethanol synthesis.

In order to find if the formation of methanol and higher alcohols are related, Elliott et al. [30] poisoned the methanol synthesis sites by adding cobalt [40]. The poisoning reduced the activity of the catalyst by more than an order of magnitude. It also inhibited the formation of both methanol and higher alcohols indicating that their formation is related. But it could not be verified using these results that a decrease in formation of higher alcohols is due to poisoning of catalytic sites active for higher alcohols or due to decrease in methanol. To determine this, they added methanol to the feed on a poisoned (with Co) catalyst. But still the formation of higher alcohols on poisoned catalyst was much lower than the unpoisoned one, suggesting that a decrease in the formation of higher alcohols was directly due to the poisoning of sites active
for higher alcohols and not due to methanol. This shows that syntheses of methanol and higher alcohols are related because they share a common active site or perhaps have the same intermediate.

Table 2.2 Reactions occurring during CO hydrogenation [37]. (Reproduced with permission from ref [37]. Copyright © 1990, OIL & GAS SCIENCE AND TECHNOLOGY - REVUE DE L'IFP.)
In another study, over a CuO/ZnO/Al$_2$O$_3$ catalyst, Elliott et al. [31] suggested that the precursor for the formation of methanol and ethanol are the same based on their experimental results where they used labeled methanol. The mechanism suggested by them is shown in Figure 2.5. It shows that syngas (CO and H$_2$) or methanol could form an adsorbed C1 species and that serves as a common precursor for both methanol and ethanol consistent with their previous study [30].

![Figure 2.5 Paths for the formation of methanol and ethanol [30].](image)

Later, Calverley et al. [20] supported the above mechanism. They observed that the yield of methanol and higher alcohol showed a maximum with alkali addition. Two possible reasons were given for this observation:

1. Formation of methanol needs Cu sites whereas higher alcohol synthesis needs alkali sites; with an increase in alkali loading methanol formation decreases which in turn deceases the production of higher alcohols.

2. Higher alcohol synthesis needs a Cu-alkali interface which increases and then decreases with alkali loading. However, the hypothesis that the formation of methanol and higher alcohols requires two different sites was later refuted by their own experiments. When methanol was added to an alkali promoted catalyst the production of higher alcohols did not increase even at higher alkali loadings. This means methanol and higher alcohols need the same type of sites.
Nunan et al. [19] proposed an alternative route for higher alcohol synthesis on a Cs/Cu/ZnO catalyst. Ethanol formation was studied by feeding $^{13}$C-enriched methanol with syngas. Isotopic labeling showed that methanol is a major source of both carbons of ethanol. Methanol synthesis is shown schematically in Figure 2.6. CO activation occurs by Cs$^+$ and its OH$^-$ ion and an adsorbed formate species forms. Then, in the second step (rate-limiting) hydrogenation occurs to produce an adsorbed formyl intermediate. Hydrogenation of this formyl group results in formaldehyde in the third step, which then transforms to methoxide in step 4. Finally hydration produces methanol in step 5.

Figure 2.7 shows the reaction scheme for ethanol synthesis. The C-C bond in ethanol formed via coupling of the C1 intermediates originating from methanol. First, one methanol molecule forms an adsorbed formyl group and another becomes formaldehyde after dehydrogenation. Then, a nucleophilic attack of the adsorbed formyl on formaldehyde produces C2 precursor and finally this precursor leads to ethanol after hydrogenation.

Figure 2.6 Mechanism for methanol formation from CO hydrogenation on Cu-based catalysts [2, 19]. (Reproduced by permission of The Royal Society of Chemistry)
An alternative scheme was suggested by Stiles et al. [15, 41] shown in Figure 2.8. According to them the actives sites are lattice–deformity sites rather than metallic. In the chain initiation step, hydrogenation of CO forms an adsorbed formaldehyde. In the chain termination step, further hydrogenation of formaldehyde produces methanol. But if the chain growth takes place then acetaldehyde forms from the incorporation of methylene radical into the formaldehyde and then immediate hydrogenation of acetaldehyde produces ethanol. Methane and higher hydrocarbons are formed from hydrogenation of methylene radical (CH$_2^*$).

![Figure 2.7 Mechanism for ethanol formation from CO hydrogenation on Cu-based catalysts [2, 19]. (Reproduced by permission of The Royal Society of Chemistry)](image)

On a Mn/Cr/Th promoted CuO/ZnO/Al$_2$O$_3$, Hofstadt et al. [28] suggested that a Cu$^+$-ZnO phase favors the formation of an oxygen containing species (CH$_3$O) and metallic copper mostly favors the formation of methylene structure (CH$_2$). They assumed that promoters such as Mn, Cr, and Th can affect the Cu$^+$/Cu$^0$ ratio and thus favor the formation of C2$^+$ alcohols. They
suggested that methanol is formed by hydrogenation of CH\textsubscript{3}O species. CH\textsubscript{3}O and CH\textsubscript{2} species combine to form C2 precursor and finally hydrogenation of this precursor produces ethanol.

Figure 2. 8 Mechanism for the formation of alcohols [15, 41]. (Reproduced with permission from ref [15]. Copyright © 1991, Elsevier.)
Subramani et al. [3] suggested the following generalized mechanism for the formation of ethanol on modified Cu-based catalysts (Figure 2.9). First, an adsorbed formyl species forms from adsorbed CO and H₂. Then, the formaldehyde forms via the hydrogenation of this formyl species. Further hydrogenation produces methanol. Then, the two adsorbed formyl species react to form an adsorbed acetyl species. Finally ethanol is formed after the hydrogenation of the acetyl species.

![Figure 2.9 Ethanol formation by CO hydrogenation via a chain-growth mechanism over modified methanol synthesis catalysts [3]. (Reproduced with permission from ref [3]. Copyright © 2008, Elsevier.]

2.1.9 Novel Catalysts

Most of the catalysts for ethanol and higher alcohols from syngas have been prepared by conventional preparation methods such as co-precipitation and impregnation. In order to further improve the activity and selectivity toward ethanol and higher alcohols, some workers used non-conventional catalysts such as Co-Cu based perovskites [42-44], Rh-Mn-Fe-Li [45] and Co-Cu [46] supported on carbon nanotubes, Co-Cu nanoparticles [47], sol-gel-derived ZrO₂ [48], K/Co/β-Mo₂C [49, 50], ultrafine Mo-Co-K [51].
In an effort to utilize high surface area of carbon nanotubes (CNTs), Pan et al. [45] used Rh-Mn and Li and Fe promoters (4-8 nm inner dia, 250-500 nm in length) to synthesize ethanol from CO and H\(_2\). Active components of the catalysts were incorporated in and onto these nanotubes by immersing these tubes in aqueous solution of salts of these metals and promoters. The suspension was ultrasonicated and stirred to assist in the filling of these tubes via capillary force. Maximum ethanol selectivity was 31.4 %C and that of C\(_2\) oxygenates (including ethanol) was 41.3 %C at reaction condition: 30 bar, H\(_2)/CO=2\), 12,000 h\(^{-1}\), 330°C when 80% of the active metal was on the inner surface of nanotubes. Selectivity to methane decreased to about 15% from 41% over a similar metal-promoter combination on supported SiO\(_2\). Another interesting finding was that the ethanol production rate on the internal surface exceeded more than an order of magnitude than the external surface. The authors attributed this to the expedited dissociation/activation of CO and higher hydrogenation rate on the inner surface than the exterior because of different metal-support interaction. These catalysts seem to be promising in terms of selectivity to ethanol, however, selectivity as high as 61.4 %C has been reported earlier for Rh-based catalysts [52]. Nevertheless, their high yield (35%) and no deactivation after 180 h make these nanotubes a promising catalyst for ethanol and other C\(_2\) oxygenates.

Conventional catalyst preparation techniques do not typically control particle size and shape. With novel methods such as wet-chemical method this can be achieved. To take advantage of the high surface area of nanomaterials, Subramanian et al. [47] synthesized Co-Cu nanoparticles by a wet-chemical method. Two types of nanoparticles were prepared: 1. Co core-Cu shell 2. Co-Cu-mixed nanoparticles. They found that an increase in temperature from
230°C to 270°C increased selectivity toward methanol, ethanol, and CO₂ and reduced methanation in some catalysts. Further increase to 300°C enhanced the selectivity toward ethane and higher hydrocarbons. Mixed metal catalysts had higher selectivity toward ethanol and higher oxygenates. Core-shell (Co core and Cu shell) catalysts were more active but less selective to ethanol. Higher Cu content produced more ethanol at 230°C but this trend was not observed at 270°C and 300°C. For Co-Cu-mixed nanoparticle catalysts - methanol, ethanol, and CO₂ selectivities go through a maximum with temperature. This was attributed to the sintering of nanoparticles at higher temperature. The highest selectivity toward ethanol was 11.4 C%. These catalysts seem to be promising owing to their high surface area and low pressure (20 bar) requirement. Further changes in morphology that can enhance the mutual interaction of reduced Co and Cu [44] may prove these catalysts more suitable for ethanol and higher alcohols synthesis.

2.2 Electrodeposited Nanowires/tubes

Possin was the first to demonstrate the electrodeposition of nanowires in a membrane/template [53]. These nanowires were composed of tin, indium, and zinc. Nanowires of different elements have been electrodeposited for a variety of applications [54, 55]. A comprehensive overview of the membrane/template based preparation method of wide variety of nanowires has been covered in several reviews [55-58].

Electrodeposition of nanowires has become an attractive field since the inception of GMR (Giant Magnetoresistance) [54, 59]. There are several techniques to make magnetic multilayers such as molecular beam epitaxy (MBE), thermal evaporation and ion beam
sputtering [60]. Nonetheless, electrodeposition is a cost effective alternative, with other advantages such as simplicity of method and high throughput.

Successful deposition of nanowires in pores depends on several factors such as applied current/potential, pulsed or direct current (DC) plating, pH, concentration, stirring, purity of solute and solvent, additives, current distribution, formation of gas bubble [55] in addition to the thermal, chemical and physical properties of the membrane [61]. For example, when the applied voltage is low, the nanowires consisted of a single crystal [62] and when the applied current was too high/low uniform wires were not obtained [63].

Metal/oxide nanowires of Mn, Cu, and Zn are of particular interest for their superconductivity [64], electrochemical capacitors [65], piezoelectric devices, sensors and solar catalysts [66] and have been fabricated by several research groups using templates. Combination of such metal/oxide nanowires might yield novel materials having superior applications. To exploit the higher surface areas of nanowires, Oh et al. [67] electrochemically deposited n-p and/or p-n nanocolumnar junction structures of Cu$_2$O, ZnO on Ni nanowires using a commercially available alumina template. An optimal potential of -1 V and a current density of -0.5 mA/cm$^2$ were applied for the electrodeposition of ZnO and Cu$_2$O, respectively. Such novel structures might respond more favorably than conventional n-p junction thin films due to its high surface active area and may eventually lead to the development of small-scale piezoelectric devices and sensors.

Electrodeposition of Mn-Cu-ZnO nanowires is reported by only one group [68, 69]; however, pulse electrodeposition of these types of nanowires has not been reported. Sima et al. [68] reported the preparation of ZnO/Mn/Cu nanowire arrays by electrodeposition from an
electrolyte containing nitrates of Mn, Cu, and Zn and lactic acid. ZnO/Mn/Cu nanowires were electrodeposited at -0.7 V vs SCE. The nanowires contained 68.98 at% Zn, 30.11 at% Cu and 0.91 at% Mn. Majority of the nanowires were about 5 micron long and 700 nm thick.

Nanowires/tubes can be fabricated using direct current (DC) or pulse electrodeposition. Pulse electrodeposition is preferred over DC deposition because latter does not result in uniform filling of the pores due to excessive cathodic side reaction that leads to local deposition in a single pore. Also, during DC plating, high reduction current/potential leads to excessive hydrogen evolution that can affect the deposition rate [70]. Pulse electrodeposition plays an important role when a desired composition of two or more metal/oxide having disparate reduction potentials is needed. Pulse electrodeposition gives more uniformity in composition of the alloy [71, 72]. During DC plating, atomic hydrogen is incorporated into the crystal lattice as a hydride, resulting in cracked deposit, whereas in pulse electrodeposition hydrogen atoms discharged during the on-time combine to form hydrogen gas during the off-time [73].

Table 2.3 shows the effect of pulse plating on the composition and microstructure of metals and alloys [74]. Pulse plating favors uniform current distribution. It also helps to reduce mass transport effects. It can control the microstructure, morphology, and composition in a better way than DC plating.

   Typical pulse schemes may include [75]:

1. Cathodic pulse followed by an off-time,
2. Cathodic pulse followed by an anodic current,
3. DC with superimposed modulations,
4. A train of cathodic pulses followed by a train of anodic pulses,
5. Modified sine-wave or Square-wave pulses,


A detailed account of pulse electrodeposition method can be found in this book [76].

Table 2.3 Possible effects of pulse electrodeposition on deposit structure [74]

<table>
<thead>
<tr>
<th>Time interval</th>
<th>Conditions that differ from d.c. plating</th>
<th>Phenomena affected</th>
</tr>
</thead>
<tbody>
<tr>
<td>On-time</td>
<td>Double layer charging</td>
<td>Nucleation rate</td>
</tr>
<tr>
<td></td>
<td>Overvoltage</td>
<td>Growth mechanism (e.g. dendrites)</td>
</tr>
<tr>
<td></td>
<td>Concentration profile near electrode</td>
<td>Electrode reaction mechanism</td>
</tr>
<tr>
<td></td>
<td>Adsorption (ions, additives, hydrogen)</td>
<td>Codeposition rate (H, alloy elements)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Additive reactions</td>
</tr>
<tr>
<td>Off-time</td>
<td>Double layer discharge</td>
<td>Surface diffusion</td>
</tr>
<tr>
<td></td>
<td>Potential relaxation</td>
<td>Surface recrystallization</td>
</tr>
<tr>
<td></td>
<td>Concentration profile relaxation</td>
<td>Corrosion, displacement reactions</td>
</tr>
<tr>
<td></td>
<td>Desorption (additives, ions, hydrogen)</td>
<td>Passivation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hydrogen diffusion</td>
</tr>
<tr>
<td>Pulse reverse-time</td>
<td>Anodic potential</td>
<td>(Selective) metal dissolution</td>
</tr>
<tr>
<td></td>
<td>Sign change of double layer charge</td>
<td>Hydrogen reoxidation</td>
</tr>
<tr>
<td></td>
<td>Concentration profile near electrode</td>
<td>Additive oxidation</td>
</tr>
<tr>
<td></td>
<td>Desorption/adsorption (additives, ions)</td>
<td>Passivation</td>
</tr>
</tbody>
</table>

Pulse electrodeposition has been applied for nanowires/tubes synthesis such as Cu/Co [77-79], Ni/Cu [60], CoNiCu [60], Bi2Te3 [80], Co/Pt [81]. It has also been used for several single metal/oxide nanowires; a few examples are Fe [82], ZnO, Cu, Cd [83], Pb [84], and Ni [70].

Nanotubes of different materials using DC or pulse electrodeposition have also been reported in the literature [85-90]. When a polycarbonate membrane is used, the reason for the formation of nanotubes is the attraction of ions in the electrolyte and the ‘molecular anchors’ provided by the pore wall [85, 86]. Gas formed during electrodeposition further helps in tube formation as gas pushes the material toward the wall [85].
Only the first pulse scheme i.e. cathodic pulse followed by a rest/off-time is discussed here due to the scope of this dissertation. It was reported that the off-time improved the homogeneity of the deposit [70, 80] and also reduced the formation of hydrogen [70]. This was ascribed to the replenishment of ions during the off-time therefore resulting in a more uniform distribution of ions at the deposition interface. Off-time also has a better control over crystallinity of the deposit [80, 84].

2.3 References


CHAPTER 3: EXPERIMENTAL DESIGN

All the chapters have their own experimental section in brief. In this chapter, all experimental methods are covered in more detail.

3.1 Synthesis of Nanowire/tube Catalysts

3.1.1 Electrodeposition Set Up

The experimental setup for the synthesis of nanowire/tube catalysts is shown in Figure 3.1. Nanowire/tube catalysts were fabricated using a direct current (DC) or pulse electrodeposition in a typical three-electrode cell. The working electrode (cathode) was a gold sputter coated (one side) hydrophilic Polycarbonate Track Etch (PCTE) membrane supplied by Sterlitech Corporation, WA. The membranes were either 10 or 25 µm thick (pore length) and had pores of 400 nm in diameter. The pore density of 10 and 25 µm thick membranes were $1 \times 10^8$ pores/cm$^2$ and $1.5 \times 10^8$ pores/cm$^2$, respectively. Gold was coated on one side of the membranes to block pores and provide a conductive film. The gold surface was kept in contact with a copper plate held inside a polyetheretherketone (PEEK) stationary holder. The counter electrode was either a 99.9% Zn sheet or a platinized Ti-mesh. The reference electrode was an Accumet saturated calomel electrode (SCE).

The cell was kept inside a water bath to maintain the required temperature at 60±2°C. Electrolyte was magnetically stirred at 320 rpm during an experiment. The reactor was immersed in a 5L glass beaker, with the electrolytes with compositions given in Table 3.1. The concentration of Cu was always kept much lower than the concentration of Zn and Mn because of its lower reduction potential. NH$_4$NO$_3$ was added because it was observed that the presence of ammonia in the baths increased the reduction potential of copper [1].
3.1.2 Potentiostat/galvanostat

Experiments with DC and long current pulses (more than 2 s) were performed using an IM-6e potentiostat/galvanostat/impedance spectrometer/function generator manufactured by BAS Zahner. A VersaSTAT3 advanced dc voltammetry system manufactured by AMETEK Princeton Applied Research, was used for experiments with very short pulses (in ms).

Table 3.1 Electrolytes for the synthesis of nanowire/tube catalysts

<table>
<thead>
<tr>
<th>Electrolyte (Used in chapter)</th>
<th>Initial pH</th>
<th>Cu(NO$_3$)$_2$ (M)</th>
<th>Zn(NO$_3$)$_2$ (M)</th>
<th>Mn(NO$_3$)$_2$ (M)</th>
<th>NH$_4$NO$_3$ (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>5.0</td>
<td>0.001</td>
<td>0.05</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>4</td>
<td>4.4</td>
<td>0.002</td>
<td>0.05</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>4</td>
<td>4.2</td>
<td>0.002</td>
<td>0.05</td>
<td>0.02</td>
<td>0.05</td>
</tr>
<tr>
<td>5</td>
<td>4.0</td>
<td>0.002</td>
<td>0.05</td>
<td>---</td>
<td>0.05</td>
</tr>
<tr>
<td>6</td>
<td>4.2</td>
<td>0.002</td>
<td>0.05</td>
<td>0.02</td>
<td>0.05</td>
</tr>
</tbody>
</table>
3.1.3 Template Based Synthesis Technique

Nanowires/tube catalysts were electrodeposited by using a template synthesis technique [3-6]. A top view of an actual membrane can be seen in Figure 3.2. Membranes were gold coated on one side to block pores and provide a conductive layer. The coating was done for 10-12 min in an inert environment (vacuum≈70 millitorr) of argon by a Hummer II sputter coater. The potential and current applied for the plasma formation was 6.5 V and 10 mA, respectively. Figure 3.3 is the schematic of the template based synthesis method. When an appropriate current was applied to the electrolyte/solution, ions started to deposit as metals/oxides from the bottom of the pores. After electrodeposition, the polycarbonate membrane was washed with de-ionized water and dried in the oven at about 65°C for 20 min. After that, it was dissolved in methylene chloride (CH₂Cl₂) solution. Thereafter, the solution was sonicated for at least 30 min to break the entangled nanowires. Centrifugation was done to separate the nanowires from rest of the solution. Separated nanowires were then dried at 110 °C in the oven for 12 h.

Figure 3.2 Top view of a PCTE membrane [7].
3.1.4 Applied Current DC/Pulse Schemes

Nanowires were both DC as well as pulse electrodeposited. In DC electrodeposition, current is applied for a specified period without any rest/off-time. A typical pulse scheme is shown in Figure 3.4.

![Diagram](image)

Figure 3.3 Schematic for nanowires fabrication (i) cross-sectional view of cylindrical pores in a polycarbonate membrane, (ii) gold sputtered membrane, (iii) filled pores after electrodeposition, and (iv) nanowires after dissolution of membrane in CH$_2$Cl$_2$. (Reproduced with permission from ref [2]. Copyright © 2009, Elsevier.)

3.1.5 Reversible Electrode Potential (E)

All the potentials reported in the present study are either standard reduction potential ($E^0$) or reversible electrode potential (E) vs SCE, the latter were calculated using the Nernst equation. Ion-ion interaction was assumed to be zero at low concentrations and therefore the concentrations of species were used in place of activity. The Nernst equation is given as:

$$E = E^0 + \frac{RT}{zF} \log \frac{[M^{z+}][e]^z}{[M]}$$

Where,
\( E \): Reversible electrode potential (V)

\( E^0 \): Standard reduction potential (V)

\( z \): electrode transferred in a reaction

\([M]\): activity of metal ‘M’ (1 in solids)

\([e]\): activity of electron (1 in solids)

For example, for the following reaction:

\[
\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}
\]

\( E \) is 0.01 V.

![Figure 3.4 Pulse scheme for nanowires.]

### 3.2 CO Hydrogenation (Syngas Conversion)

CO hydrogenation studies were performed in a tubular fixed bed reactor. First, 10% O\(_2\) in He was passed through the catalyst for 2 h at 400\(^\circ\)C to oxidize any carbon left after dissolution of the polycarbonate membrane. This step was also done with the co-precipitated catalyst to have the same pretreatment condition. Then, the catalyst was reduced using pure H\(_2\) at 320\(^\circ\)C for 2 h. The reaction was performed at varying temperature, pressure, and H\(_2\)/CO
ratio. Reaction conditions employed are given in respective chapters. The product stream was analyzed by a Gas Chromatography-Mass Spectrometer supplied by Agilent Technologies.

### 3.2.1 Fixed Bed Reactor

The fixed bed reactor (AMI-200R-HP) was manufactured and supplied by Altamira Instruments, Inc. Figure 3.5 is the schematic of the reactor system. Ultra high purity (UHP) gases supplied by various vendors (for eg., Airgas, Capitol Welders) were fed to the reactor at different inlets. Flow rates of gases were controlled and monitored by mass flow controllers (5850E) manufactured by Brooks Instrument. The reactor is controlled by the AMI 2000 software.

Catalysts were placed inside a glass lined reactor tube (0.25“ OD, 0.15” ID, 12” long; stable to about 800 C; manufacturer: SGE Incorporated) using quartz wool as shown in Figure 3.6. Reactant gases were fed to the bottom of the reactor. Products were fed into Agilent GC-MS (discussed in the next section) for online analysis. Reactor system also has a thermal conductivity detector (TCD) and a Quadrupole Mass Spectrometer/Residual Gas Analyzer supplied by GOW-MAC Instrument CO. and Ametek, respectively. TCD was used during the temperature programmed reduction (TPR) experiments.

### 3.2.2 Gas Chromatograph–Mass Spectrometer (GC-MS)

GC-MS was a 6890N Network GC System supplied by Agilent Technologies. System configuration/instrumentation was done by Wasson ECE. The instrument was equipped with a 5975B Mass Selective Detector (MSD), connected to the GC via a heated transfer line. The GC also had two TCDs, mounted on its top. UHP grade Helium was the carrier gas for both MSD and
Figure 3.5 Schematic of the reactor [13].

Figure 3.6 Closer view of the tube reactor.
front TCD. Rear TCD was for hydrogen analysis; therefore carrier gas was N\textsubscript{2} because He and H\textsubscript{2} have very small difference in their thermal conductivities.

There were two separate methods for detection of product gases on MSD. A detailed plumbing schematic of columns is given in Appendix A. The system is equipped with several columns as can be seen in the Figure A. However, only columns used in this work are discussed here. First method detected and quantified methanol, ethanol, i-propanol, n-propanol, n-butanol, i-butanol acetone, acetaldehyde, i-butyne, n-butyne, and hexane. Column 5 was used to separate these analytes. Second method was used to quantify light gases - CO, methane, CO\textsubscript{2}, ethane, propadiene, propylene, and propane. Column 4 was used to accomplish this. Column 3a & b were guard columns so that heavier gases do not enter the Column 4. All the columns discussed here were proprietary capillary types supplied by Wasson ECE with no further detail except that shown in Table 3.2.

Table 3.2 GC column specifications

<table>
<thead>
<tr>
<th>Column no.</th>
<th>ID (mm)</th>
<th>Length (m)</th>
<th>Max temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>0.53</td>
<td>15</td>
<td>220</td>
</tr>
<tr>
<td>3b</td>
<td>0.53</td>
<td>1</td>
<td>165</td>
</tr>
<tr>
<td>4</td>
<td>0.53</td>
<td>50</td>
<td>210</td>
</tr>
<tr>
<td>5</td>
<td>0.25</td>
<td>100</td>
<td>210</td>
</tr>
</tbody>
</table>

Operation and data analysis of the GC-MS system were controlled by the Agilent ChemStation software. The system was calibrated frequently and a set of calibration files is presented in Appendix B.
3.3 Characterization

3.3.1 H₂ Temperature Programmed Reduction (H₂ TPR)

TPR studies were performed in order to determine different oxidation states of species present in a catalyst that are reducible in the temperature range (30-500°C) studied. TPR also provided qualitative information about the interaction of different species. TPR experiments were carried out at atmospheric pressure using the AMI-200R-HP reactor discussed earlier. The catalyst was placed in the tubular reactor between two quartz wool plugs as shown in Figure 3.6. First, He was flown at 120°C for 30 min and then cooled down to 30°C to remove any moisture present in the catalyst due to the atmospheric exposure during storage/transfer. Then, 10% H₂/Ar with a flow rate of 100 scc/min passed through the catalyst and temperature was ramped from 30°C to 470°C at the rate of 10°C/min. A TCD was used to record the signal generated from the hydrogen consumption by the catalyst.

3.3.2 Inductively Coupled Plasma-Optical/Atomic Emission Spectrometry (ICP-OES/AES)

The bulk elemental analysis was performed by a Perkin Elmer Optima 3300 DV dual view ICP-OES and a Varian Vista AX CCD Simultaneous ICP-AES.

3.3.3 X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES)

X-ray Photoelectron Spectroscopy and Auger Electron Spectroscopy analyses were done with a PHI Quantum 2000/PHI 5600 and a SSX-100 (Surface Science Instruments) having an x-ray source of monochromated Alkα (hv = 1486.6 eV). Charge correction was done by using the signal C1s (B.E. = 284.8 eV) from adventitious carbon. BE calibration was done by monitoring the BE difference between a Au and Cu metal foil.
3.3.4 X-ray Diffraction (XRD)

The XRD patterns were obtained with an automated X-ray powder diffractometer (Bruker/Siemens D5000, CuKα radiation).

3.3.5 Scanning Electron Microscopy (SEM)

The SEM imaging was done by a JSM-840A manufactured by JEOL, operated at accelerating voltage of 15-20 kV, beam current: 1-5 nA, and working distance of 10-25 mm. High resolution TEM imaging was done by a FEI TITAN 80-300, operated at 200 kV.

3.4 References


CHAPTER 4: ELECTRODEPOSITED Cu-ZnO AND Mn-Cu-ZnO NANOWIRE/TUBE CATALYSTS FOR HIGHER ALCOHOLS FROM SYNGAS

4.1 Introduction

The synthesis of higher alcohols from syngas has attracted attention recently as these compounds have been studied for use as neat fuels and fuel additives [1], as well as hydrogen carriers [2, 3]. Because syngas can be produced from a wide range of feedstocks such as biomass, coal, and natural gas, the choice of higher alcohols as a potential end product is attractive given the wide range of possible end uses for these oxygenates.

The hydrogenation of CO to produce $C_2^+\text{ alcohols has been studied on a number of catalysts, including supported rhodium [4], modified Fischer-Tropsch catalysts [5], sulfides [6], and promoted Cu-based catalysts [7]. Although Rh-based catalysts typically show the greatest selectivity to higher alcohols, the high cost of rhodium may limit its use in large-scale processes. The relatively low cost of Cu-based catalysts, and the fact that they can be modified to increase their selectivity to higher alcohols, suggest that these materials be studied further. Much of the work reported on these catalysts is based on the addition of alkali promoters to methanol synthesis catalysts. However, the hydrogenation of CO to produce higher alcohols is typically limited by low selectivities due to excessive methane and CO$_2$ formation [2, 8].}

Catalysts for the synthesis of higher alcohols have most often been prepared by conventional methods such as wet impregnation and co-precipitation. Recently, there has been increased interest in developing novel synthesis approaches such as coating of nanoparticles [9], and the use of shape-selective carbon nanotubes as supports [10].

---

Here, we report a novel synthesis method to prepare Cu-based catalysts to synthesize alcohols from syngas, based on electrodeposited nanowires and nanotubes of Cu-ZnO and Mn-Cu-ZnO. Electrodeposition is a process in which metals/oxides are deposited on a substrate (cathode) from an aqueous salt solution when an appropriate current/potential is applied. The main advantage of electrodeposition over conventional techniques is the control of the active metal environment, a critical property of a catalyst.

In the present study, two types of catalysts prepared by electrodeposition are compared: Cu-ZnO catalysts representing an unpromoted methanol synthesis catalyst, and Cu-Mn-ZnO, a nominally similar catalyst promoted with Mn. The choice of Mn as a promoter is based on its reported ability to increase selectivity to higher alcohols [7], and the fact that it can be electrochemically co-reduced with Cu in the electrodeposition process used here. Although alkali metals are often used as promoters for Cu-based catalysts [11], their high negative reduction potential, limits the ability to electrodeposit them along with Cu.

To the best of our knowledge, electrodeposited Cu-Zn-based nanowires have not been used as heterogeneous catalysts. However, electrodeposition of ZnO nanowires has been studied for their application in solar cells and sensors [12, 13]. Electrodeposited nanowires of Cu$_2$O have been examined for their photocatalytic properties [13, 14], and Cu-Mn-ZnO nanowires have been prepared to enhance the semiconducting properties of ZnO [15]. Electrodeposition of nanowires has become an attractive field since the inception of GMR (Giant Magnetoresistance) [16]. A comprehensive overview of the method and its applications can be found elsewhere [17-19].
4.2 Experimental

4.2.1 Electrodeposition

The experimental setup for the electrodeposition of the Cu-based catalysts is shown in Figure 4.1. A gold sputtered polycarbonate membrane (Sterlitech®) was used as cathode. The counter electrode was a 99.9% Zn sheet. The reference electrode was an Accumet® saturated calomel electrode (SCE). The electrolytes were aqueous solutions containing varying amount of nitrates of Cu, Zn, Mn, and NH₃. The cell was kept inside a water bath to maintain the required temperature (60±2°C). Electrolytes were magnetically stirred during experiments to ensure proper mixing of ions and to prevent depletion of ions near the electrode surface. Experiments were performed using an IM-6e potentiostat/galvanostat/impedance spectrometer supplied by BAS Zahner.

![Figure 4.1 Electrochemical Deposition Setup. (1) Electrolyte, (2) Cathode (gold sputtered polycarbonate membrane), (3) Anode (99.9 % pure Zn plate), (4) Reference Electrode (saturated calomel electrode), (5) Computer, and (6) Potentiostat.

The nanowires/tubes were electrochemically deposited by using a template synthesis technique [19] in which an appropriate current/potential is applied to the solution, causing the
metals/oxides to deposit within the pores of the gold-sputtered membrane (Figure 4.2). The pore length and diameter of the membrane were 10 μm and 400 nm, respectively. After deposition, the membrane was dissolved in CH$_2$Cl$_2$ and sonicated for 30 min to release the nanowires/tubes.

![Figure 4.2 Schematic for nanowires fabrication](image)

(i) 10 μm pores (ii) After gold sputtering (iii) 400 nm pores (iv) Gold layer

Nanowires/tubes

After membrane dissolution

Figure 4.2 Schematic for nanowires fabrication (i) cross-sectional view of cylindrical pores in a polycarbonate membrane, (ii) gold sputtered membrane, (iii) filled pores after electrodeposition, and (iv) nanowires after dissolution of membrane in CH$_2$Cl$_2$.

4.2.2 Characterization

The bulk elemental analysis was done by a Perkin Elmer Optima 3300 DV dual view inductively coupled plasma optical emission spectrometer (ICP/OES). The SEM imaging was done by a model JSM-840A manufactured by JEOL. The XRD analysis was carried out by a Bruker/Siemens D5000 automated powder X-ray diffractometer.

Temperature programmed reduction (TPR) was carried out at atmospheric pressure using an Altamira AMI-200R-HP. First, 10% O$_2$ in He was passed through the catalyst for 2 h at 400°C to oxidize any carbon left after dissolution of the polycarbonate membrane. TPR was
then carried out in 10% H₂/Ar with a flow rate of 100 scc/min and temperature was ramped from 30°C to 470°C at the rate of 10°C/min.

4.2.3 Syngas Reaction

The fixed bed reaction studies were also carried out in the Altamira AMI-200R-HP. First, 10% O₂ in He was passed through the catalyst for 2 h at 400°C. Then, the catalyst was reduced using pure H₂ at 320°C. The reaction was performed at 270°C, 10-20 bar, and H₂/CO ratio of 2/1. The product stream was analyzed by a 5975x Gas Chromatography-Mass Spectrometer (model: G3171A) supplied by Agilent Technologies.

4.3 Results and Discussion

4.3.1 Electrodeposition

First, appropriate current densities were found using polarization curves. An example of polarization curve is shown in Figure 4.3, representing the effect of potential (V) on current (I) when a potential is applied to the electrode (2) in Figure 4.1. It relates a range of total current densities with potential. When the applied potential (V) is low, the current (I) varies linearly with potential. At slightly higher potential, the I-V relationship is exponential (kinetically controlled). When the potential is yet higher, the rate becomes mixed controlled (kinetic and mass transport), and finally at even higher potential the rate of deposition is controlled by mass transfer [20].

In Figure 4.3, the left side of the vertical line at about -0.20 V represents a region where there is mostly copper deposition. Copper was deposited according to the following reaction [21], where E° is the standard reduction potential:

\[ \text{Cu}^{2+} + 2e^- \rightarrow \text{Cu} \quad (E^o=+0.10 \text{ V}) \]  (1)
Copper deposition was found to be mass transfer controlled, since increasing potential from -0.05 V to -0.23 V did not increase the current density significantly.

Figure 4.3 Polarization curve of electrolyte containing 0.002 M Cu(NO$_3$)$_2$ and 0.05 M Zn(NO$_3$)$_2$.

The sharp increase in the current when potential was more negative than -0.25 V is due to the reduction of nitrate ions as shown in reaction 2. This reaction changed the local pH of the electrolyte from acidic to alkaline:

\[
\text{NO}_3^- + H_2O + 2e^- \rightarrow \text{NO}_2^- + 2OH^- \quad (E^\circ = -0.23 \text{ V}) \quad (2)
\]

The following reactions show the deposition of other species and standard reduction potential ($E^\circ$) vs saturated calomel electrode (SCE).

Cupric oxide can be deposited according to the following reactions [22]:

\[
\text{Cu}^{2+} + 2OH^- \rightarrow \text{Cu(OH)}_2 \quad \text{N/A} \quad (3)
\]

\[
\text{Cu(OH)}_2 \rightarrow \text{CuO} + H_2O \quad \text{N/A} \quad (4)
\]

Cuprous oxide can be deposited according to the following reaction [21, 23]:

\[
2\text{Cu(OH)}_2 + 2e^- \rightarrow \text{Cu}_2O + 2OH^- + H_2O \quad (E^\circ = -0.30 \text{ V}) \quad (5)
\]
Zinc oxide can be deposited via the following sequence of reactions:

\[
\begin{align*}
\text{NO}_3^- + \text{H}_2\text{O} + 2e^- & \rightarrow \text{NO}_2^- + 2\text{OH}^- \quad (E^0=-0.23 \text{ V}) \\
\text{Zn}^{2+} + 2\text{OH}^- & \rightarrow \text{Zn(OH)}_2 \\
\text{Zn(OH)}_2 & \rightarrow \text{ZnO} + \text{H}_2\text{O}
\end{align*}
\]

Cu-ZnO Nanowires

Table 4.1 shows the effect of electrolyte composition on bulk elemental composition for the two Cu/ZnO catalysts. Increasing copper ions concentration from 0.001 M to 0.002 M at constant zinc concentration increased the copper content in the nanowires.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Electrolyte</th>
<th>Initial pH</th>
<th>Current applied (mA/cm²)</th>
<th>Cu (wt%)</th>
<th>Zn (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.001 M Cu(NO₃)₂ and 0.05 M Zn(NO₃)₂</td>
<td>5.0</td>
<td>-5.18</td>
<td>10.1</td>
<td>89.9</td>
</tr>
<tr>
<td>B</td>
<td>0.002 M Cu(NO₃)₂ and 0.05 M Zn(NO₃)₂</td>
<td>4.4</td>
<td>-5.18</td>
<td>28.6</td>
<td>71.4</td>
</tr>
</tbody>
</table>

To change the atomic level interaction of Cu and Zn, a rest time was introduced, as shown in Figure 4.4. First, a cathodic current was applied for deposition, followed by a rest time (zero current) to avoid depletion of copper ions, with the goal of obtaining both a uniform composition and higher copper content in the nanowires. Current density, deposition time, and electrolyte concentration were held constant to observe the effect of rest time on copper content in nanowires, as shown in Table 4.2. After introducing 20 and 120 s of rest time during electrodeposition the copper content increased from 28.6% to 42.6% and 42.3%, respectively. The change in rest time from 20 to 120 s did not affect the Cu content, indicating that 20 s was
enough time for copper ions to diffuse to the electrode surface, consistent with theory showing that Cu ions will take 0.1 s to reach the electrode surface from bulk for a 10 µm thick membrane. The time is calculated as follows [24]:

\[ t = \frac{l^2}{D} = \frac{(10 \times 10^{-4})^2 \text{ cm}^2}{10^{-5} \text{ cm}^2 \text{s}^{-1}} = 0.1 \text{ s} \]

Where \( t \) is the time, \( l \) is the distance to be traveled, and \( D \) is the diffusion coefficient of the ions.

Table 4.3 Cu-ZnO nanowires with different rest times (Electrolyte: 0.002 M Cu(NO$_3$)$_2$, 0.05 M Zn(NO$_3$)$_2$)

<table>
<thead>
<tr>
<th>Current density (mA/cm$^2$)</th>
<th>Deposition Time (s)</th>
<th>Rest time (s)</th>
<th>wt% Cu</th>
<th>wt% Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>-5.18</td>
<td>7200</td>
<td>0</td>
<td>28.6</td>
<td>71.4</td>
</tr>
<tr>
<td>-5.18</td>
<td>20</td>
<td>20 (short)</td>
<td>42.6</td>
<td>57.4</td>
</tr>
<tr>
<td>-5.18</td>
<td>20</td>
<td>120 (long)</td>
<td>42.3</td>
<td>57.7</td>
</tr>
</tbody>
</table>

Figure 4.5 is an SEM image of these catalysts, showing that they are in the form of nanowires. The thickness and length of the nanowires were 400 nm and 7 µm, respectively.

Figure 4.4 Pulse scheme for Cu-ZnO nanowires.
Figure 4.5 SEM micrograph of nanowires from electrolyte containing 0.002 M Cu(NO$_3$)$_2$ and 0.05 M Zn(NO$_3$)$_2$ and pulse of 5.18 mA/cm$^2$ for 20 s, 0 for 120 s.

**Cu-ZnO Nanotubes**

In addition to nanowires, nanotubes can be produced by electrodeposition. The tube morphology has the advantage of higher surface area, and possibility of shape selectivity which has been shown to increase alcohol selectivity for Rh-based catalysts [10]. Therefore, nanotubes were fabricated using a direct current of -50.8 mA/cm$^2$. One of the possible mechanisms for the formation of nanotubes at this high current density is that hydrogen bubbles formation forces the ions to the wall of the membrane (Figure 4.6), resulting in no deposition in inner parts of the pores [25]. Figure 4.7 shows the nanotubes having inner and outer diameters of 220±20 nm and 400 ±20 nm, respectively, and containing 2 wt% Cu and 98 wt% Zn.
Figure 4.6 Generic schematic of nanotube formation.

Figure 4.7 SEM micrograph of nanotubes from electrolyte containing 0.001 M Cu(NO3)2, 0.01 M Zn(NO3)2, and 0.1 M NH4(NO3)2.

**Mn Promoted Cu-ZnO Nanowires**

Table 4.4 summarizes the synthesis conditions and bulk elemental composition of the Mn-promoted Cu-ZnO nanowires. Manganese is expected to deposit as MnO in the nanowires.
Higher current density was used in order to deposit manganese in the nanowires. Due to the increase in current density from -5.18 to -25.38 mA/cm$^2$, Cu content decreased from 28.6 wt% to 13.5 wt% and ZnO content increased from 71.4 wt% to 82.7 wt% (Table 4.1 and Table 4.4). An increase in current density did not increase the deposition rate of Cu since it was mass transport controlled. However, increasing current density increased the deposition rate of ZnO since it was kinetically controlled, resulting in less Cu and more ZnO in the nanowires. Even though manganese ion concentration in the electrolyte was 10 times more than Cu, the nanowires had more Cu (13.8%) than Mn (3.8 wt%), since Cu is more easily deposited than MnO.

Table 4.4 Deposition conditions and composition of Mn-Cu-ZnO Nanowires

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Initial pH</th>
<th>Current applied (mA/cm$^2$)</th>
<th>Cu (wt%)</th>
<th>Zn (wt%)</th>
<th>Mn (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.002 M Cu(NO$_3$)$_2$,</td>
<td>4.2</td>
<td>-25.38</td>
<td>13.5</td>
<td>82.7</td>
<td>3.8</td>
</tr>
<tr>
<td>0.05 M Zn(NO$_3$)$_2$,</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05 M NH$_4$(NO$_3$)$_2$,</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.02 M Mn (NO$_3$)$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.3.2 CO Hydrogenation

To study the catalytic properties of the nanowires for syngas conversion, reactions were carried out at varying reaction conditions. Table 4.5 summarizes the results from different types of nanowire/tube catalysts.

Cu-ZnO Nanowires

Figure 4.8 shows that an increase in copper content in the nanowires increased the selectivity toward alcohols by reducing the CO$_2$ formation. Methanol selectivity was more than
doubled and ethanol selectivity increased more than 14 times with an increase in copper content. Also, the formation of C3-C4 alcohols significantly increased for the nanowires containing more copper. Increasing Cu content from 10.1 wt% to 28.6 wt% also increased CO conversion from 0.17% to 0.64%, decreased CO\(_2\) selectivity and increased methane selectivity slightly.

Table 4.5 Catalytic performance of Cu-ZnO and Mn-Cu-ZnO nanowires/tubes at H\(_2\)/CO=2/1, P=10 bar, GHSV= 10,000 scc/h-gcat, temp=270°C

<table>
<thead>
<tr>
<th>Catalyst wt%</th>
<th>Morphology</th>
<th>Selectivity (%C)(^a)</th>
<th>CO Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>Zn</td>
<td>Mn</td>
<td>Methanol</td>
</tr>
<tr>
<td>10.1</td>
<td>89.9</td>
<td>-</td>
<td>wire</td>
</tr>
<tr>
<td>28.6</td>
<td>71.4</td>
<td>-</td>
<td>wire</td>
</tr>
<tr>
<td>42.6</td>
<td>57.4</td>
<td>-</td>
<td>wire</td>
</tr>
<tr>
<td>(short rest time)</td>
<td>42.3</td>
<td>57.7</td>
<td>-</td>
</tr>
<tr>
<td>(long rest time)</td>
<td>2</td>
<td>98</td>
<td>-</td>
</tr>
<tr>
<td>13.5</td>
<td>82.7</td>
<td>3.8</td>
<td>wire</td>
</tr>
</tbody>
</table>

\(^a\) Selectivity (%C) = \(\frac{N_C x 100}{\sum N_C_i}\)

Where \(N_i\) is the number of carbon atoms in product and \(C_i\) is its concentration (mol%). The products analyzed by GC/MS but not reported here include higher alkanes, n-hexane, and propylene. Collectively, these products constitute less than 8%.

When the rest time was introduced during electrodeposition, total alcohol selectivity decreased, CO\(_2\) selectivity decreased, and methane selectivity increased (compare Figure 4.8 and 4.9). This difference in their catalytic performance may be due to different compositional uniformity along the length of the nanowires.

Two different rest times of 20 s and 120 s were introduced during electrodeposition. Because the two nanowires prepared using different rest times have the same composition (Table 4.6), and presumably the same compositional uniformity, the same catalytic behavior might be expected; however, there was a significant increase in higher alcohol selectivity for
the nanowires prepared with a 120 s rest time (Figure 4.9). Methane and methanol selectivity remained almost same and CO$_2$ selectivity decreased from 20.7% to 17.5% with the increase in rest time. Increasing the rest time decreased the CO conversion slightly from 0.11 to 0.09%. At other reaction conditions (H$_2$/CO=2/1, P=20 bar, GHSV= 33,000 scc/h-gcat, temp=270°C; Figure 4.10), methanol and higher alcohol selectivity increased. However methane and CO$_2$ selectivity decreased slightly. This may be due to different degree of re-crystallization of the electrode surface and hydrogen release from freshly deposited surface during different rest times [27].

![Selectivities on Cu-ZnO nanowires. Reaction conditions: H$_2$/CO=2/1, P=10 bar, GHSV= 10,000 scc/h-gcat, temp=270°C.](image)

To understand the difference in their catalytic selectivity, the potential transients were analyzed. Figure 4.11 shows the potential transients for short and long rest times during electrodeposition. For nanowires having short rest times, the potential did not reach a steady state value after 20 s, indicating that the time was not sufficient for ions to be uniformly redistributed in the diffusion layer [28]. However the potential almost reached a steady state
value for nanowires that have longer rest time. Rest potentials were different for the two rest times probably due to different degree of passivation (oxide formation) [27].

Figure 4.9 Selectivities on Cu-ZnO nanowires having different rest times. Reaction conditions: \( \text{H}_2/\text{CO}=2/1, \ P=10 \text{ bar}, \ \text{GHSV}= 10,000 \text{ scc/h-gcat}, \ \text{temp}=270^\circ \text{C} \).

Figure 4.10 Selectivities on Cu-ZnO nanowires having different rest times. Reaction conditions: \( \text{H}_2/\text{CO}=2/1, \ P=20 \text{ bar}, \ \text{GHSV}= 33,000 \text{ scc/h-gcat}, \ \text{temp}=270^\circ \text{C} \).
Figure 4.11 Potential transients of Cu-ZnO nanowires.

To gain insight into the reducibility of the metal oxides in these nanowires, temperature programmed reduction (TPR) studies were carried out. Figure 4.12 shows that both nanowires have lower reduction temperature (260-270°C) than bulk CuO (400°C) [29]. This difference in reduction temperature is due to strong interaction between ZnO and CuO observed by other researchers for similar catalysts [30]. The small peak at ≈ 400°C is due to residual CuO reduction.

Figure 4.12 also shows that increasing the rest time increased the reduction temperature slightly. The reason could be the more compact structure of the nanowires having more rest time possibly due to more hydrogen bubble release and also due to different crystalline structure [31]. There is a shoulder between 230°C and 270°C for nanowires with long rest time due to the reduction of more dispersed or isolated CuO [32], which appears not to be present in the nanowires prepared with short rest time.
Similarly, XRD analysis (Figure 4.13) revealed that different rest times resulted in different crystalline structures. Crystalline ZnO was found in both types of nanowires. However, nanowires with short rest time have crystalline Cu$_2$O, whereas nanowires with long rest time have crystalline Cu. Crystalline CuO is not found in any of the nanowires, suggesting that any CuO is amorphous.

**Cu-ZnO Nanotubes**

The selectivity of the Cu-Zn nanotubes toward methanol was 15%, which is greater than for the nanowires (Table 4.5). However, ethanol selectivity was only 0.14% and C$_3$-C$_4$ alcohol selectivity was less than the detection limit due to excessive methane formation. The reason could be non-uniform composition due to direct deposition and low copper content. During direct deposition, a constant current was applied without any rest time.
Figure 4.13 XRD patterns of Cu-ZnO nanowires: (a) short rest time and (b) long rest time.

Mn Promoted Cu-ZnO Nanowires

Figure 4.14 shows the TPR results of Mn-Cu-ZnO nanowires. The first peak is due to the reduction of CuO to metallic copper and second peak corresponds to the reduction of MnO$_2$ to Mn$_3$O$_4$ [33].

Figure 4.14 TPR profile of Mn-Cu-ZnO nanowires.
The addition of manganese increased the selectivity toward ethanol and higher alcohols, consistent with previous studies [7, 34] (Figure 4.15). This happened due to reduction in methanol and methane formation, however, CO₂ selectivity more than doubled. It is evident from Figure 4.15 that the C₃- C₄ alcohols selectivity increased approximately 9 times due to the presence of manganese in Cu-ZnO catalyst.

![Figure 4.15](image)

Figure 4.15 Selectivities on nanowires with and without manganese. Reaction conditions: H₂/CO=2/1, P=10 bar, GHSV= 10,000 scc/h-gcat, temp=270°C.

4.4 Conclusions

Electrodeposited Cu-ZnO nanowires/ tubes and Mn-Cu-ZnO nanowires have been successfully prepared using template synthesis method from aqueous electrolytes. For the Cu-ZnO nanowires, deposition and rest times of 20 s and 120 s, respectively, resulted in higher C₂-C₄ alcohols selectivity compared to a rest time of 20 s. However nanowires without any rest time showed the highest selectivity for higher alcohols.
Although the $C_2$ alcohol selectivity was at most 15.7%, the electrodeposited nanowires may prove to be promising catalysts because of their enhanced selectivity toward higher alcohols at low reaction pressure.

Cu-ZnO nanotubes showed very low selectivity toward alcohols due to excessive methane and CO$_2$ formation. Therefore, optimization of electrodeposition conditions is required to increase the amount of copper and compositional uniformity and to take advantage of the higher surface area of this morphology.

Addition of manganese to Cu-ZnO nanowires improved the selectivity toward $C_2$-$C_4$ alcohols by reducing methane and methanol formation. More research is needed to further enhance the selectivity toward higher alcohols and this can be achieved by optimizing operating variables such as pulse scheme and composition of nanowires.

4.5 References


CHAPTER 5: PULSE ELECTRODEPOSITION OF Cu-ZnO AND Mn-Cu-ZnO NANOWIRES

5.1 Introduction

Metal and metal oxide nanowires [1, 2] have applications in microelectronics [3-5] chemical sensors [6-8] medicine, biology [9] and catalysis [10]. The use of pulse electrodeposited nanowire catalysts for CO hydrogenation is particularly beneficial because of its ability to control the surface properties of multimetallic catalysts in a way not possible with conventional catalyst preparation methods such as co-precipitation and impregnation [11]. Cu-ZnO and Mn-Cu-ZnO nanowires/tubes were electrodeposited and used recently as novel catalysts for the first time for the synthesis of alcohols from CO hydrogenation [10]. The nanowire catalysts seemed to be promising catalysts because of their enhanced selectivity toward higher alcohols at low reaction pressure.

Nanowires can be fabricated by diversified techniques including lithographic patterning [12, 13], vapor transport techniques [14-19], and other synthesis methods [20-24]. Most of these techniques are either slow, and/or fabrication cost is high. However, template based synthesis involving electrodeposition is more promising owing to its specific advantages of low cost and control over the nanowire properties via changing the electrolyte composition, pH, temperature and applied potential/current [25]. Possin was the first to report the electrodeposition of nanowires using template based method [26]. A comprehensive overview of the membrane/template based preparation method for a wide variety of nanowires has been covered in various reviews [2, 25, 27, 28]. In the present study, we fabricated and characterized Cu-ZnO and Mn-Cu-ZnO nanowires in the nanochannels of Polycarbonate Track Etch (PCTE) membranes by the pulse electrodeposition process.
To the best of our knowledge, there are no prior reported studies focused on pulse electrodeposited Mn-Cu-ZnO nanowires. However, DC electrodeposition has been reported before [10, 29, 30]. Pulse electrodeposition is preferred over direct deposition because latter does not result in uniform filling of the pores due to excessive cathodic side reaction that leads to local deposition in a single pore. Also, pulsing avoids excessive hydrogen evolution that can affect the deposition rate [31].

5.2 Experimental

Cu-ZnO and Mn-Cu-ZnO nanowires are pulse electrodeposited using a template synthesis technique [26, 32] in a typical three electrode cell. Polycarbonate Track Etch (PCTE) membranes (Sterlitech Corporation, WA) (pore diameter: 400 nm and thickness: 25 µm) are sputter coated with an Au film and used as working electrodes. The gold surface is kept in contact with a copper plate held inside a polyetheretherketone (PEEK) stationary holder. A platinized Ti-mesh is used as a counter electrode and a saturated calomel electrode (SCE) is used as the reference electrode. Any anode deposition (typically 98 wt% Mn, 0.9 wt% Cu, and 1.1 wt% Zn) was etched after each experiment. The reactor is immersed in a 5L glass beaker, with the electrolytes (compositions given in Table 5.1). A water bath is used to maintain the temperature at 60 ± 2°C and the electrolyte is magnetically stirred at 320 rpm during experiments. All the experiments are carried out with a VersaSTAT^3 potentiostat/galvanostat (AMETEK Princeton Applied Research, TN). Membranes are dissolved in methylene chloride (CH₂Cl₂) and sonicated for 30 min to release the nanowires. Thereafter, nanowires are separated from CH₂Cl₂ by centrifugation and dried in the oven at 110°C for 12 h. Bulk elemental compositions are determined using a Varian Vista AX CCD Simultaneous ICP-AES. Scanning
Electron Microscopy (SEM) micrographs of the nanowires are obtained using a JEOL 840. X-ray diffraction (XRD) patterns are obtained with an automated X-ray powder diffractometer (Bruker/Siemens D5000, CuKα radiation). XPS analyses are done using a PHI Quantum 2000/PHI 5600 and a SSX-100 (Surface Science Instruments) with an x-ray source of monochromated Alkα (hv = 1486.6 eV).

Table 5.1 Electrolytes used for deposition of Cu-ZnO and Mn-Cu-ZnO nanowires

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Initial pH</th>
<th>Cu(NO₃)₂ (M)</th>
<th>Zn(NO₃)₂ (M)</th>
<th>Mn(NO₃)₂ (M)</th>
<th>NH₄NO₃ (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuZn</td>
<td>4.0</td>
<td>0.002</td>
<td>0.05</td>
<td>---</td>
<td>0.05</td>
</tr>
<tr>
<td>MnCuZn</td>
<td>4.2</td>
<td>0.002</td>
<td>0.05</td>
<td>0.02</td>
<td>0.05</td>
</tr>
</tbody>
</table>

5.3 Results and Discussion

Cu-ZnO and Mn-Cu-ZnO nanowires are pulse electrodeposited. During pulse electrodeposition varying off-times (100-600 ms) are used in order for the diffusion layer to attain equilibrium. This section includes the mechanism of the probable reactions occurring at the electrode-electrolyte interface, imaging, pulse scheme, potential transients, and compositional characterization of Cu-ZnO and Mn-Cu-ZnO nanowires.

Electrodeposition of two elements with disparate reduction potentials such as Cu and Mn is very challenging, even more in nanopores because the deposition of one of the species (Cu in the present case) is usually mass transport controlled. The situation becomes more complex when the deposition of species such as ZnO is known to occur only via chemical reactions [33, 34]. In order to obtain the desired composition of alloy, an understanding of detailed mechanisms of reactions occurring at the cathode is necessary.
Figure 5.1 shows the voltammetric behavior of dilute CuZn and MnCuZn electrolytes on gold coated membranes with three distinct regions: I, II, and III. Region I (E< -0.19 V), represents Cu deposition under kinetic control. Region II (between -0.19 and -0.5 V) shows a current plateau due to the mass transport limited deposition of copper:

\[ \text{Cu}^{2+} + 2e \rightarrow \text{Cu} \quad (E= +0.01 \text{ V}) \]  

(1)

At high current densities (Region III), nitrate reduction [33, 35] and proton reduction (until the electrolyte is acidic near the vicinity of the cathode) occur simultaneously. Both reactions cause the local pH to increase, depending on current density.

\[ \text{NO}_3^- + \text{H}_2\text{O} + 2e \rightarrow \text{NO}_2^- + 2\text{OH}^- \quad (E= -0.26 \text{ V}) \]  

(2)

Figure 5.1 Linear voltammograms of CuZn and MnCuZn electrolytes. Scan rate: 10mV/s.

As seen in the Pourbaix diagram for Cu in Figure 5.2, the thermodynamically stable copper species is Cu(OH)$_2$. The hydroxide may be reduced by the following reaction which also increases the local pH.

\[ \text{Cu}_2\text{O} + \text{H}_2\text{O} + 2e \rightarrow 2\text{Cu} + 2\text{OH}^- \quad (E= +0.02 \text{ V}) \]  

(3)
\[
\text{Cu(OH)}_2 + 2e \rightarrow \text{Cu} + 2\text{OH}^- \quad (E = -0.55 \text{ V}) \quad (3)
\]

Figure 5.2 E-pH diagram of Mn-Cu-N-Zn-H\textsubscript{2}O system at 60°C and 1 atm using Cu as the main element.

If the local pH is less than 7.5 and potential is more negative than -1.5 V vs SCE, manganese may be reduced (Figure 5.3).

\[
\text{Mn}^{2+} + 2e \rightarrow \text{Mn} \quad (E = -1.49 \text{ V}) \quad (4)
\]

At pH > 7.5 manganese exists as Mn(OH)\textsubscript{2} and may be deposited in the form of MnO via the following chemical reactions (Figure 5.3).

\[
\text{Mn}^{2+} + 2\text{OH}^- \rightarrow \text{Mn(OH)}_2 \quad (5)
\]

\[
\text{Mn(OH)}_2 \rightarrow \text{MnO} + \text{H}_2\text{O} \quad (6)
\]

Further, at potentials more positive than -0.9 V vs SCE and pH > 5.5, ZnO precipitates (Figure 5.4) and is included in the deposit [33, 34].

\[
\text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2 \quad (7)
\]
\[ \text{Zn(OH)}_2 \rightarrow \text{ZnO} + \text{H}_2\text{O} \] \hspace{2cm} (8)

Main side reactions are the reduction of protons and water to form hydrogen (eq. 9 and 10).

\[ 2\text{H}^+ + 2e \rightarrow \text{H}_2 \hspace{2cm} (E= -0.37 \text{ V}) \] \hspace{2cm} (9)

\[ 2\text{H}_2\text{O} + 2e \rightarrow \text{H}_2 + 2\text{OH}^- \hspace{2cm} (E= -1.01 \text{ V}) \] \hspace{2cm} (10)

Figure 5.3 E-pH diagram of Mn-Cu-N-Zn-H_2O system at 60°C and 1 atm using Mn as the main element.

Based on the three reaction regimes observed here, a high cathodic current density of 50.7 mA/cm^2 was applied because the reduction potential of Mn is very negative (eq. 4). Waveforms are expected to play a critical role in alloy composition because DC electrodeposition is found to be very inefficient due to excessive hydrogen generation (eq. 9 and 10) in nanopores. To improve alloy uniformity in these dilute Cu solutions, off-time is given after each cathodic pulse to allow replenishment of ions from the bulk electrolyte. A waveform with a forward pulse time of 50 ms (greater than the charging time and less than the transition
time [36]) and an off-time of more than 225 ms (greater than the time taken by a Cu ion to reach the double layer [37]) is used to improve Cu concentration uniformity in these dilute Cu solutions (0.002 M). Experiments with off-times <350 ms did not yield reproducible alloy compositions from all the experiments, suggesting insufficient time for ion transport or non-uniform filling of pores.

Figure 5.4 E-pH diagram of Mn-Cu-N-Zn-H₂O system at 60 °C and 1 atm using Zn as the main element.

Figure 5.5 shows the potential transients at varying off-times. It is observed that the potential transients attain a steady state value and are nearly the same with varying off-times, suggesting that potential and concentration profiles are well relaxed, which is required for homogeneous composition of the nanowires [38]. However, the potential transients did not attain a steady state value for off-time less than 400 ms as shown in Figure 5.5 therefore suggesting a non-homogeneous composition of the nanowires.
To gain insight into the effect of off-time on composition of the nanowires, off-time was varied from 0 to 600 ms. Table 5.2 shows the bulk composition of Mn-Cu-ZnO nanowires obtained employing varying off-times. Cu content increases whereas Zn and Mn content decreases with the increase in off-time. The desired composition is obtained at off-times 400, 500, and 600 ms and therefore these waveforms are further studied in detail.

An example of nanowires is shown in Figure 5.6. The nanowires contained Mn, Cu, and ZnO synthesized with a 400 ms off-time. The nanowires are 400 nm in diameter and lengths ranging from 1 to 8 µm. This wide range is expected due to the sonication process during their dissolution in CH$_2$Cl$_2$. All the nanowires Cu-ZnO as well as Mn-Cu-ZnO look nearly identical. Figure 5.7 is a SEM micrograph for DC electrodeposited Mn-Cu-ZnO nanostructures when the applied current density was 50.7 mA cm$^{-2}$. The bulk composition of these nanostructures is 10.9
wt% Mn, 10.5 wt% Cu, and 78.6 wt% Zn. It can be clearly seen by comparing Figure 5.6 and Figure 5.7 that nanostructures produced by pulse electrodeposition are more uniform than the one formed by DC electrodeposition. Nanostructures formed by DC electrodeposition are tubes due to hydrogen evolution during deposition process [39]. Encircled portions in Figure 5.7 depict the deposits having random shapes neither wire nor tube because the deposition is also occurring in the space created by the partial dissolution of the membrane. This might have happened due the increase in local pH; which is supported by the fact that a bluish white precipitate is seen on the membrane after the experiment.

Table 5.2 Effect of off-time on bulk composition of Mn-Cu-ZnO nanowires

<table>
<thead>
<tr>
<th>Nanostructure</th>
<th>Bulk composition (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td>MnCuZn-0 ms-off-time (DC)</td>
<td>10.5</td>
</tr>
<tr>
<td>MnCuZn-100 ms-off-time</td>
<td>19.2</td>
</tr>
<tr>
<td>MnCuZn-200 ms-off-time</td>
<td>31.8</td>
</tr>
<tr>
<td>MnCuZn-300 ms-off-time</td>
<td>60.9</td>
</tr>
<tr>
<td>MnCuZn-400 ms-off-time</td>
<td>79.7</td>
</tr>
<tr>
<td>MnCuZn-500 ms-off-time</td>
<td>90.5</td>
</tr>
<tr>
<td>MnCuZn-600 ms-off-time</td>
<td>92.2</td>
</tr>
</tbody>
</table>

Figure 5.8 shows the variation in copper and zinc content in the nanowires with varying off-times. Cu content increases and Zn content decreases with the increase in off-time. A similar trend is observed for the nanowires deposited with two different electrolytes (with and without Mn). The trend indicates that the copper deposition is mass transport controlled. Copper content increased by approximately ~50% and zinc content decreased by more than ~60% for all off-times when Mn is added to the electrolyte. This behavior may be attributed to
the following displacement reaction between Cu ion and freshly deposited Mn during the off-times [40, 41].

\[
\text{Cu}^{2+} + \text{Mn} \rightarrow \text{Cu} + \text{Mn}^{2+}
\]

Figure 5.6 SEM micrograph of pulse electrodeposited Mn-Cu-ZnO nanowires with 50 ms on-time (i=50.7 mA cm\(^{-2}\)) and 400 ms off-time

It is also observed that Mn content decreased (from 2.8 to 1.5 wt%) with an increase in off-time due to the displacement reaction between Cu and Mn. It is also possible for protons to displace the freshly deposited Mn [41].

\[
\text{Mn} + 2\text{H}^+ \rightarrow \text{Mn}^{2+} + \text{H}_2
\]

More Cu and less Mn is desirable for catalysts during CO hydrogenation because Cu provides the main active sites and Mn is one of many promoters [42, 43] added to enhance higher alcohols formation. Also, higher promoter content can block the active sites and thus inhibit the higher alcohol synthesis [44-47].
Figure 5.7 SEM micrograph of DC electrodeposited Mn-Cu-ZnO nanostructures (i=50.7 mA cm$^{-2}$).

Figure 5.8 Effect of off-time on bulk copper and zinc content.

Figure 5.9 shows the XRD patterns obtained from the Cu-ZnO nanowires and Mn-Cu-ZnO nanowires with an off-time of 500 ms. All the Cu-ZnO nanowires at different off-times are
composed of a well crystalline material containing Cu and ZnO except for 600 ms off-time, minor Cu$_2$O peaks are observed. However, Pourbaix diagrams depict the formation of metallic Cu and ZnO. Mn-Cu-ZnO nanowires with different off-times also depict dominant Cu and ZnO peaks consistent with the Pourbaix diagrams. This suggest that the Cu$_2$O is not electrodeposited rather it is formed due to the oxidation of Cu during storage and transfer time between fabrication and XRD testing. All the Mn-Cu-ZnO nanowires exhibit nearly the same crystalline features. Interestingly, no Mn is detected which shows that all the Mn is present in amorphous form or doped into the ZnO lattice [48]. Copper hkl planes are found to be (111), (200), and (220) for any type of nanowires suggesting a FCC crystal lattice for copper [49, 50]. The dominant peak for the (111) plane shows that the nanowires preferentially grew in this plane [51].

Figure 5.9 XRD patterns of Cu-ZnO nanowires and Mn-Cu-ZnO nanowires with an off-time of 500 ms. (■) Cu, (△) ZnO, (○) Cu$_2$O.
To understand the effect of off-time and Mn on the morphology of the nanowires, crystallite sizes are calculated using the Scherrer formula [52]:

\[ L = \frac{K\lambda}{\beta \cos \theta} \]

where,

\( L \): crystallite size (nm), \( K \): constant (often taken as 1), \( \lambda \): x-ray wavelength (in the present work Cu K\( \alpha \) = 0.154056 nm), \( \beta \): peak width (radians), \( \theta \): angle between the beam and the normal on the reflecting plane (radians).

Figure 5.10 is a bar plot for the mean crystallite sizes of copper for all the nanowires. It is evident that the crystallite size increases with an increase in off-time for both Cu-Zn and Mn-Cu-Zn nanowires. This happened due to the recrystallization phenomena during the off-times. Smaller crystallites/grains are thermodynamically less stable than the larger ones due to high surface energy and therefore recrystallize like in bubble coalescence during the off-time to attain a more stable state [53]. The results also show that the addition of Mn increases the crystallite size of nanowire for any off-time. This is probably due to the displacement reaction between Cu ion and Mn, discussed earlier. However, it is evident from Figure 5.11 that there is no trend for the ZnO crystallites with varying off-times that might be due to poor crystallinity of ZnO in the nanowires.

XRD also revealed that some of the Cu and Mn are doped into the ZnO lattice because of the shift in peaks for ZnO [48, 54, 55]. Table 5.3 shows the peak shift for ZnO in nanowires with 400 ms off-time. A negative shift is observed for other nanowires too. The lower angle shift suggests the nonuniform substitution of Cu ion into the ZnO site [54, 56].
Figure 5.10 Effect of off-time on mean crystallite size of Cu.

Figure 5.11 Effect of off-time on mean crystallite size of ZnO.
Table 5.3 ZnO peak shift (XRD) for the nanowires with 400 ms off-time

<table>
<thead>
<tr>
<th>2θ</th>
<th>CuZn-nanowires-400ms-off-time</th>
<th>MnCuZn-nanowires-400ms-off-time</th>
</tr>
</thead>
<tbody>
<tr>
<td>31.769</td>
<td>-0.087</td>
<td>-0.182</td>
</tr>
<tr>
<td>34.421</td>
<td>-0.041</td>
<td>-0.18</td>
</tr>
<tr>
<td>36.252</td>
<td>-0.032</td>
<td>-0.216</td>
</tr>
<tr>
<td>56.602</td>
<td>-0.123</td>
<td>-0.108</td>
</tr>
<tr>
<td>62.862</td>
<td>-0.081</td>
<td>-0.252</td>
</tr>
</tbody>
</table>

Surface composition is very critical for a catalyst in heterogeneous catalysis because, all the reactions occur on the surface. XPS survey scans revealed that there is less Cu and more Zn on the surface than the bulk for any type of nanowires at a given off-time as shown in Figure 5.12. It is evident that the surface has an increase in the Cu content in the Mn-Cu-ZnO nanowires for longer off-times, but it is significantly less than the bulk (Figure 5.8 and 5.12). Cu content increased by more than two times whereas Zn content decreased by more than 75% at the surface for all the off-times when Mn is added to the electrolyte. This is ascribed to the displacement reaction between Cu ions and freshly deposited Mn during the off-times [40, 41]. The displacement reaction seems to be more favorable at the surface than the bulk because the latter had only about 50% increase in the Cu content. This is further confirmed by the fact that no Mn is detected on the surface of any Mn-Cu-ZnO nanowires. All these variations in the compositions of nanowires may be attributed to the different atomic environment for the bulk and the surface species during the time of deposition. Bulk material of the nanowires is formed at the bottom of the pores. Nonetheless, surface of the nanowires is formed due to the
deposition of ions near the pore wall which is coated with polyvinylpyrrolidone (PVP) to make the pores more hydrophilic and more easily wettable. PVP has more affinity toward Zn$^{2+}$ than Cu$^{2+}$ [57]; therefore the interface near the pore wall contains more Zn$^{2+}$ ions resulting in higher Zn content than the bulk.

Most of the copper on the surface for any type of nanowires is present as Cu$_2$O confirmed by Auger signal shown in Figure 5.13. Nonetheless, Pourbaix diagram and XRD show that most of the Cu in the nanowires is in metallic form. This indicates that the Cu$_2$O is not electrodeposited rather it is formed due to the oxidation of Cu during storage and transfer time between fabrication and XPS testing. Also, the presence of a “shake-up” peak at ~ 945 eV in the spectrum (Figure 5.14) suggests that some of the Cu might have oxidized to CuO [58, 59].

![Figure 5.12 Effect of off-time on surface composition of the nanowires.](image_url)
Zinc is present as ZnO because all the binding energies for any type of nanowires are greater than metallic zinc and even ZnO (Table 5.4). This supports the XRD findings that zinc is present as ZnO, which is confirmed by the Auger signal too (Figure 5.15).

Table 5.4 Binding energies of zinc for nanowires with varying off-times

<table>
<thead>
<tr>
<th></th>
<th>Binding Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn (0) standard</td>
<td>1021.9</td>
</tr>
<tr>
<td>Zn (II) standard</td>
<td>1022.3</td>
</tr>
<tr>
<td>Cu-Zn Nanowires</td>
<td></td>
</tr>
<tr>
<td>Off-time-400 ms</td>
<td>1022.6</td>
</tr>
<tr>
<td>Off-time-500 ms</td>
<td>1022.4</td>
</tr>
<tr>
<td>Off-time-600 ms</td>
<td>1022.4</td>
</tr>
<tr>
<td>Mn-Cu-Zn Nanowires</td>
<td></td>
</tr>
<tr>
<td>Off-time-400 ms</td>
<td>1022.9</td>
</tr>
<tr>
<td>Off-time-500 ms</td>
<td>1023.0</td>
</tr>
<tr>
<td>Off-time-600 ms</td>
<td>1023.2</td>
</tr>
</tbody>
</table>

Figure 5.13 Auger signal for Cu from Mn-Cu-ZnO nanowires with 50 ms on-time and 400 ms off-time.
Figure 5.14 XPS spectra of Cu 2p$_{3/2}$ from Mn-Cu-ZnO nanowires with 50 ms on-time and 400 ms off-time.

Figure 5.15 Auger signal for ZnO on Mn-Cu-ZnO nanowires with 50 ms on-time and 400 ms off-time.
5.4 Conclusions

Cu-ZnO and Mn-Cu-ZnO nanowires are successfully fabricated by pulse electrodeposition. The results with an off-time of 400 ms are found to be appropriate to obtain the desired composition of nanowires which is dictated by their use as catalysts in CO hydrogenation reactions. Uniform composition of the nanowires is expected as all the potential-time transient curves suggested a uniform re-distribution of ions near the electrode. Copper and zinc are present as Cu and ZnO, respectively in the nanowires whereas manganese might be present as MnO. Interestingly, there is significant difference in the bulk and surface composition. Nanowires contained more Zn and no Mn at the surface. Another interesting finding is the increase in Cu content when Mn is added to the electrolyte, which can be attributed to a displacement reaction between Cu ion and Mn. XRD showed a FCC crystal lattice for Cu and that the nanowires grew preferentially in the (111) direction. Cu crystallite size increased with an increase in off-time due to higher degree of recrystallization with increasing off-times. It also increased with the addition of Mn probably due to the displacement reaction between Cu ion and freshly deposited Mn.

The results of the present work demonstrate that a desired composition and morphology of the nanowires can be achieved with an appropriate selection of various parameters during pulse electrodeposition even when the two species such as Cu and Mn have very disparate reduction potentials. We believe that the study presented in this work will provide a method of preparing novel catalysts.

5.5 References


CHAPTER 6: SYNTHESIS OF ETHANOL FROM CO HYDROGENATION USING NOVEL ELECTRODEPOSITED Mn-Cu-ZnO NANOWIRE CATALYSTS

6.1 Introduction

There is a need for alternative fuels because of limited oil supply [1], increased oil demand [1], and persistent increase in oil prices [2]. One such alternative fuel/additives is ethanol or a mixture of ethanol and higher alcohols [3-5]. Another important application of ethanol is that it can be used for transporting hydrogen. For example, fuel cells (an efficient source of energy) require hydrogen as energy carrier; can be supplied with hydrogen in the form of ethanol. Ethanol can then be steam reformed or partially oxidized to produce hydrogen [3, 6, 7].

Syngas conversion to ethanol seems to be a promising renewable alternative source of energy due to its environmental friendliness and cost because of easily accessible raw material. Ethanol and higher alcohol synthesis from syngas is being explored by many researchers using different types of catalysts [3, 8-11]. It is worth mentioning that the conversion of syngas to methanol over Cu/ZnO supported with Al₂O₃ or Cr₂O₃ catalysts is a very efficient industrial process with over 99% yield [5, 12]. Nevertheless, the yields of ethanol and higher alcohols are generally below 15% from CO hydrogenation even though ethanol is more thermodynamically favored than methanol. Therefore, the problem is one of kinetic control [8].

To date, rhodium-based catalysts have been the most promising but their prohibitive cost and limited supply hinder their ability to be used as industrial catalysts [11]. Thus, much less expensive copper-based catalysts [13, 14] are an attractive option. These catalysts are alkali-promoted Cu/ZnO/Al₂O₃ or Cu/ZnO/Cr₂O₃ [9, 13, 15-17], non-alkali promoted Cu-ZnO-Al₂O₃ [13], Cu-Mn-ZrO₂ [18-20], and alkali-promoted/unpromoted different combinations of all
or some of these components - Cu, Co, Zn, Al [21-24]. Promoters are added to Cu-based because they have been shown to enhance ethanol and higher alcohol synthesis [3, 11, 17].

Generally, heterogeneous catalysts are prepared by conventional methods such as co-precipitation and impregnation. To further increase the performance of these catalysts, a control over the atomic level morphology is essential. Therefore, it has become necessary to explore novel catalyst preparation methods that can provide some control over the morphology and structure of these catalysts that cannot be achieved with conventional methods. Novel catalyst preparation methods have been used by some workers and found promising results [25-27].

A potential promising alternative is electrodeposited nanowires/tubes because it offers a means to control the surface properties of multimetallic catalysts in a way not possible with conventional catalyst preparation techniques. A principle advantage of electrodeposition over conventional methods centers on its ability to control the active metal environment at the atomic level. In a previous work, Cu-Zn and Mn-Cu-ZnO nanowire/tube catalysts were shown to promising catalyst for ethanol and higher alcohols [28]. However, only DC electrodeposition was used for Mn-Cu-ZnO nanowire catalysts. In this work, pulse electrodeposition was used to fabricate Mn-Cu-ZnO nanowires with different composition and morphology. To the best of our knowledge, this is the first time that pulse electrodeposited Mn-Cu-ZnO nanowires have been used as catalysts for any heterogeneous chemical reaction. Pulse electrodeposition is preferred over direct deposition because latter does not result in a good deposit due to excessive cathodic side reaction that leads to local deposition in a single pore. Also, during DC electrodeposition, high reduction current/potential leads to excessive hydrogen evolution that
can affect the deposition rate [29]. Pulse electrodeposition plays an important role when a desired composition of two or more metal/oxide having disparate reduction potentials, is needed. Pulse electrodeposition gives more uniformity in composition of the alloy when the two species have different reduction potential [30].

6.2 Experimental

6.2.1 Electrodeposition

Nanowire/tube catalysts were fabricated using pulse electrodeposition in a typical three-electrode cell [28]. The working electrode (cathode) was a gold sputter coated (one side) hydrophilic Polycarbonate Track Etch (PCTE) membrane supplied by Sterlitech Corporation, WA. The membranes were 10 µm thick (pore length) and had pores of 400 nm in diameter. Gold was coated on one side of the membranes to block pores and provide a conductive film. A platinized Ti-mesh and an Accumet saturated calomel electrode were used as anode and reference electrode, respectively. The aqueous electrolyte (0.002 M Cu(NO₃)₂ + 0.05 M Zn(NO₃)₂ + 0.02 M Mn(NO₃)₂ + 0.05 M NH₄NO₃) was magnetically stirred at 320 rpm during experiments. NH₄NO₃ was added because it was observed that the presence of ammonia in the baths increases the reduction potential of copper [31]. The electrolyte’s pH was 4.2. The cell was kept inside a water bath to maintain the required temperature at 60±2°C. Experiments were performed using a VersaSTAT3 advanced dc voltammetry system manufactured by AMETEK Princeton Applied Research. Nanowires/tube catalysts were electrodeposited by using a template synthesis technique [32-35].

Table 6.1 Pulse conditions during electrodeposition of nanowire catalystsshowss the pulse schemes applied during the electrodeposition of nanowire catalysts. During the on-time,
a cathodic current was applied so that ions in the electrolyte deposit in the pores of the membrane. An off-time represents a period when the current is zero. Two types of nanowire catalysts were prepared by varying the off-time only.

Table 6.1 Pulse conditions during electrodeposition of nanowire catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Current applied during on-time (mA/cm²)</th>
<th>On-time (ms)</th>
<th>Off-time (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Short off-time</td>
<td>-25.38</td>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td>Long off-time</td>
<td>-25.38</td>
<td>50</td>
<td>200</td>
</tr>
</tbody>
</table>

After electrodeposition, the polycarbonate membrane was washed with de-ionized water and dried in the oven at about 65°C for 20 min. After that, it was dissolved in methylene chloride (CH₂Cl₂) solution. Thereafter, the solution was sonicated for at least 30 min to break the entangled nanowires. Centrifugation was done to separate the nanowires from rest of the solution. Separated nanowires were then dried at 110°C in the oven for 12 h. More experimental details are presented elsewhere [28].

6.2.2 Characterization

H₂-Temperature Programmed Reduction (H₂-TPR)

TPR experiments were carried out at atmospheric pressure using the AMI-200R-HP reactor discussed earlier. First, He was flown at 120°C for 30 min and then cooled down to 30°C to remove any moisture present in the catalyst due to the atmospheric exposure during storage/transfer. Then, 10% H₂/Ar with a flow rate of 100 scc/min passed through the catalyst and temperature was ramped from 30°C to 700°C at the rate of 10°C/min. A TCD was used to record the signal generated from the hydrogen consumption by the catalyst.
**Inductively Coupled Plasma-Optical/Atomic Emission Spectrometry (ICP-OES/AES)**

The bulk elemental analysis was performed by a Perkin Elmer Optima 3300 DV dual view ICP-OES and a Varian Vista AX CCD Simultaneous ICP-AES.

**X-ray Photoelectron Spectroscopy (XPS)**

XPS analysis was done with a SSX-100 (Surface Science Instruments) having an x-ray source of monochromated Alk$_\alpha$ (hv = 1486.6 eV). Charge correction was done by using the signal C1s (B.E. = 284.8 eV) from adventitious carbon. BE calibration was done by monitoring the BE difference between a Au and Cu metal foil.

**X-ray Diffraction (XRD)**

The XRD patterns were obtained with an automated X-ray powder diffractometer (Bruker/Siemens D5000, CuKα radiation).

**Scanning Electron Microscopy (SEM)**

The SEM imaging was done by a JSM-840A manufactured by JEOL, operated at accelerating voltage of 15-20 kV, beam current: 1-5 nA, and working distance of 10-25 mm.

**6.2.3 CO Hydrogenation**

CO hydrogenation studies were performed in a tubular fixed bed reactor (AMI-200R-HP) supplied by Altamira Instruments, Inc. Catalysts were placed inside a glass lined reactor tube (0.25“ OD, 0.15” ID, 12” length; stable to about 800°C; manufacturer: SGE Incorporated) using quartz wool. First, 10% O$_2$ in He was passed through the catalyst for 2 h at 400°C to oxidize any carbon left after dissolution of the polycarbonate membrane. Then, the catalyst was reduced using pure H$_2$ at 320°C for 2 h. The reaction was performed at varying temperature, pressure,
and H₂/CO ratio. The product stream was analyzed by a GC-MS (6890N Network GC System) supplied by Agilent Technologies.

6.3 Results and Discussion

6.3.1 Electrodeposition of Nanowires (Pulse Schemes)

The metal environment was controlled by applying two types of current pulses (Table 6.1) during electrodeposition of nanowires. Short current pulses of a few milliseconds were given in order to obtain uniform composition of the nanowires. During pulse electrodeposition, it is very critical for a pulse scheme to have suitable on- and off-times. The on-time should be more than the double layer (accumulation of opposite charges at the metal-solution interphase) charging time to have an impact of pulse electrodeposition on the resulting alloy. If it is less than the double layer charging time then the electrodeposition is nearly direct deposition [36]. At the onset of electrodeposition the total current applied (I), consists of capacitative part (Iₐ) and Faradic part (I₇). Charging time is defined as the time elapsed for the value of I₇ to become 99% of I. Whereas, the discharging time is defined as the time elapsed for I₇ to become 1% of I from 99.9% of I. The double layer charging and discharging time were calculated as follows [36]:

\[ t_c = \frac{17}{I} \]

\[ t_d = \frac{120}{I} \]

Where,

= charging time (µs)

= discharging time (µs)
\[ I = \text{current applied (A/cm}^2\text{)} \]

For the present system, charging time and discharging time were 0.34 ms and 2.37 ms, respectively. Therefore, on-time was chosen to be more than 0.34 ms. To determine the upper limit for on-time, the Sand equation was used to calculate the transition time when the concentration of a species becomes virtually zero at the Outer Helmholtz Plane (OHP) \([37, 38]\).

\[
\tau = \left( \frac{nFc_b}{2l} \right)^2 \pi D
\]

Where,

\[ \tau = \text{Transition time (s)} \]

\[ n = \text{No. of electrons involved in an electrochemical reaction} \]

\[ F = \text{Faraday's constant (96485 C/eq)} \]

\[ c_b = \text{Bulk concentration (mol/cm}^3\text{)} \]

\[ I = \text{Applied current (A/cm}^2\text{)} \]

\[ D = \text{Diffusivity (cm}^2\text{/s)} \]

Using the above equation, transition time was 73.1 ms. Hence, the on-time was chosen to be less than 73.1 ms.

To obtain the compositionally uniform nanowires, it is necessary that an appropriate off-time is given after each on-time when the deposition of one or more of the species is mass transport controlled, so that they have sufficient time to diffuse from bulk to the electrode surface. The time taken by an ion to reach the double layer is calculated by the following equation \([39]\), assuming bulk composition at a distance of 10 µm (membrane thickness) from the double layer.

\[ t = \frac{I^2}{D} = 100 \text{ ms} \]
Where,

\[ t = \text{Time spent by an ion to reach the double layer} \]
\[ l = \text{Distance traveled during this time} \]
\[ D = \text{Diffusion coefficient of ion.} \]

Therefore, for the current system, a pulse scheme with an on-time of 50 ms (more than the charging time and less than the transition time) and an off-time of more than 100 ms and 200 ms (greater than the time taken by an ion to reach the double layer) had been employed.

Figure 6.1 shows an example of nanowire catalysts when the off-time was 100 ms. The thickness and length of the nanowires were 400 nm and 4 µm, respectively. Similar nanowires were obtained for the longer off-time.

Figure 6.1 SEM micrograph of nanowire catalysts with short off-time.
6.3.2 Characterization

Composition

Table 6.2 shows the variation in copper and zinc content (both bulk and surface) in the nanowire catalysts at two different off-times. Copper content increased by two times when the off-time was doubled because of diffusion controlled copper deposition [28, 40]. Zinc content decreased with the increase in off-time due to increased rate of copper deposition. However, there was no effect of off-time on Mn content.

Surface had slightly more copper than the bulk for nanowire catalysts with short off-time. However, when the off-time increased from 100 ms to 200 ms, there was less Cu and more ZnO on the surface. In general, the surface would have more ZnO because it is formed due to the deposition of ions near the pore wall which is coated with polyvinylpyrrolidone (PVP) to make the pores more hydrophilic and more easily wettable. PVP has more affinity toward Zn$^{2+}$ than Cu$^{2+}$ [41]; therefore the interface near the pore wall contains more Zn$^{2+}$ ions resulting in higher Zn content than the bulk. Another difference in the surface composition was that there was no Mn on the surface of the nanowires which could be due the following displacement reactions of Cu and H$^+$ ions with freshly deposited Mn near the pore wall during the off-times [42, 43], consistent with our previous findings [40].

\[ \text{Cu}^{2+} + \text{Mn} \rightarrow \text{Cu} + \text{Mn}^{2+} \]  \hspace{1cm} (1)

\[ \text{Mn} + 2\text{H}^+ \rightarrow \text{Mn}^{2+} + \text{H}_2 \]  \hspace{1cm} (2)

XRD

XRD analysis (Figure 6.2) revealed that the different off times resulted in different crystalline structures. Both the nanowire catalysts were composed of a well crystalline material
containing major Cu, ZnO, and minor MnO. Copper \( hkl \) planes were found to be (111), (200), and (220) for both type of catalysts indicating a FCC crystal lattice for copper [44, 45]. The dominant peak for the (111) plane suggests that the nanowires grew preferentially in this plane [40].

Table 6.2 Bulk and surface composition of nanowire catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Bulk (ICP)</th>
<th>Surface (XPS)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wt% Cu</td>
<td>wt% Zn</td>
</tr>
<tr>
<td>Short off-time (100 ms)</td>
<td>33.7</td>
<td>66.0</td>
</tr>
<tr>
<td>Long off-time (200 ms)</td>
<td>66.1</td>
<td>33.5</td>
</tr>
</tbody>
</table>

Error ± 3%

To gain insight into the effect of off-time on the morphology of the nanowire catalysts, crystallite sizes were calculated using the Scherrer formula [46]:

\[
L = \frac{K\lambda}{\beta \cos \theta}
\]

Where,

- \( L \): crystallite size (nm), \( K \) = constant (often taken as 1), \( \lambda \) = x-ray wavelength (Cu K\(\alpha\) = 0.154056 nm), \( \beta \) = peak width (radians), \( \theta \) = angle between the beam and the normal on the reflecting plane (radians).

Figure 6.3 is a bar plot showing the mean crystallite sizes of Cu and ZnO for both the catalysts. The Cu crystallite size increased with an increase in off-time due to enhanced recrystallization at a longer off-time. Bigger crystallites/grains formed from recrystallization of smaller ones. Smaller crystallites are thermodynamically less stable than the bigger ones and therefore recrystallize to attain a stable state [47]. However, the mean crystallite size of ZnO
decreased with an increase in off-time probably due to the blockage of the growth centers of its crystallites by the adsorption of an inhibitor such as nitrate ion in the electrolyte [47].

Figure 6.2 XRD patterns of Mn-Cu-ZnO nanowire catalysts. (■) Cu, (△) ZnO, (○) MnO.

Figure 6.3 Mean crystallite size of Cu and ZnO for nanowire catalysts.
Temperature Programmed Reduction (TPR)

Figure 6.4 shows the TPR profiles of both types of nanowire catalysts. For both the nanowire catalysts, the major peak at ca. 260°C is due to the reduction of Cu$^{2+}$ to Cu$^{0}$ [48, 49]. It is evident that both catalysts have lower reduction temperature (257 and 265°C) than the bulk Cu nanowires (353°C) (not shown in the figure) due to strong interaction between ZnO and CuO observed by other workers too for Cu-Zn catalysts [50]. Increasing the off-time increased the reduction temperature slightly previously observed for similar nanowire catalysts [28]. It could be due to different crystalline structure [51], different composition [52] and/or increased particle size [53]. Shoulder peak at 161°C (for short off-time) and 189°C (for long time) could be due to the reduction of more dispersed or isolated CuO [32] or amorphous CuO [52, 54] or surface CuO [55]. Another shoulder peak at 272°C for long off-time nanowires could be due to Cu$^{2+}$ to Cu$^{1+}$ and finally to Cu [48]. The peak at 343°C for short off-time nanowires could be due to Cu$^{1+}$ to Cu$^{0}$ [56], however this peak is not observed for long off-time nanowires. The plateaus with no defined peaks starting from 386°C for short off-time and 328°C for long off-time are due to ongoing ZnO reduction and decomposition of carbonate present in the nanowires because of their precursor membranes [57, 58]. Copper is strongly interacting with ZnO and enhancing its reducibility because the ZnO reduction does not begin even up to 600°C [52].

6.3.3 CO Hydrogenation (Syngas Conversion)

The CO hydrogenation reactions were carried out at differential conditions. During CO hydrogenation, major products were methanol, ethanol, methane, ethane, propane, propylene, and CO2. Minor products were higher alcohols (n-propanol, i-propanol, and i-butanol), C4+
hydrocarbons (i-butane, n-butane, n-hexane), and acetone. All the experiments were carried out at 10 bar because most of the syngas generating gasifiers operate between 1 and 30 bar [59, 60].

![Figure 6.4 TPR profiles of nanowire catalysts.](image)

**Effect of Temperature**

Table 6.3 shows how the temperature affects the product distribution over nanowire catalysts. Selectivity toward ethanol, higher alcohols, and higher alkanes goes through a maximum at 290°C. This trend in ethanol and higher alcohols selectivity had been observed by other workers too for Cu-based catalysts [13, 20, 22, 61]. However, for methanol this maximum was observed at a lower temperature i.e. 270°C, similar to what was reported by Majocchi *et al.*
[62] on Cu-based catalysts. Selectivity toward CO$_2$, propylene, and methane was minimum at 290°C in the temperature range studied. In general, conversion increased with temperature.

However, temperatures as high as 350°C [63] and 375°C [5] were found to be suitable for some catalysts. But higher temperatures should be avoided because of the instability of some oxygenates at temperatures above 450°C [10], increased formation of CO$_2$ and methane at temperatures above 280°C [5, 13, 20], and deactivation of the catalyst due to sintering [62, 64, 65]. Therefore, rest of the reactions in this work were carried out at 290°C.

Table 6.3 Effect of temperature on selectivities of various products over nanowire catalysts with long off-time

<table>
<thead>
<tr>
<th>Temperature (C)</th>
<th>Methanol</th>
<th>Ethanol</th>
<th>C3-C4 Alcohols</th>
<th>Methane</th>
<th>C2-C6 Hydrocarbons</th>
<th>Propylene</th>
<th>CO$_2$</th>
<th>CO Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>15.9</td>
<td>6.35</td>
<td>1.6</td>
<td>40.2</td>
<td>7.22</td>
<td>7.11</td>
<td>10.4</td>
<td>0.32</td>
</tr>
<tr>
<td>270</td>
<td>18.3</td>
<td>8.44</td>
<td>1.72</td>
<td>39.1</td>
<td>10.2</td>
<td>6.06</td>
<td>13.3</td>
<td>0.41</td>
</tr>
<tr>
<td>290</td>
<td>13.9</td>
<td>9.42</td>
<td>1.95</td>
<td>35.5</td>
<td>10.9</td>
<td>6.73</td>
<td>16.3</td>
<td>0.54</td>
</tr>
<tr>
<td>310</td>
<td>10.1</td>
<td>7.77</td>
<td>1.46</td>
<td>37.3</td>
<td>8.92</td>
<td>6.93</td>
<td>18.7</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Acetone <0.5%
Error: ± 10%

$^a$ Selectivity (%C) = \( \frac{N_C x 100}{\sum N_i C_i} \)

Where \( N_i \) is the number of carbon atoms in product and \( C_i \) is its concentration (mol%).

**Effect of H$_2$/CO Ratio**

The H$_2$/CO feed ratio is a critical parameter for ethanol synthesis [15]. Unless the experiments are carried out at differential conversions, this ratio can change with reactor position because of the water-gas-shift reaction (WGS) [10]. Table 6.4 shows how the H$_2$/CO ratio affects the product distribution over nanowire catalysts. Selectivities toward ethanol and higher alcohols decrease with the increase in H$_2$/CO ratio in agreement with the reported
literature [10, 15, 62, 66]. However, methanol selectivity increased with the increase in H₂/CO ratio, similar trends were found by other researchers [10, 17, 23, 67]. In general, low H₂/CO ratios favor the coke formation and C-C chain growth, and therefore higher alcohol selectivity. Higher H₂/CO ratios favor methanol synthesis [10, 15, 62, 66]. Conversion and methane selectivity increased with the increase in H₂/CO ratio. Selectivities toward propylene and CO₂ decreased with the increase in H₂/CO ratio.

Table 6.4 Effect of H₂/CO ratio on selectivities of various products over nanowire catalysts with long off-time

<table>
<thead>
<tr>
<th>H₂/CO</th>
<th>Methanol</th>
<th>Ethanol</th>
<th>C3-C4 Alcohols</th>
<th>Methane</th>
<th>C2-C6 Hydrocarbons</th>
<th>Propylene</th>
<th>CO₂</th>
<th>CO Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.0</td>
<td>12.3</td>
<td>1.89</td>
<td>3.00</td>
<td>13.2</td>
<td>9.85</td>
<td>17.7</td>
<td>1.11</td>
</tr>
<tr>
<td>2</td>
<td>14.3</td>
<td>8.8</td>
<td>1.75</td>
<td>31.9</td>
<td>14.7</td>
<td>9.31</td>
<td>14.8</td>
<td>1.24</td>
</tr>
<tr>
<td>2.5</td>
<td>14.1</td>
<td>6.83</td>
<td>1.52</td>
<td>36.8</td>
<td>14.1</td>
<td>8.95</td>
<td>13.7</td>
<td>1.87</td>
</tr>
<tr>
<td>3</td>
<td>15.5</td>
<td>6.44</td>
<td>1.66</td>
<td>38.5</td>
<td>12.7</td>
<td>8.52</td>
<td>13.2</td>
<td>1.94</td>
</tr>
</tbody>
</table>

Error ± 10%

Effect of Off-time during Electrodeposition of Nanowires

Figure 6.5 shows the selectivity toward various products on nanowire catalysts at the best conditions (H₂/CO = 1/1, P = 10 bar, GHSV = 7,500 scc/h gcat, temperature = 290°C) found from the above discussions. Longer off-time increased the ethanol selectivity from 9.65% to 12.3%. Selectivity toward propylene and CO₂ also increased with the increase in off-time. However, selectivity to higher alcohols decreased slightly from 2.20% to 1.89% with the increase in off-time. Methanol selectivity remained almost the same. Selectivity toward methane and higher alkanes decreased with the increase in off-time. Increasing the off-time decreased the CO conversion slightly from 1.34% to 1.11%.
Figure 6.5 Selectivities over Mn-Cu-ZnO nanowire catalysts with different off-times. Reaction conditions: H₂/CO = 1/1, P = 10 bar, GHSV = 7,500 scc/h gcat, temperature = 290°C.

Most of these results are consistent with one of our previous works on Cu-ZnO nanowires [28] except for higher alcohols and CO₂ selectivity possibly due to different composition and morphology. Present work showed more selectivity toward ethanol and higher conversion than the catalysts used in our previous study for Cu-ZnO [28]. It can be attributed to the presence of Mn in the nanowire catalyst because Mn is believed to partly oxidize the Cu to Cu⁺ and these ions could then become active centers [61]. For instance, Li et al. reported that the addition of Mn increased dispersion of Cu and thus catalytic activity of the catalyst [55]. Even Mn-Cu-ZnO from previous work had less ethanol selectivity which could be ascribed the non-uniform composition and inclusion of hydrogen in the nanowires during DC electrodeposition.
Different catalytic behavior of these catalysts was due to different composition and atomic environment. The atomic environment can significantly change due to several phenomena occurring during off-time such as surface diffusion, recrystallization, and passivation of the freshly deposited material [68, 69]. Another important reason could be the hydrogen gas release because hydrogen atoms in the deposit combine to form molecular hydrogen during the off-time and escape from the deposit [70].

**Suggested Mechanism for Ethanol and Other Products on Nanowire Catalysts**

Due to different product distribution on nanowire catalysts than the modified Cu-based catalyst it became necessary to adapt several mechanisms to justify the formation of various products [10, 11, 16, 63, 71]. Catalytic behavior of nanowire catalysts seems like a combination of modified methanol synthesis catalysts [20, 61, 72] and modified Fischer–Tropsch (FT) catalysts [22, 73, 74].

It is believed that active sites for alcohol formation are Cu\(^+\) species [63, 71, 75] and Cu\(^0\) for alkanes [63]. Herman et al. [76] reported that during methanol synthesis, chemisorption and activation of CO occurs on the Cu\(^+\) sites and of hydrogen on ZnO. Moreover, Schulz-Flory distributions (Figure 6.6 and 6.7) of the products suggest that the synthesis of alcohols and hydrocarbons require different sites because of different chain growth probability factors (\(\alpha\)) [19]. The \(\alpha\) values for alcohol formation for nanowire catalysts with short-off-time and long-off-time were 0.19 ±0.007 and 0.18 ±0.008, respectively. For hydrocarbon formation, the \(\alpha\) values were 0.24 ±0.015 and 0.28 ±0.017 for short and long off-time, respectively.

Literature shows the existence of surface species such as formate, carbonate, methylene [55], adsorbed formate species, methoxy [77, 78], adsorbed atomic oxygen, and
formaldehyde [78] on methanol synthesis catalysts during CO hydrogenation. On modified methanol catalysts also, existence of similar species such as adsorbed formic acid (HCOOH) and H₂CO (formaldehyde) had been reported [61].

Figure 6.6 Schulz-Flory distribution of linear C₁-C₄ alcohols for long off-time nanowire catalysts. Reaction conditions: H₂/O = 1/1, P = 10 bar, GHSV = 7500 scc/h gcat, temperature = 290°C.

Figure 6.7 Schulz-Flory distribution of linear C₁-C₆ (except C₅) hydrocarbons for long off-time nanowire catalysts. Reaction conditions: H₂/O = 1/1, P = 10 bar, GHSV = 7500 scc/h gcat, temperature = 290°C.
Based on the above discussion, following reaction mechanisms are proposed here for the synthesis of ethanol and other major products. Ethanol can form via the following reaction sequence (Figure 6.8) [11]. First, an adsorbed formyl species forms from adsorbed CO and H (step 1). Then, the two adsorbed formyl species react to form an adsorbed acetyl species (step 2). Finally ethanol is formed after the hydrogenation of the acetyl species (step 3). Higher alcohols can form from a reaction of formyl species with the acetyl species.

![Figure 6.8 Reaction mechanism for ethanol synthesis on nanowire catalysts.](image)

Figure 6.9 shows the reaction pathways for methanol synthesis [11]. Adsorbed formyl species hydrogenates to form adsorbed formaldehyde (step 1). Further hydrogenation of the formaldehyde produces methoxy species (step 2). And finally methanol forms via the hydrogenation of methoxy species (step 3).

Figure 6.10 shows a possible reaction pathway for methane formation [10]. CO adsorbs dissociatively (step 1) and then adsorbed C and adsorbed H form a CH\textsubscript{x} species (step 2). Further hydrogenation of this species forms methane (step3).

Figure 6.11 shows a possible reaction pathway for propylene formation [10]. Two adsorbed CH\textsubscript{x} species can combine to form an adsorbed C\textsubscript{2}H\textsubscript{y} species (step 1). Then this species
can react with a CH₉ species to form propylene (step 2).

Figure 6.9 Reaction mechanism for methanol synthesis on nanowire catalysts.

Figure 6.10 Reaction mechanism for methane synthesis on nanowire catalysts.

Figure 6.11 Reaction mechanism for the formation of propylene on nanowire catalysts.

CO₂ formation can occur via the following reaction sequence Figure 6.12. A reaction of CO with adsorbed atomic oxygen can form CO₂ [78].

Figure 6.12 Reaction mechanism for the formation of CO₂ on nanowire catalysts.
6.4 Conclusions

Mn-Cu-ZnO nanowire catalysts were fabricated by pulse electrodeposition. Their atomic environment was tailored by introducing an off-time during electrodeposition. Different off-times resulted in different bulk and surface composition. XRD showed that nanowire catalysts contained mostly containing major Cu, ZnO, and small amount of MnO. Nanowires grew preferentially in the (111) direction. It also showed that with the increase in off-time Cu crystallite size increased whereas that of ZnO decreased. TPR studies showed strong interaction between CuO and ZnO.

The pulse electrodeposited Mn-Cu-ZnO nanowire catalysts were then used as catalysts for syngas conversion reaction. Temperature was varied from 250°C and 300°C while keeping other parameters constant. It was found that the selectivity toward ethanol, higher alcohols, and higher alkanes goes through a maximum at 290°C. Nonetheless, selectivity toward CO₂, propylene, and methane was minimum at 290°C in the temperature range studied. It was also found that the conversion increased with temperature. The increase in H₂/CO ratio (1 to 3) decreased the selectivity toward ethanol and higher alcohols. However, selectivity to methanol and methane, conversion increased with its increase. Nanowire catalysts showed higher selectivity toward ethanol and higher alcohols when H₂/CO is 1; it is good because most of the gasifiers produce H₂/CO ratio close to 1 [15].

Longer off-time during electrodeposition resulted in enhanced selectivity to ethanol, which increased from 9.65% to 12.3%. Also, selectivity toward propylene and CO₂ increased with longer off-time. However, selectivity to higher alcohols decreased slightly from 2.20% to 1.89% with the increase in off-time.
Nanowires are shown to be promising catalysts. However, experimental studies such as FTIR and isotopic labeling of its reactants during syngas conversion reaction are necessary to devise a mechanism that specifically works on these types of catalysts.

6.5 References


CHAPTER 7: ELECTRODEPOSITION OF CuNiW ALLOYS: THIN FILMS, NANOSTRUCTURED MULTILAYERS AND NANOWIRES*

7.1 Introduction

Electrodeposition of tungsten alloys are of interest because of their superior properties such as hardness, wear resistance, thermal resistance and corrosion resistance [1-4]. In addition, their electrodeposition behavior is unique since tungsten cannot be deposited from an aqueous electrolyte, nonetheless it can readily be deposited in the presence of iron group metal ions such as cobalt, nickel, and iron [5, 6]. This type of electrodeposition is known as ‘induced codeposition’ a term coined by Brenner [5]. The present work utilizes tungsten codeposition with both nickel and copper to form a ternary alloy for the fabrication of multilayers.

Multilayered alloys are materials in which the composite of alternative layers is modulated. Since copper is more noble than nickel or tungsten it can be preferentially deposited as one layer. Nickel and tungsten are chosen as the other components of the bilayer in a multilayer stack due to the superior properties of its alloy [3-5, 7-9], and they are typically deposited from ammonia containing electrolytes. Due the presence of ammonia in the baths, the reversible potential of copper is moved to a more negative potential range [10], hindering the ability to form multilayers. Without ammonia, there is a larger separation of the reversible potential of copper and nickel-tungsten, that facilitates multilayer fabrication, however a lower ammonia concentration or no ammonia, lowers the current efficiency appreciably for nickel-tungsten codeposition [11].

Electrodeposition of multilayers is a cost effective and versatile method for developing a wide variety of micro-devices [12-14]. Electrodeposited multilayers have already been applied to many sectors such as electronics, aerospace, automotive, etc. due to low cost and straightforward implementation. There have been many studies on multilayer deposition due to a significant improvement in electrical properties [15-18], magnetic properties [15, 19-24] and mechanical properties such as hardness [22, 25-28] and tensile strength [19, 22, 27, 29-31].

Electrodeposition of multilayers followed by preferential etching of sacrificial layers can potentially be used as an inexpensive alternative stamp for nanoimprint lithography (NIL) [32-37] applications. NIL has already been shown to find potential applications in bio-chemical analysis systems [34, 37], electronic storage media [34] and optical elements [37, 38] and CD/DVD optical pick up units [39]. It can also be used for fabricating in-fiber gratings in optical fibers [38]. Other applications of electrodeposited multilayers followed by selective etching of one layer are in fabricating micro-electro-mechanical devices such as microgears [14] and liquid-core waveguides [40]. For example, electrodeposited multilayers have recently been demonstrated to fabricate nanostamps using Cu/Ni, Cu/NiFe and CoFeNiCu/Cu systems [41, 42]. The present work includes tungsten in one bilayer to create a more robust nanostamp.

A non-destructive method of visualizing multilayers is to electrodeposit multilayered nanowires and examine them using TEM. Electrodeposition of nanowires has become an attractive field since the inception of GMR (giant magnetoresistance) [20, 23, 43]. The properties of nanowires depend on electrolyte composition, temperature, pH, and applied potential/current. When single layer thickness in nanowires is only a few nanometers, the nanowires exhibit a great decrease in electrical resistance when an external magnetic field is
applied. For GMR purposes they consist of alternative layers of ferromagnetic metals such as Ni, Co, Fe or their alloys and paramagnetic metals such as Cu. There are several techniques to fabricate magnetic multilayers such as molecular beam epitaxy (MBE), thermal evaporation and ion beam sputtering [21]. Nonetheless, electrodeposition is a cost effective alternative with other advantages such as simplicity of method and high throughput. To the best of our knowledge, this is the time first time CuNiW multilayered nanowires have been fabricated, complimenting the different types of nanowires reported in the literature [e.g., 44-47].

7.2 Experimental

7.2.1 Electrodeposition Characterization

Electrolytes

Electrolytes used in all the experiments contained 0.6 M Na$_3$C$_6$H$_5$O$_7$, 0.2 M Na$_2$WO$_4$, 0.3 M NiSO$_4$ and varying amount of CuSO$_4$. All the chemicals were certified A.C.S. The electrolyte solutions were prepared using deionized water. The electrolyte temperature was maintained at 70 ± 2 °C. NH$_4$OH was added to the electrolytes, 2.0, 1.5, 1.4% v/v, containing 0.03, 0.01 and 0.003 M CuSO$_4$, respectively to establish the initial pH of 8.0 ± 0.2, and the pH was maintained by periodically adding NH$_4$OH between experiments. Experiments were performed using a rotating cylinder electrode (RCE) with a uniform current distribution, a rotating cylinder hull cell (RCHC) with a non-uniform current distribution (Figure 7.1) and a rotating disk electrode (RDE) to obtain flat alloy deposits.

Rotating Cylinder Electrode (RCE) and Rotating Cylinder Hull Cell (RCHC)

The RCE and RCHC were used as cathodes with a controlled rotation rate to facilitate a
constant hydrodynamic environment near the electrode surface. The electrode materials were a 410 stainless steel (area = 15 cm$^2$) cylinder surrounded by a platinized, titanium counter electrode. The RCE, with a uniform current distribution along its length, was used to obtain current-potential relationships (polarization curves) at a constant rotation rate. The RCHC, with an induced current distribution, shown in Figure 7.1, was used to assess the effect of the applied current density on the deposit composition, thickness and partial current densities. The difference between RCE and RCHC set-up is that the former does not have a plastic shield around the cylindrical cathode. The absence of the shield promotes a uniform current distribution.

Figure 7.1 A Rotating Cylinder Hull Cell (RCHC), (http://yanco.com.tr/products/Eco%20Chemie/rotahull.pdf).
The Hull cell configuration, with the shield, is designed in such a way that current varies along the length of the cylinder when the total current rises rapidly with potential. Under these conditions, the current distribution is greatest due to the geometry and the ohmic limitations of the electrolyte, referred to as primary current distribution. The lower end of the cylinder has the highest current density and it decreases along the electrode length. Figure 7.2 presents the current density, $i$, variation, normalized to the average applied current density, $i_{\text{avg}}$, along the cylindrical cathode length, $x$, in a RCHC [48], shown as a normalized parameter with the total electrode length, $L$. The anode is closest to the cathode at $x L^{-1} = 0$, where the current density is at a maximum. The calculated points on Figure 7.2 represents a primary current distribution. If the reactions are sluggish then the distribution will be smaller.

![Figure 7.2 Current distribution along the cylindrical electrode in a RCHC [44].](image)
After obtaining electrodeposition conditions for different alloys, these were used to estimate conditions to deposit multilayered alloys onto a rotating disc electrode (RDE) and into nanoporous membranes.

**Rotating Disc Electrode (RDE)**

Alloys were deposited using a rotating disc electrode (RDE) with a high precision rotator supplied by Pine Instrument Company, Grove City, USA, and electrodeposited under pulsed current conditions. A single compartment cell was used with 410 stainless steel working electrodes (area = 0.28 cm$^2$), a Pt counter electrode and a saturated calomel reference. Experiments were performed using an IM-6e potentiostat/galvanostat/impedance spectrometer supplied by BAS Zahner.

The cell was kept inside a water bath to maintain the required temperature. Before experiments the cylindrical pellet was cleaned by soap and rinsed with deionized water. The working electrode was a cylindrical pellet having an area of 0.283 cm$^2$. The pellet was polished using a 4000 sand paper followed by 3 µm diamond spray (Struers).

Linear sweep voltammetry was done to obtain polarization curves for different electrolytes using an IM-6e Potentiostat/Function generator/ FRA. A slow scan rate of 2 mV s$^{-1}$ was applied to all scans in order to ensure steady state conditions. Impedance spectroscopy was done to find solution resistance (ohmic drop) by varying the frequency of 1 K Hz to 1 M Hz. The ohmic drop was then applied to all polarization curves.

Alloy deposits were obtained at several current densities to obtain varying amount of Cu, Ni, and W suitable for multilayer deposition under normal and pulse plating conditions. The deposits were sufficiently thick (more than 0.5 µm) to carry out composition analysis.
7.2.2 Multilayer Electrodeposition and Etching

All multilayers were electrodeposited using a rotating disc electrode under pulsed current conditions. Table 7.1 shows the copper, nickel, tungsten and sodium citrate compositions of electrolytes used and the current densities used for alloy and multilayer deposition. The etching solution to preferentially etch one layer of the CuNi/CuNiW multilayers was 0.034 M K$_2$Cr$_2$O$_7$, 0.36 M H$_2$SO$_4$, 0.012 M HCl [45].

Table 7.1 Electrolytes and corresponding current densities used for multilayer deposition

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>CuSO$_4$</th>
<th>Ni-rich (mA cm$^{-2}$)</th>
<th>Cu-rich (mA cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.03 M</td>
<td>-35.38</td>
<td>-7.08</td>
</tr>
<tr>
<td>B</td>
<td>0.01 M</td>
<td>-35.38</td>
<td>-1.76</td>
</tr>
<tr>
<td>C</td>
<td>0.003 M</td>
<td>-35.38</td>
<td>-0.71</td>
</tr>
</tbody>
</table>

A: 0.6 M Na$_3$C$_3$H$_5$O(CO$_2$)$_3$, 0.2 M Na$_2$WO$_4$, 0.3 M NiSO$_4$ and 0.03 M CuSO$_4$
B: 0.6 M Na$_3$C$_3$H$_5$O(CO$_2$)$_3$, 0.2 M Na$_2$WO$_4$, 0.3 M NiSO$_4$ and 0.01 M CuSO$_4$
C: 0.6 M Na$_3$C$_3$H$_5$O(CO$_2$)$_3$, 0.2 M Na$_2$WO$_4$, 0.3 M NiSO$_4$ and 0.003 M CuSO$_4$

7.2.3 Nanowire Electrodeposition

Figure 7.3 shows a schematic of nanowire fabrication using a membrane. The nanowires were electrodeposited into alumina membranes (Whatman Anodisc) having a pore length and diameter of 60 μm and 200 nm, respectively. The membranes were gold sputtered on one side for electrical contact. The gold sputtered membrane and a platinum mesh served as cathode and anode, respectively. The electrolyte contained 0.6 M Na$_3$Cit, 0.2 M Na$_2$WO$_4$, 0.3 M NiSO$_4$ and 0.03 M CuSO$_4$ (solution A). Temperature and pH were 70 ± 2°C and 8.0 ± 0.2, respectively. Other experimental variables are given in Table 7.2. The potentials shown in the following table are chosen corresponding to the current densities values for multilayer deposition.
7.2.4 Characterization

The compositional analyses of the films deposited on the cylinder electrodes were measured by energy dispersive X-Ray Fluorescence (XRF), model Omicron by Kevex. The XRF analyses were performed at an X-ray energy of 50 kV, current of 1.7 mA and acquisition time of 100 s. Multilayer characterization (a few microns to submicron size), was carried out by a scanning electron microscope (model JSM-840A) and a transmission electron microscope (model JEOL 100CX), manufactured by JEOL.

![Figure 7.3 Schematic for nanowires fabrication](image)

(i) cross-sectional view of cylindrical pores in an alumina membrane, (ii) sputtered gold on membrane bottom surface (iii) filled pores with electrodeposited multilayered structure, and (iv) multilayered nanowires protruding from gold layer after dissolution of membrane in 1 M KOH.

Table 7.2 Electrolytes and corresponding applied potential for nanowires electrodeposition

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>CuSO₄</th>
<th>NiW-rich (V vs SCE)</th>
<th>Cu-rich (V vs SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.03 M</td>
<td>1.4 -1.8</td>
<td>0.6 -0.9</td>
</tr>
<tr>
<td>C</td>
<td>0.003 M</td>
<td>1.4 -1.8</td>
<td>0.6 -0.9</td>
</tr>
</tbody>
</table>

A: 0.6 M Na₃C₃H₅O(CO₂)₃, 0.2 M Na₂WO₄, 0.3 M NiSO₄ and 0.03 M CuSO₄
C: 0.6 M Na₃C₃H₅O(CO₂)₃, 0.2 M Na₂WO₄, 0.3 M NiSO₄ and 0.003 M CuSO₄
7.3 Results and Discussion

7.3.1 Electrodeposition Characterization

Rotating Cylinder Electrode (RCE)

Figure 7.4 shows the polarization curves of the electrolytes containing different amounts of copper obtained using the RCE at a rotation rate of 400 rpm. The plateau region of the curves (-0.6 to -0.8 V vs SCE) that increase with copper in the electrolyte indicate the region where the Cu limiting current density occurs. At potentials more noble to this region, the deposits are primarily copper while at less noble potentials, in the region beyond the limiting current density of Cu, deposits are an alloy containing nickel, copper and tungsten. The composition, thickness and resulting partial current densities were determined by using the RCHC.

Figure 7.4 Ohmic drop corrected polarization curves with rotating cylinder electrodes (rpm = 400) from electrolytes having different Cu ion concentrations.
Rotating Cylinder Hull Cell (RCHC)

Guided by the polarization curves in Figure 7.4, the applied average current density to the RCHC was -13.33 mA cm\(^{-2}\) and resulted in a deposit that varied in composition along the electrode length. Figure 7.5 shows the variation of copper along the length of the cylinder, expressed in terms of the estimated applied current density. The copper content in the alloy increases with copper in the solution and decreases with the applied current density consistent with a mass transport control. When copper is decreased from 0.03 to 0.01 M the copper content in the alloy decreases by 40 wt\%, and it is reduced by 62 wt\% when the copper concentration is further decreased to 0.003 M at lower current density.

![Graph showing Cu content in the CuNiW alloy deposited from electrolytes having different Cu ion concentrations.](image)

Figure 7.5 Cu content in the CuNiW alloy deposited from electrolytes having different Cu ion concentrations.
The nickel content in the alloy is always higher than tungsten for all the electrolytes (Figure 7.6 and 7.7). The amount of tungsten increases slightly with an increase in current density and the amount of nickel stays about the same. Figure 7.6 and 7.7 also shows that the nickel and tungsten content in the alloy decreases with more copper in the system as expected. At lower current densities, the difference in the nickel content from the different solutions is more than at the higher current densities. The amount of tungsten in the alloy is high at higher current densities consistent with other literature studies [5]. The highest amount of tungsten achieved was 31 wt % from electrolyte containing 0.003 M Cu (II).

In an attempt to better understand the system and the interaction among all species, the partial current densities were determined and expressed as a function of potential. The partial current density $i_k$ (mA cm$^{-2}$) of $k^{th}$ species in the electrolyte is calculated as

$$i_k = \frac{(1000)(X_k)(n_k)(m)(F)}{(AW_k)(t)}$$

(1)

where $k$ represents copper, nickel and tungsten, $X_k$ is the weight fraction, $n_k$ (eq mol$^{-1}$) is the number of electrons involved in balanced equation for reduction, $m$ (g cm$^{-2}$) is the total mass deposited per unit area, $F$ (96485 C eq$^{-1}$) is the Faraday’s constant, $AW_k$ (g mol$^{-1}$) is the atomic weight and $t$ (s) is the total electrodeposition time.

The mass per unit area, $m$ is determined from the thickness measurement.

$$m = \frac{\theta}{\frac{X_{Cu}}{\rho_{Cu}} + \frac{X_{Ni}}{\rho_{Ni}} + \frac{X_{W}}{\rho_{W}}}$$

(2)

where $\theta$ (cm) is the thickness of the deposit and $\rho_{Cu}, \rho_{Ni},$ and $\rho_{W}$ are the densities of copper, nickel and tungsten, respectively.
Figure 7.6 Ni content in the CuNiW alloy deposited from electrolytes having different Cu ion concentrations.

Figure 7.7 W content in the CuNiW alloy deposited from electrolytes having different Cu ion concentrations.
The side reaction is defined as

\[ i_S = i_{Total} - (i_{Cu} + i_{Ni} + i_{W}) \]  

where \( i_{Total} \) is the total current applied and \( i_{Cu}, i_{Ni} \) and \( i_W \) are partial current densities of copper, nickel and tungsten respectively. Current efficiency is determined from the ratio of the metal partial current densities to the total current density applied.

Figure 7.8-7.10 represent the calculated partial current densities determined from measured composition and thickness data plotted against an interpolated potential from the polarization curves (Figure 7.4). In Figure 7.8, the partial current density of copper is highest for the electrolyte containing 0.03 M Cu (II) and lowest for the electrolyte with 0.003 M Cu (II), as expected for a mass transport control. Although, at the highest amount of Cu (II), 0.03 M, there is evidence of a mixed kinetic control since the partial current increases with potential. The negligible change of the partial current density with potential of copper from the dilute electrolytes clearly indicates a mass transport control. The partial current density of nickel (Figure 7.9) for all the electrolytes, increases when potential becomes more negative, indicating kinetic control. The nickel partial current densities are almost the same up to -1 V. For the potentials more negative than -1 V, it increases as the copper content in the electrolyte increases, this trend is consistent with past study of Cu-Ni codeposition in citrate electrolyte [46]. Figure 7.10 depicts the tungsten partial current density, which is lowest for the electrolyte containing the highest amount of copper. The addition of copper in the electrolyte thus affects the tungsten partial current density.

The side reaction is primarily H\(_2\) evolution which becomes more favorable at higher negative potentials as shown in Figure 7.11. The side reaction was significantly reduced in the
whole range of potential with the addition of copper in the electrolyte. There is no effect on the side reaction when the copper ion concentration is reduced from 0.03 to 0.01 M. However, as the copper electrolyte concentration is reduced to 0.003 M the side reaction increases, accompanied with an increase in tungsten. Another way of representing the same data is in the calculation of the current efficiency, Figure 7.12. The current efficiency follows the same trend for all the electrolytes, decreasing with the current density. The highest current efficiency occurs with the deposits containing the most amount of copper from 0.03 M Cu (II) and the lowest current efficiency (24%) was recorded from the electrolyte containing the lowest amount of copper (0.003 M Cu (II)).

Figure 7.8 Partial current density of Cu from electrolytes having different Cu ion concentration.
Figure 7.9 Partial current density of Ni from electrolytes having different Cu ion concentration.

Figure 7.10 Partial current density of W from electrolytes having different Cu ion concentration.
Figure 7.11 Partial current density of side reaction from electrolytes having different Cu ion concentration.

Figure 7.12 Current efficiency for electrolytes having different Cu ion concentration.
7.3.2 Multilayer Thin Film Deposition

Rotating Disc Electrode (RDE)

The rotating disc electrode was used to create flat deposits using the conditions obtained in the previous section, for multilayer fabrication. Figure 7.13 shows the ohmic drop (iR) corrected polarization curves for the three electrolytes containing different concentrations of copper at 900 rpm. The curves are qualitatively similar to the polarization curves generated by the RCE Figure 7.4. The compositional analysis of the alloy films from the electrolytes at two applied current densities for multilayer deposition was investigated. The lower current density was chosen to obtain a CuNi alloy in one layer. Since the limiting current density is dependent upon the concentration, the low current density value will vary for the different electrolytes. Approximately the same ratio (0.25) of total current to the limiting current was maintained. At an applied current density of -7.08, -1.76 and -0.71 mA cm\(^{-2}\), the copper wt% was 95, 97 and 99. At the higher applied current density of -35.38 mA cm\(^{-2}\) the composition was 59, 26 and 11 wt\% for copper in the three electrolytes. The nickel and tungsten concentrations were 36, 58, 69 and 5, 16, 19 wt\%, respectively.

Etching Characteristics

Polarization curves of the Cu-rich and NiW-rich CuNiW alloys were examined to assess the etching characteristics of individual layers during chemical etching in a chromic acid electrolyte. Figure 7.14 shows the etching of the deposits created from the 0.03 M Cu (II) electrolyte and Figure 7.15 from the low 0.003 M Cu (II) electrolyte. The cathodic part of the curves arise from H\(^+\) and O\(_2\) reduction and the anodic part is due to the etching of the deposit. The corrosion current densities and respective corrosion potentials of Cu-rich and NiW-rich
deposits are presented in Table 7.3. Both electrolytes have a higher corrosion current density for Cu-rich deposits indicating that this layer will dissolve at a faster rate than the NiW-rich deposits. The Cu-rich alloy has a less noble corrosion potential than NiW-rich alloys. The larger the difference between the corrosion current densities and potential of the Cu-rich and NiW-rich alloys, the better will be the selectivity of etching chemical. Therefore, the results suggest that multilayers can be preferentially etched, and that the deposit containing the least amount of copper in the NiW-rich alloy side, deposited from the electrolyte containing 0.003 M Cu (II), would be most selectively etched. Differences in the corrosion potential and current density may be attributed to not only the composition changes, but also deposit structure and variability in passivation.

Figure 7.13 Ohmic drop corrected polarization curves with a rotating disc electrode (rpm = 900) from electrolytes having different Cu ion concentrations.
Figure 7.14 Polarization curves of Cu-rich deposit (●) and NiW-rich deposit (□) from electrolyte A (0.03 M Cu (II)).

Figure 7.15 Polarization curves of Cu-rich deposit (●) and NiW-rich deposit (□) from electrolyte C (0.003 M Cu (II)) during electrochemical etching.
Table 7.3 Corrosion results for various deposits

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Deposit</th>
<th>Current Density (mA cm(^{-2}))</th>
<th>Corrosion Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyte A</td>
<td>CuNi</td>
<td>3.3</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td>CuNiW</td>
<td>2.3</td>
<td>83</td>
</tr>
<tr>
<td>Electrolyte C</td>
<td>CuNi</td>
<td>2.7</td>
<td>71</td>
</tr>
<tr>
<td></td>
<td>CuNiW</td>
<td>0.5</td>
<td>131</td>
</tr>
</tbody>
</table>

SEM

Figure 7.16-7.18 are SEM micrographs of multilayer examples after selective etching of the Cu-rich layer. The Cu-rich layers are darker than the NiW-rich layers. In all the images, layers are deposited from bottom to top. In Figure 7.16 Cu-rich (85 ± 32 nm) and NiW-rich (124 ± 25 nm) layers obtained from the electrolyte containing 0.003 M Cu (II) were electrodeposited at -0.71 mA cm\(^{-2}\) for 10 min and -35.38 mA cm\(^{-2}\) for 12 s, respectively. In Figure 7.17 the Cu-rich layer (99 ± 18 nm) was deposited at -7.08 mA cm\(^{-2}\) for 1 min and NiW-rich (140 ± 16 nm) layer was deposited at -35.38 mA cm\(^{-2}\) for 15 s from electrolyte containing 0.03 M Cu (II). A better quality of deposition and etching was observed using the concentrated Cu (II) electrolyte, even though the etching should have been more selective when the layers are electrodeposited from the more dilute Cu (II) solution. Thus, the conditions of electrodeposition are more critical than for etching.

Multilayers in Figure 7.18 were deposited at the same current conditions as discussed above but the time of the deposition was doubled for both the layers along with the etching time (from 30 s to 1 min). The thicknesses of Cu-rich and NiW-rich layers are 205 ± 13 nm and 280 ± 19 nm, respectively. The thicknesses of Cu-rich and NiW-rich layers are doubled by doubling the time, consistent with Faraday’s law. The multilayered features in all of these images have uniform layers with well defined interfaces. A disadvantage of using the more
concentrated electrolyte is that the deposit contains more copper and less tungsten in the NiW-rich layer. However it has been observed that even low amounts of tungsten in a NiW deposit can appreciably increase hardness [47].

Figure 7.16 SEM micrograph of multilayers from electrolyte 0.003 M Cu (II).

Figure 7.17 SEM micrograph of multilayers from electrolyte 0.03 M Cu (II).
Figure 7.18 SEM micrograph of multilayers from electrolyte 0.03 M Cu (II).

### 7.3.3 Nanowires

Figure 7.19 shows the polarization curve for the concentrated Cu (II) electrolyte using the nanoporous template electrode. The plateau reached at potentials more noble than -0.8 V is due to copper’s mass transport controlled deposition. Nickel and tungsten deposition start just after -0.8 V and -1.0 V, respectively. Water reduction also occurs after -0.8 V. Therefore, potentials ranging from -0.6 V to -1.0 and -1.0 V to -1.8 V were expected to obtain Cu-rich and NiW-rich multilayers, respectively, in a pulsed fashion.

Figure 7.20 and 7.21 present TEM results of nanowires deposited at -0.7 V for 80 s and -1.3 V for 10 s, where, dark and light layer thicknesses are 77 ± 6 nm and 7 ± 2 nm, respectively (Figure 7.20) and another case when the lower potential is deposited for a longer time, 120 s (Figure 7.21). Figure 7.22 is another example of nanowires deposited at -0.94 V for 60 s and -1.3 V for 10 s. The layer thickness is difficult to measure as the interface is not clear. Inspection of the current transients showed that at potential more positive than -0.93 V the current was
positive and hence oxidation took place (Figure 7.23), even though at steady state the current was expected to be negative and reductive. Current transients for the pulses between -0.94 V for 60 s and -1.3 V for 10 s, are all negative currents (Figure 7.24).

Figure 7.19 Ohmic drop corrected polarization curve with an alumina membrane.

Figure 7.20 TEM micrograph of multilayered nanowires, pulse: -0.7 V for 80 s and -1.3 V for 10 s.
Figure 7.21 TEM micrograph of multilayered nanowires, pulse: -0.7 V for 120 s and -1.3 V for 10 s.

Figure 7.22 TEM micrograph of multilayered nanowires, -0.94 V for 60 s and -1.3 V for 10 s.
Figure 7.23 Current transients during nanowire deposition, -0.7 V for 80 s and -1.3 V for 10 s.

Figure 7.24 Current transients during nanowire deposition, -0.94 V for 60 s and -1.3 V for 10 s.
In the region where an oxide can develop, the more positive potential was varied from -0.7 to -0.9 V (maintaining a constant potential and time of -1.3 V, 10 s for the other pulse).

Table 7.4 summarizes the layer thickness results. It was found that the CuNiW alloy (dark) layer thickness increased even at constant higher potential (-1.3 V) and time (10 s), when the lower potential was changed.

Table 7.4 Effect of lower potential on layer thickness

<table>
<thead>
<tr>
<th>Sample</th>
<th>Potential (V)</th>
<th>Time (s)</th>
<th>Layer thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-0.7</td>
<td>40</td>
<td>6 ± 3</td>
</tr>
<tr>
<td></td>
<td>-1.3</td>
<td>10</td>
<td>78 ± 7</td>
</tr>
<tr>
<td>B</td>
<td>-0.8</td>
<td>40</td>
<td>5 ± 2</td>
</tr>
<tr>
<td></td>
<td>-1.3</td>
<td>10</td>
<td>91 ± 5</td>
</tr>
<tr>
<td>C</td>
<td>-0.9</td>
<td>40</td>
<td>4 ± 1</td>
</tr>
<tr>
<td></td>
<td>-1.3</td>
<td>10</td>
<td>96 ± 9</td>
</tr>
</tbody>
</table>

It was also observed that an increase in time at the more positive potential did not increase the layer thickness which is consistent with a chemical step controlling the formation of an oxide. Table 7.5 summarizes these findings. Layer thickness did not increase proportional to time; when time is doubled to 80 s, there was an increase of 17 % but when it was further increased to 120 s, no change was observed in thickness. Longer time (120 s) at the lower potential resulted in multilayered features (Figure 7.21). In addition, the pulse nature of the deposit helps to reduce the amount of gas accumulated in the pores. At applied potentials more negative than -1.3 V the pores become blocked by excessive gas evolution.

Table 7.5 Effect of time on layer thickness

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>40</th>
<th>80</th>
<th>120</th>
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<td>Dark (alloy) layer thickness (nm)</td>
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7.4 Conclusions

Electrodeposition conditions were evaluated to achieve a disparity in deposit composition and smooth morphology for CuNi and CuNiW deposits. The larger amount of copper ions in the electrolyte lowered the amount of tungsten in the deposit. The current densities of $-35.38 \text{ mA cm}^{-2}$ and $-7.08 \text{ mA cm}^{-2}$ were found to be suitable for higher tungsten and copper contents in the alloy, respectively for thin film, multilayer fabrication.

The partial current densities of the metal reaction and side reactions were investigated. The Cu partial current densities increased with more copper in the electrolyte, as expected for a transport control. The Ni partial current densities were under kinetic control and observed to be the same for all three electrolytes up to -1.0 V, and then decreased as the copper amount in the electrolyte was reduced. The W partial current densities were affected by the addition of copper only when the copper concentration was reduced to 0.01 M from 0.03 M. No effect was observed when the copper concentration was further reduced to 0.003 M. The copper addition in the electrolyte decreased tungsten content in the alloy but improved the current efficiency.

The etching studies of the multilayers showed that the Cu-rich deposits etched preferentially compare to the NiW-rich deposits. The etching parameters of bulk Cu-rich and NiW-rich alloys were examined with rotating disk electrodes. The selectivity between the deposits were greater when deposited from electrolytes having less Cu (II) (0.003 M) compared to the electrolytes containing higher Cu (II) concentration (0.03 M), due to a greater disparity in deposit composition. Nevertheless, even a higher selectivity with regard to etching not always resulted in sharp and well defined multilayers. This indicated that the multilayered features were governed by electrodeposition rather than etching.
Multilayered nanowires of CuNiW and its oxide having nanometric scale were deposited for pulse potential conditions: -0.7 V, (x s); -1.3 (10 s), where the time, x ranged from 40 to 120 s. Increasing this time during the more positive potential, -0.7 V, did not change the layer thickness consistent with a non-metallic deposit, despite having a metallic deposit on rotating electrodes at this potential. Thus, multilayered deposition in this system is confounded by the formation of interfacial oxide at the low potential region and can be avoided by choosing a more negative potential.

7.5 References


8.1 Electrodeposition and Characterization of Nanowire/tube Catalysts

Cu-ZnO nanowire/tube and Mn-Cu-ZnO nanowire catalysts having different composition and morphology have been successfully prepared by pulse and direct electrodeposition from aqueous electrolytes using the template synthesis method. Their atomic environment was tailored by introducing varying off-times during deposition. Different off-times resulted in different bulk and surface composition. High direct current density resulted in tube morphology due to hydrogen bubbles generation inside the pores of the membranes. Pulse deposited nanowires were more homogeneous and uniform than their DC deposited counterparts due to uniform filling of the pores because of off-time. During an off-time, the electrode is replenished with ions therefore avoiding excessive cathodic side reaction that leads to local deposition in a single pore. Also, pulsing avoids excessive hydrogen evolution that can affect the deposition rate. Higher off times were found to be appropriate to obtain the uniform composition of nanowires as all the potential-time transient curves suggested a uniform redistribution of ions near the electrode.

Interestingly, there was a significant difference in the bulk and surface composition. Nanowires contained more ZnO and no MnO on the surface. During pulse electrodeposition, Cu content increased when Mn is added to the electrolyte, which can be attributed to a displacement reaction between Cu ion and freshly deposited Mn.

XRD showed that both Cu-ZnO and Mn-Cu-ZnO nanowire catalysts synthesized at different off-times were composed of a well crystalline material containing metallic Cu and ZnO with minor Cu$_2$O peaks in some nanowires which could be due to the oxidation of some of the
copper during transfer and storage because E-pH diagram suggested that the copper should be
deposited as metallic Cu. XRD also showed FCC crystal lattice for Cu and that the nanowires
grew preferentially in the (111) direction. Cu crystallite size increased with an increase in off-
time due to higher degree of recrystallization with increasing off-times.

TPR results showed that Cu-ZnO and Mn-Cu-ZnO nanowire catalysts had lower
reduction temperature (255–270°C) than bulk CuO nanowires (330°C). This difference in
reduction temperature is due to strong interaction between ZnO and CuO. TPR also showed
that increasing the rest time increased the reduction temperature slightly. The reason could be
more compact structure of the nanowires having more rest time possibly due to more
hydrogen bubble release and also due to different crystalline structure.

The results of the present work demonstrate that a desired composition and
morphology of the nanowires can be achieved with an appropriate selection of various
parameters during pulse electrodeposition even when the two species such as Cu and Mn have
very disparate reduction potentials and therefore difficult to obtain a desired composition.

In the future, nanowires thinner than 400 nm can be prepared by using their precursor
membranes having smaller pore size. This will help in increasing the active surface area and
thus their activity during CO hydrogenation. Nanowires with different morphology can also be
synthesized by using different pulse schemes such as cathodic pulse followed by an anodic
current, cathodic pulse followed by an anodic current and then an off-time, and a train of
cathodic pulses followed by a train of anodic pulses. Mn content in nanowires can be increased
on the surface by adding an additive agent or applying a suitable pulse. Supported
nanowire/tube catalysts can also be prepared by addition of nanoparticles of the support such as silica to the electrolyte.

To further enhance the surface area, nanotubes can be synthesized. Compositionally uniform nanotubes can be obtained by coating the walls of the membrane pores with metal or molecular anchors so that deposition begins from the wall rather than the bottom of the pores. Another approach could be – the use of an electrolyte containing only Cu ions subjected to very high current density so that deposition occurs only on the wall of the membrane resulting in very thin (a few atomic layers) tubes and then putting this membrane is another electrolyte containing all the ions of interest. As the wall is conductive because of Cu on it, the deposition will occur on the wall and thus final nanostructures will be nanotubes.

HR-TEM/STEM analysis should be done to understand how the composition and morphology along the length and cross-section of a nanowire/tube changes when electrodeposition conditions are varied and how it affects the activity and selectivity toward various products during CO hydrogenation (syngas conversion).

8.2 CO Hydrogenation over Nanowire/tube Catalysts

The nanowire/tube catalysts were then used as catalysts for syngas conversion reactions. Temperature was varied from 250°C and 310°C while keeping other parameters constant. It was found that the selectivity toward ethanol, higher alcohols, and higher alkanes goes through a maximum at 290°C. Nonetheless, selectivity toward CO₂, propylene, and methane was minimum at 290°C in the temperature range studied. It was also observed that the conversion increased with the temperature. The increase in H₂/CO ratio (1 to 3) decreased the selectivity toward ethanol and higher alcohols. However, selectivity to methanol and methane, conversion
increased with its increase. Nanowire catalysts showed higher selectivity toward ethanol and higher alcohols when H₂/CO is 1; it is good because most of the gasifiers produce H₂/CO ratio close to 1 [1].

Longer off-time during electrodeposition resulted in enhanced selectivity to ethanol, which increased from 9.65% to 12.3%. Also, selectivity toward propylene and CO₂ increased with longer off-time. However, selectivity to higher alcohols decreased slightly from 2.20% to 1.89% with the increase in off-time. Different catalytic behavior of these catalysts was due to different composition and atomic environment. The atomic environment can significantly change due to several phenomena occurring during off-time such as surface diffusion, recrystallization, and passivation of the freshly deposited material [2, 3]. Another important reason could be the hydrogen gas release because hydrogen atoms in the deposit combine to form molecular hydrogen during the off-time and escape from the deposit [4].

Cu-ZnO nanotubes showed very low selectivity toward alcohols due to very less Cu content. Therefore, optimization of electrodeposition conditions is required to increase the amount of copper and compositional uniformity to take advantage of the higher surface area of this morphology. Addition of manganese to Cu-ZnO nanowires improved the selectivity toward C₂-C₄ alcohols. It can be attributed to the oxidizing nature of Mn because it is believed to partly oxidize the Cu to Cu⁺ and these ions could then become active centers [5].

Schulz-Flory distributions of the products suggest that the synthesis of alcohols and hydrocarbons require different sites [6]. Alcohol formation does not follow Schulz-Flory distribution well, whereas hydrocarbon synthesis behave like modified Fischer–Tropsch catalysts [7, 8].
Based on the literature and product distribution, it can be suggested that ethanol can form via the hydrogenation of the acetyl species, which in turn formed from a reaction between two adsorbed formyl species. Higher alcohols can form from a reaction of formyl species with the actetyl species [9].

In the future, however, experimental studies such as FTIR and isotopic labeling of its reactants during syngas conversion reaction can be done to devise a mechanism that specifically works on these types of catalysts. FTIR studies should be done with a MSD to monitor the surface intermediates and final products under continuous or transient flows of reactant gases. In particular, changes in CO adsorption and stretching frequency may be related to the CO dissociation and therefore ethanol/methane selectivity. Transient switching between reactant gases and inert components will allow dynamic information about desorption and reaction rates to be obtained. Correlation between downstream reaction products and the surface species can be used to learn how the reaction progresses. Addition of isotopically labeled compounds such as CO, methanol, and ethanol can be done to better understand the reaction mechanism. A computational model of CO hydrogenation on nanowire/tube catalysts can also be devised to better understand the reaction mechanism. Kinetic study and development of a kinetic model can also be done. Cost analysis for nanowire catalysts can be done for its potential commercialization.

8.3 References


Figure A1. Drawing of the columns and valves installed in the GC
APPENDIX B: CALIBRATION OF GC-MS

The GC-MS system was periodically calibrated by using gas cylinders having known compositions of the components to be analyzed. The following graphs were generated during one of the calibrations.

- Methanol: $y = 1.739 \times 10^2 x$

- Ethanol: $y = 3.911 \times 10^3 x$
Acetaldehyde
\[ y = 7.860 \times 10^2 \times x \]

Acetone
\[ y = 9.531 \times 10^3 \times x \]
Isopropanol

Response

1.00e+006
5.00e+005
0.00e+000

0
50
100
Concentration

$y = 1.052e+004x$

1-Propanol

Response

2.00e+004
0.00e+000

0
50
100
Concentration

$y = 3.350e+002x$
Isobutanol

Response

2.00e+004

0

Concentration

0

50

100

$y = 3.010e+002 \times$

1-Butanol

Response

1.00e+005

0

Concentration

0

50

100

$y = 1.450e+003 \times$
y = 1.965e+003 x

y = 5.265e+003 x
n-Hexane

Response

Concentration

$y = 6.358e+003 \times$

Carbon Monoxide

Response

Concentration

$y = 9.226e+004x$
Methane

$y = 7.033 \times 10^4 x$

Carbon Dioxide

$y = 1.064 \times 10^5 x$
APPENDIX C: ERROR ANALYSIS

Selectivity of a component is given by:

\[ \text{Selectivity (S)} = \frac{100NiCi}{\sum NiCi} \]

Where, \( Ni \) is the number of carbon atoms in a product and \( Ci \) is its concentration (mol%). Selectivity is a nonlinear function of concentration.

For such functions mean (E) is given by,

\[ E(S) = \mu_{Ci} = h(\mu_{Ci}) \]

And variance (V) is determined by the following formula,

\[ V(S) = \sum_{i=1}^{n} \left( \frac{\partial h}{\partial Ci} \right)^2 \sigma_{Ci} \]

Where the partial derivative are evaluated at \( \mu_{Ci} \).

An example of the error estimation is presented in the following table.

Table A : Error estimation for the CO hydrogenation results on the nanowire catalyst with long off-time covered in Chapter 6

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<th>σ²</th>
<th>σ</th>
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<th>%C</th>
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Electrodeposited Cu–ZnO and Mn–Cu–ZnO nanowire/tube catalysts for higher alcohols from syngas

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1. Introduction

The synthesis of higher alcohols from syngas has attracted attention recently as these compounds have been studied for use as neat fuels and fuel additives [1], as well as hydrogen carriers [2,3]. Because syngas can be produced from a wide range of feedstocks such as biomass, coal, and natural gas, the choice of higher alcohols as a potential end product is attractive given the wide range of possible end uses for these oxygenates.

The hydrogenation of CO to produce C1+ alcohols has been studied on a number of catalysts, including supported rhodium [4], modified Fischer–Tropsch catalysts [5], sulfides [6], and promoted Cu-based catalysts [7]. Although Rh-based catalysts typically show the greatest selectivity to higher alcohols, the high cost of rhodium may limit its use in large-scale processes. The relatively low cost of Cu-based catalysts, and the fact that they can be modified to increase their selectivity to higher alcohols, suggest that these materials be studied further. Much of the work reported on these catalysts is based on the addition of alkali promoters to methanol synthesis catalysts. However, the hydrogenation of CO to produce higher alcohols is typically limited by low selectivities due to excessive methane and CO2 formation [2,8].

Catalysts for the synthesis of higher alcohols have most often been prepared by conventional methods such as wet impregnation and co-precipitation. Recently, there has been increased interest in developing novel synthesis approaches such as coating of nanoparticles [9], and the use of shape-selective carbon nanotubes as supports [10].

Here, we report a novel synthesis method to prepare Cu-based catalysts to synthesize alcohols from syngas, based on electrodeposited nanowires and nanotubes of Cu–ZnO and Mn–Cu–ZnO. Electrodeposition is a process in which metals/oxides are deposited on a substrate (cathode) from an aqueous salt solution when an appropriate current/potential is applied. The main advantage of electrodeposition over conventional techniques is the control of the active metal environment, a critical property of a catalyst.

In the present study, two types of catalysts prepared by electrodeposition are compared: Cu–ZnO catalysts representing an unpromoted methanol synthesis catalyst, and Cu–Mn–ZnO, a nominally similar catalyst promoted with Mn. The choice of Mn as a promoter is based on its reported ability to increase selectivity to higher alcohols [7], and the fact that it can be electrochemically co-reduced with Cu in the electrodeposition process used here. Although alkali metals are often used as promoters for Cu-based catalysts [11], their high negative reduction potential, limits the ability to electrodeposited them along with Cu.

To the best of our knowledge, electrodeposited Cu–ZnO-based nanowires have not been used as heterogeneous catalysts. However, electrodeposition of ZnO nanowires has been studied for their application in solar cells and sensors [12,13]. Electrodeposited nanowires of CuO have been examined for their photocatalytic properties [13,14], and Cu–Mn–ZnO nanowires have been prepared to enhance the semiconducting properties of...
VITA

Mayank Gupta was born in December, 1978, in Sandhi, Tehsil-Orai, District-Jalaun, Uttar Pradesh (UP), India. He grew up in Orai, Uttar Pradesh. He completed his high school from Uttar Pradesh Sainik School, Lucknow, Uttar Pradesh. He received his Bachelor of Technology degree in pulp and paper engineering in 2001 from Indian Institute of Technology (IIT) Roorkee. He then worked for a year at ITC Limited in India. He then moved to the United States for his graduate studies and completed his master of science degree in paper science and engineering from University of Minnesota, Twin Cities, in 2004. After that he started his doctoral studies in chemical engineering at LSU in Fall 2004. He received a master’s degree (non-thesis) in chemical engineering in 2008 while pursuing the doctorate. He expects to graduate in May 2010.