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Catalytic Hydrogenation of CO to Higher Alcohols

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CATALYTIC HYDROGENATION OF CO TO HIGHER ALCOHOLS

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

Nachal Devi Subramanian
B.Tech., Central Electrochemical Research Institute, India, 2006
May 2011
Dedication

This work is dedicated to my loving family
Acknowledgements

It would not have been possible to achieve this major academic accomplishment without the help, guidance, and support of some very important people in my life. I hope they share this tremendous joy and achievement with me. First and foremost, I would like to thank my parents and grandparents, for their love, support, patience, encouragement and countless sacrifices throughout my life. I thank my aunts and uncles, brothers and cousins for their endless love and support. I can never forget the joyful occasions and festivals I have spent with my loving family. I thank the Almighty God, for the gift of life, love, knowledge and understanding.

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Abstract

The interest in converting synthesis gas to alcohols and oxygenated fuel additives via CO hydrogenation is growing rapidly due to the increasing rise in oil prices. Among the potential end products, ethanol is desirable since it serves as a clean alternative fuel, a gasoline blend, and a hydrogen carrier to supply fuel cells. The high cost and limited availability of the most active/selective Rh-based catalysts has led to the development of base metal catalysts such as modified Cu-based catalysts. Literature suggests that a combination of Co (or Mn) with Cu can facilitate higher alcohol formation by a non-dissociative adsorption of CO on the Cu sites, followed by insertion of CO into growing hydrocarbon chains formed from dissociated CO on the Co (or Mn) sites. The goal of this research work was to synthesize, characterize and test two types of copper-based catalysts – bimetallic nanoparticles and pyrochlores, for the hydrogenation of CO to higher alcohols, particularly ethanol.

Copper-based bimetallic nanoparticles with core-shell morphologies synthesized using wet-chemical methods were the major focus of this dissertation. Uniformly dispersed and highly reproducible Cu core-Mn$_3$O$_4$ shell (Cu@Mn$_3$O$_4$) and Cu core-Co$_3$O$_4$ shell (Cu@Co$_3$O$_4$) nanoparticles were synthesized with a porous shell, thereby making the copper core accessible. DRIFTS (in-situ FTIR) showed that the Cu@Mn$_3$O$_4$ nanoparticles have a greater CO adsorption capacity and a lower CO dissociation activity, while the Cu@Co$_3$O$_4$ nanoparticles showed a higher selectivity towards alcohols and oxygenates, with the total alcohols/oxygenates being 48% of the total products. An ethanol selectivity of 15% (with a corresponding methane selectivity of 11%) was achieved at 10 bar, 270 °C and H$_2$/CO=2.

Another focus was on Cu-ZnO based catalysts supported on La$_2$Zr$_2$O$_7$ pyrochlores which are believed to be promising candidates as supports for stable and active copper catalysts for CO
hydrogenation. Mn or Co promoted Cu-ZnO-La$_2$Zr$_2$O$_7$-Li$_2$O catalysts were synthesized by coprecipitation. Addition of Mn or Co promoter increased the overall extent of reduction of the catalysts. DRIFTS studies showed increased CO chemisorption and negligible methanation on the Mn promoted catalyst under the conditions tested, while methane was the major product on the Co-promoted catalyst.
Chapter 1: Introduction

1.1 Research Objective

The purpose of the research described here is to synthesize copper-based catalysts for the hydrogenation of CO to higher alcohols with the following objectives in mind:

• Achieve uniformly dispersed copper-based core-shell nanoparticles using wet-chemical synthesis methods with high reproducibility.

• Synthesize Cu-ZnO based catalysts supported on La$_2$Zr$_2$O$_7$ pyrochlores.

• Characterize the nanoparticles and pyrochlores using various techniques (including synchrotron radiation based tools) and real time (in-situ) studies to develop structure-activity relationships for CO hydrogenation.

1.2. Rationale for This Research

With today’s increasing oil and energy prices, there is a need to look for alternative commercially viable energy sources $^1$. Figure 1.1 shows the production and consumption of the various fossil fuels (coal, natural gas and petroleum) since 1950 in the United States $^2$. The analysis shows that the U.S. produced sufficient amounts of coal for its requirements, whereas the natural gas production was less than its consumption after the year 1967. Of all the three fuels, petroleum production never satisfied domestic demand and hence the U.S. relies more heavily on imported supplies. It is apparent that the economical and efficient way to become energy independent is to use the domestic resources. Alternatively, renewable fuels (derived from biomass, solar, wind, geothermal, etc.) as opposed to the non-renewable fuels (produced
from fossil fuels) is receiving increased attention because these resources can have less net environmental impact through lower greenhouse gas emissions.

![Figure 1.1: Production as share of consumption for coal, natural gas and petroleum in the United States](image)

According to the International Energy Outlook 2010, the projections indicate an increase in the consumption of liquid fuels and other petroleum-based fuels from 86.1 million barrels per day in 2007 to 110.6 million barrels per day in 2035. To satisfy this increase in world liquids demand, liquids production is projected to increase by 26 million barrels per day from 2007 to 2035. This includes the production of both conventional liquid supplies (crude oil and lease condensate, natural gas plant liquids, and refinery gain) and unconventional supplies (biofuels, oil sands, extra-heavy oil, coal-to-liquids, gas-to-liquids, and shale oil). World oil prices reached historically high levels in 2008, mainly because of a strong increase in demand for transportation fuels, particularly in emerging non-OECD economies. The sustained high world oil prices allow for the economical development of unconventional resources and the use of enhanced oil recovery technologies to increase production of conventional resources. This brings
in the necessity of innovative research for the cost-effective conversion of domestic coal/biomass reserves into clean fuels.

Bio-based fuel resources, particularly ethanol, have been studied extensively in the recent years as clean, sustainable and transportable fuel alternatives \(^1\text{,}^4\). The major routes to produce ethanol are categorized as biochemical and thermochemical routes. The biochemical route involves the fermentation of sugars derived from corn or sugarcane \(^5\text{–}^6\), and the thermochemical route is mainly gasification of biomass (which can be mixed with coal or natural gas) to produce a gaseous mixture called synthesis gas (or syngas) which can then be catalytically converted to ethanol and other higher alcohols \(^5\). Biochemical processes result in higher selectivities towards specific end products, but their reaction rates are orders of magnitude lower than that of the thermochemical processes and the product is an aqueous mixture that must be separated before it can be used. Thus the thermochemical routes to produce ethanol are more economically competitive \(^5\).

A typical syngas mixture obtained from industrial coal/biomass gasifiers contains primarily CO and H\(_2\), with some CO\(_2\) and H\(_2\)O. The H\(_2\)/CO ratio of the syngas mixture depends mainly on the type of feedstock used and the operating conditions of the gasifier \(^7\). The catalytic hydrogenation of CO is one of the most promising technologies for the synthesis of ethanol and higher alcohols from syngas. This process has been studied for over a hundred years \(^6\), but it is not yet an economically and commercially viable process.

Among the potential end products of catalytic CO hydrogenation, ethanol is more desirable since it serves as a clean alternative fuel \(^8\text{–}^{10}\), a gasoline blend, and as a hydrogen carrier to supply fuel cells \(^6\). In addition to its potential application as a transportation fuel, ethanol has been
considered as a feedstock for the synthesis of variety of chemicals, fuels and polymers\textsuperscript{11-12}. However, the major application of ethanol for which a widespread market exists is its use as a fuel additive\textsuperscript{5}. It is estimated that biomass-derived ethanol could replace as much as one-third of the domestic petroleum use in the near future\textsuperscript{13}. The use of ethanol as a transportation fuel is shown to produce lower greenhouse gas emissions\textsuperscript{5-6}.

1.3. Thermodynamics of CO Hydrogenation

The hydrogenation of CO to produce ethanol is a highly exothermic and thermodynamically favorable reaction:

\[
2CO + 4H_2 \rightarrow C_2H_5OH + H_2O
\]

\[\Delta H_r^\circ = -61.20 \text{ kcal mol}^{-1}\]

\[\Delta G_r^\circ = -29.32 \text{ kcal mol}^{-1}\]

Two important side reactions are the water gas shift and methanation reactions. Oxygenates and hydrocarbons are always accompanied by the production of water, which can react further to form CO\textsubscript{2} through the water–gas-shift (WGS) reaction\textsuperscript{14}

\[
CO + H_2O \leftrightarrow CO_2 + H_2
\]

\[\Delta H_r^\circ = -9.84 \text{ kcal mol}^{-1}\]

\[\Delta G_r^\circ = -6.85 \text{ kcal mol}^{-1}\]

The WGS reaction is desirable for syngas feed with a low H\textsubscript{2}/CO ratio as the reaction generates additional H\textsubscript{2}, but it is undesirable for feeds containing a high H\textsubscript{2}/CO ratio. Coal-derived syngas
has a H₂/CO ratio of ~0.7, which can be adjusted via the water gas shift reaction to that required for ethanol synthesis. However, higher H₂/CO ratios may lead to the formation of hydrocarbons, particularly methane, while at lower H₂/CO ratios, higher oxygenate selectivity would be expected.

Another important side reaction is the methanation:

\[ CO + 3H₂ \rightarrow CH₄ + H₂O \]

\[ \Delta H_r^\circ = -49.26 \text{ kcal mol}^{-1} \]

\[ \Delta G_r^\circ = -33.97 \text{ kcal mol}^{-1} \]

Methane is the most thermodynamically favored product. Figure 1.2 shows the result of a thermodynamic analysis of the CO hydrogenation reaction for a wide range of products (methane, CO₂, H₂O, ethanol and C₂⁺ oxygenates) as a function of temperature, assuming a stoichiometric mixture of CO and H₂ (H₂/CO = 2.0) at 20 bar. Ethanol selectivity at equilibrium is virtually zero at all temperatures when methane is allowed as a product. Thus, to increase the ethanol yield and selectivity, the thermodynamically favored methane formation must be kinetically limited.

1.4. Mechanism Involved in CO Hydrogenation

The general mechanism of C₂⁺ oxygenates formation from syngas has been extensively studied, with the overall objective of finding a catalyst with high yields and selectivities towards C₂⁺ alcohols and oxygenates, while, at the same time, minimizing the side reactions such as methanation, methanol formation, and water gas shift reactions. Spivey and Egbebi reported a
Figure 1.2: Equilibrium composition for the hydrogenation of CO to ethanol, with methane and C$_2$+ oxygenates formation allowed (H$_2$/CO = 2, 20 bar, calculated using HSC software).

simplified sequence of reaction steps involved in the CO hydrogenation mechanism on Rh based catalysts (Figure 1.3) $^5$. CO dissociation is believed to be the first step. The resulting surface carbon is then hydrogenated to form a surface hydrocarbon species, (CH$_x$)$_{ads}$. This (CH$_x$)$_{ads}$ species can then undergo: (a) CO insertion to form oxygenates, or (b) hydrogenation to form methane, or (c) chain growth to form higher hydrocarbons. In a parallel reaction sequence, associatively adsorbed CO can be hydrogenated directly to form methanol $^{5,17,20}$. Methane is the most thermodynamically favored product, but is economically undesirable. Thus, hydrocarbon formation, which typically accompanies high catalyst activity, must be suppressed kinetically to maximize the ethanol selectivity.
1.5. Catalysts

Generally, a catalyst active for higher oxygenate synthesis must contain both adsorbed molecular CO, and surface carbon species produced by dissociative adsorption of CO. So the catalyst must be able to dissociate only a portion of the CO molecules and must balance this with the hydrogenation of the intermediate to form alcohols. Hydrogenation of the \((\text{CH}_x)_{\text{ads}}\) intermediate produces undesirable methane \(^5\). However, the formation of ethanol can be significantly enhanced by the addition of suitable promoters \(^{21-23}\).

Promoted Rh-based catalysts have been reported to show the highest activity and selectivity for the formation of ethanol and other C\(_2^+\) oxygenates due to their ability to catalyze both CO dissociation and CO insertion \(^{16,18,24-27}\). For example, Hu et al. recently reported 56\% selectivity to ethanol on a 6\% Rh-Mn/SiO\(_2\) powdered catalyst \(^{28}\). However, the high cost and limited
availability of the Rh metal makes it difficult to achieve an economical process. This has led to the development of base metal catalysts such as the Cu-based, Fischer-Tropsch, or Mo-based catalysts. Novel materials such as carbon nanotube-based Rh catalysts, Cu-Co based nanoparticles, electrodeposited Cu-Zn based nanowires, Rh catalysts in microchannel reactors have also been reported recently for this reaction.

1.6. Outline of the Dissertation

Chapter 1 describes the major research objectives of this work. It introduces the concept behind the need for alternative energy sources and the processes used for converting coal or biomass derived syngas to C$_2$+ alcohols. It also describes the thermodynamics involved in CO hydrogenation and the major side reactions limiting the activity and selectivity of the catalysts towards higher alcohols and oxygenates. The general mechanism involved in the C$_2$+ alcohol/oxygenate formation during CO hydrogenation is also discussed.

Chapter 2 reviews the literature on the major catalyst types that have been studied for the hydrogenation of CO. The effect of promoters, supports, catalyst synthesis methods and the necessity to atomically control the catalyst compositions are discussed. Finally, the choice of catalysts for this particular work and a brief literature review of the types studied have been described.

Chapters 3-7 are written in journal style. Chapter 3 has been published in a peer-reviewed journal; Chapters 4 and 6 have been submitted for publication and are currently under review; Chapters 5 and 7 will be submitted for publication [These stand-alone journal chapters have some overlap or duplication in some subsections with regards to the introduction and experimental methods used, however the results are unique and address various aspects of the
experimental objectives]. In addition to these chapters, the effect of reaction conditions - temperature, pressure, H₂/CO ratio and space velocity - on the activity and selectivity of Rh/SiO₂-based catalysts (synthesized at Clemson University) has been published in a peer-reviewed journal ²⁴.

**Chapter 3** examines the CO hydrogenation activity and selectivity towards C₂+ alcohols and oxygenates on two sets of novel Co-Cu bimetallic nanoparticles synthesized by wet chemical methods: (i) Co core-Cu shell and (ii) Co-Cu mixed nanoparticles. The effect of reaction temperature on their activity and selectivity is studied.

**Chapter 4** demonstrates a wet-chemical approach for the synthesis of Cu core (~6.1 nm) - porous Mn₃O₄ shell (~3.4 nm thick) nanoparticles and focuses on various characterization techniques, including synchrotron radiation-based SAXS and XANES tools, to confirm the core-shell structure. While the optical properties of the core Cu nanoparticles are influenced by the Mn₃O₄ shell, the magnetic properties of the core-shell particles were found to be similar to those of Mn₃O₄ nanoparticles reported in the literature.

**Chapter 5** is a Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) or *in situ* FTIR study on Cu core-Mn oxide shell (Cu@Mn₃O₄) and Cu core-Co oxide shell (Cu@Co₃O₄) nanoparticles. The evidence for the lack of CO adsorption on the catalysts in the presence of organic surfactant ligands is provided and the DRIFTS results of CO adsorption and CO hydrogenation on the ligand-free nanoparticles are discussed. A comparison between the CO adsorption properties of Cu@Mn₃O₄ vs. Cu@Co₃O₄ nanoparticles, together with the CO hydrogenation results at 10 bar and 270 °C are provided.
Chapters 6 and 7 are focused on Cu-ZnO-La$_2$Zr$_2$O$_7$ based catalysts. Chapter 6 is an *in-situ* XRD and XANES study of Mn- or Co-promoted copper-rare earth zirconate (Cu-ZnO-La$_2$Zr$_2$O$_7$-Li$_2$O) pyrochlore catalysts under H$_2$-TPR conditions. The focus of this study is to investigate the structural and chemical changes in the local environment of copper induced by the transition metal promoters under reducing environments.

Chapter 7 investigates the CO adsorption properties of Mn- or Co- promoted Cu-ZnO-La$_2$Zr$_2$O$_7$-Li$_2$O pyrochlore catalysts by *in-situ* FTIR (DRIFTS) study coupled with mass spectrometry (MS) at 1 bar using CO and H$_2$ as probe molecules. DRIFTS, equipped with an online mass spectrometer for continuous monitoring of the product stream, permits monitoring the surface species during steady state or transient reaction conditions. The nature of the active sites and the surface intermediates involved in CO hydrogenation are discussed.

Chapter 8 summarizes the conclusions drawn from Chapters 3-7 and also offers recommendations for future work.

### 1.7. References


Chapter 2: Literature Review

It is well known that syngas conversion to C$_2$+ alcohols and oxygenates is often limited by the formation of methane and methanol. However, C$_2$+ alcohols are more desirable products, both as neat fuels$^{1-3}$, fuel additives, or as carriers for hydrogen to supply fuel cells. Hence, the development of a suitable and efficient catalyst to produce higher alcohols from syngas, coupled with an understanding of the underlying reaction mechanism, is very important.

2.1. Catalyst Types Being Studied

The majority of catalysts that have been studied for CO hydrogenation can be broadly classified into the following four categories$^4$:

(1) Rh-based catalysts

(2) Modified methanol synthesis catalysts (Cu-based)

(3) Modified Fischer-Tropsch based catalysts

(4) Modified Mo-based catalysts

Rh-based catalysts have been found, so far, to be the most active/selective catalysts for the synthesis of higher alcohols from CO hydrogenation$^{4-12}$. The high activity and selectivity of C$_2$+ oxygenate synthesis on Rh catalysts has been attributed to their ability to catalyze both CO dissociation and CO insertion$^{7,13}$. The most relevant feature of Rh is its ability to adsorb reactive CO both associatively and dissociatively, allowing it to form both hydrocarbons and oxygenates. This is in agreement with the catalytic behavior of Rh in CO hydrogenation since it has been suggested that metals which adsorb CO strongly enough to activate the molecule, but not dissociate it readily, are active catalysts for the formation of C$_2$+ oxygenates$^{12,14-15}$. Hu et al.
reported 56% selectivity to ethanol with a 25% CO conversion on a 6% Rh-Mn/SiO$_2$ powdered catalyst $^9$. Subramanian et al. achieved 52% selectivity to ethanol with an 8% CO conversion on a 1.5% Rh/La/V/SiO$_2$ catalyst $^{11}$.

The high cost and limited availability of the Rh metal $^5$ has led to the development of base metal catalysts such as modified Cu-based catalysts. However, methanol remains the dominant product on most Cu-based catalysts, although the formation of C$_2$+ alcohols and oxygenates can be greatly enhanced by the addition of suitable promoters. Modified copper-based catalysts have been widely studied for this reaction $^{16-24}$. Various alkali promoters such as Li, Na, K, Rb and Cs have been explored on Cu-based catalysts and higher alcohol synthesis has been found to increase with increasing alkali atomic size, in the order Li < Na < K < Rb < Cs $^4$. These alkali promoters are reported to neutralize the surface acidity (acid sites) thereby suppressing unwanted side reactions, and provide basic sites necessary for the C-C and C-O bond forming reactions $^4$. However, the promoter type, concentration and catalyst support, among other factors, affect the degree of promotion. K or Cs promoted Cu/ZnO-based methanol synthesis catalysts supported on either Al$_2$O$_3$ or Cr$_2$O$_3$ were found to produce a mixture of linear and branched C$_1$-C$_6$ alcohols, with a small amount of other oxygenates and hydrocarbons $^5$.

A wide range of Cu-Co-based catalysts have been reported in the literature for higher alcohol synthesis $^5$, $^{20}$, $^{24-25}$. The high yield and selectivity of higher alcohols on these catalysts has been attributed to the synergistic interaction between Cu and Co, and properties such as particle size, dispersion and reducibility $^{16}$. Cu-Co catalysts have been tested on support materials like MgO, La$_2$O$_3$, CeO$_2$, TiO$_2$, ZrO$_2$ and SiO$_2$, and the selectivity towards higher alcohols on SiO$_2$ and ZrO$_2$ were found to be the highest with 29 and 25% respectively $^{16}$. Rare-earth oxide supports like La$_2$O$_3$ and LaYO$_3$ have also been reported to promote higher alcohol formation, but they suffer
from carbon deposition and deactivation. Thus the CO hydrogenation activity is strongly affected by the presence of promoters, catalyst cluster size and shape, support, synthesis methods, pretreatment, and reaction conditions. The advantage of having mixed metals (alloy, core–shell, or physical mixture) is that they can be used to prepare catalysts with different metal-promoter morphologies and to control atomic-level interactions. This may lead to further improvement in the selectivity to desired products.

2.2. Catalyst Synthesis Methods

The activity and selectivity of catalysts is strongly influenced by the preparation method. The metal clusters need to be uniform in size, evenly spaced to avoid agglomeration and resistant to sintering at high temperatures. Scalability, batch-to-batch reproducibility and cost-effectiveness are also important factors to be considered in a catalyst preparation method. Typical catalyst preparation techniques include impregnation, co-precipitation, deposition–precipitation, sol-gel process, hydrothermal method, etc. Co-precipitation, using a precipitating agent like urea, ammonia or oxalic acid, is the most frequently applied method of catalyst preparation. It is reported to yield catalysts with higher metal loadings, greater dispersion, and homogeneity compared to other methods. Impregnation methods are suitable for lower metal loadings (< 10%) and they are very less time-consuming compared to other methods, but they are difficult to control and can lead to non-uniform deposition of the impregnated material on the support.

However, achieving desired metal-promoter morphologies and atomic-level control over the structure of the catalysts is still limited with these conventional techniques. The achievement of such an atomic-level control may lead to further improvement in the selectivity to desired products. Atomically controlled nanoparticles are being given considerable attention due to their
interesting properties and potential applications as catalysts that are not found in their respective bulk counterparts. There are several methods that have been reported for the controlled synthesis of such nanoparticles (See Section 2.4 for further details).

2.3. Catalyst Types in This Work

The work reported here focuses on two types of copper-based catalysts – bimetallic nanoparticles and pyrochlores. Cu-based bimetallic nanoparticles studied here were synthesized by wet chemical methods using organic surfactants. The intention of developing bimetallic nanoparticles through wet chemical methods was to achieve atomic level control over catalyst compositions and metal-metal interactions.

Second, Cu-ZnO-La$_2$Zr$_2$O$_7$ based pyrochlores were synthesized by coprecipitation. La$_2$Zr$_2$O$_7$ pyrochlores are believed to be promising candidates as supports for stable and active copper catalysts for CO hydrogenation to higher alcohols and oxygenates, due to their excellent thermal and chemical stability towards deactivation and low sintering rates (See section 2.5 for further details).

2.4. Nanoparticles as Catalysts

The study of catalysis with nanoparticle surfaces is growing rapidly. Nanomaterials are transforming modern science and technology due to their unique optical, electronic, catalytic, and magnetic properties that are not found in the corresponding bulk materials. Their unusual properties have been attributed to their high surface to volume ratios, inter-particle interactions, and surface electronic structure. Several methods have been reported for the synthesis of nanostructured materials, and the control of particle size and shape is an
important factor in exploiting their applications in diverse fields including catalysis, optics, biosensors, drug delivery, and electrochemistry.

Lately, bimetallic nanoparticles (either alloy or core-shell type structures) are receiving interest since they exhibit improved electronic, optical, physiochemical and catalytic performances compared to the monometallic nanoparticles. Core-shell nanoparticles are of economic interest as well, since precious materials can be deposited on inexpensive cores. They provide excellent control over surface properties through modulation of shell and core dimensions. Although core–shell type catalysts have only one type of surface metal, their electronic structure and catalytic properties are substantially modified because of the interactions of the shell atoms with the core atoms.

Core-shell nanoparticles have been investigated both as a means to improve the stability and surface chemistry of the core nanoparticle and as a way of accessing unique physical properties that are not possible from one nanomaterial alone. In addition, the nanoporosity of the shell is an interesting property of core-shell particles which promises to have great potential in the field of catalysis. Reactants and products can diffuse through the porous shell, thus allowing catalysis to occur at the peripheral or interfacial areas between the core and the shell. There are many literature reports on Ru-Pt, Au-Ag, Au-Pd, Au-Pt, Co-Cu, Au-Ru, Fe-Au, Cu-Au, Cu-Pd, Cu-Pt, Fe-Pd, Fe-Pt bimetallic (alloy or core-shell) nanoparticle systems. Synthesis methods include microemulsion techniques, displacement reactions, high-temperature transmetallation reactions, hydrothermal method, sol–gel method and polyol process.
Among various metal nanoparticles reported, copper is one of the most commonly studied transition metals. Copper nanoparticles have been used as catalysts, heat transfer fluids and optical sensors, and as a result are being explored as a substitute for expensive metals such as Au, Ru, Rh, Pt and Pd. Some of the reported preparation methods for synthesizing copper nanoparticles include chemical reduction \(^2^5, 4^0, 5^3\), sonochemical reduction \(^3^7, 5^2, 5^7, 6^6\), photolytic reduction \(^5^4, 6^6\), radiolytic reduction \(^5^5, 6^6\), microwave-assisted synthesis, laser ablation \(^6^6\), metal evaporation \(^5^6\), thermal decomposition \(^7^5\) and microfluidic synthesis \(^4^1, 7^6\). Copper is also a well known plasmonic (optical) material which when combined with a magnetic material, results in a system that shows excellent magneto-optical (magnetoplasmonic) \(^4^3\) properties.

Wet chemical (bottom-up) synthesis methods are being widely used for the controlled synthesis of nanoparticles. Surfactants play a vital role in controlling the particle size and shape of nanoparticles synthesized using such wet-chemical methods. There are numerous literatures that reported surfactant-assisted synthesis of nanoparticles with controlled sizes and shapes \(^1^7, 3^7, 4^0-4^1, 4^8, 5^9, 7^1, 7^6-7^8\). However, the surfactants used during the synthesis may be retained on the surfaces, blocking the surface adsorption sites required for catalysis and thus may also lead to loss of catalytic activity \(^4^6, 6^3, 7^9-8^0\). For example, one plausible reason for the low selectivities of the Co-Cu bimetallic nanocatalysts \(^1^7\) could be decomposition of excess surfactant at elevated reaction temperatures leading to particle agglomeration and/or formation of an amorphous or nanocrystalline shell of carbon around the particles \(^4^6\). Thus, the presence of surfactants is unfavourable for catalytic applications as they leave carbon residues on the catalyst surface when subjected to high temperatures \(^7^9\). Hence, the excess surfactants bonded to the nanoparticles must be removed from their surfaces in order for them to be suitable as catalysts \(^7^9-8^0\).
Since a catalyst active for higher alcohol/oxygenate synthesis must contain both adsorbed molecular CO, and surface carbon species produced by dissociative adsorption of CO, the catalyst must be able to dissociate only a portion of the CO molecules and must balance this with the hydrogenation of the intermediate to form alcohols. Taking this into consideration, we choose the combination of Cu and metals like Co or Mn for most of the catalysts studied in this research work due to the following reasons: Copper assists in non-dissociative activation of CO, e.g., in methanol synthesis. Co has been found to increase the selectivity to higher alcohols as well as alkenes, and even a very small amount of Co promotion reduces the yield of methanol. Both Mn and Co help in CO dissociation and hydrogenation of the surface carbon species into hydrocarbons. Mn also promotes the adsorption and dissociation of CO, accelerates the hydrogenation steps, and creates new active sites for the CO insertion reaction.

Thus, when Co/Mn is combined with copper, it is expected to facilitate higher alcohols formation by creating a balance between dissociated and undissociated CO. For example, in the case of Cu-Co combination, it might be expected to adsorb molecular CO on the Cu, which can then react preferentially with the carbon chains generated on the Co, thereby leading to higher alcohols (see Figure 2.1 for schematic illustration).

In the beginning stages of this research work, Co core-Cu shell and Co-Cu mixed (synthesized by simultaneous reduction of precursors) nanoparticles were studied as catalysts for CO hydrogenation. The highest ethanol selectivity achieved was 11.4% (with 17.2% methane selectivity) at differential conversions for the Co-Cu mixed nanoparticles (See Chapter 3). The low selectivities towards ethanol and high selectivities towards hydrocarbons in the case of Co core-Cu shell nanoparticle catalyst may be either due to large concentrations of cobalt, an active
Figure 2.1: Schematic illustration of the mechanism: role of (1) cobalt alone, (2) copper alone and (3) combination of copper and cobalt.

Fischer Tropsch catalyst, resulting in an increased conversion of CO into hydrocarbons, or due to the excess surfactants on the catalyst surface which decompose at elevated reaction temperatures leaving carbon residues on the surface which affects the activity/selectivity of the catalyst. The surfactant ligands may also block the adsorption sites, decreasing the active surface area available for catalysis and hence lead to a loss of catalytic activity. Thus, in order to achieve maximum alcohol formation:

(i) copper must be viewed as the primary metal and cobalt must be a secondary metal (or promoter) in minor amounts, and

(ii) the excess surfactants bonding to the nanoparticles must be removed.

Keeping these factors in mind, the later part of the project focuses on reverse core-shell design: that is, copper being the primary core metal and the shell containing Mn or Co, with some
changes in the synthesis method, and the surfactants retained on the nanoparticle surfaces after synthesis were removed before conducting the catalytic reactions.

2.5. Pyrochlores as Catalysts

A promising class of materials for the catalytic hydrogenation of CO is based on rare earth zirconate supports with cubic pyrochlore structures, such as La$_2$Zr$_2$O$_7$, which have an excellent thermal and chemical stability towards deactivation $^{18-19}$ and low sintering rates $^{42}$. These pyrochlores show potential to incorporate noble metals and other elements into their lattice structure to form a stable catalyst that resists deactivation $^{85}$. A pyrochlore has the general stoichiometry A$_2$B$_2$O$_7$, where the A-site is usually a rare earth element coordinated with 8 oxygen anions and the B-site is a smaller cation (usually transition metal) coordinated with 6 oxygen anions $^{85}$. Metal (or other element) substitution into the pyrochlore structure may create structural defects which result in oxygen vacancies, thereby increasing the lattice oxygen mobility in the bulk material $^{42, 85}$. The increased oxygen ion mobility is believed to reduce carbon formation on the surface.

Rh and Ru substituted La$_2$Zr$_2$O$_7$ pyrochlores synthesized by Pechini method have been shown to be active catalysts for the catalytic partial oxidation (CPOX) of a diesel surrogate fuel with minimum deactivation and carbon deposition $^{85-86}$. La$_2$TM$_{0.3}$Zr$_{1.7}$O$_{7-δ}$ (TM = Mn, Co, or Fe) catalysts prepared by coprecipitation have been tested for the catalytic combustion of methane and La$_2$Fe$_{0.3}$Zr$_{1.7}$O$_{7-δ}$ was found to give the highest catalytic activity $^{87}$. However, some researchers developed copper catalysts supported on these La$_2$Zr$_2$O$_7$ pyrochlore materials, rather than substituted into the lattice, for reactions such as the transformation of ethanol into acetone and the formation of methanol from syngas $^{18-19, 26, 88}$. This pyrochlore is believed to be a
promising candidate as a support for a stable and active copper catalyst for C₂+ oxygenate synthesis ²⁶. These authors reported that the formation of carbonates under the reaction conditions could be prevented by using such a mixed oxide support with both basic and acidic properties. These supported pyrochlore catalysts were synthesized by coprecipitation techniques as opposed to impregnation or other methods, because coprecipitation yields catalysts with higher metal loadings, greater dispersion, and homogeneity ¹⁹, ²⁶. High temperature calcination (~700 °C) is required to form well defined pyrochlores with cubical crystal structures ¹⁸-¹⁹, ²⁶, ⁸⁸.

Cu-ZnO supported on La₂Zr₂O₇ pyrochlores are shown to be effective catalysts for the formation of methanol with minimum deactivation ¹⁸-¹⁹, ²⁶. The generally accepted role of copper in these catalysts is to assist in non-dissociative activation of CO ¹⁶-¹⁷, whereas ZnO stabilizes the catalytic activity without affecting the catalytic sites, thus limiting the deactivation observed on ZnO-free catalysts ⁸⁹. ZnO has also been reported to enhance the hydrogenation properties of copper catalysts by forming H---ZnO species ⁹⁰-⁹¹.

A balance between dissociated and non-dissociated surface CO required for higher alcohol formation can be achieved by combining suitable transition metal (eg., Co, Mn) and/or alkali (eg., Li) promoters with Cu-La₂Zr₂O₇ based catalysts ¹⁷. Both Mn and Co help in CO dissociation and hydrogenation of the surface carbon species into hydrocarbons ¹⁶-¹⁷. Mn also accelerates the hydrogenation steps and creates new active sites for the CO insertion reaction ⁸³,⁸⁴. Li₂O, like other alkali promoters, increases the yield and selectivity of higher alcohols by suppressing hydrocarbon formation ⁴-⁵. For example, Tien-Thao et al. reported that even very small amounts of such residual alkali ions (0.05-0.75 wt%) are sufficient to promote catalytic activity and selectivity to higher alcohols ²⁴. Thus, in a portion of this work, Co or Mn promoted Cu-ZnO-La₂Zr₂O₇ pyrochlore based catalysts were studied for CO hydrogenation.
2.6. References


48. Han, S. W.; Kim, Y.; Kim, K. J. Colloid Interface Sci. 1998, 208 (1), 272-278.


Chapter 3: Development of Cobalt–Copper Nanoparticles as Catalysts for Higher Alcohol Synthesis from Syngas*

3.1. Introduction

Bio-based fuel resources, particularly ethanol, have been studied extensively in the recent years as clean, sustainable and transportable fuel alternatives. One promising process for bio-fuel production involves the conversion of bio-derived synthesis gas (syngas) to fuels and oxygenates. Syngas derived from biomass or coal is particularly interesting since both sources are abundant, and biomass is a renewable feedstock. It is well known that syngas conversion to C$_2$+ oxygenates is often limited by the formation of methane and methanol. However, C$_2$+ alcohols are more desirable products, both as neat fuels, fuel additives and as a carrier for hydrogen to supply fuel cells. In addition to its potential application as a transportation fuel, ethanol has been considered as a feedstock for the synthesis of variety of chemicals, fuels and polymers. Hence, the development of a suitable and efficient catalyst to produce higher alcohols from syngas, coupled with an understanding of the underlying reaction mechanism, is clearly important.

Herein, we report the synthesis, characterization and catalytic activity of Co–Cu nanoparticles in the conversion of syngas to higher alcohols. Cobalt–copper nanoparticles were synthesized by wet chemical methods to achieve either core–shell nanoparticles or mixed nanoparticles and then tested for CO hydrogenation reaction in a fixed bed microreactor system. The focus of the present research is to investigate the Co–Cu nanoparticle catalysts for the synthesis of C$_2$+ oxygenates from syngas via CO hydrogenation and the impact of reaction temperature on...
their activity and selectivity. We are aware of no literature reports that use Co–Cu bimetallic nanoparticles as catalysts for CO hydrogenation reaction.

3.2. Experimental

All the catalyst syntheses were carried out under inert atmospheric conditions using commercially available reagents. Cobalt chloride, copper chloride, dodecyl-N,N-dimethy-3-ammonio-1-propanesulfonate (sulfobetaine SB-12, 98%), sodium borohydride, copper sulfate and sodium citrate hexahydrate were purchased from Aldrich Chemical Company and were used without further purification. All the solvents used were degassed prior to use.

3.2.1. Synthesis of Cobalt (Core) @ Copper (Shell) Nanoparticles

3.2.1.1. Synthesis of Cobalt (Core) Nanoparticles:

Cobalt nanoparticles were synthesized using a modified version of the synthesis method reported by Guo et al \(^8\). A mixture of cobalt chloride and SB-12 was placed in a three-necked flask which was evacuated and then filled with nitrogen three times. Degassed water was added to the flask under sonication and the contents were dissolved. Sodium borohydride was dissolved in water separately and this solution was added drop wise into the earlier CoCl\(_2\) mixture over a period of 30 min. The pale pink solution turned black immediately upon addition, indicating the formation of cobalt nanoparticles. After the addition is complete, the reactants were stirred for an additional hour to ensure completion of the reaction, followed by the addition of 15 ml of acetone to destroy the excess reducing agent. The resulting cobalt nanoparticles were separated, washed thoroughly with degassed water followed by ethanol, and dried to obtain a fine powder.
3.2.1.2. Displacement Formation of Copper Shell Around Cobalt Nanoparticles:

The procedure as described by Guo et al. was used to develop a copper shell around the cobalt nanoparticles. In a typical process, cobalt nanoparticles were added to a copper–citrate electrolyte, containing 0.25 M CuSO$_4$·5H$_2$O and 0.3 M C$_6$H$_5$Na$_3$O$_7$·2H$_2$O at a pH of 4.0. The reactants were sonicated for an hour under nitrogen environment. The particles were then washed thoroughly with degassed water followed by ethanol, then dried to obtain a fine powder. The final core–shell catalyst obtained is designated as Co@Cu-1 in this chapter.

3.2.2. Synthesis of Co–Cu Mixed Nanoparticles

A mixture of cobalt chloride, copper chloride and SB-12 was placed in a three-necked flask which was evacuated and then filled with nitrogen three times. Degassed water was added to the flask under sonication and the contents were dissolved. Sodium borohydride was dissolved in water separately and this solution was added drop wise into the earlier CoCl$_2$ mixture over a period of 30 min. After the addition is complete, the reactants were stirred for an additional hour to ensure completion of the reaction, followed by the addition of 15 ml of acetone to destroy the excess reducing agent. The resulting Co-Cu mixed nanoparticles were washed thoroughly with degassed water followed by ethanol, and dried to obtain a fine powder. This synthesis may lead to two possible forms of these Co–Cu mixed nanoparticles: a mixture of copper and cobalt, or Co–Cu alloy nanoparticles. This catalyst is designated as Co–Cu(1:24) in this chapter (the ratio in parentheses indicates the final atomic ratio of Co and Cu as obtained by ICP-AES results).
3.2.3. Characterization

The Co–Cu core–shell and mixed nanoparticles were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Inductively coupled plasma atomic emission spectrometry (ICP-AES). TEM gives information on the size of the particles, the polydispersity of the nanoparticle population, as well as an idea of the type of shapes formed by the nanoparticles. TEM experiments were carried out using Hitachi H-7600 with a 125 kV accelerating voltage and operated on a JEOL 100CX at 80 kV. Samples for TEM were prepared in inert atmospheric conditions by dispersing the Co–Cu nanoparticles in ethanol and then placing them on carbon-coated gold grids. X-ray diffraction (XRD) patterns were recorded on a Bruker/Siemens D5000 automated powder X-ray diffractometer, using Cu Kα radiation (\(\lambda = 1.540562 \text{ Å}\)) with Rietveld analysis software. XPS studies were performed on a Kratos AXIS 165 X-ray Photoelectron Spectroscope and Scanning Auger Microscope equipped with standard Mg/Al source and high performance Al monochromatic source. Inductively coupled plasma (ICP) atomic emission spectrometry was used for the determination of the bulk metal content in each sample. The ICP measurements were performed with a Spectro Ciros Inductively Coupled Plasma Analyzer in the Central Analytical Instruments Research Laboratory, LSU Ag Center, LSU.

3.2.4. CO Hydrogenation Studies

CO hydrogenation reactions were performed in a fixed bed microreactor system at differential conversions. The schematic of the fixed bed reactor system and the analytical equipment is shown in Figure 3.1. The catalyst (0.2 g) was loaded between quartz wool and axially centered in the reactor tube, with the temperature monitored by a thermocouple close to the catalyst packing.
Prior to reaction, the catalyst was reduced at 300 °C in flowing 75% H₂/He for 2 h at atmospheric pressure. Then, gas flow was switched to H₂/CO mixture at the reaction temperature and pressure. The products were analyzed for both oxygenates and hydrocarbons in an Agilent GC 6890 with MSD and TCD.

![Schematic of the reactor and the analytical equipment.](image)

Figure 3.1: Schematic of the reactor and the analytical equipment.

The catalysts were tested at three different temperatures (230, 270 and 300 °C) at a pressure of 20 bar, H₂/CO ratio of 2:1 and space velocity (SV) of 18,000 scc/(h gcat). Product selectivities are reported in terms of carbon efficiencies, which is defined as

\[
\text{Carbon efficiency} = \frac{n_iC_i}{\Sigma(n_iC_i)}
\]

where \(n_i\) is the number of carbon atoms and \(C_i\) is the molar concentration of the carbon-containing products.
Calibration of the GC/MS was carried out using standard gas mixtures (Air Liquide, Houston, TX) containing certified concentrations of each product gas. Multiple calibration injections were made prior to each experiment and the errors reported here are based on 95% confidence limits. See Appendix A for more details on error estimation.

3.3. Results and Discussion

3.3.1. TEM

Figure 3.2 shows the TEM micrographs of Co@Cu-1 and Co–Cu(1:24) nanoparticles respectively. The morphology of all the particles irrespective of the synthetic conditions is spherical in nature. The mean diameters are roughly around 9 nm and 25 nm respectively for Co@Cu-1 and Co–Cu(1:24) nanoparticles. In the sample synthesized by core–shell method, the expected core–shell structure is not clearly distinguishable from the TEM images and this may be due to very small difference in atomic numbers between Co and Cu \(^8\). There is also a possibility of a discontinuous shell around cobalt nanoparticles, in which case, both cobalt and copper will be accessible at the surface.

![TEM images of (a) Co@Cu-1 (9±2 nm) and (b) Co–Cu(1:24) (25±1.9 nm) nanoparticle catalysts.](image)

Figure 3.2: TEM images of (a) Co@Cu-1 (9±2 nm) and (b) Co–Cu(1:24) (25±1.9 nm) nanoparticle catalysts.
3.3.2. XRD

Figure 3.3 shows the XRD patterns for the two Co–Cu nanoparticles. The peaks can be identified as face-centered cubic Cu. As can be seen, for both the catalysts, a single pattern corresponding to Cu is prominent, similar to pure copper nanoparticles (Figure 3.3(c)), probably indicating either the higher dispersion or the amorphous nature of cobalt. XRD peaks are observed at $d = 2.09$, 1.81 and 1.28 Å, which are in a good agreement with the standard XRD pattern, ICDD(040836) of metallic Cu. However, a small peak at around $2\theta = 36.2^\circ$ and $d = 2.48$ Å for the case of Co–Cu(1:24) catalyst (Figure 3.3(b)) indicates the presence of minor amounts of Cu$_2$O based on ICDD(030892). No clear or distinct peak was detected for Co, consistent with the results of others$^9$. For the case of Co–Cu(1:24) mixed nanoparticles, there is no evidence for the formation of an alloy. This suggests that a mixture of cobalt and copper nanoparticles was formed in this catalyst.

![X-ray diffraction patterns](image.png)

Figure 3.3: X-ray diffraction patterns of (a) Co@Cu-1, (b) Co–Cu(1:24) and (c) Cu nanoparticles.
3.3.3. XPS and ICP-AES

XPS studies of the as-prepared samples were carried out in order to study the chemical state of the elements at the catalytic surface. Table 3.1 gives the data in terms of binding energies of the main cobalt and copper peaks. Table 3.1 also summarizes the Cu/Co bulk atomic ratios of the nanoparticle catalysts obtained from ICP-AES results.

Table 3.1: XPS & ICP-AES analysis of Co–Cu nanoparticle catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Binding energies (eV)</th>
<th>Cu/Co bulk atomic ratio by ICP-AES</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu 2p$_{3/2}$</td>
<td>Co 2p$_{3/2}$</td>
</tr>
<tr>
<td>Co@Cu-1</td>
<td>932.6</td>
<td>779.3</td>
</tr>
<tr>
<td>Co–Cu (1:24)</td>
<td>931.9</td>
<td>782.3</td>
</tr>
</tbody>
</table>

For the Co@Cu-1 catalyst, the Cu 2p$_{3/2}$ main peak is centered at 932.6 eV while the Co 2p$_{3/2}$ main peak is positioned at 779.3 eV; for copper, the binding energy suggests that it is present as Cu$^+$ or Cu$^0$ species and cobalt ions remain in the form of Co$_3$O$_4$\(^{10}\). In the case of Co–Cu(1:24) sample, the Cu 2p$_{3/2}$ peak at 931.9 eV suggests that copper is present in +1 oxidation state. The binding energy of the Co 2p$_{3/2}$ peak increased to 782.3 eV with the shake-up satellite appearing at higher binding energy. This value seems higher compared to a spectrum characteristic of Co$^{2+}$ (781 ± 0.5 eV) in the form of CoO. But as reported in literature, cobalt may be present as the divalent ion\(^{10}\). Further evidence for this is given by the fact that the difference in binding energy between Co (2p$_{3/2}$) and Co (2p$_{1/2}$) is 15.4 eV which is in agreement with the literature\(^{11}\). The surface oxidation in all the catalysts may be due to the exposure to air during sample preparation. The nanoparticles, especially the metallic cobalt nanoparticles, are extremely
sensitive to atmospheric oxygen\textsuperscript{8} and a thin layer of cobalt oxide is readily formed\textsuperscript{12} which could be a major reason for the oxidation signatures in XPS measurements.

3.3.4. CO Hydrogenation Results

The influence of the reaction temperature on the product selectivities has been examined in the range of 230–300 °C under 20 bar and H\textsubscript{2}/CO = 2 over the two catalysts investigated here (Table 3.2). It is evident that the reaction temperature has a profound effect on the selectivity of the catalyst. Oxygenates and hydrocarbons are always accompanied by the production of water, most of which appears to be converted to CO\textsubscript{2} through the water–gas-shift reaction\textsuperscript{13}.

Table 3.2: Effect of temperature on the product selectivities of Co–Cu nanoparticle catalysts\textsuperscript{a}.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Selectivity (% C)\textsuperscript{b}</th>
<th>CO\textsubscript{2}</th>
<th>CH\textsubscript{4}</th>
<th>MeOH</th>
<th>EtOH</th>
<th>C\textsubscript{2+} Oxy\textsuperscript{c}</th>
<th>C\textsubscript{2+} HC\textsuperscript{d}</th>
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</thead>
<tbody>
<tr>
<td>(a) Product selectivities of Co–Cu nanoparticle catalysts at 230 °C</td>
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<tr>
<td>Co@Cu-1</td>
<td>9.5</td>
<td>59.1</td>
<td>0.9</td>
<td>0.6</td>
<td>5.0</td>
<td>25.2</td>
<td></td>
</tr>
<tr>
<td>Co–Cu(1:24)</td>
<td>39.8</td>
<td>16.7</td>
<td>5.6</td>
<td>9.6</td>
<td>28.3</td>
<td>0.03</td>
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<tr>
<td>(b) Product selectivities of Co–Cu nanoparticle catalysts at 270 °C</td>
<td></td>
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<tr>
<td>Co@Cu-1</td>
<td>16.6</td>
<td>40.2</td>
<td>1.3</td>
<td>2.1</td>
<td>2.6</td>
<td>37.4</td>
<td></td>
</tr>
<tr>
<td>Co–Cu(1:24)</td>
<td>48.8</td>
<td>17.2</td>
<td>6.6</td>
<td>11.4</td>
<td>16.0</td>
<td>0.1</td>
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<tr>
<td>(c) Product selectivities of Co–Cu nanoparticle catalysts at 300 °C</td>
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<tr>
<td>Co@Cu-1</td>
<td>41.6</td>
<td>30.5</td>
<td>0.3</td>
<td>0.7</td>
<td>1.4</td>
<td>25.6</td>
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<tr>
<td>Co–Cu(1:24)</td>
<td>30.7</td>
<td>15.6</td>
<td>3.5</td>
<td>6.0</td>
<td>41.5</td>
<td>2.7</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}Catalyst: 0.2 g; reaction conditions: P = 20 bar, H\textsubscript{2}/CO =2, space velocity=18,000 scc/(h gcat). 95% confidence limits on selectivities are less than ± 0.2% for all values except CO\textsubscript{2} (within ± 1.7%) and CH\textsubscript{4} (within ± 2.7%). Product selectivities varied no more than ± 5% upon repetition of the 230 °C run.

\textsuperscript{b}Product selectivities are reported in terms of carbon efficiencies defined as, Carbon efficiency = \(n_i C_i/\Sigma(n_i C_i)\) where \(n_i\) is the number of carbon atoms and \(C_i\) is the concentration of the carbon-containing products.

\textsuperscript{c}Oxygenates with 2 or more carbons except ethanol (acetaldehyde, acetone, i-propanol, i-butanol, n-propanol and n-butanol).

\textsuperscript{d}Hydrocarbons with 2 or more carbons (ethane, propane, i-butane, n-butane, n-hexane and propylene).
From the results presented in Table 3.2, it is clearly evident that the mixed Co–Cu(1:24) nanoparticles have higher ethanol and C₂⁺ oxygenates selectivity at all the temperatures tested. For this catalyst, the selectivity to ethanol, methanol, methane and CO₂ go through a maximum as a function of temperature. In the case of core–shell catalyst, a major portion of the products comprises of hydrocarbons (HCs). Methane and higher HCs are always higher on the core-shell catalyst than on the mixed nanoparticles at all three temperatures tested. Higher selectivities towards hydrocarbons on the core-shell nanoparticles may be attributed to the presence of large concentrations of cobalt which is a good Fischer-Tropsch catalyst and results in an increased conversion of CO into hydrocarbons.

Cobalt is active in the dissociative adsorption of CO, C–C chain growth and hydrocarbon production. Nonetheless, relative suppression of hydrocarbon formation was seen on the mixed nanoparticle catalyst, perhaps due to enhanced stability of the CH₃ species on the surface, followed by CO insertion into the M–C bond of the surface CH₃ species and hydrogenation to produce alcohols. The termination and alcohol production step can be attributed to the role of copper which assists in non-dissociative activation of CO. Among the two catalysts, the Co–Cu(1:24) catalyst showed the highest selectivity towards ethanol with the maximum at 270 °C (11.4%) with reduced methane selectivity (17.2%). The C₂⁺ oxygenates selectivity was also found to be the highest on this catalyst at 300 °C.

Figure 3.4 depicts the variations in the rates of CO conversion (reported in μmoles/gcat/s) as a function of temperature for the two catalysts. The CO conversion rate increased rapidly with reaction temperature for the case of the core–shell catalyst, whereas, it goes through a minimum at 270 °C for the mixed nanoparticle catalyst. However, the rates of the Co-Cu(1:24) catalyst is only a few percent (0.2-4%) of those for the core-shell catalyst. Hence, we find that the Co–Cu
mixed nanoparticle catalyst is much less active than the core–shell catalyst, but is more selective towards ethanol formation. This might be because hydrocarbon formation, which typically accompanies high catalytic activity, is suppressed on this catalyst.

Figure 3.4: CO conversion rate as a function of temperature (H₂/CO = 2, 20 bar, 18,000 scc/(h gcat)).

3.4. Conclusions

Co–Cu core–shell and mixed nanoparticle catalysts were synthesized and tested for CO hydrogenation. It was found that the mixed nanoparticle catalyst is more selective to ethanol and higher oxygenates than the core–shell catalyst whereas the latter is more active but not selective to ethanol. The mixed nanoparticle catalyst is not active because hydrocarbon formation, which typically accompanies high catalytic activity, is suppressed. The present investigation also indicates that the CO conversion and product selectivity of the Co–Cu bimetallic catalysts is strongly influenced by reaction temperature. Under the reaction conditions of this study, the
highest ethanol selectivity achieved was 11.4% for the Co–Cu(1:24) catalyst with 17.2% methane selectivity.

The low selectivities towards ethanol and high selectivities towards hydrocarbons in the case of core-shell nanoparticle catalyst may be either due to large concentrations of cobalt, an active Fischer Tropsch catalyst, resulting in an increased conversion of CO into hydrocarbons, or due to the excess surfactants on the catalyst surface which decompose at elevated reaction temperatures leading to particle agglomeration and/or formation of an amorphous or nanocrystalline shell of carbon around the particles. The surfactant ligands may also block the adsorption sites, decreasing the active surface area available for catalysis and hence lead to a loss of catalytic activity.

Even though the mixed nanoparticles showed a higher ethanol and C$_2$+ oxygenates selectivity, the uniformity and batch-to-batch reproducibility of such nanoparticles is limited. On the other hand, the core-shell nanoparticles can be reproducible and uniformly dispersed (see Appendix B). Thus, further modifications in the design of our core-shell nanoparticle catalysts are necessary in order to balance between the catalyst activity and selectivity to obtain a high yield of ethanol.

Keeping these factors in mind, the second phase of the project focused on synthesis of nanoparticles with (i) reverse core-shell design with copper being the primary core material and the shell containing either Mn or Co, and (ii) removal of excess surfactants retained on the nanoparticle surface before the catalytic reactions. Manganese or cobalt, added as a secondary metal in minor amounts around copper core nanoparticles, may act as a promoter, and the core-
shell type structure (rather than an alloy) may provide improved properties that are beneficial for higher alcohol synthesis. The next two chapters focus on these core-shell nanoparticles.

3.5. References


4.1. Introduction

Nanomaterials are transforming modern science and technology due to their unique optical \(^1\)-\(^3\), electronic \(^4\)-\(^7\), catalytic \(^8\)-\(^{11}\), and magnetic \(^5\),\(^{12}\)-\(^{15}\) properties that are not found in the corresponding bulk materials. Among the various transition metal nanoparticles, copper is one of the most commonly studied materials \(^16\). Copper nanoparticles can be used as catalysts, heat transfer fluids, optical sensors, and as substitute for more expensive metals such as Au, Ru, Rh, Pt and Pd. Copper is also a well known plasmonic (optical) material which when combined with a magnetic material, such as Mn, can result in a system with excellent magneto-optical (magnetoplasmonic) \(^1\) properties.

Manganese oxide nanoparticles are receiving great attention due to their diverse applications in various fields including catalysis, ion exchange, batteries and MRI contrast agents \(^17\)-\(^{18}\). Their magnetic properties also differ widely from their bulk counterparts due to their high atomic moments and magnetic alignments \(^19\)-\(^{21}\). Mn\(_3\)O\(_4\) nanoparticles are reported to show ferrimagnetic behavior with a slight shift in their Curie temperatures compared to bulk Mn\(_3\)O\(_4\) \(^19\),\(^{22}\). For example, the magnetic coercivity of the Mn\(_3\)O\(_4\)/MnO nanoparticles is found to be greater than that of bulk Mn\(_3\)O\(_4\) by a factor of three \(^19\). Mn\(_3\)O\(_4\) nanoparticles are also known to be active catalysts for various oxidation and reduction reactions \(^22\)-\(^{23}\).

Compared to monometallic nanoparticles, bimetallic nanoparticles (either alloy or core-shell type structures) exhibit improved electronic, optical, physiochemical and catalytic properties \(^2\),\(^{6\,9\,12\,14\,24\,38}\). In addition, the nanoporosity of the shell is an interesting property of core-shell particles.
which promises to have great potential in the field of catalysis. Reactants and products can diffuse through the porous shell, thus allowing catalysis to occur at the peripheral or interfacial areas between the core and the shell \(^3\). Therefore, core-shell nanostructures consisting of both an optically active plasmonic material, such as Cu, and a magnetically active porous Mn-oxide component may have potential for simultaneous optical, magnetic and catalytic applications. However, we are aware of no reports for the synthesis of Cu-Mn bimetallic core-shell nanoparticles for any of the above mentioned (optical, magnetic or catalytic) applications.

Here, we demonstrate a wet-chemical synthesis approach to synthesize a Mn oxide shell around Cu core nanoparticles (referred to as Cu@Mn\(_3\)O\(_4\)) and provide characterization results confirming the core-shell structure.

### 4.2. Experimental

#### 4.2.1. Synthesis of Cu@Mn\(_3\)O\(_4\) Bimetallic Nanoparticles

All the syntheses were carried out under inert atmospheric conditions using commercially available reagents. The synthesis method reported by Mott et al. \(^{40}\) was used for the copper nanoparticles. First, a mixture of copper acetylacetonate salt (12 mmol) and hexadecanediol (reducing agent, 24 mmol) was placed in a three-necked flask which was evacuated and then filled with nitrogen three times. 120 ml diphenyl ether was added to the flask, while being stirred using a magnetic stirrer. Then, the contents were heated to 105 °C and held for 5-10 minutes before adding oleic acid (24 mmol) and trioctylphosphine (24 mmol) surfactants. After adding the surfactants, the whole reaction mixture was heated to 200 °C and held for 20 minutes, then cooled down to room temperature. The resulting copper nanoparticles were washed thoroughly with degassed methanol followed by ethanol and dried to obtain a fine powder.
For the bimetallic nanoparticles, manganese acetylacetonate salt (4 mmol) was added along with lithium triethylborohydride (LiEt₃BH) to the copper nanoparticle colloidal mixture at 200 °C and held there for another 20 minutes. The particles were then washed thoroughly with degassed methanol followed by ethanol and dried. The initial molar ratios of Cu and Mn were 3:1 by mole.

4.2.2. Characterization

The Cu@Mn₃O₄ bimetallic nanoparticles were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Ultraviolet-Visible spectroscopy (UV-Vis), Fourier transform infrared spectroscopy (FTIR), Small angle X-ray scattering (SAXS), X-ray absorption near edge spectroscopy (XANES) and by means of a superconducting quantum interference device (SQUID). SAXS, XPS, XRD and FTIR instrument details are provided in Appendix C.

TEM experiments were carried out using a Hitachi H-7600 microscope with a 125 kV accelerating voltage and operated on a JEOL 100CX at 80 kV. Samples for TEM were prepared in inert atmospheric conditions by dispersing the bimetallic nanoparticles in toluene and then placing a drop of the solution on carbon-coated gold grids. UV-Visible spectroscopy measurements were performed using a Varian Cary 5000 spectrophotometer. Halogen incandescent lamp was used to study the optical properties in the wavelength range of 400-1000 nm using a 1 cm path length quartz cuvette at room temperature. Dilute solutions of toluene-dispersed nanoparticles were used as samples for these experiments.

XANES K-edge experiments were performed at the Double Crystal Monochromator beamline of the J. Bennett Johnston, Sr., Center for Advanced Microstructures and Devices, Louisiana State University, using Ge (220) crystals. The storage ring operated with an electron energy of 1.3
GeV and a current between 90 and 190 mA. Powder samples placed between two kapton tapes were used for XANES measurements. Magnetic studies were carried out using a Quantum Design MPMS-5S SQUID magnetometer. The magnetization temperature dependence was measured in an applied magnetic field of 100 G between 5 and 300 K using zero-field-cooled (ZFC) and field-cooled (FC) procedures. The field dependence of magnetization was measured at 5 and 300 K. The core-shell nanoparticle samples for magnetic studies were placed in gelatin capsules in powder form, before being inserted into the sample space of the magnetometer.

4.3. Results and Discussion

4.3.1. Structural Characterization of Cu@Mn₃O₄ Nanoparticles

Figure 4.1 illustrates the synthesis method (see Experimental Section for a detailed description) and a schematic view of the porous core-shell particle. One can envisage the growth of the Mn₃O₄ shell around the Cu core due to the differences in their standard reduction potentials, which are 0.34V and 1.51V for Cu²⁺/Cu⁰ and Mn³⁺/Mn²⁺, respectively. The galvanic replacement reaction is possible due to the higher reduction potential of Mn³⁺. Hence, copper nanoparticles may act as crystal centers for the deposition of Mn₃O₄ over their surface.

![Diagram of synthesis method and nanoparticle structure](image_url)

Figure 4.1: Synthesis of copper and Cu@Mn₃O₄ (core@shell) nanoparticles, with a schematic view of a single nanoparticle with a porous shell.
Figure 4.2(a) shows a HRTEM image of Cu@Mn₃O₄ nanoparticles. The particles are uniformly dispersed and exhibit a core-shell structure with a porous shell. Figure 4.2(b) shows a narrow size distribution of the nanoparticles with a size of 13 ± 0.35 nm. The Cu core size is ~6.1 nm and the shell has an average thickness of ~3.45 nm. The inset of Figure 4.2(b) shows an EDX spectrum of the core-shell nanoparticles. The intense Cu peaks originate from the core and the weak Mn peaks arise from the shell. Notice that the Mn peaks are hardly visible, suggesting that the Mn concentration is very small. XPS gives a surface Cu/Mn ratio of 2.2:1, indicating a surface enrichment of copper which is likely to be due to the Cu-core being easily accessible through the porous shell. However, the presence of Cu oxide in the shell cannot be ruled out either (see Appendix C for XPS results, Table C.1). SAXS measurements showed that the Cu@Mn₃O₄ nanoparticles had a very narrow and symmetric, unimodal size distribution indicating the absence of any particle agglomeration (see Appendix C, Figure C.1).

![Figure 4.2](image)

Figure 4.2: (a) HRTEM image of the Cu@Mn₃O₄ nanoparticles (inset shows a single particle with core-shell structure). (b) Particle size distribution. The mean size is 13 nm with a standard deviation of 0.35 nm. Inset shows the EDX spectrum.

Photographs of Cu@Mn₃O₄ and pure Cu nanoparticles dispersed in toluene are shown in Figure 4.3(a). The complete dispersion of these nanoparticles in nonpolar solvents suggests that the
surface of the particles is bound to non-polar surfactants - oleic acid (OA) and trioctylphosphine (TOP), which were used during the synthesis. FTIR spectra of the as-prepared Cu@Mn$_3$O$_4$ nanoparticles further confirmed the presence of certain bands characteristic of the COO$^-$ group of oleic acid as well as C-P stretching modes of TOP, and CH$_2$ vibrations due to both surfactants (see Appendix C, Figure C.2). However, the $\nu$(C=O) stretching mode of the carboxylic group found in pure oleic acid, was present only as a small broad shoulder at 1709 cm$^{-1}$. A decrease of the intensity of this band indicates the chemical adsorption of oleic acid on the surface of the nanoparticles. Sharma et al. attributed the absence of this peak on oleic acid stabilized CoNi nanoparticles to this same adsorption process. The presence of organic ligands on the surface of the nanoparticles also explains the absence of agglomeration as seen in the TEM and SAXS results.

Figure 4.3: (a) Photographs and (b) UV visible absorption spectra of Cu and Cu@Mn$_3$O$_4$ nanoparticles dispersed in toluene.
Figure 4.3(a) shows the change in color of the solution before and after the formation of the shell indicating that the surface plasmon resonance of copper is influenced by the formation of the shell $^{1,3,43}$. Figure 4.3(b) displays the UV-visible absorption spectra of the nanoparticles. The peak associated with the plasmon resonance of the Cu core is seen at about 559 nm for the pure Cu nanoparticles, while it is absent in Cu@Mn$_3$O$_4$ nanoparticles. The Cu@Mn$_3$O$_4$ nanoparticles display a very broad peak ranging from 600-700 nm. This indicates the chemical damping of the surface plasmon by the shell, which is consistent with Yeshchenko et al. $^{44}$ who reported a large effect on the optical spectra of Mn nanoparticles by the damping of free electron oscillations. Schladt et al. $^{45}$ also observed a similar result with Au@MnO “nanoflowers”, where the MnO shell in the form of petals red-shifted the plasmon resonance of Au nanoparticles. They attributed this red-shift to an increase in the effective local dielectric function around the gold core. Hence, the different colors of the nanoparticle dispersions and the UV-Visible spectral features suggest that the bimetallic nanoparticles are not a simple mechanical mixture of two different monometallic clusters. The fact that the optical absorption spectrum does not show only one plasmon band between the absorption peaks of the two pure metal nanoparticles also indicates the absence of an alloy formation.

Figure 4.4(a) shows the derivative spectrum of the normalized Cu K-edge XANES for the Cu@Mn$_3$O$_4$ nanoparticles. The spectrum exhibits the absorption edge at 8979 eV, along with shape resonance, in good agreement with the spectrum of fcc copper foil. Although most of the features closely resemble those of Cu foil, there are minor contributions from Cu$_2$O. This is consistent with the XPS results (see Appendix C). Therefore, it is possible that the nanoparticles contain traces of copper oxide due to their air sensitivity.
Figure 4.4: First derivatives of the normalized XANES spectra for (a) Cu K-edge and (b) Mn K-edge of Cu@Mn$_3$O$_4$ nanoparticles.
Figure 4.4(b) shows the derivative spectrum of the normalized Mn K-edge XANES. The Mn K-edge spectrum has the absorption edge at 6547 eV and the pre-edge and post-edge features match the Mn$_3$O$_4$ standard. This is also consistent with XRD findings (see Appendix C, Figure C.3). However, there are some differences in the spectral features of both Cu and Mn edges which can be attributed to the unique behavior of nanoparticles as opposed to bulk metal standards and also to the interactions between Cu and Mn at the interface.

4.3.2. Magnetic Properties

The temperature-dependent magnetization measured under zero-field-cooled (ZFC) and field-cooled (FC) conditions between 5 and 300 K in a 100 Oe field is shown in the left panel of Figure 4.5. The Cu@Mn$_3$O$_4$ nanoparticles display an apparent phase transition from ferromagnetic to paramagnetic ground state at around 41 K. We determine the blocking temperature ($T_B$) from the maximum in the ZFC curve. Below $T_B$ the nanoparticles become ferromagnetic whereas they are paramagnetic above $T_B$. The observed blocking temperature of 41 K is consistent with previously reported values for Mn$_3$O$_4$ nanoparticles of approximately 10 nm size $^{23, 46-48}$. Berkowitz et al. observed a similar blocking temperature for MnO/Mn$_3$O$_4$ core-shell nanoparticles with a 4 nm thick Mn$_3$O$_4$ shell $^{49}$.

The right panel of Figure 4.5 shows the field dependence of the magnetization at 5 K for both Cu@Mn$_3$O$_4$ and Cu nanoparticles. At 300 K (well above the blocking temperature), the magnetization does not show any hysteresis as evidenced by lack of coercivity and remnant magnetization, indicative of the paramagnetic state; whereas at 5 K, well below the blocking temperature, the Cu@Mn$_3$O$_4$ nanoparticles display a clear hysteresis with a coercive field of about 3.5 kOe, greater than that of bulk Mn$_3$O$_4$ $^{50}$. Berkowitz et al. $^{49}$ reported a coercive field of
Figure 4.5: Left panel: Temperature dependence of the magnetization at 100 Oe after cooling in 100 Oe (FC, circles) and after cooling in zero field (ZFC, squares); (a) displays the magnetization of Cu@Mn$_3$O$_4$ nanoparticles; (b) shows Cu nanoparticles. Right panel: Hysteresis curves at 5 K for (a) Cu@Mn$_3$O$_4$ and (b) Cu nanoparticles.

5.8 kOe at 5 K after field cooling in 50 kOe on MnO core-Mn$_3$O$_4$ shell nanoparticles, where, the Mn$_3$O$_4$ shell was ~4 nm thick, comparable to our nanoparticle shell thickness. The saturation magnetization ($M_s$) from Figure 4.5 is 55 emu/(g·Mn), or equivalently 39.6 emu/(g·Mn$_3$O$_4$), and the remanent magnetization ($M_r$) is 20 emu/(g·Mn), or 14.4 emu/(g·Mn$_3$O$_4$), where we suppose all the Mn is in the form of Mn$_3$O$_4$. These values are very close to the saturation and remanent magnetization in bulk Mn$_3$O$_4$. Thus the remanence ratio ($M_r/M_s$) of Cu@Mn$_3$O$_4$ nanoparticles is calculated as 0.36. It should be noted that the hysteresis loop at 5 K is very similar in shape to that of reported Mn$_3$O$_4$ nanoparticles. The magnetization data on pure Cu nanoparticles indicates paramagnetic behavior. The fact that the Cu@Mn$_3$O$_4$ nanoparticles exhibit behavior
similar to that of Mn$_3$O$_4$ nanoparticles reported in the literature, combined with the blocking temperature obtained from Figure 4.5, are consistent with the presence of Mn$_3$O$_4$ in the shell.

4.4. Conclusions

In conclusion, we have demonstrated a wet-chemical approach for the synthesis of a porous Mn$_3$O$_4$ shell of approximately 3.5 nm thickness around 6 nm copper core nanoparticles. The core-shell structure with uniform shell thickness was confirmed by HRTEM images. XANES analysis showed that the shell is composed of manganese in the form of Mn$_3$O$_4$. Interestingly, the Cu@Mn$_3$O$_4$ nanoparticles exhibited a magnetic behavior (both in their temperature dependent as well as field dependent magnetization) very similar to that of Mn$_3$O$_4$ nanoparticles reported in the literature. Thus, when a paramagnetic material like copper, with well known plasmonic (optical) properties, is combined with a magnetic material like Mn$_3$O$_4$, the resulting system is anticipated to show excellent magnetoplasmonic characteristics, thereby providing a way to harness both optical and magnetic properties from a single material. Design of such core-shell nanostructures is anticipated to pave the way for the development of novel materials with combined optical, magnetic and catalytic properties.

See Appendix C for other supporting characterization results obtained by means of SAXS, XPS, XRD and FTIR (Figures C.1-C.3 and Table C.1).

4.5. References


5.1. Introduction

Syngas conversion to higher alcohols via the catalytic hydrogenation of CO has been extensively studied over a wide range of catalysts \(^1\)\(^-\)\(^2\). The high cost and limited availability of the most active/selective Rh-based catalysts, for this application, has led to the development of base metal catalysts such as modified Cu-based catalysts \(^2\). Although copper-based catalysts are active and selective for methanol synthesis, addition of suitable promoters can significantly enhance the formation of higher alcohols \(^3\)\(^-\)\(^5\). Since copper can assist in non-dissociative adsorption of CO, a promoter that would dissociate portion of the adsorbed CO, thereby forming CH\(x\) surface species, is required for the higher alcohol formation. Cobalt and manganese would be expected to possess such properties – cobalt dissociates CO and hydrogenates the resulting surface carbon species into hydrocarbons, e.g., in F-T synthesis \(^6\), and manganese can promote the adsorption and dissociation of CO \(^7\)\(^-\)\(^9\), accelerate the hydrogenation steps \(^10\) and create new active sites for the CO insertion reaction \(^11\). Hence Cu-Co and Cu-Mn catalysts are potential candidates for CO hydrogenation to higher alcohols.

The interaction of catalyst and promoter appears to be a crucial property in determining the activity and selectivity to higher alcohols. The catalysts that have been studied for CO hydrogenation are typically synthesized using conventional impregnation or coprecipitation methods. However, achieving desired metal-promoter morphologies and atomic-level control over the structure of the catalysts is limited with these techniques. The achievement of such atomic-level control may lead to further improvement in the selectivity to desired products.
Atomically controlled nanoparticles are receiving considerable attention due to their interesting properties and potential applications as catalysts that are not found in their respective bulk counterparts \(^{12-15}\). Bimetallic core-shell nanoparticles are also very interesting since they provide excellent control over surface properties through modulation of shell and core dimensions. Their electronic structure and catalytic properties are substantially modified due to the interactions between the shell and the core atoms \(^{16}\).

Wet chemical synthesis methods are being widely used for the controlled synthesis of such nanoparticles. Surfactants play a vital role in controlling the particle size and shape of nanoparticles synthesized using such wet-chemical methods \(^{12,17}\). There are numerous reports that reported surfactant-assisted synthesis of nanoparticles with controlled sizes and shapes \(^{12-13,17-24}\). However, the surfactants used during the synthesis are retained on the surfaces, blocking the active adsorption sites required for catalysis and thus may also lead to loss of catalytic activity \(^{25-28}\). The excess surfactants can sometimes be removed by repeated washing, but if not, their decomposition at elevated reaction temperatures may lead to particle agglomeration and/or formation of an amorphous or nanocrystalline shell of carbon around the particles, thus making them catalytically inactive \(^{26}\). Hence, the excess surfactants bonded to the nanoparticles must be removed from their surfaces in order for them to be suitable as catalysts \(^{25,28}\).

Time resolved (in-situ) characterization techniques are critical in understanding the structural and chemical changes of a catalyst under reaction conditions and to develop structure-activity relationships. Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) or in-situ FTIR is a useful technique to study the adsorption behavior of catalysts under reaction conditions using probe molecules such as CO and H\(_2\) \(^{29-39}\). The active sites involved in the CO hydrogenation reaction and the surface intermediates formed can be determined from DRIFTS
Since catalytic reactions occur mainly on catalyst surfaces, it is very important to study the surface under reaction conditions.

In order to provide control over the catalyst composition at the scale of a few nanometers, we have used wet-chemical synthesis routes to synthesize Cu core-Mn oxide shell (denoted as Cu@Mn$_3$O$_4$) and Cu core-Co oxide shell (denoted as Cu@Co$_3$O$_4$) nanoparticles using oleic acid and trioctylphosphine surfactants. Here we provide the evidence for the lack of CO adsorption on the nanoparticle catalysts in the presence of organic ligands and report the DRIFTS results of CO adsorption and CO hydrogenation on the ligand-free nanocatalysts. A comparison between the CO adsorption properties of Cu@Mn$_3$O$_4$ vs. Cu@Co$_3$O$_4$ is provided.

5.2. Experimental

5.2.1. Synthesis of Cu@X (X=Mn$_3$O$_4$ or Co$_3$O$_4$) Bimetallic Nanoparticles

All the syntheses were carried out under inert atmospheric conditions using commercially available reagents. First, a mixture of copper acetylacetonate salt (12 mmol) and hexadecanediol (reducing agent, 24 mmol) was placed in a three-necked flask which was evacuated and then filled with nitrogen three times. 120 ml diphenyl ether was added to the flask, while being stirred using a magnetic stirrer. The contents were heated to 105 °C and held for 5-10 minutes before adding oleic acid (24 mmol) and trioctylphosphine (24 mmol) surfactants. This mixture was then heated to 200 °C and held for 20 minutes, after which manganese or cobalt acetylacetonate salt (4 mmol) was added along with lithium triethylborohydride (LiEt$_3$BH) and held at 200 °C for another 20 minutes. The resulting nanoparticles were then washed thoroughly with degassed methanol followed by ethanol and dried to obtain a fine powder.
These nanoparticles are designated as Cu@Mn$_3$O$_4$ and Cu@Co$_3$O$_4$ in this chapter, since they were found to have a core containing copper and a porous shell containing manganese oxide (in the form of Mn$_3$O$_4$) or cobalt oxide (in the form of Co$_3$O$_4$), as will be discussed in the Results section.

5.2.2. Characterization

The nanoparticles were characterized by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), X-ray absorption near edge structure (XANES), Ex-situ Fourier Transform Infrared Spectroscopy (Ex-situ FTIR) and Temperature programmed reduction (TPR). TEM experiments were carried out using a Hitachi H-9500 (acceleration voltage 200 kV). Samples for TEM were prepared in inert atmospheric conditions by dispersing the bimetallic nanoparticles in toluene and then placing a drop of the solution on carbon-coated copper or molybdenum grids. X-ray photoelectron spectroscopy (XPS) studies were performed on a Kratos AXIS 165 X-ray Photoelectron Spectroscope and Scanning Auger Microscope equipped with standard Mg/Al source and high performance Al monochromatic source. XANES K-edge experiments were performed at the Double Crystal Monochromator beamline of the J. Bennett Johnston, Sr., Center for Advanced Microstructures and Devices, Louisiana State University, using Ge (220) crystals. The storage ring operated with an electron energy of 1.3 GeV and a current between 90 and 190 mA. Powder samples placed between two kapton tapes were used for XANES measurements.

Ex-situ FTIR spectra were obtained using a Thermo Nicolet 6700 spectrometer equipped with a MCT detector. A diamond crystal attenuated total reflectance (ATR) accessory was used for these measurements. A small amount of the powder sample was placed on the diamond crystal
and IR spectra were collected at 4 cm$^{-1}$ resolution and 32 scans. TPR experiments were carried out in a fixed bed micro reactor system. 50 mg of the sample was placed in a ¼ inch reactor tube and reduced in a 10% H$_2$/Ar mixture while the temperature was linearly ramped from room temperature to 500 ºC at 5 ºC/min. A thermal conductivity detector (TCD) was used to follow H$_2$ consumption as a function of temperature. The TCD was calibrated with known amounts of silver oxide in order to calculate the total hydrogen consumption of the nanoparticles.

5.2.3. In-situ FTIR (DRIFTS)

A Thermo Nicolet 6700 FTIR spectrometer equipped with a MCT detector and a Harrick Praying Mantis cell was employed for the Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) studies. The cell contains a temperature controlled reaction chamber, which is thermally isolated from the outer wall by a water-cooled jacket. The powdered sample was placed into the sample cup and prior to exposure to the reaction gas, the sample was heated under flowing He (30 scc/min) to 400 ºC and treated with 10% O$_2$/He (50 scc/min) at 400 ºC for 10 h to remove the surfactant ligands. The catalyst was then reduced in-situ in 10% H$_2$/He (50 scc/min) at 400 ºC for 2 h, followed by He flushing and then cooled down to room temperature in He. Background spectra were collected at different temperatures. Then the reactant gas (or gas mixture) was fed to the cell and the infrared spectra were taken at 4 cm$^{-1}$ resolution with 32 scans. 5% CO/He and 10% H$_2$/He gas mixtures were used. CO adsorption and CO hydrogenation DRIFTS experiments were carried out at different temperatures and pressures as described in the respective sections. A Hiden HPR-20 QIC Benchtop Gas Analysis System equipped with a quadrupole mass spectrometer was connected to the DRIFTS reactor to be able to monitor the reaction products online as they were eluting the reactor.
5.2.4. CO Hydrogenation

CO hydrogenation was performed in a fixed bed microreactor. The catalyst (0.2 g) was loaded between quartz wool and axially centered in the reactor tube, with the temperature monitored by a thermocouple. Prior to reaction, the catalyst was reduced at 400 °C in H₂ flow for 2 h at atmospheric pressure. Then, gas flow was switched to a 2:1 H₂/CO mixture at 270 °C and 10 bar. The products were analyzed for both oxygenates and hydrocarbons in an Agilent GC 6890 equipped with MSD and TCD. Product selectivities are reported in terms of carbon efficiencies which is defined as,

\[
\text{Carbon efficiency} = \frac{n_iC_i}{\sum(n_iC_i)}
\]

where \( n_i \) is the number of carbon atoms and \( C_i \) is the molar concentration of the carbon-containing products. Calibration of the GC/MS was carried out using standard gas mixtures (Air Liquide, Houston, TX) containing certified concentrations of each product gas.

5.3. Results and Discussion

5.3.1. Structural Characterization of As-prepared Nanoparticles

Figure 5.1 and 5.2 show the HRTEM images and particle size distributions of the as-prepared Cu@Mn₃O₄ and Cu@Co₃O₄ nanoparticles. The nanoparticles appear in spherical forms with distinguishable contrast between inner and outer regions suggesting core-shell structures. The particles are uniformly dispersed and show a narrow size distribution with a size of 13 ± 0.35 nm (for Cu@Mn₃O₄) and 11.4 ± 0.73 nm (for Cu@Co₃O₄). The Cu core size is ~6.1 nm and the shell is ~3.45 nm thick in the case of Cu@Mn₃O₄ nanoparticles, while the Cu@Co₃O₄ nanoparticles have a core of ~5 nm and a shell ~3.2 nm thick.
Figure 5.1: HRTEM image and particle size distribution of the as-prepared Cu@Mn$_3$O$_4$ nanoparticles. Mean size: 13 nm with a standard deviation of 0.35 nm.

Table 5.1 gives the XPS binding energies and Cu/Mn or Cu/Co surface atomic ratios. The surface atomic ratios for both the nanoparticles indicate a surface enrichment of copper, which could be due to either the presence of Cu oxide in the shell or the Cu-core being accessible through the porous shell, as was discussed in Chapter 4. The Cu 2p$_{3/2}$ peak is observed at similar positions in both the nanoparticles and it corresponds to Cu$^0$ and/or Cu$_2$O. Although the presence of metallic copper is most probable due to the absence of any shake up satellites corresponding
to Cu$_2$O, there is still a possibility of the copper core being partially oxidized by exposure to air during sample loading since the shell is porous. The Mn 2p$_{3/2}$ peak is positioned at 641.7 eV and the difference between the binding energy values of Mn 2p$_{3/2}$ and Mn 2p$_{1/2}$ level is 11.9 eV, which matches values for Mn$^{2+}$ and/or Mn$^{3+}$ oxides. Therefore, the discrimination becomes very difficult and a definite conclusion about the oxidation state of Mn cannot be derived from the XPS results. Similarly the Co 2p$_{3/2}$ peak positioned at 781.5 eV, can be attributed to either Co$^{2+}$ or Co$^{3+}$ states.

Table 5.1: XPS analysis of Cu@Mn$_3$O$_4$ and Cu@Co$_3$O$_4$ nanoparticles (X=Mn or Co).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Binding energies (eV)</th>
<th>Cu/X surface atomic ratio</th>
<th>Oxidation states</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu 2p$_{3/2}$</td>
<td>X 2p$_{3/2}$</td>
<td></td>
</tr>
<tr>
<td>Cu@Mn$_3$O$_4$</td>
<td>932.6</td>
<td>641.7</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>Cu$^{0}$ and/or Cu$_2$O</td>
<td>Mn$^{2+}$ and/or Mn$^{3+}$</td>
<td></td>
</tr>
<tr>
<td>Cu@Co$_3$O$_4$</td>
<td>932.5</td>
<td>781.5</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>Cu$^{0}$ and/or Cu$_2$O</td>
<td>Co$^{2+}$ and/or Co$^{3+}$</td>
<td></td>
</tr>
</tbody>
</table>

Figures 5.3 and 5.4 show the derivative spectrum of the normalized Cu K-edge and Mn (or Co) K-edge XANES for the Cu@Mn$_3$O$_4$ and Cu@Co$_3$O$_4$ nanoparticles. The Cu K-edge XANES spectrum for both the nanoparticles exhibits the absorption edge at 8979 eV, in agreement with the spectrum of fcc copper foil. Although most of the features closely resemble those of Cu foil, there are minor contributions from Cu$_2$O. This is consistent with the XPS results. Therefore, it appears that the nanoparticles contain traces of copper oxide due to their air sensitivity.
Figure 5.3: First derivatives of the normalized XANES spectra for (a) Cu K-edge and (b) Mn K-edge of the Cu@Mn\(_3\)O\(_4\) nanoparticles.

The Mn K-edge spectrum (Figure 5.3b) has the absorption edge at 6547 eV and the pre-edge and post-edge features match the Mn\(_3\)O\(_4\) standard. The absorption edge of the Co K-edge spectrum is observed at 7718 eV (Figure 5.4b) and it closely resembles that of a Co\(_3\)O\(_4\) standard. However, there are some differences in the spectral features of all the edges which can be attributed to the unique behavior of nanoparticles as opposed to bulk metal standards and also to the interactions between core and shell atoms at the interface. These results suggest that the core is metallic copper and the shell comprises of Mn\(_3\)O\(_4\) (in Cu@Mn\(_3\)O\(_4\)) and Co\(_3\)O\(_4\) (in Cu@Co\(_3\)O\(_4\)) nanoparticles, but the presence of minor amounts of copper oxide (Cu\(_2\)O) in the shell cannot be ruled out.
5.3.2. Removal of Surfactant Ligands from As-prepared Core-Shell Nanoparticles

The as-prepared (ligand-capped) core-shell nanoparticles are catalytically inactive since their surfaces are covered by organic ligands of the surfactants. The complete dispersion of these nanoparticles in nonpolar solvents suggests that the surface of the particles is bound to nonpolar surfactants - oleic acid and trioctylphosphine (TOP), which were used during the synthesis. Figure 5.5 shows the ex-situ FTIR spectra of the as-prepared Cu@Mn₃O₄ and Cu@Co₃O₄ nanoparticles which confirm the presence of certain bands characteristic of the COO⁻ group of oleic acid as well as C-P stretching modes of TOP, and CH₂ vibrations due to both surfactants. The peaks at 2848 and 2916 cm⁻¹ can be assigned to the symmetric and asymmetric CH₂ stretching modes and the peak at 3002 cm⁻¹ is due to the ν(C-H) mode of the C-H bond adjacent to the C=C bond. All these bands in the region 2850-3000 cm⁻¹ are characteristic of both OA and TOP surfactants. The bands at 1530 and 1395 cm⁻¹ in the case of Cu@Mn₃O₄ (1536 and 1402
cm$^{-1}$ for Cu@Co$_3$O$_4$) can be attributed to the symmetric and asymmetric vibrations of –COO$^-$ group of oleic acid, indicating the presence of bidentate carboxylate bonding to the nanoparticles. However, the $\nu$(C=O) stretching mode of the carboxylic acid group found in pure oleic acid$^{19}$, was present only as a small broad shoulder at around 1709 cm$^{-1}$, and a decrease of the intensity of this band is indicative of the chemical adsorption of oleic acid to the surface of the nanoparticles$^{40}$.

![Ex-situ FTIR spectra](image)

Figure 5.5: Ex-situ FTIR spectra of the as-prepared nanoparticles in the 700-3200 cm$^{-1}$ region: (a) Cu@Mn$_3$O$_4$ and (b) Cu@Co$_3$O$_4$ nanoparticles.

The peaks in the range 1000-1170 cm$^{-1}$ are due to the C–P stretching modes of TOP$^{41}$. Also, the bands that originate from the terminal methyl groups of TOP can be seen as shoulders on the major bands in the 1360-1500 cm$^{-1}$ region$^{41}$. Overall, the bands arising specifically due to TOP adsorption are relatively lower in intensity compared to those due to oleic acid. This indicates that the metal-TOP complexes decompose at the synthesis temperature (200 °C) whereas oleic
acid strongly chemisorbs on the nanoparticle surface. All the bands observed in the ex-situ FTIR spectra show that organic ligands from the surfactants are capped onto the nanoparticle surface, thereby preventing further agglomeration of the particles.

In-situ CO adsorption experiments on such ligand-capped nanoparticles by DRIFTS does not show any bands attributable to chemisorbed CO which indicates that CO does not adsorb on these materials. This is because all the adsorption sites are blocked by the surfactant ligands. Hence the organic ligands must be removed before using them as catalysts. This was achieved by treating the nanoparticles at 400 °C in 10% O₂/He while monitoring mass 44 (for CO₂) in an online mass spectrometer. The oxidation treatment was continued until the CO₂ levels came down to the baseline value, which took about 10 h.

Figure 5.6 shows the ex-situ FTIR spectra of the Cu@Mn₃O₄ and Cu@Co₃O₄ nanoparticles after treating them with 10% O₂/He at 400 °C for 10 h. The major bands characteristic of the surfactants, which were observed on the as-prepared nanoparticles (Figure 5.5), are either absent or insignificant in the case of oxygen-treated nanoparticles (Figure 5.6). The band at 1629 cm⁻¹ for Cu@Mn₃O₄ nanoparticles (1632 cm⁻¹ for Cu@Co₃O₄), accompanied with a broad band in the range 3000-3500 cm⁻¹, can be attributed to the stretching and bending vibrations of adsorbed water which is a major product of oxidation. The absence of bands due to the surfactants in the IR spectra indicates their removal in the O₂-treated nanoparticles.

The morphology and size of the particles after oxidation was studied by HRTEM. [Figures 5.1 and 5.2 showed the TEM images of as-prepared (ligand-capped) nanoparticles]. Figure 5.7 shows the HRTEM images of the O₂-treated (ligand-free) Cu@Mn₃O₄ and Cu@Co₃O₄ nanoparticles. The nanoparticles after high temperature oxidation show a polyhedron-like
morphology. It should be noted that their outer region show well-ordered layer structures. The core-shell structures are retained after high temperature oxidation, but the particles are slightly agglomerated, indicating the removal of surfactants.

Figure 5.6: Ex-situ FTIR spectra of the O$_2$-treated (ligand-free) nanoparticles: (a) Cu@Mn$_3$O$_4$ and (b) Cu@Co$_3$O$_4$ nanoparticles.

Figure 5.7: HRTEM images of the nanoparticles after removing the surfactant ligands by oxidation at 400 °C for 10 h - (a) Cu@Mn$_3$O$_4$ and (b) Cu@Co$_3$O$_4$. 
5.3.3. TPR of As-prepared and O$_2$-treated Nanoparticles

Since the oxidation pretreatment results in completely oxidized catalysts, they have to be reduced in H$_2$ before the DRIFTS experiments. Temperature programmed reduction (TPR) experiments were carried out on the as-prepared (ligand-capped) and O$_2$-treated (ligand-free) nanoparticle catalysts to understand their reduction behavior. Figures 5.8 and 5.9 show the TPR profiles of the Cu@Mn$_3$O$_4$ and Cu@Co$_3$O$_4$ nanocatalysts - as-prepared and O$_2$-treated.

![Figure 5.8: TPR profiles of as-prepared nanoparticles – (a) Cu@Mn$_3$O$_4$ and (b) Cu@Co$_3$O$_4$.](image)

The as-prepared Cu@Mn$_3$O$_4$ nanoparticle catalyst has a major TPR peak centered at 261 °C, whereas that of the as-prepared Cu@Co$_3$O$_4$ is at 269 °C (Figure 5.8). Since the as-prepared nanoparticles have a copper core and a porous shell containing oxides of manganese (in Cu@Mn$_3$O$_4$) or cobalt (in Cu@Co$_3$O$_4$), this TPR peak can be attributed to the reduction of
copper oxide on the surface of the core resulting from the exposure to atmosphere through the porous shell during sample preparation and loading, or to the reduction of surfactant ligands that are present in the as-prepared nanoparticles. However, the appearance of the TPR peak at similar positions (and shapes) mostly supports the consumption of hydrogen by the ligands. In the case of Cu@Co₃O₄, a broad peak is also observed between 400 and 600 °C which may be assigned to the reduction of cobalt oxides in the shell. But for Cu@Mn₃O₄, there is no significant peak in the high temperature region, which may indicate the very small concentrations of manganese oxide or the irreducibility of manganese oxide under these conditions.

Figure 5.9: TPR profiles of O₂-treated nanoparticles – (a) Cu@Mn₃O₄ and (b) Cu@Co₃O₄.

After oxidation at 400 °C for 10 h, the nanoparticles are completely oxidized (both the core and the shell) and thus require higher temperatures to undergo reduction as evident in the TPR profiles of the O₂-treated catalysts (Figure 5.9). The O₂-treated Cu@Mn₃O₄ nanoparticles start to reduce at a much higher temperature than the corresponding as-prepared catalyst (Figure 5.8a). It
has a very small peak at 245 °C, but the major reduction peak is centered at 421 °C. On the other hand, the TPR profile of the O₂-treated Cu@Co₃O₄ nanoparticles is characterized by two peaks centered at 271 °C and 319 °C, respectively. Unlike the Cu@Mn₃O₄ nanoparticles, the onset of reduction is the same in both the as-prepared and O₂-treated Cu@Co₃O₄ nanoparticles. Since most of the surfactant ligands are removed in the O₂-treated nanoparticles, the differences in their reducibility (Figure 5.9) can be attributed to the effect of shell material. Thus, it is clear that manganese significantly inhibits the reduction of copper.

The area under the TPR peaks can be related to total H₂ consumed during the TPR experiments, using the silver oxide calibration. Table 5.2 presents the calculated H₂ consumption values for all the four nanoparticles. It is clear that the O₂-treated (ligand-free) nanoparticles consume about 2.5 times more H₂ than the corresponding as-prepared (ligand-capped) nanoparticles.

Table 5.2: TPR peak maxima and H₂ consumption for the Cu@Mn₃O₄ and Cu@Co₃O₄ nanocatalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Peak Maxima (°C)</th>
<th>Total H₂ consumed (μmol)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu@Mn₃O₄ – as prepared</td>
<td>261</td>
<td>85.7</td>
</tr>
<tr>
<td>Cu@Mn₃O₄ – O₂-treated</td>
<td>245, 421</td>
<td>222.0</td>
</tr>
<tr>
<td>Cu@Co₃O₄ – as prepared</td>
<td>269</td>
<td>131.2</td>
</tr>
<tr>
<td>Cu@Co₃O₄ – O₂-treated</td>
<td>271, 319</td>
<td>291.2</td>
</tr>
</tbody>
</table>

* H₂ consumption for 50 mg of catalyst (calibrated using silver oxide) – experimental error is within ±4%.
5.3.4. DRIFTS Studies on Ligand-free Nanoparticles at 1 bar

5.3.4.1. Cu@Mn₃O₄

(i) CO Adsorption at 25 °C Followed by He Flushing at 25 °C, 1 bar:

As described in the Experimental section, the O₂-treated ligand-free nanoparticles were reduced in-situ at 400 °C in 10% H₂/He for 2 h before the DRIFTS experiment. 5% CO/He was adsorbed on the reduced catalyst surface at 25 °C for 10 min, followed by He flushing to remove the physisorbed CO.

Figure 5.10 shows the DRIFTS spectra of CO adsorption on the reduced ligand-free Cu@Mn₃O₄ nanoparticles at 25 °C followed by He flushing. After 2 min of contact with CO, the major peaks observed in the IR spectra are in the carbonyl stretching region (2000-2200 cm⁻¹) that can be attributed to various forms of adsorbed CO. The doublet bands attributed to gaseous CO could be removed by flushing with He for about 10 min. Linearly adsorbed CO species become visible after He flushing. The band at 2136 cm⁻¹ with shoulders on either side (2126 cm⁻¹, 2148 cm⁻¹ and 2174 cm⁻¹) are due to the linearly chemisorbed carbonyl species. The principal band at 2120-2136 cm⁻¹ is assigned to Cu⁺-CO species by many authors. However, when the copper is highly dispersed, Cu⁰-CO species can also adsorb at the same frequency as Cu⁺-CO carbonyl in which case these two surface species can be distinguished by their stability: the Cu⁰-CO species are easily removed during flushing or evacuation. In the case of Cu@Mn₃O₄ catalyst, the 2136 cm⁻¹ band was highly resistant to He flushing and can be assigned to carbonyl species on Cu⁺ sites. The high stability and intensity of the band suggests that these Cu⁺-CO species are predominant on the surface, although minor contributions from metallic copper carbonyls to the band cannot be excluded. Although the catalyst was reduced before the DRIFTS experiment, the
results provide the evidence for the presence of Cu$^+$ sites, which can be either due to the interaction of the Cu atoms with either CO in the feed, thereby keeping the surface Cu atoms in a partially oxidized state \(^{44}\), or with the hydroxyl groups present on the surface after hydrogen reduction. Another plausible explanation could be that the reduction at 400 °C for 2 h before the DRIFTS experiment may not have been sufficient to reduce the catalyst entirely to its metallic state.

Figure 5.10: DRIFTS spectra of CO adsorption on the ligand-free Cu@Mn$_3$O$_4$ nanoparticles at 25 °C and 1 bar followed by He flushing.

The 2126 cm$^{-1}$ band in Figure 5.10 can be due to another kind of Cu$^+$-CO species since it is also found to be stable with He flushing. If so, there may be two kinds of Cu$^+$ sites present on the surface. However, some reports suggest that the typical band positions of Cu$^+$-(CO)$_2$ dicarbonyl species are characterized by the symmetric ($v_s$) and antisymmetric ($v_{as}$) vibrational modes at
2160 and 2115 cm\(^{-1}\) respectively \(^{35}\). With regard to this, the bands observed at 2126 and 2174 cm\(^{-1}\) in our case (Figure 5.10) can also be assigned to these dicarbonyl species, if a component of the band at 2174 cm\(^{-1}\) can be assigned to the symmetric mode of Cu\(^{+}\)-(CO)\(_2\) species, the respective antisymmetric vibrations being at 2126 cm\(^{-1}\).

The other small band at 2148 cm\(^{-1}\), which decreased in intensity with He flushing and eventually disappeared, can be assigned to the CO adsorbed over highly dispersed copper sites (or small copper particles) \(^{45}\) or CO hydrogen-bonded to the surface hydroxyl groups present after hydrogen reduction \(^{37}\). The doublet in the region 2320-2380 cm\(^{-1}\), which corresponds to gaseous CO\(_2\), varies randomly throughout the experiment. Although the sample compartment is sealed from the atmosphere, the instrument is extremely sensitive to even very small changes in CO\(_2\) in the lab atmosphere due to which the CO\(_2\) bands were not taken into account and no conclusions were drawn from them.

The spectra after 2 min of CO adsorption did not have any significant IR bands below 1700 cm\(^{-1}\), whereas the spectra after He flushing for 20 min and higher revealed some IR bands in the low frequency region that may be due to various surface bound carbonates or carboxylates \(^{46}\). The absence of these bands in the initial 2 min spectrum indicates that they originated from the desorbed CO as a result of He flushing. The bands at 2923, 2955 and 2854 cm\(^{-1}\) can be assigned to the C–H stretching vibrations of the saturated alkyl groups \(^{47-48}\). The bands in the region 1300-1650 cm\(^{-1}\) found in the 28 min and 40 min spectra can be attributed to the vibrations of surface bound carbonate species or carboxylate species of the formate or acetate type, and/or to the CH\(_3\)O\(_{ad}\) and C\(_2\)H\(_5\)O\(_{ad}\) species, as reported elsewhere \(^{47-49}\). These bands in conjunction with the C–H stretching region could indicate the presence of adsorbed oxygenated compounds on the catalyst surface. Although no hydrogen was admitted in this experiment, these species can be
produced by an interaction of CO with already present residual hydroxyl groups or residual hydrogen that is left over after the reduction step\(^{46}\). The band at 1176 cm\(^{-1}\) can be due to some hydrogen-carbonate species that is also formed upon interaction of desorbed CO with the residual hydrogen\(^{46}\). This may indicate that more CO desorbed with He flushing over time which then reacts with the left-over hydrogen or OH groups to form these new species.

(ii) Effect of Temperature on CO Adsorption at 1 bar:

CO was adsorbed on the reduced Cu@Mn\(_3\)O\(_4\) nanoparticles at three different temperatures followed by 20 min of He flushing. Figure 5.11 shows the IR spectra recorded after 20 min of He flushing. The intensity of the linearly adsorbed carbonyl species on copper sites decreases with temperature. The spectrum at 25 °C is the same as that in Figure 5.10. At 100 °C, a less intense band at 2138 cm\(^{-1}\) is detected after He flushing, which can be attributed to Cu\(^{+}\)-CO species, while

![IR spectra](image)

Figure 5.11: IR spectra recorded after CO adsorption at 1 bar followed by 20 min of He flushing at 25 °C, 100 °C, and 270 °C on the ligand-free Cu@Mn\(_3\)O\(_4\) nanoparticles.
at 270 °C, only gaseous CO was observed and no linear carbonyl bands were present after He flushing. This indicates that at higher temperatures, CO may be adsorbed in an IR inactive form (or dissociative form) \(^{50}\). The absence of chemisorbed CO bands at higher temperatures may also be due to a weak interaction between CO and Cu\(^+\).

(iii) Coadsorption of CO and H\(_2\) at 1 bar:

In this experiment, a mixture of 5% CO/He and 10% H\(_2\)/He was co-adsorbed on the reduced Cu@Mn\(_3\)O\(_4\) nanoparticles for 10 min at 25 °C, followed by flushing with H\(_2\)/He (at 25 °C, 100 °C and 270 °C). Simultaneous adsorption of CO and H\(_2\) did not affect the positions of the CO stretching bands, but flushing with H\(_2\) after CO+H\(_2\) adsorption resulted in a faster desorption/reaction of the adsorbed CO species, as evidenced by a significant decrease in their intensity, compared to flushing with He alone. [The IR spectra are not shown since they are similar to CO adsorption spectra as in Figures 5.10 and 5.11, except that H\(_2\) flushing resulted in a faster desorption of the chemisorbed CO]. The carboxylate species (< 1700 cm\(^{-1}\)), which are considered to be the intermediates for alcohol/oxygenate products \(^{46}\), and, bands in the C-H stretching region (2830-2950 cm\(^{-1}\)), decreased in intensity with H\(_2\) flushing over time, indicating their reaction with either H\(_2\) or desorbed CO. Thus, coadsorption of CO and H\(_2\) decreases the absorbance for the adsorbed CO which may be attributed to the decrease in dipole-dipole interactions as a result of dilution by adsorbed hydrogen.

However these DRIFTS results alone cannot be used to conclusively identify the products formed. Reactor studies under similar conditions are necessary to support these findings.
5.3.4.2. Comparison of CO Adsorption on Cu@Mn₃O₄ vs. Cu@Co₃O₄ Nanoparticles at 1 bar

Figure 5.12 compares the DRIFTS spectra after CO adsorption followed by 20 min of He flushing at 25 °C and 1 bar over the ligand-free Cu@Mn₃O₄ and Cu@Co₃O₄ nanoparticles. The CO chemisorption is much more stable and intense on Cu@Mn₃O₄ than on Cu@Co₃O₄ nanoparticles. The CO uptake is very high and the linearly adsorbed CO band is highly stable to He flushing on the Cu@Mn₃O₄ nanoparticles. The higher wavenumbers and high stability indicate the presence of Cu⁺ active sites, whereas on the Cu@Co₃O₄ nanoparticles, the linear carbonyl bands are only partially stable to He flushing indicating the possibility of both Cu⁰-CO and Cu⁺-CO species.

Figure 5.12: DRIFTS spectra after CO adsorption followed by 20 min of He flushing at 25 °C and 1 bar over ligand-free nanoparticles (a) Cu@Mn₃O₄ and (b) Cu@Co₃O₄.
As seen in Figure 5.12, the CO stretching region for both the nanoparticles shows a major peak with shoulders on either side. But the frequencies (wavenumbers) are higher in the case of Cu@Mn$_3$O$_4$ nanoparticles, where all the bands have blue-shifted. The shift towards higher frequency (blue-shift) with Mn promoter on Cu catalysts was also observed by Xu et al. $^{29,51}$, who attributed the blue-shift to lowering of the Lewis basicity (or electron density) of the surface Cu metal atoms by the presence of Mn$^{2+}$, consequently increasing the strength of the C≡O bond, leading to higher vibrational frequencies. Higher frequencies represent the weakening of Cu–CO bond and strengthening of the C–O bond which may be expected to enhance the associative adsorption of CO during CO hydrogenation $^{52}$. The weakening of the Cu-CO bond by Mn is due to the electron withdrawing effect of Mn which results in an increased population of Cu$^+$ species on the catalyst surface. The lowering of the electron density of the surface Cu atoms by Mn$^{2+}$ can be used to explain the TPR results as well. That is, due to the decrease in electron density, Cu atoms tend to remain in an oxidized state, which makes their reduction difficult. Therefore, the reduction of copper is inhibited by Mn, as evidenced by the TPR profile of the O$_2$-treated Cu@Mn$_3$O$_4$ nanoparticles (Figure 5.9a). Hence two major observations can be made: first, CO chemisorption increases (more intense linear CO band) because Mn provides more sites for CO adsorption, and second, CO dissociation is less on the Mn-containing catalyst, making most of the adsorbed CO desorb as molecular CO. The latter point is consistent with the effect of Mn on CuMnZrO$_2$, as previously reported, where Mn oxide weakened the Cu-CO bond $^{29}$.

On the other hand, lower wavenumbers in the case of Cu@Co$_3$O$_4$ nanoparticles suggests that the C-O bond is relatively weaker (or Cu-CO bond is stronger) than the Cu@Mn$_3$O$_4$ nanoparticles. The presence of both Cu$^+$ and Cu$^0$ sites may suggest that CO adsorbs in both associative and dissociative forms on Cu@Co$_3$O$_4$ nanoparticles. The stronger the adsorption between CO and
metal the more likely it is to be dissociated, suggesting that CO is less likely to dissociate on the Mn-containing nanoparticles.

5.3.5. DRIFTS Experiments at 10 bar: Hydrogenation of Pre-adsorbed CO

5.3.5.1. Cu@Mn₃O₄ - 10 bar

In this set of experiments, CO adsorption followed by hydrogenation of the pre-adsorbed CO was studied at 10 bar. Figure 5.13 shows the IR spectra of CO adsorption at 25 °C and 10 bar followed by He flushing at 25 °C to remove the gaseous CO and then flowing H₂/He at various temperatures for the ligand-free Cu@Mn₃O₄ nanoparticles. Longer flushing times are required to remove the gaseous CO in the case of 10 bar experiments, while 10 min or less was sufficient at 1 bar. The spectrum after 40 min of He flushing and that after 75 min of H₂/He flushing at 25 °C in Figure 5.13 show the presence of three bands in the CO stretching region, but all of them seem to have blue-shifted compared to CO adsorption at 1 bar (See Figure 5.10). The 2148 cm⁻¹ band can be assigned to linearly adsorbed CO on Cu⁺ sites based on its high stability even after H₂/He flushing at 25 °C. The other two bands (2132 and 2175 cm⁻¹) were observed to follow similar trends in that they increased in intensity with time in the beginning and then decreased in intensity with flushing in a consistent manner. For this reason, they can be attributed to the Cu⁺-(CO)₂ dicarbonyl species with the symmetric and antisymmetric modes of vibrations at 2175 and 2132 cm⁻¹ respectively. A comparison between the CO adsorption at 1 bar and 10 bar on the same catalyst indicates that the linear CO uptake at 10 bar is roughly about 8 times greater than that at 1 bar. Thus, increase in the total pressure resulted in an increase in the intensity of the linear CO and an upward shift of its wavenumber.
Admission of H$_2$ to the reactor at 25 °C over the pre-adsorbed CO did not affect the positions of any of the bands, but decreased their intensities which suggest that the adsorbed CO undergoes reaction with hydrogen. The decrease in the intensity of the linear CO with hydrogen can be attributed to the reduction in the dipole-dipole coupling interactions as a result of the removal of the adsorbed CO by reaction with hydrogen. As the temperature was increased to 270 °C under hydrogen flow, the linear CO bands disappeared and the CO stretching region is now characterized by a doublet band attributable to physisorbed (gaseous) CO and new bands appeared at 2916 and 2948 cm$^{-1}$, corresponding to C-H vibrations. These observations indicate the reaction between desorbed linear CO and H$_2$ thereby resulting in the formation of hydrocarbon intermediate species.
When the temperature was further raised to 400 °C in H\(_2\), no linear CO bands were detected and the gaseous CO that was observed at 270 °C also disappeared which indicates that all the pre-adsorbed CO had reacted with H\(_2\) or dissociated, leading to almost complete consumption of gaseous CO. The band at 1615 cm\(^{-1}\) with a shoulder at 1632 cm\(^{-1}\), which was observed at 25 °C, decreased with increasing temperature and disappeared completely at 400 °C. This band can be attributed to the presence of molecular water\(^{44}\). At 400 °C, there are new bands in the 1400-1700 cm\(^{-1}\) region which are due to the surface bound carboxylate species, probably of the formate/acetate type\(^{46}\). The vibrations due to C-H modes were also observed at 2927 and 2948 cm\(^{-1}\). The new band at 3015 cm\(^{-1}\) accompanied by another new band at 1307 cm\(^{-1}\) at 400 °C can be assigned to gaseous CH\(_4\)\(^{47,53}\). Thus, at 400 °C, the complete consumption of the entire pre-adsorbed CO (including the gaseous CO) indicates the dissociation of CO, which is further supported by the appearance of IR bands corresponding to gaseous methane. An analysis of the effluents from the DRIFTS cell using a mass spectrometer also showed a sharp increase in mass 15 at 400 °C, consistent with the IR band.

5.3.5.2. Cu@Co\(_3\)O\(_4\) - 10 bar

Figure 5.14 shows the IR spectra of CO adsorption at 25 °C and 10 bar followed by He flushing at 25 °C and then flowing H\(_2\)/He at various temperatures for the ligand-free Cu@Co\(_3\)O\(_4\) nanoparticles. The spectrum after 70 min of He flushing is characterized by several CO bands in the 2000-2200 cm\(^{-1}\) region which are blue-shifted and higher in intensity compared to CO adsorption at 1 bar on the same catalyst (See Figure 5.12). The blue-shifts and higher CO uptakes observed with increasing pressure in both the catalysts (Figures 5.13 and 5.14) indicate that higher pressures increase the strength of the C≡O bond, resulting in a weak Cu–CO bond. This may be expected to enhance the CO insertion step during CO hydrogenation.
Figure 5.14: DRIFTS spectra recorded during CO adsorption at 25 °C and 10 bar followed by He flushing at 25 °C and then flushing with H₂/He at various temperatures for the ligand-free Cu@Co₃O₄ nanoparticles.

The highly stable band at 2137 cm⁻¹ in Figure 5.14 can be assigned to linearly adsorbed CO on Cu⁺ sites as seen in the previous sections. The two bands at 2116 and 2164 cm⁻¹ can again be attributed to antisymmetric and symmetric modes of the Cu⁺-(CO)₂ dicarbonyl species. The band at 2116 cm⁻¹ can also be due to CO adsorbed on Co⁺ ions or CO complexes with partially-reduced cations. The higher frequency bands in the range 2160-2180 cm⁻¹ can be assigned to CO linearly adsorbed on oxidized Co species (Co²⁺ or Co³⁺).

Upon hydrogenation at 25 °C after He flushing, the band positions were not affected significantly similar to the case of Cu@Mn₃O₄ and all the bands except that at 2137 cm⁻¹ decreased in intensity with H₂, but the intensity of the linear CO band at 2137 cm⁻¹ increased with hydrogen flow at 25 °C. A careful inspection of the spectra and the literature indicates that
it is possible for the Cu\(^{+}\)-(CO)\(_2\) dicarbonyl species to decompose into monocarbonyl species, thereby resulting in an intense linear CO band \(^{55}\). Thus, the rise in intensity of the 2137 cm\(^{-1}\) band during hydrogenation could be a result of decomposition of the dicarboxyls to linear Cu\(^{+}\)-CO complexes. As the temperature was raised to 270 °C in hydrogen flow, the linear CO band becomes very weak due to the presence of gaseous CO, indicating the possible reaction between desorbed linear CO and H\(_2\).

### 5.3.6. DRIFTS Experiments Coupled with Mass Spectrometry

The products of DRIFTS CO hydrogenation experiments carried out at 270 °C on the Cu@Mn\(_3\)O\(_4\) and Cu@Co\(_3\)O\(_4\) nanoparticles were analyzed by an online mass spectrometer. Figure 5.15 shows the mole fractions of masses 31 and 15 observed at 1 bar and 10 bar (both at 270 °C), which can be attributed to the formation of alcohols and methane respectively.

![Figure 5.15](image)

Figure 5.15: Masses 31 and 15 monitored on a mass spectrometer during CO hydrogenation DRIFTS experiment at 270 °C: (a) 1 bar and (b) 10 bar (Note that the y-axis scales are different).
There are no significant differences in mass 15 at 1 bar. Increasing the pressure to 10 bar increases the yields to all products, indicating an increase in overall CO conversion (note the different y-axis scales in Figure 5.15 (a) and (b)). At both the pressures, mass 31 is higher in the case of Cu@Co$_3$O$_4$ nanoparticles, suggesting that they produce more alcohols than the Cu@Mn$_3$O$_4$ nanoparticles.

5.3.7. CO Hydrogenation Results

Table 5.3 summarizes the product selectivities of the two nanoparticle catalysts tested at 10 bar, 270 °C, H$_2$/CO=2, space velocity (S.V.)=18,000 scc/(h gcat) and differential conversions. These conditions were chosen for the reactor studies to allow for a direct comparison with the DRIFTS/MS results.

The high selectivities towards CO$_2$ formation can be attributed to the presence of copper which enhances the water gas shift reaction. It is evident that the Cu@Co$_3$O$_4$ nanoparticles produces more alcohols and methane compared to the Cu@Mn$_3$O$_4$ nanoparticles, consistent with the DRIFTS/MS results at 10 bar (Figure 5.15b). The highest ethanol selectivity achieved at this condition is 15% on the Cu@Co$_3$O$_4$ nanoparticles with relatively low methane selectivity (11%), and the total selectivity towards alcohols and oxygenates is 47.5%.

These results are consistent with the DRIFTS results which suggested a higher CO uptake in an associative form and a lower CO dissociation activity on the Cu@Mn$_3$O$_4$ nanoparticles. This might result in a lower concentration of CH$_x$ species on the surface, thus limiting the rate of the CO insertion step required to form higher alcohols. On the other hand, the DRIFTS results suggest that the Cu@Co$_3$O$_4$ nanoparticles adsorb CO in both forms (dissociative and associative), which may be the reason for higher selectivities towards alcohols on this catalyst.
Lower methane selectivity and higher alcohol selectivity may be attributed to the enhanced stability of the CH\textsubscript{x} species on the surface, followed by CO insertion into the M-C bond of the surface CH\textsubscript{x} species and hydrogenation to produce alcohols.

Table 5.3: Product selectivities of Cu@Mn\textsubscript{3}O\textsubscript{4} and Cu@Co\textsubscript{3}O\textsubscript{4} nanoparticles \textsuperscript{a}.

<table>
<thead>
<tr>
<th>Products</th>
<th>Selectivity (C %) \textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu@Mn\textsubscript{3}O\textsubscript{4}</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>69.3</td>
</tr>
<tr>
<td>MeOH</td>
<td>9.6</td>
</tr>
<tr>
<td>EtOH</td>
<td>5.2</td>
</tr>
<tr>
<td>C\textsubscript{3}+ Oxy \textsuperscript{c}</td>
<td>6.8</td>
</tr>
<tr>
<td>CH\textsubscript{4}</td>
<td>9.0</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Catalyst: 0.2 g; reaction conditions: P = 10 bar, 270 °C, H\textsubscript{2}/CO = 2, space velocity=18,000 scc/(h gcat).

\textsuperscript{b}Product selectivities are reported in terms of carbon efficiencies defined as, Carbon efficiency = \( n_i C_i / \Sigma (n_i C_i) \), where \( n_i \) is the number of carbon atoms and \( C_i \) is the molar concentration of the carbon-containing products.

\textsuperscript{c}Propanol, butanol and acetone.

5.4. Summary and Conclusions

Cu core-Mn oxide shell (Cu@Mn\textsubscript{3}O\textsubscript{4}) and Cu core-Co oxide shell (Cu@Co\textsubscript{3}O\textsubscript{4}) nanoparticles were synthesized using surfactant-assisted wet chemical synthesis methods and their CO adsorption properties were studied using DRIFTS. The removal of surfactant ligands from the nanoparticle surfaces was found to be necessary for CO adsorption during DRIFTS experiments. CO adsorbed in both linear and dicarbonyl forms on the ligand-free nanoparticles, and the desorbed CO as a result of He flushing over time led to the formation of surface bound carboxylate species, probably by reacting with the residual hydroxyl groups present after hydrogen reduction. The intensity of the linearly adsorbed carbonyl species decreased with
temperature and only gaseous CO was found at 270 °C, indicating either the weak interaction of CO with Cu\(^+\) or adsorption of CO in an IR inactive (or dissociative) form.

The CO uptake was very high and the linearly adsorbed CO band was highly stable to He flushing on the Cu@Mn\(_3\)O\(_4\) nanoparticles, indicating the presence of only Cu\(^+\) active sites, whereas the partially stable linear carbonyl species on the Cu@Co\(_3\)O\(_4\) nanoparticles indicated the possible presence of both Cu\(^0\) and Cu\(^+\) sites. The shift towards higher frequencies (blue-shift) in the case of Cu@Mn\(_3\)O\(_4\) nanoparticles can be attributed to the lowering of the Lewis basicity (or electron density) of the surface Cu metal atoms by the presence of Mn\(^{2+}\), consequently increasing the strength of the C≡O bond, which may result in an enhanced associative adsorption of CO during CO hydrogenation.

The effect of pressure on CO adsorption and hydrogenation was also studied using DRIFTS. Longer flushing times were required to remove the weakly adsorbed gaseous CO in the case of experiments conducted at 10 bar. Increase in the total pressure resulted in an increase in the intensity of the linear CO and an upward shift of its wavenumber. The linear CO uptake at 10 bar was roughly about 8 times greater than that at 1 bar. Hydrogenation of the pre-adsorbed CO at 270 °C indicated the disappearance of strongly pre-adsorbed linear CO in both Cu@Mn\(_3\)O\(_4\) and Cu@Co\(_3\)O\(_4\) nanoparticles, indicating the reaction of linear CO with H\(_2\).

CO hydrogenation studies at 10 bar and 270 °C showed a highest ethanol selectivity of 15% on the Cu@Co\(_3\)O\(_4\) nanoparticles with relatively low methane selectivity (11%), and a total alcohols/oxygenates selectivity of 47.5%. These results are in agreement with the DRIFTS results which indicated a lower CO dissociation activity on the Cu@Mn\(_3\)O\(_4\) nanoparticles, and
both dissociative and associative forms of CO adsorption on the Cu@Co₃O₄ nanoparticles, which may be the likely reason for higher selectivities towards alcohols/oxygenates on this catalyst.

5.5. References


Chapter 6: Transition Metal Promoted Copper-Rare Earth Zirconate Catalysts - *In-situ* Time-resolved XRD and XANES Studies

Chapters 6 and 7 focus on the second type of copper-based catalysts (pyrochlores) that were studied in this research work.

6.1. Introduction

Ethanol production has attracted attention as oil prices have risen and the search for cheaper alternatives to conventional fuels is growing rapidly \(^1-^2\). Ethanol and other oxygenates can be used as fuels or fuel additives to reduce greenhouse gas emissions \(^2-^5\). They also have the potential to serve as hydrogen carriers for fuel cell applications \(^2-^3,^6\). Among all the processes involved in the synthesis of higher alcohols and oxygenated fuel additives, the most promising route is the one from syngas, which can be derived from biomass, coal or natural gas. Catalytic conversion of syngas to ethanol and other higher alcohols has been studied for over a hundred years \(^2\), but it is not yet an economically and commercially viable process. This has led to the growing need for an active/selective catalyst. The general mechanism of C\(_{2+}\) oxygenates formation from syngas has been extensively studied \(^3,^7-^10\), with the overall objective of finding a catalyst with high yields and selectivities towards C\(_{2+}\) alcohols and oxygenates, while, at the same time, minimizing the side reactions such as methanation, methanol formation, and water gas shift reactions.

Rh-based catalysts have so far been the most selective and active for ethanol \(^1,^3,^7,^11-^13\). However, Rh is an expensive, rare metal that may be impractical for a commercial process \(^2\). Other catalysts have been studied, such as the modified Cu, Fischer-Tropsch, or Mo-based catalysts \(^2-^3\). Cu-Co catalysts have been tested on support materials like MgO, La\(_2\)O\(_3\), CeO\(_2\), TiO\(_2\), ZrO\(_2\) and
SiO$_2$, and the selectivity towards higher alcohols on SiO$_2$ and ZrO$_2$ were found to be the highest with 29 and 25% respectively $^{14}$. Rare-earth oxide supports like La$_2$O$_3$ and LaYO$_3$ have been reported to promote higher alcohol formation, but they suffer from carbonation and deactivation $^{15-16}$.

A promising class of materials is based on rare earth zirconate supports with cubic pyrochlore structures, such as La$_2$Zr$_2$O$_7$, which have an excellent thermal and chemical stability towards deactivation $^{15, 17}$ and low sintering rates $^{18}$. This pyrochlore is believed to be a promising candidate as a support for a stable and active copper catalyst for C$_2+$/oxygenate synthesis $^{16}$. Cu-ZnO supported on La$_2$Zr$_2$O$_7$ pyrochlores are effective catalysts for the formation of methanol with minimum deactivation $^{15-17}$. The generally accepted role of copper in these catalysts is to assist in non-dissociative activation of CO $^{14, 19}$, whereas ZnO stabilizes the catalytic activity without affecting the catalytic sites, thus limiting the deactivation observed on ZnO-free catalysts $^{20}$. ZnO has also been reported to enhance the hydrogenation properties of copper catalysts by forming H---ZnO species $^{21-22}$.

Copper catalysts supported on La$_2$Zr$_2$O$_7$ supports are prepared using high temperature calcination ($>700$ °C) to make well defined pyrochlores with cubic crystal structures $^{15-17, 23}$. The addition of promoters does not hinder the formation of La$_2$Zr$_2$O$_7$ pyrochlore. Coprecipitation methods, as opposed to impregnation techniques, have been used in this study to synthesize these catalysts because coprecipitation yields catalysts with greater metal loadings, dispersion, and homogeneity $^{15-16}$. The following mechanism has been proposed to occur during the calcination of these supported Cu-La$_2$Zr$_2$O$_7$ catalysts $^{15-16}$:
\[
\text{CuO} + \text{La}_2\text{O}_3 \rightarrow \text{CuLa}_2\text{O}_4 \quad (400 \, ^\circ \text{C})
\]

\[
\text{CuLa}_2\text{O}_4 + 2\text{ZrO}_2 \rightarrow \text{CuO} + \text{La}_2\text{Zr}_2\text{O}_7 \quad (> 550 \, ^\circ \text{C})
\]

Higher alcohol formation requires a certain balance of dissociated and non-dissociated surface CO\textsuperscript{19}. This balance can be achieved by combining suitable transition metal (e.g., Co, Mn) and/or alkali (e.g., Li) promoters with Cu-La\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} based catalysts. For example, Co has been found to increase the selectivity of higher alcohols as well as alkenes, and even a very small amount of Co promotion reduces the yield of methanol\textsuperscript{15, 17}. Both Mn and Co help in CO dissociation and hydrogenation of the surface carbon species into hydrocarbons\textsuperscript{14, 19}. Mn also promotes the adsorption and dissociation of CO\textsuperscript{24-26}, accelerates the hydrogenation steps\textsuperscript{27}, and creates new active sites for the CO insertion reaction\textsuperscript{28}. Li\textsubscript{2}O, like other alkali promoters, increases the yield and selectivity of higher alcohols by suppressing hydrocarbon formation\textsuperscript{2-3}. For example, Tien-Thao et al. reported that even very small amounts of such residual alkali ions (0.05-0.75 wt%) are sufficient to promote catalytic activity and selectivity to higher alcohols\textsuperscript{29}.

Time-resolved and element-specific studies are critical in understanding the pyrochlore structure and the role of metal substitution into its lattice, in order to be able to develop structure-activity relationships. Thus, this paper is focused on the \textit{in-situ} characterization of the catalysts.

Here, we describe the synthesis of a series of transition metal promoted Cu-ZnO-La\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}-Li\textsubscript{2}O catalysts and provide the results of \textit{in-situ} X-ray diffraction (XRD) as well as synchrotron-based X-ray absorption near-edge structure spectroscopy (XANES) experiments carried out under H\textsubscript{2}-TPR conditions. The focus of this study is to investigate the structural and chemical changes in the local environment of Cu and the significance of transition metal promotion. Insights into how
the transformation into metallic phases occurs can help in designing the pretreatment or activation procedures that will produce catalysts with improved properties\textsuperscript{30-32}.

6.2. Experimental

6.2.1. Catalyst Synthesis

Cu-ZnO-La\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}-Li\textsubscript{2}O catalysts were synthesized by coprecipitation of a mixed solution of copper nitrate, zinc nitrate, lithium nitrate, lanthanum nitrate and zirconium acetylacetonate in ethanol using oxalic acid, as reported elsewhere\textsuperscript{15, 17}. After dropwise addition of oxalic acid, the mixture was stirred for 2-3 h. The precipitate was then washed with ethanol, dried overnight at 110 °C and finally calcined in air at 550 °C for 3.5 h followed by 710 °C for 30 min\textsuperscript{15}. Co or Mn was added to the catalyst in a similar way. All the nitrate salts were coprecipitated using oxalic acid, washed, dried and calcined as above. In this chapter, the Cu-ZnO-La\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}-Li\textsubscript{2}O catalyst is denoted as CZLL, with Mn promotion as CMnZLL, and with Co promotion as CCoZLL.

6.2.2. Catalyst Characterization

The catalysts were characterized by BET, inductively coupled plasma atomic emission spectrometry (ICP-AES), X-ray photoelectron spectroscopy (XPS), temperature programmed reduction (TPR), \textit{in-situ} X-ray diffraction (XRD), and \textit{in-situ} X-ray absorption near-edge structure spectroscopy (XANES) techniques. The BET surface areas of the calcined catalysts were measured by N\textsubscript{2} adsorption/desorption at liquid nitrogen temperature (77 K), using an Altamira AMI-200R catalyst characterization instrument. ICP-AES was used for the determination of the bulk metal content in each sample. These (ICP-AES) measurements were performed with a Spectro Ciros Inductively Coupled Plasma Analyzer in the Central Analytical
Instruments Research Laboratory, LSU Ag Center, LSU. XPS studies were performed on a Kratos AXIS 165 X-ray Photoelectron Spectroscope and Scanning Auger Microscope equipped with standard Mg/Al source and high performance Al monochromatic source. TPR experiments were carried out in a fixed bed micro reactor system. 50 mg of the sample was placed in a ¼ inch reactor tube and reduced in a 10% H₂/Ar mixture while the temperature was linearly ramped from room temperature to 500 °C at 5 °C/min. A thermal conductivity detector (TCD) was used to follow H₂ consumption as a function of temperature. The TCD was calibrated with known amounts of silver oxide in order to calculate the extent of reduction of the catalysts.

*In-situ* time-resolved XRD patterns were recorded on a PANalytical X’Pert Pro MPD vertical θ/θ goniometer using Cu Kα radiation, at the Center for Nanophase Materials Sciences, Oak Ridge National Laboratory. The instrument is equipped with Anton Paar XRK 900 high-temperature reaction chamber (RT to 900°C) with rotating sample stage. Diffraction patterns were collected under reducing conditions in 4% H₂/Ar atmosphere, while ramping the temperature. HighScore Plus (v.3.0.1) Crystallography and Rietveld software was used for data analysis.

*In-situ* XANES experiments were carried out on the Cu K-edge of the pyrochlores under H₂ TPR conditions at the DCM beamline of the J. Bennett Johnston Sr. Center for Advanced Microstructures and Devices (CAMD), Baton Rouge, LA. The synchrotron was operated with an electron energy of 1.3 GeV and a current between 100-230 mA. The DCM had Ge (220) crystals and was calibrated with a Cu foil for the *in-situ* XANES study. The XANES scanning parameters are given in Table 6.1. An *in-situ* Lytle cell was used with a Variac temperature controller to ramp the temperature from 25 °C to 362 °C at a rate of 2 °C/min. A mixture of 20 mg catalyst diluted in 20 mg amorphous silica was loaded into the cell and enclosed within two pieces of kapton tape. XANES spectra were collected in transmission mode at the Cu K-edge (8979 eV) at
increments of 25 °C under 10% H₂/Ar flow and a reference foil was placed after the sample and scanned in transmission mode simultaneously to maintain energy calibration during the XANES scans. All the experiments were limited to 362 °C due to the design limitations of the Lytle cell.

Data reduction for the Cu K-edge XANES spectra were performed using the Athena software.\textsuperscript{34} All the spectra were calibrated to account for shifts in the edge position of the reference foil, which was measured independently for each scan. CuO, Cu₂O and Cu foil were used as standards. Their spectra were collected in transmission mode at the same beamline and processed in a similar way. Linear combination fitting (LCF) was performed using Athena’s analysis package to determine the fractional composition of each of the standard phases (CuO, Cu₂O and Cu\textsuperscript{0}) represented during each measurement.

Table 6.1: Cu K-edge XANES scanning parameters.

<table>
<thead>
<tr>
<th>Scan interval relative to Cu K-edge (8979 eV)</th>
<th>-50, -15, 50, 100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step size (eV)</td>
<td>1, 0.5, 1</td>
</tr>
<tr>
<td>Integration time (s)</td>
<td>1</td>
</tr>
</tbody>
</table>

6.3. Results and Discussion

6.3.1. BET

The BET surface areas of the three calcined catalysts are listed in Table 6.2. The values are comparable to those reported in literature for various Cu-La\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} pyrochlore-based catalysts calcined between 700-710 °C.\textsuperscript{15-17} It can be seen from Table 6.2 that the Co promoted catalyst (CCoZLL) has a slightly higher surface area than the unpromoted CZLL catalyst, whereas that of the Mn promoted catalyst (CMnZLL) is twice as that of CZLL. The higher surface area of
CMnZLL indicates that it has smaller particles (and/or pores) compared to the other two catalysts.

Table 6.2: BET surface areas, and ICP & XPS compositions of the calcined catalysts (T: Target; I: ICP; X: XPS).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CZLL</th>
<th>CMnZLL</th>
<th>CCoZLL</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET S.A. (m²/g)</td>
<td>15</td>
<td>31</td>
<td>20</td>
</tr>
<tr>
<td>Wt % Cu</td>
<td>T</td>
<td>20</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>I</td>
<td>25.4</td>
<td>14.2</td>
</tr>
<tr>
<td></td>
<td>X</td>
<td>4.7</td>
<td>3.2</td>
</tr>
<tr>
<td>Wt % Zn</td>
<td>T</td>
<td>16</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>I</td>
<td>19.9</td>
<td>11.3</td>
</tr>
<tr>
<td></td>
<td>X</td>
<td>12.8</td>
<td>8.4</td>
</tr>
<tr>
<td>Wt % Mn</td>
<td>T</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>I</td>
<td>-</td>
<td>6.2</td>
</tr>
<tr>
<td></td>
<td>X</td>
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<tr>
<td>Wt % Co</td>
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<td>-</td>
</tr>
<tr>
<td></td>
<td>X</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

6.3.2. ICP-AES and XPS

Table 6.2 gives the bulk (ICP-AES) as well as the surface (XPS) atomic compositions of the calcined catalysts. The ICP compositions of the transition metals in the final calcined catalysts are very similar to the target compositions used for the synthesis, indicating the accuracy of the synthesis method. However, a very small amount of Li was evident in all the calcined catalysts which indicates a relatively much lower precipitation rate in the case of lithium. Li content, measured by ICP, was less than 1 wt% in all the catalysts (Target composition – 4.5%).
XPS gives the compositions of each element present on the surface. From Table 6.2, it is clear that the XPS compositions of all the elements are different from their ICP values except for manganese. The difference is especially noticeable in the case of copper. A similar surface and bulk composition of manganese serves as evidence for uniform substitution of Mn into the pyrochlore lattice, whereas the different XPS and ICP values for other elements (Cu, Zn and Co) suggests that these elements are partially substituted into the lattice and some of them are present on the surface of the pyrochlore, which acts as a support. This argument will be further supported by XRD results in the next section where CuO, ZnO and Co$_3$O$_4$ were detected as separate phases, but not Mn$^{2+}$/Mn$^{3+}$ species.

### 6.3.3. In-situ XRD

Figures 6.1 and 6.2 display the results of the in-situ X-ray diffraction experiments that were carried out under H$_2$-TPR conditions for each of the three catalysts. All the catalysts showed the typical diffraction peaks distinctive to the pyrochlore material and can be attributed to La$_2$Zr$_2$O$_7$ with a cubic unit cell structure$^{18}$. The XRD signal from the samples at room temperature showed the presence of a crystalline La$_2$Zr$_2$O$_7$ pyrochlore phase along with peaks that correspond to CuO and ZnO. The formation of the pyrochlore phase in all the catalysts is consistent with the fact that addition of structural and alkali promoters do not alter the formation of pyrochlore structure$^{17,23}$. There is no evidence for mixed metal oxides, alloys, or perovskites in the diffractograms. The appearance of the reflections due to the oxides of copper and zinc in the room temperature XRD patterns of all calcined catalysts indicates the formation of well-dispersed CuO and ZnO on the framework of the pyrochlore lattice (phase rejection process)$^{15-16}$, rather than being completely substituted into it, as reported in the case of similar Cu-La$_2$Zr$_2$O$_7$ catalysts$^{15-16}$. This result is also consistent with the XPS surface atomic compositions as discussed earlier.
The *in-situ* XRD experiments under H\textsubscript{2}-TPR conditions show that the catalysts undergo reduction only beyond 225 °C since no significant changes were observed in the diffraction patterns up to 225 °C. The pyrochlore structure was found to be stable with increasing temperature and did not transform or decompose to any other forms such as perovskites or alloys. As seen from the ICP results, Li\textsubscript{2}O concentration was very small in all the catalysts and is not detected in the XRD patterns.

![Figure 6.1](image)

Figure 6.1: (a) *In-situ* XRD diffractograms under H\textsubscript{2}-TPR conditions and (b) XRD patterns during isothermal reduction at 400 °C for 2 h in H\textsubscript{2}/Ar flow for the Cu-ZnO-La\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}-Li\textsubscript{2}O (CZLL) catalyst. Major phases above 250 °C: La\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} (*), ZnO (•), Cu\textsuperscript{0} (Δ).

In the case of CZLL (Figure 6.1(a)), the major phases were La\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}, CuO, and ZnO at room temperature. The diffractograms during TPR showed the appearance of a metallic copper phase.
at around 275 °C along with a Cu$_2$O phase. Reduction to Cu$^0$ was complete by 300 °C. Isothermal reduction at 400 °C for 2 hrs (Figure 6.1(b)) did not change the XRD patterns, indicating that La$_2$Zr$_2$O$_7$ and ZnO phases were stable with temperature under these reducing conditions. Similar XRD experiments on the Mn or Co promoted catalysts showed that addition of Mn or Co promotors did not limit the formation of pyrochlore structure, but increased the reducibility of copper as discussed in the section below.

In the case of CMnZLL (Figure 6.2(a)), the diffraction patterns show a less crystalline structure compared to other catalysts. This indicates that the particle (or crystallite) size in the case of CMnZLL is smaller, leading to a higher BET surface area (Table 6.2). The crystallinity of the catalyst increased with reduction temperature as seen by the XRD profiles. Cheng et al. also observed an increase in the crystallization temperature of the pyrochlore phase with the introduction of Mn$^{23}$.

At room temperature, the major phases were La$_2$Zr$_2$O$_7$, CuO, and ZnO, with traces of Mn$_2$O$_3$. Copper oxide reduction occurred at around 250 °C, where metallic copper phases began to appear. Above 250 °C, only minor traces of Mn$_3$O$_4$ and MnO were detected which suggests that a major portion of the manganese is substituted uniformly into the pyrochlore lattice, unlike the copper and zinc, which are present as separate phases outside the pyrochlore lattice. The incorporation of manganese into the pyrochlore lattice is consistent with the results of Cheng et al., who attributed the absence of transition metals as separate phases in the XRD patterns to their uniform substitution into the pyrochlore lattice$^{23}$. This is also consistent with our XPS and ICP results which showed that the surface and bulk compositions of manganese were the same, indicating that manganese was well distributed into the pyrochlore structure.
Figure 6.2: \textit{In-situ} XRD diffractograms under H$_2$-TPR conditions for the (a) Cu-Mn-ZnO-La$_2$Zr$_2$O$_7$-Li$_2$O (CMnZLL) and (b) Cu-Co-ZnO-La$_2$Zr$_2$O$_7$-Li$_2$O (CCoZLL) catalysts.

The XRD patterns of the Co-promoted catalyst (CCoZLL-Figure 6.2(b)) showed similar results. Besides the major phases (La$_2$Zr$_2$O$_7$, ZnO and CuO), a Co$_3$O$_4$ phase was also detected at room temperature and the diffraction patterns were similar up to 225 °C. CuO reduction began at 250 °C (similar to other catalysts) and was complete by 275 °C. A small peak at 41.9° corresponding to CoO also appeared at 250 °C along with Co$_3$O$_4$, suggesting the formation of CoO through the reduction of Co$_3$O$_4$. CoO and Co$^0$ followed opposite trends with temperature and CoO was completely reduced to Co metal at around 375 °C. No changes were observed with further increase in temperature. In this catalyst, cobalt is reduced at a lower temperature than bulk cobalt oxide \(^29\) which indicates that the presence of copper atoms on the pyrochlore support strongly promotes the reducibility of cobalt oxides.
6.3.4. H₂-TPR

Figure 6.3 shows the TPR profiles of the three pyrochlore catalysts. The TPR profile of non-zinc Cu-La₂Zr₂O₇-Li₂O (CLL) catalyst is also shown for comparison (this catalyst was synthesized in a similar manner as others, but without Zn, Mn, or Co). All the catalysts, except CCoZLL, show a single major peak between 150 and 325 °C, but CCoZLL is characterized by two prominent peaks in the range 150-460 °C. The assumption that CuO, Co₃O₄ and Mn₂O₃ are the only reducible species is valid because La₂Zr₂O₇ does not undergo reduction under our TPR conditions as reported by Cheng et al. 23, who attribute a TPR peak centered at 851 °C to the reduction of Zr⁴⁺ to Zr³⁺ that is present in La₂Zr₂O₇. Also, ZnO is not expected to be reduced at such low temperatures 35. The peak maxima, the amount of hydrogen consumed by each catalyst during the TPR experiments, and the percent reducibility of the reducible species are listed in Table 6.3.

Figure 6.3: TPR profiles of (a) CLL (b) CZLL (c) CMnZLL and (d) CCoZLL catalysts.
Table 6.3: TPR peak maxima, H₂ consumption and percent reducibility of the reducible species.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Peak Maxima (°C)</th>
<th>Total H₂ consumed (μmol)</th>
<th>Extent of reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CLL</td>
<td>239</td>
<td>220.6</td>
<td>70 (CuO→Cu⁰)</td>
</tr>
<tr>
<td>CZLL</td>
<td>253</td>
<td>109.5</td>
<td>78 (CuO→Cu⁰)</td>
</tr>
<tr>
<td>CMnZLL</td>
<td>227</td>
<td>128.0</td>
<td>96 (CuO→Cu⁰ &amp; Mn₂O₃→MnO)</td>
</tr>
<tr>
<td>CCoZLL</td>
<td>221, 375</td>
<td>143.7</td>
<td>100 (CuO→Cu⁰ &amp; Co₃O₄→CoO)</td>
</tr>
</tbody>
</table>

¹ H₂ consumption for 50 mg of catalyst (calibrated using silver oxide) – experimental error is within ±5%.
² Assuming only CuO, Mn₂O₃ and Co₃O₄ are the reducible species.
³ Complete reduction to Cu⁰ and Mn₂O₃, but partial reduction to MnO.
⁴ Complete reduction to Cu⁰ and CoO and partial reduction to Co⁰.

For the non-zinc CLL pyrochlore (Figure 6.3(a)), the major peak is centered at 239 °C and the reduction is complete by 310 °C. The amount of H₂ consumed corresponds to only 70% reduction of copper (Table 6.3). Addition of zinc (CZLL - Figure 6.3(b)) delays the onset of reduction by 34 °C and shifts the peak maxima by 14 °C. This catalyst has a major peak centered at 253 °C with a small shoulder at 287 °C. Assuming the area under this peak corresponds solely to the Cu²⁺ → Cu⁰ transition, the amount of H₂ consumed corresponds to only 78% reduction. However, the tail on the TPR peak is an indication that more than one species contributes to the overall reduction at higher temperatures.

Mn promotion (CMnZLL - Figure 6.3(c)) increases the reducibility of copper. Reduction starts at the same temperature as that of the unpromoted CLL but the major peak is centered at 227 °C and the reduction is complete by 274 °C. Unlike CLL and CZLL, the total H₂ consumed by CMnZLL through the major peak corresponds to complete reduction of copper (Cu²⁺ to Cu⁰) as
well as partial reduction of Mn$^{3+}$/Mn$^{2+}$ species. Based on the assumption that Mn$_2$O$_3$ is the major phase present in the calcined catalyst at room temperature, calculations show that Mn$_2$O$_3$ can be completely reduced to Mn$_3$O$_4$ and partially (~60%) to MnO. This is also consistent with the XRD results after reduction at 400 °C, which revealed the presence of Mn$_3$O$_4$ and traces of MnO. In addition, a single TPR peak with no shoulder may indicate a strong interaction between copper and manganese. The increase in the reducibility of copper promoted by manganese could also be due to the uniform distribution of manganese throughout the pyrochlore structure, as indicated by the XPS and XRD results.

Cobalt promotion (CCoZLL – Figure 6.3(d)) does not alter the onset of reduction. However, some noticeable changes can be observed. The two reducible species (CuO and Co$_3$O$_4$) reduce in the temperature range between 150 and 460 °C, with two peaks centered at 221 °C and 375 °C respectively. The first peak with a shoulder can be assigned to the combined reduction of Cu$^{2+}$ to Cu$^0$ and Co$_3$O$_4$ to CoO. The second peak is assigned to the reduction of a portion of the CoO to Co$^0$. The total amount of H$_2$ consumed corresponds to complete reduction of CuO $\rightarrow$ Cu$^0$ and Co$_3$O$_4$ $\rightarrow$ CoO. However the measured H$_2$ consumption is slightly greater than that required theoretically for these reduction steps, indicating that some amount of CoO further reduces to Co metal at temperatures between 300 and 460 °C. This result is also consistent with the XRD results which showed that both CoO and metallic Co were present after reduction. Hence it is clear that cobalt promotion increases the reducibility of copper compared to the non-Co promoted CZLL catalyst. The reduction temperature of bulk cobalt oxide has been previously reported to be much higher than what is observed here $^{29,37}$, indicating that copper promotes the reduction of cobalt. The process may involve the reduction of copper oxide, yielding metallic...
copper, which then accelerates the reduction of cobalt ions. Tien Thao et al. proposed similar interaction between copper and cobalt \textsuperscript{29,37}.

Thus the TPR results of the transition-metal substituted pyrochlores (CMnZLL and CCoZLL) indicate significant differences in reducibilities, suggesting a strong interaction between copper, zinc, and manganese/cobalt. As copper and manganese/cobalt sites are atomically distributed on the pyrochlore lattice, the interaction between such ions could affect their reducibility. The TPR profile of the unpromoted CZLL catalyst showed an increase in the reduction temperature of copper, compared to Mn and Co-promoted catalysts as well as other reported non-pyrochlore based (supported or perovskite type) catalysts \textsuperscript{29,38-39}, and a lower percentage reducibility. This may be due to the strong interaction of surface oxygen or hydroxyl groups retained on the pyrochlore support with the Cu ions, thus slowing down the reduction rate and preventing complete reduction.

However, for CMnZLL and CCoZLL, the reduction temperature was lower and the extent of reduction was higher than CZLL even though the surface oxygen or hydroxyl groups of the pyrochlore support are still present, similar to that of CZLL. This can be attributed to the promotion effects of manganese and cobalt on the reducibility of copper, indicating a synergistic interaction on the surface. Once metallic copper is formed, it then acts as a reduction promoter to reduce the manganese/cobalt oxides.

6.3.5. \textit{In-situ} XANES

The normalized Cu K-edge XANES spectra and the relative phase composition of copper species based on linear combination fitting (LCF) as a function of temperature during \textit{in-situ} H\textsubscript{2}-TPR, are shown for the three catalysts: CZLL, CMnZLL and CCoZLL in Figures 6.4 - 6.6. The
XANES spectra also show the standards for comparison; the rationale for fitting standards of CuO, Cu$_2$O, and Cu$^0$ phases to the XANES spectra are based on the XRD results showing the presence of these three phases. In the case of CZLL (Figure 6.4), the initial spectrum at 25 °C is in agreement with the CuO standard and does not change until 250 °C, after which the white line starts to broaden and reduce in intensity with increasing temperature. Although the pre-edge feature is very similar to that of CuO, the broadening might indicate some contribution from Cu$_2$O. The distribution plot derived from LCF suggests an onset of reduction at around 250 °C with significant increases in Cu$_2$O and Cu$^0$ concentrations. The proportion of Cu$^0$ is greater than that of Cu$_2$O at all temperatures.

There are no major changes in the XANES spectra above 350 °C and the LCF distribution plot indicates 77% Cu$^0$ at 362 °C. Within experimental error, this is consistent with the H$_2$ consumption calculation from the TPR profile of CZLL which indicated 78% reduction to metallic copper. The temperature was maintained at 362 °C for an additional hour to see if the reducibility increased. As seen in the LCF plot, after 16 min at 362 °C, the sample had 87% Cu$^0$ and 13% Cu$_2$O. Isothermal reduction at 362 °C for additional time did not further change the compositions significantly. However, the in-situ XRD results for this catalyst indicated a complete reduction of CuO to Cu$^0$ by 300 °C. However, it is possible that some irreducible CuO or partially reduced Cu$_2$O are present in amorphous form or as small particles at 300 °C, which were not detected by XRD, whereas XANES technique can detect poorly crystalline or amorphous materials. Also, the temperature at which metallic copper starts to appear is slightly lower in the XANES spectra compared to XRD patterns, indicating that the initially formed copper metal particles are too small to be detected by XRD.
Figure 6.4: Normalized *in-situ* XANES transmission spectra at the Cu K-edge and linear combination fitting results as a function of temperature (X-axis labels with underscores denote the hold time (minutes) at that temperature) for the CZLL pyrochlore during H$_2$-TPR.

Figure 6.5 shows the *in-situ* XANES spectra and phase distribution plot for the CMnZLL pyrochlore. The spectrum of the as-prepared catalyst (25 ºC) resembles that of the CuO standard and is consistent with a significant proportion of CuO species in the LCF fit. The broadening of the white line and intensity decrease occur at around 200 ºC and the shape of the spectrum resembles that of Cu$^0$ at temperatures above 250 ºC. The LCF fitting also shows the onset of reduction at 200 ºC, accompanied by a steep rise in Cu$^0$ composition. The reduction seems to be complete by 325 ºC with 87% Cu$^0$. Maintaining the temperature at 362 ºC for additional time did not alter the shape or composition of the spectra greatly, suggesting no further reduction of Cu$_2$O. Figure 6.4 showed that the onset of CZLL reduction occurred at 250 ºC which is greater than that of CMnZLL. Also, the LCF fitting shows that CMnZLL has 87% Cu$^0$ at 325 ºC whereas the CZLL catalyst had only 60% Cu$^0$ at the same temperature. This suggests that Mn promotion increases the reducibility of copper, consistent with TPR and XRD findings.
Figure 6.5: Normalized \textit{in-situ} XANES transmission spectra at the Cu K-edge and linear combination fitting results as a function of temperature for the CMnZLL pyrochlore during H$_2$-TPR.

Figure 6.6: Normalized \textit{in-situ} XANES transmission spectra at the Cu K-edge and linear combination fitting results as a function of temperature for the CCoZLL pyrochlore during H$_2$-TPR.
The CuO species in the CCoZLL pyrochlore (Figure 6.6) reduces rapidly beyond 225 °C, similar to CMnZLL. The XANES spectra do not change after 325 °C and the LCF fit suggests a complete reduction at 362 °C with 97% Cu⁰. Hence the XANES results indicate that both manganese and cobalt promoters enhance the reduction of copper, but the effect is greater in the case of cobalt promotion. Thus, the interaction between Mn or Co and Cu greatly affects the reduction behavior of the catalyst.

6.4. Conclusions

In-situ XRD and XANES studies under H₂-TPR conditions revealed that transition metal promoters (Mn and Co) increased the reducibility of copper in Cu-ZnO-La₂Zr₂O₇-Li₂O catalysts. Once formed, metallic copper accelerated the reduction of the Mn and Co oxides. TPR results indicated that the Mn or Co promoter also increased the overall extent of reduction of the catalysts, suggesting a synergistic interaction between Cu and Mn or Co. Room temperature XRD indicated the presence of crystalline phases of CuO, ZnO and Co₃O₄ on the framework of the pyrochlore lattice (phase rejection process), rather than being completely substituted into the pyrochlore structure. But only minor traces of Mn₂O₃ were detected in XRD suggesting that a major portion of the manganese was substituted into the pyrochlore lattice, consistent with the XPS results. In-situ XRD during H₂-TPR confirmed the formation of a cubic pyrochlore structure irrespective of the promoter metal used and the pyrochlore phase was found to be stable under high temperature activation conditions. Additionally, in-situ XANES experiments on the Cu K-edge of the catalysts allowed for a comparison of the reduction behavior of copper with the TPR and in-situ XRD results. This study emphasizes that the presence of copper sites in close proximity to the Mn or Co promoter atoms affects the dispersion and the reducibility of the catalyst.
6.5. References


Chapter 7: A DRIFTS Study of Mn or Co Promoted Cu-ZnO-La$_2$Zr$_2$O$_7$ Based Catalysts for CO Hydrogenation

7.1. Introduction

CO hydrogenation to higher alcohols has been extensively studied over a variety of catalysts$^{1-3}$, with Rh-based catalysts being the most active and selective. Recently, there has been an interest in less costly catalysts. One promising class of materials is based on rare-earth zirconate pyrochlores (such as La$_2$Zr$_2$O$_7$) because of their excellent thermal and chemical stability under reaction conditions$^{4-6}$. Transition metal substituted pyrochlores, in particular, are attracting great attention as catalysts for CO hydrogenation$^{4,6}$. La$_2$Zr$_2$O$_7$ pyrochlores have been used as supports for copper catalysts and are reported to be highly selective for methanol synthesis while being resistant to carbonation$^{4-6}$. Higher alcohol synthesis requires the catalyst surface to have both adsorbed molecular CO, and surface carbon species produced by dissociative adsorption of CO$^7$. Taking this into consideration, we believe that the selectivity of Cu-ZnO-La$_2$Zr$_2$O$_7$ catalysts to C$_2$$_+$$alcohols and oxygenates can be increased by adding suitable transition metal promoters (eg., Co, Mn), which enhance CO dissociation and hydrogenation of the surface carbon species into hydrocarbons$^{7-8}$ and create new active sites for the CO insertion reaction$^9$, and alkali promoters (eg., Li), which increase the yield and selectivity of higher alcohols by suppressing hydrocarbon formation$^{1-2}$. Thus, a combination of these promoters and Cu might be expected to adsorb molecular CO on the Cu, which can then react preferentially with the carbon chains generated on the promoters, thereby leading to higher alcohols and oxygenates$^7$.

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) is an useful technique to probe the adsorption sites on the surface of the catalysts and to elucidate the nature of the
active sites and the surface intermediates involved in the reaction. CO and CO+H\textsubscript{2} are common probe molecules used to study the catalyst surface for CO hydrogenation. DRIFTS, equipped with an online mass spectrometer for continuous monitoring of the product stream, permits monitoring the surface species during steady state or transient reaction conditions. In the present work, an \textit{in-situ} FTIR (DRIFTS) reactor coupled with a mass spectrometer (MS) was used to study the catalyst surface under reaction conditions and to relate the structure of the catalyst to its function in CO hydrogenation. Here we report the DRIFTS results on Cu-ZnO-La\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}-Li\textsubscript{2}O catalysts as well as the effects of transition metal promoters (Mn or Co) on CO adsorption and hydrogenation.

7.2. Experimental

7.2.1. Catalyst Synthesis

Cu-ZnO-La\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}-Li\textsubscript{2}O catalysts were synthesized by coprecipitation of a mixed solution of copper nitrate, zinc nitrate, lithium nitrate, lanthanum nitrate and zirconium acetylacetonate in ethanol using oxalic acid, as reported elsewhere. After dropwise addition of oxalic acid, the mixture was stirred for 2-3 h. The precipitate was then washed with ethanol, dried overnight at 110 °C and finally calcined in air at 550 °C for 3.5 h followed by 710 °C for 30 min. Co or Mn was added to the catalyst in a similar way. All the nitrate salts were coprecipitated using oxalic acid, washed, dried and calcined as above. The Cu-ZnO-La\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}-Li\textsubscript{2}O catalyst is hereafter denoted as CZLL, the Mn-promoted catalyst as CMnZLL and the Co-promoted catalyst as CCoZLL.
7.2.2. Characterization

The catalysts were characterized by inductively coupled plasma atomic emission spectrometry (ICP), X-ray photoelectron spectroscopy (XPS), temperature programmed reduction (TPR), *in-situ* X-ray diffraction (XRD), and *in-situ* X-ray absorption near-edge structure spectroscopy (XANES) techniques. Details of these analyses are given in Chapter-6.

7.2.3. *In-situ* FTIR (DRIFTS)

A Thermo Nicolet 6700 FTIR spectrometer equipped with a MCT detector and a Harrick Praying Mantis cell was employed for the *in-situ* FTIR studies. The cell allowed collection of spectra in a temperature controlled reaction chamber, which is thermally isolated from the outer wall by a water-cooled jacket. About 20-30 mg of powdered sample was placed into the sample cup and flattened to obtain high IR reflectivity. Prior to exposure to the reaction gas, the sample was heated under flowing He (30 scc/min) to 400 °C, reduced *in-situ* in 10% H$_2$/He (50 scc/min) at 400 °C for 2 h, followed by He flushing and then cooled down to room temperature in He. Background spectra were collected at different temperatures. Then the reactant gas (or gas mixture) flow was started to the cell and the infrared spectra were taken at 4 cm$^{-1}$ resolution with 32 scans. CO adsorption and CO hydrogenation experiments were carried out for all the catalysts. A Hiden HPR-20 QIC Benchtop Gas Analysis System equipped with a quadrupole mass spectrometer was connected to the DRIFTS reactor to be able to monitor the reaction products online as they were eluting the reactor. All the DRIFTS experiments in this study were carried out at 1 bar.
7.3. Results and Discussion

7.3.1. DRIFTS Studies

7.3.1.1. CO Adsorption at 25 °C

In this experiment, CO/He was adsorbed on the reduced catalytic surface for 10 min followed by He flushing to remove the physisorbed CO. Figure 7.1 shows the DRIFTS results of CO adsorption at room temperature (25 °C) followed by He flushing for the Cu-Mn-ZnO-La$_2$Zr$_2$O$_7$-Li$_2$O (CMnZLL) catalyst. The spectra collected after 1 min of CO flow has peaks in the region 2000-2200 cm$^{-1}$ that can be attributed to various forms of adsorbed CO. The bands attributed to gaseous CO could readily be removed by flushing with He for less than 10 min. A band at 2110 cm$^{-1}$ with a shoulder at 2144 cm$^{-1}$ is formed readily upon first contact of the reduced catalyst with CO at room temperature. The shoulder at 2144 cm$^{-1}$ can be attributed to CO adsorbed over highly dispersed copper sites or CO hydrogen-bonded to the surface hydroxyl groups$^{14}$ of the pyrochlore support.

The band at 2110 cm$^{-1}$ may be assigned to CO chemisorbed linearly on either Cu$^+$ or highly dispersed Cu$^0$ sites$^{14}$, but the predominant type of site can be determined based on the stability of the band to He flushing. Cu$^+$-CO species are characterized by a high stability compared to CO on metallic Cu sites$^{14-16}$. In our case, for the CMnZLL catalyst (Figure 7.1), this band was found to be highly resistant to He purging over a period of 2 h. Thus, taking into account the high stability of the carbonyl species, this band can be unambiguously ascribed to Cu$^+$-CO species in accordance with previous work$^{14-16}$. 

120
Figure 7.1: CO adsorption at 25 °C, followed by He flushing at 25 °C for the CMnZLL catalyst.

The doublet in the region 2320-2380 cm\(^{-1}\) corresponds to gaseous CO\(_2\) which varies randomly throughout the experiment. Although the sample compartment is sealed from the atmosphere, the instrument is extremely sensitive to even very small changes in CO\(_2\) in the lab atmosphere. Hence the CO\(_2\) bands were not taken into account and no conclusions were drawn from them.

The catalyst was reduced at 400 °C for 2 h before the DRIFTS experiment which would be expected to reduce all the copper oxide to metallic copper\(^\text{17-18}\). But the DRIFTS results (in Figure 7.1) provide the evidence for the presence of partially oxidized Cu\(^+\) sites, which can be due to the interaction of the Cu atoms with the surface hydroxyl groups of the pyrochlore or with the CO, thereby keeping the surface Cu atoms in a partially oxidized state\(^\text{19}\). This is a likely result from the spillover of oxygen or OH groups from the support onto the Cu atoms. Millar et al. attributed the presence of a partially reduced catalyst surface during CO+CO\(_2\) hydrogenation to the role of CO in the feed\(^\text{19}\).
The IR bands below 1700 cm\(^{-1}\) are due to various surface bound carboxylates and possibly other reaction products. The bands at 1544 and 1348 cm\(^{-1}\) are similar to those reported for surface bound carbonate species or carboxylate species of the formate/acetate type \(^{20}\). These bands increase in intensity with the adsorption time and are resistant to He flushing. Although no hydrogen was admitted in this experiment, formate species can be produced by an interaction of CO with surface hydroxyl groups on the pyrochlore support or with the residual hydrogen that is present after the reduction step \(^{20}\). The high stability of these bands upon He flushing indicates that these species are chemisorbed to the surface and not physically bound. The 1215 cm\(^{-1}\) band can be assigned to some hydrogen-carbonate species that are also formed by interaction of CO with the residual hydrogen present after reduction \(^{20}\). The bands at 1060 and 1137 cm\(^{-1}\) can be assigned to either the CH\(_3\) rocking vibrations or the bidentate and monodentate C–O vibration modes of the carboxylate species \(^{21}\). The 856 cm\(^{-1}\) band cannot be conclusively assigned, but it is most likely also due to a stretching mode of a surface carboxylate species \(^{21}\).

**7.3.1.2. Hydrogenation of Pre-adsorbed CO**

The catalyst with pre-adsorbed CO after He flushing (as was seen in Figure 7.1) was hydrogenated at 25 °C, then the temperature was increased to 270 °C, then 400 °C in H\(_2\) flow and held at these two temperatures until the stabilization of the masses in the MS occurred; which took about 30 min. The FTIR spectra recorded during hydrogenation of pre-adsorbed CO for the CMnZLL catalyst are presented in Figure 7.2. [The CO adsorption spectra are not included in this figure since they were shown in Figure 7.1]. The cell was flushed with helium until the 55 min spectra were recorded, after which H\(_2\) flow was started at 25 °C. Figure 7.2 shows that hydrogen flow at 25° C did not change the positions of any of the IR bands and resulted in a significant decrease in the intensity of the CO stretching bands (2100-2150 cm\(^{-1}\)).
H$_2$/He flushing resulted in a faster desorption of the adsorbed CO species as evidenced by a significant decrease in their intensity compared to He alone. This indicates that part of the adsorbed linear CO reacts with hydrogen to form products. As the temperature was increased to 400 °C in hydrogen flow, the linearly chemisorbed CO bands disappeared immediately and the carbonate/formate species (1544 and 1348 cm$^{-1}$) observed during CO adsorption shifted to new positions (1492 and 1370 cm$^{-1}$), which can be attributed to the formation of formate/methoxy species. The 1060 cm$^{-1}$ band observed during CO adsorption has shifted to 1087 cm$^{-1}$ during hydrogenation at 400 °C (Figure 7.2), which also corresponds to CH$_3$ rocking vibrations of the carboxylate species.

![Figure 7.2: Hydrogenation of the pre-adsorbed CO at 25 °C and 400 °C for the CMnZLL catalyst.](image)

Formate species are a result of the hydrogen reduction of the carbonates, while methoxy species are a result of the reduction of the formates (Figure 7.3), both of which were formed during
CO adsorption. Both the methoxy and formate species are considered to be intermediates for alcohol synthesis\textsuperscript{20}. However, the IR bands in the high temperature spectrum are less intense than those at 25 °C, indicating that the surface species participate in the hydrogenation reaction at high temperatures. The intensities of the bands in the lower frequency region (<1600 cm\textsuperscript{-1}) corresponding to hydrocarbon fragment species are much weaker upon hydrogenation at high temperatures than those formed at 25 °C. This indicates the reaction of the surface held hydrocarbon/formate species with H\textsubscript{2}, and their subsequent desorption from the surface as reaction products.

![Reaction schemes for the conversion of carbonates to formates, and formates to methoxy species.](image)

Figure 7.3 Reaction schemes for the conversion of carbonates to formates, and formates to methoxy species.

Figure 7.4 ((a) and (b)) compares the DRIFTS results on CZLL and CCoZLL catalysts for a similar experiment - CO adsorption at 25 °C followed by He flushing, and hydrogenation (at 25 °C and 270 °C). The spectra are very similar for these two catalysts, indicating that Co-promotion does not affect the adsorption of CO significantly. Upon CO adsorption, the bands

\[ \text{Carbonates} + 3\text{H}_2 \rightarrow \text{Formates} \]

\[ \text{Formates} + 2\text{H}_2 \rightarrow \text{Methoxy} + \text{H}_2\text{O} \]
Figure 7.4: CO adsorption at 25 °C, followed by hydrogenation at 25 °C and 270 °C for the catalysts (a) CZLL and (b) CCoZLL.
attributable to linearly adsorbed CO over copper sites (2107 cm\(^{-1}\)) and CO over either highly dispersed copper sites or CO hydrogen bonded to the surface hydroxyl groups of the pyrochlore (2144 cm\(^{-1}\)) are present in both the catalysts, as was the case for CMnZLL (Figure 7.1). However, the intensities are much less than those on CMnZLL. Also, these bands are only partially stable to He flushing, suggesting the presence of both Cu\(^+\) and Cu\(^0\) sites \(^{14-16}\). On the Co-promoted catalyst (CCoZLL), a very weak band at 2167 cm\(^{-1}\) is detected upon CO adsorption which desorbs faster with He flushing. This weak band can be attributed to CO linearly adsorbed on Co\(^{2+}\) or Co\(^{3+}\) ions as reported in literature \(^{22}\).

Upon hydrogenation, the CO bands decrease in intensity at room temperature and completely disappear at higher temperatures (Figure 7.4(a) and (b)), a behavior that is similar to the CMnZLL catalyst. It is interesting to note that the IR bands for linear CO species were not observed for any of the three catalysts at high temperatures (in H\(_2\) flow), which may be due to CO dissociation and reaction with H\(_2\) or to the CO being present in an IR inactive form, as reported by Venter et al. \(^{23}\). It is also possible that at high temperatures, CO adsorbs over Cu\(^0\) sites which disappear immediately upon He or H\(_2\)/He flushing.

The linearly adsorbed CO band, observed at 2107 cm\(^{-1}\) for the CZLL and CCoZLL catalysts (Figure 7.4), was found at 2110 cm\(^{-1}\) in the case of CMnZLL catalyst (Figure 7.1). The shift towards higher frequency (blue-shift) with Mn promoter on Cu catalysts was also observed by Xu et al. \(^{24-25}\), who attributed the blue-shift to lowering of the Lewis basicity of the surface Cu metal atoms by the presence of Mn\(^{2+}\), consequently increasing the strength of the C≡O bond, leading to higher vibrational frequencies. Higher frequencies represent the weakening of Cu–CO bond and strengthening of the C–O bond which may be expected to enhance the associative adsorption of CO during CO hydrogenation. The high intensity indicates that Mn provides more
sites for CO adsorption and a stronger C-O bond suggests that CO dissociation is less on the Mn-containing catalyst, making most of the adsorbed CO desorb as associated CO species. Higher wavenumbers can also be attributed to higher dispersion of copper\textsuperscript{14, 25}, as was seen in our previous TPR and \textit{in-situ} XRD results (See Chapter-6). In this earlier study, the TPR profile of this Mn-promoted catalyst revealed a single peak at 227 °C indicating a strong interaction between copper and manganese suggesting a higher dispersion. Also, XRD results indicated that this catalyst was less crystalline which can be attributed to smaller particle size and therefore higher dispersion.

The bands in the lower frequency region (< 1700 cm\textsuperscript{-1}) upon CO adsorption in Figure 7.4(a) and (b) can again be attributed to the carbonate species or formate species formed by the interaction of CO with either surface hydroxyl groups or residual hydrogen left after reduction. Similar to CMnZLL, these carbonate/formate bands are transformed to formate/ methoxy species upon hydrogenation at 270 °C and 400 °C.

Hence, the important difference between CO adsorption over the three catalysts is that the CO uptake is very high and the linearly adsorbed CO band is highly stable to He flushing on the CMnZLL catalyst compared to CCoZLL and CZLL, indicating the presence of predominantly Cu\textsuperscript{+} active sites on CMnZLL. Hence it can be inferred that Mn promotion increases the CO adsorption sites and enhances the associative CO adsorption property of the pyrochlore catalyst for CO hydrogenation.

\textbf{7.3.1.3. Hydrogenation of Pre-adsorbed CO as Observed in Mass Spectrometer (MS)}

Several products were monitored on a mass spectrometer throughout the FTIR experiments. Figure 7.5 displays the trend of mass 15 (methane) for all the three catalysts during
hydrogenation of the pre-adsorbed CO at various temperatures. Upon hydrogenation at 270 °C, negligible methane formation can be observed in the case of CZLL and CMnZLL, whereas a large peak is evident for CCoZLL. As the temperature is increased to 400 °C, another large peak is observed for CCoZLL and the intensity of both the peaks is roughly 100 times greater than those of the other two catalysts. This suggests that the pre-adsorbed CO undergoes rapid dissociation at high temperatures to form predominantly methane on the Co-promoted catalyst. On the other hand, the Mn promoted catalyst showed the minimum methanation under these same conditions. This is consistent with the CO adsorption properties, which showed that CO is less likely to dissociate on the Mn promoted catalyst, thereby leading to less methanation.

Figure 7.5: Mass 15 formation during hydrogenation of the pre-adsorbed CO at 270 °C and 400 °C for (a) CZLL (b) CCoZLL and (c) CMnZLL catalysts.
7.4. Conclusions

The CO adsorption properties of Mn and Co promoted Cu-ZnO-La\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}-Li\textsubscript{2}O pyrochlore catalysts were investigated using Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) coupled with a mass spectrometer at 1 bar. Mn promoter significantly influenced the CO adsorption on Cu-ZnO-La\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}-Li\textsubscript{2}O pyrochlore, whereas the Co promoter affected only the product distribution. On the Mn-promoted catalyst (CMnZLL), Cu\textsuperscript{+}-carbonyl species were detected, whereas the partially stable linear carbonyl species on the unpromoted (CZLL) and Co-promoted (CCoZLL) catalysts indicated the presence of both Cu\textsuperscript{+} and Cu\textsuperscript{0} sites. The linear CO band was observed at a slightly higher frequency (blue-shift) on the Cu-Mn-ZnO-La\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}-Li\textsubscript{2}O (CMnZLL) catalyst and this shift can be attributed to the lowering of the Lewis basicity (or electron density) of the surface Cu metal atoms by the presence of Mn\textsuperscript{2+} as reported in literature, consequently increasing the strength of the C≡O bond, leading to higher vibrational frequencies. Mn-promotion enhanced the intensity and stability of the linear CO species on copper sites, and weakened the Cu-CO bond, which may be expected to enhance the associative adsorption of CO during CO hydrogenation.

Carbonate/formate species were formed during CO adsorption due to the interaction of CO with either surface hydroxyl groups or with the residual hydrogen present after the reduction step. These species were reduced to formate/methoxy species upon hydrogenation at high temperatures, which are considered to be the intermediates for alcohol/oxygenate synthesis.

MS results indicated that the C\textsubscript{2}\textsuperscript{+} alcohol/oxygenate formation on the Cu-ZnO-La\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}-Li\textsubscript{2}O catalysts decreases in the following order under the tested reaction conditions: CMnZLL > CZLL > CCoZLL. Mass 15 (methane) was identified to be the major product on the Co-promoted
catalyst and was present in the reaction product stream at concentrations around 100 times greater than that on the other two catalysts, whereas the Mn-promoted catalyst showed negligible methanation under the same conditions, consistent with the CO adsorption properties.

7.5. References


Chapter 8: Conclusions and Recommendations

8.1. Conclusions

The main objective of this research work was to synthesize, characterize and test different copper-based catalysts for CO hydrogenation to higher alcohols. This work focused on two types of copper-based catalysts - bimetallic nanoparticles and pyrochlores. Based on the results obtained in this study, the following conclusions can be made.

(i) Bimetallic Nanoparticles:

- A wet-chemical approach for the synthesis of uniformly dispersed and highly reproducible copper-based core-shell nanoparticles has been demonstrated.
- DRIFTS (in-situ FTIR) experiments indicate that the Cu@Mn$_3$O$_4$ nanoparticles showed a greater CO adsorption capacity than the Cu@Co$_3$O$_4$ nanoparticles, but a weaker Cu-CO bond which is expected to lower the CO dissociation rate and adsorb CO in an associative form, while the Cu@Co$_3$O$_4$ nanoparticles showed a moderately stronger Cu-CO bond, expected to assist in achieving a proper balance between dissociative and associative forms of CO adsorption, thereby resulting in higher alcohol/oxygenate formation.
- CO hydrogenation results at 10 bar, 270 °C and H$_2$/CO=2 were consistent with the DRIFTS findings. The Cu@Co$_3$O$_4$ nanoparticles showed a higher selectivity towards alcohols and oxygenates, with the total alcohols/oxygenates being 48% of the total products.

(ii) Pyrochlores:

- Mn or Co promoted Cu-ZnO-La$_2$Zr$_2$O$_7$-Li$_2$O pyrochlore catalysts were synthesized by coprecipitation and studied for CO hydrogenation using DRIFTS.
• Addition of Mn or Co promoter shifted the reduction temperature of copper to lower values compared to the non-Mn or non-Co catalysts. The reduced copper then accelerated the reduction of Mn or Co oxides. The promoters also increased the overall extent of reduction of the catalysts as evidenced by TPR, in-situ XRD, and synchrotron-based in-situ XANES experiments under H₂-TPR conditions.

• DRIFTS coupled with mass spectrometry was used to identify the nature of the active sites and the surface intermediates involved during CO hydrogenation. Among the three pyrochlore-based catalysts, the Mn promoted catalyst showed superior CO adsorption properties and negligible methanation under the reaction conditions studied, whereas methane was the major product on the Co-promoted catalyst and was present in the reaction product stream at concentrations around 100 times greater than that on the other two catalysts.

8.2. Recommendations for Future Work

Following are some recommendations for future work based on the results presented in this work, and considering the experiments previously performed in the literature:

• Catalytic activity testing: Only limited tests of the nanoparticles for CO hydrogenation were carried out. Hence future work would be to test the nanoparticles and pyrochlores for CO hydrogenation at various reaction conditions and quantify the products using an analytical system (GC/MS); calculate the CO conversion and product selectivities; optimize the reaction conditions for the best catalyst in terms of space velocity, temperature, pressure and H₂/CO ratio.

• EXAFS studies: EXAFS would be a useful technique to obtain detailed element-specific information on the local atomic structure of the core-shell nanoparticles. While XANES
provides useful information on the average oxidation state, EXAFS gives a quantitative idea of the distance to neighboring atoms (average bond length), coordination number and type of neighboring atoms.

- *In-situ* EXAFS and XANES measurements carried out under CO hydrogenation conditions can provide information about the structural changes in the local environment of the nanoparticles. These experiments can be useful in correlating the activity and selectivity of the catalysts to their atomic structures.

- Use of a support for the nanoparticles can increase their dispersion which could probably have an effect on the activity and selectivity. The core-shell nanoparticles studied in this work have been supported on SiO$_2$, but the supported nanoparticles have not yet been tested for their catalytic activities.

- Tests with H$_2$O and CO$_2$ in addition to CO + H$_2$ in the reactant stream can provide insights into ethanol formation under realistic syngas compositions.
Appendix A: Calibration of GC/MS and Error Estimation

A.1. Calibration of the Gas Chromatograph/Mass Spectrometer (GC/MS)

An Agilent gas chromatograph 6890N / mass spectrometer MSD 5975B (GC/MS) was used for the analysis of the reaction products. The GC/MS has been configured by Wasson ECE Instrumentation and Agilent technologies for the analysis of various hydrocarbons, light molecular weight oxygenates, and some fixed gases. The instrument is equipped with three detectors: an Agilent 5975B mass selective detector (MSD), and two thermal conductivity detectors (TCD). The oxygenates (methanol, ethanol, n-propanol, n-butanol, acetaldehyde and acetone) and light gases (methane, ethane, propane and butane) were analyzed using the mass spectrometer and the gases CO, CO2 and H2 were analyzed using the TCD. The calibration of the GC/MS was done using different calibration levels of each component. The calibration responses were used for the estimation of errors associated with the concentration measurements, which were then used to estimate the errors in the product selectivities.

Multiple injections of calibration gases with known concentrations (C_cal) give the corresponding responses in area counts (A_cal). For example, the calibration data for ethanol is presented in Table A.1 with the resultant calibration curve depicted in Figure A.1.

Table A.1: Calibration data for ethanol.

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<th>Concentration ppm (C_cal)</th>
<th>Response area ct. (A_cal)</th>
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<td>9.3</td>
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<td>133394</td>
</tr>
<tr>
<td>99.3</td>
<td>133175</td>
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Figure A.1: Calibration curve for ethanol.

A.2. Error Estimation

Assuming a linear relationship between response and concentration, we have, $A_{\text{cal}} = m \cdot C_{\text{cal}}$. The mean and variance of the slope $m$ can be calculated which in turn, can be used to calculate the variance of an experimental concentration, $C_{\text{exp}}$, for a measured area, $A_{\text{exp}}$, using the equations given in Engineering Statistics by Montgomery et al., for a linear function.

From Engineering Statistics by Montgomery et al., the approximate variance, $V(Y)$ of a linear function can be computed as

$$V(Y) = \sigma_Y^2 = \sum \left( \frac{dh}{dX_i} \right)^2 \sigma_{X_i}^2$$

where, $\sigma_{X_i}^2$ is the variance of the variable $X_i$ and the derivative $\frac{dh}{dX_i}$ is evaluated at $X_i$. 

$$y = 1392.4x - 4983.9$$
$$R^2 = 1$$
Applying to our case, where, \( h = C_{\text{exp}} = \frac{A_{\text{exp}}}{m} \),

\[
V(Y) = \sigma_{c_{\text{exp}}}^2 = \left( \frac{dC_{\text{exp}}}{dm} \right)_m^2 \ast \sigma_m^2
\]

\[
V(Y) = \sigma_{c_{\text{exp}}}^2 = \left( \frac{-A_{\text{exp}}}{m^2} \right)_m^2 \ast \sigma_m^2
\]

The variance of \( C_{\text{exp}} \) accounts for the error due to calibration as well as that due to the repeat measurements at the same reaction condition. The variances in measured concentrations are computed for all the products in a similar way. Now the errors in selectivities have to be calculated based on the errors in the corresponding measured concentrations. The selectivity of a product \( i \) can be computed as

\[
S_i = \left( \frac{C_i}{\Sigma C_i} \right) \ast 100
\]

Thus the variance of \( S_i \) as given by the formula from Montgomery et al., after simplification becomes

\[
\sigma_{S_i}^2 = \left[ 100 \ast \frac{\Sigma C_i - C_i}{(\Sigma C_i)^2} \right]^2 \ast \sigma_{C_i}^2
\]

where, \( \sigma_{C_i}^2 \) is equal to the variance of measured concentration, \( \sigma_{c_{\text{exp}}}^2 \), of product \( i \). The 95% confidence limits on the selectivity values can then be calculated using the variances in the selectivities.
Appendix B: Batch-to-batch Reproducibility of Nanoparticles

One very important factor, that is essential for a catalyst development method to be successful, is the batch-to-batch reproducibility of the synthesized catalysts, especially during a scale-up process. The properties such as particle size, monodispersity and morphology should be reproducible.

Several batches of the nanoparticles, used as catalysts in this study, were synthesized and tested for batch-to-batch reproducibility. HRTEM and UV-Visible spectroscopy techniques were used to test the repeatability between different batches. No significant deviation between the batches could be found. Figures B.1 and B.2 show the HRTEM images of different batches of Cu@Mn$_3$O$_4$ and Cu@Co$_3$O$_4$ nanoparticles. The particles seem to be uniform in size and shape between the batches and the core-shell structure is also reproducible. However, there seems to be more reproducibility in the case of Cu@Mn$_3$O$_4$ nanoparticles than that of Cu@Co$_3$O$_4$ nanoparticles.

Figure B.1: HRTEM images of Cu@Mn$_3$O$_4$ nanoparticles synthesized in three different batches.
Figure B.2: HRTEM images of Cu@Co$_3$O$_4$ nanoparticles synthesized in two different batches.

Figure B.3 shows the UV-Visible spectral features displayed by two different batches of nanoparticles. There are no significant variations, which indicate that the synthesis method produces nanoparticles with great reproducibility. Also, the nanoparticles synthesized in different batches showed similar colors when dispersed in toluene. Hence, the synthesis method used reduces the batch-to-batch variations significantly and produces nanoparticles with good reproducibility.

Figure B.3: UV-Visible spectra of the nanoparticles dispersed in toluene: (a) Cu@Mn$_3$O$_4$ and (b) Cu@Co$_3$O$_4$. 
Appendix C: Supplemental Characterization Results on Cu@Mn$_3$O$_4$ Nanoparticles

This appendix contains the supporting characterization results (SAXS, XRD, XPS and FTIR) on Cu@Mn$_3$O$_4$ core-shell nanoparticles discussed in Chapter 4.

C.1. Experimental Methods

In order to characterize the size distribution of the Cu@Mn$_3$O$_4$ nanoparticles, small angle X-ray scattering (SAXS) experiments were carried out using the SAXS beamline at LSU/CAMD. A double-crystal monochromator allows photons with energy range from ~3-14 KeV. SAXS pattern is imaged with 200 mm x 200 mm multiwire gas detector with a resolution of 200-250 μm FWHM in a 1024 x 1024 array. A segmented flight path allows q-range from 0.0015 to 0.44 Å$^{-1}$ to be studied. Dilute toluene solutions of dispersed nanoparticles were filled into 1 mm quartz capillary tubes in inert atmosphere and sealed.

X-ray diffraction (XRD) patterns were recorded on a Bruker/Siemens D5000 automated powder X-ray diffractometer, using Cu Kα radiation ($\lambda = 1.540562$ Å) with Rietveld analysis software. X-ray photoelectron spectroscopy (XPS) studies were performed on a Kratos AXIS 165 X-ray Photoelectron Spectroscope and Scanning Auger Microscope equipped with standard Mg/Al source and high performance Al monochromatic source. Fourier transform infrared spectroscopy (FTIR) spectra were obtained using a Thermo Nicolet 6700 spectrometer equipped with a MCT detector. A diamond crystal attenuated total reflectance (ATR) accessory was used for measurements. Spectra were collected at 4 cm$^{-1}$ resolution and 32 scans.
C.2. Results and Discussion

(a) XPS

The Cu/Mn surface atomic ratios as well as the binding energies of the main peaks were obtained by XPS measurements for the Cu@Mn₃O₄ nanoparticles (Table C.1). The results indicate that the surface Cu/Mn ratio is 2.2:1, indicating a surface enrichment of copper. This could be due to either the presence of Cu oxide in the shell or the Cu-core being accessible through the porous shell. The Cu 2p₃/₂ peak at 932.6 eV corresponds to Cu⁰ and/or Cu₂O, but the XPS spectrum did not reveal any shake up satellites corresponding to Cu₂O. Also, the difference in the 2p₃/₂ and 2p₁/₂ energies is about 19.9 eV, corresponding to metallic copper. However, although it is most probable the presence of metallic copper, there is also the possibility of the copper core getting partially oxidized during sample loading since the shell is porous. The Mn 2p₃/₂ peak is positioned at 641.7 eV and the difference between the binding energy values of Mn 2p₃/₂ and Mn 2p₁/₂ level is 11.9 eV, which matches values for many types of manganese oxides. Therefore, the discrimination becomes very difficult and a definite conclusion about the oxidation state of Mn cannot be derived from the XPS results.

Table C.1: XPS analysis of Cu@Mn₃O₄ nanoparticles.

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<th>Binding energies (eV)</th>
<th>Cu/Mn surface atomic ratio</th>
<th>Oxidation states</th>
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<tr>
<td>Cu 2p₃/₂</td>
<td>Mn 2p₃/₂</td>
<td>2.2</td>
</tr>
<tr>
<td>932.6</td>
<td>641.7</td>
<td>Cu⁰ and/or Cu₂O \Mn^{2+}\ and/or \Mn^{3+}\</td>
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</table>
(b) SAXS

Figure C.1 shows the SAXS data for pure copper and Cu@Mn₃O₄ nanoparticles. SAXS data represent the scattering cross section per unit sample volume, I(Q), as a function of scattering vector Q. Figure C.1 also displays the particle size distribution derived from the SAXS data assuming the spheroid particle model and a non-negative least squares (NNLS) fitting method.

A unimodal size distribution is observed in both systems. The approximate average particle size of Cu nanoparticles (Figure C.1a) is around 7-12 nm, while the Cu@Mn₃O₄ nanoparticles (Figure C.1b) have a very narrow unimodal size distribution of around 17-20 nm. The symmetrical size distribution indicates the absence of any particle agglomeration, and the average particle size of the nanoparticles is found to increase with the shell coating. However,
the particle sizes obtained from SAXS fits are slightly larger than those obtained from the TEM. This difference could be attributed to the fact that SAXS information is generated from a large sampling volume and hence a larger number of particles are probed compared to TEM. Also, the fitting method and the particle model assumed for fitting the data could have led to some disparities.

(c) FTIR

In order to confirm the adsorption of surfactants used during synthesis – oleic acid (OA) and trioctylphosphine (TOP), FTIR spectra of the as-prepared Cu@Mn₃O₄ nanoparticles was recorded. The resulting infrared spectra in the 700-3200 cm⁻¹ region is shown in Figure C.2. It has been reported that oleic acid binds to nanoparticle surfaces through the –COO⁻ group in both monodentate and bidentate forms²-³ and TOP binds via C-P modes. From Figure C.2, the peaks at 2847 and 2916 cm⁻¹ can be assigned to the symmetric & asymmetric CH₂ stretching modes and the peak at 3001 cm⁻¹ is due to the ν(C-H) mode of the C-H bond adjacent to the C=C bond. All these bands in the region 2850-3000 cm⁻¹ are characteristic of both OA and TOP surfactants.

The bands at 1530 and 1395 cm⁻¹ can be attributed to the symmetric and asymmetric vibrations of the –COO⁻ group of oleic acid, indicating the presence of bidentate carboxylate bonding to the nanoparticles. However, the ν(C=O) stretching mode of the carboxylic acid group found in pure oleic acid², was present only as a small broad shoulder at 1709 cm⁻¹, and a decrease of the intensity of this band after surfactant binding on the nanoparticles is indicative of the chemical adsorption of oleic acid to the surface of the nanoparticles. Sharma et al. attributed the absence of this peak on oleic acid stabilized CoNi nanoparticles to a similar assignment³. Peaks in the low frequency region (< 1500 cm⁻¹) arise from complex combinations of C-C and C-O stretches, CH₂
deformations, etc. The peaks in the range 1000-1170 cm$^{-1}$ are due to the C–P stretching modes of TOP. Also, the shoulders at 1462, 1456 and 1377 cm$^{-1}$ are reported to originate from the terminal methyl groups of TOP. Overall, the bands arising specifically due to TOP adsorption are relatively lower in intensity compared to those due to oleic acid. This might indicate that the metal-TOP complexes decompose at the synthesis temperature (200 °C) whereas oleic acid strongly chemisorbs on the nanoparticle surface. All the bands observed in the FTIR spectra point toward the existence of organic ligands from surfactants that are capped onto the nanoparticle surface, thereby preventing further agglomeration of the particles. This was also further confirmed by the detection of CO$_2$, CH$_4$ and H$_2$O as products when the nanoparticles were oxidized under 10% O$_2$/He.

![FTIR spectrum](image)

Figure C.2: FTIR spectrum of Cu@Mn$_3$O$_4$ nanoparticles in the 800-3200 cm$^{-1}$ region.

(d) XRD

The major peaks in the XRD pattern (Figure C.3) can be identified as face-centered cubic Cu. XRD peaks are observed at 2θ values of around 43.4°, 50° and 74°, which are in a good
agreement with the standard XRD pattern of metallic Cu $^5$, consistent with the XPS assignments. The diffraction peaks at $2\theta = 29.3^\circ, 36.5^\circ, 61^\circ, 74^\circ$ can be attributed to Mn$_3$O$_4$ $^6$-$^9$.

![X-ray diffraction pattern of Cu@Mn$_3$O$_4$ nanoparticles](#)

**Figure C.3:** X-ray diffraction pattern of Cu@Mn$_3$O$_4$ nanoparticles.

### C.3. References


Appendix D: Academic Activity – Publications and Presentations

D.1. Journal Publications:


2. Nachal D. Subramanian and James J. Spivey, “A DRIFTS study of Mn or Co promoted Cu-ZnO-La$_2$Zr$_2$O$_7$ based catalysts for CO hydrogenation”, to be submitted.


4. Nachal D. Subramanian, Andrew Campos, Andrew Payzant and James J. Spivey, “*In-situ* time-resolved XRD and XANES studies of transition metal promoted copper-rare earth zirconate catalysts”, Submitted to *Journal of Physical Chemistry C* (under review).


D.2. Conference Presentations: (Presenter underlined)

1. Nachal Subramanian, Andrew Campos and James J. Spivey, “*In-situ* time-resolved XRD and XANES studies of copper-rare earth oxide pyrochlore catalysts”, 22nd North American Catalysis Society Meeting, Detroit, MI, June 5-10, 2011.


3. Nachal Subramanian, Sivakumar Vasireddy and James J. Spivey, “Effect of transition metal promters on copper-rare earth oxide catalysts for higher alcohol synthesis from syngas”,

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D.3. Conference Proceedings and Preprints:


D.4. Submitted Abstracts:

Appendix E: Permission to Use Copyright Materials

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Development of cobalt–copper nanoparticles as catalysts for higher alcohol synthesis from syngas

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\textbf{ABSTRACT}

The synthesis of higher alcohols from syngas has been studied over different types of Cu-based catalysts. In order to provide control over the catalyst composition at the scale of a few nanometers, we have synthesized two sets of Co–Cu nanoparticles with core–shell structures by wet chemical methods, namely, (a) cobalt core–copper shell (Co@Cu) and (b) cobalt–copper mixed (synthesized by simultaneous reduction of metal precursor) nanoparticles. These catalysts were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and temperature programmed reduction (TPR). A study was conducted for CO hydrogenation at temperatures ranging from 230°C to 300°C, 20 bar and 18000 sccm/hr (gcat), and it was observed that the Co–Cu mixed nanoparticles with higher Cu concentration exhibited a greater selectivity towards ethanol and C\textsubscript{2} alcohols. The highest ethanol selectivity achieved was 11.4% with corresponding methane selectivity of 17.2% at 270°C and 20 bar.

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1. Introduction

With today’s increasing oil prices and declining fossil fuel resources, there is a need to look for alternative commercially viable energy sources. Bio-based fuel resources, particularly ethanol, have been studied extensively in the recent years as a clean, sustainable and transportable fuel alternative [1]. One promising process for bio-fuel production involves the conversion of bio-derived synthesis gas (syngas) to fuels and oxygenates. Syngas derived from biomass or coal is particularly interesting since both sources are abundant, and biomass is a renewable feedstock [2]. It is well known that syngas conversion to C\textsubscript{2} oxygenates is often limited by the formation of methane and methanol. However, C\textsubscript{2} alcohols are more desirable products, both as neat fuels [3–5], fuel additives or as a carrier for hydrogen to supply fuel cells. In addition to its potential application as a transportation fuel, ethanol has been considered as a feedstock for the synthesis of various chemicals, fuels and polymers [6,7]. It is estimated that ethanol could replace as much as one-third of the domestic petroleum use in the near future [8]. Hence, the development of a suitable and efficient catalyst to produce higher alcohols from syngas, coupled with an understanding of the underlying reaction mechanism, is clearly important.

The general mechanism of C\textsubscript{2} oxygenate formation from syngas has been extensively studied and the main steps are believed to be: (a) dissociative adsorption of CO and H\textsubscript{2} and (b) formation of surface hydrocarbon (\textit{CH}_{n=1-4}) and hydroxyl (OH\textsubscript{n=1}) species and (c) CO insertion to form the C–C bond [9]. Ethanol formation is favored by a catalyst that selectively promotes the CO insertion reaction instead of the hydrogenation of the \textit{CH}_{n=1-4} surface species, since hydrogenation of \textit{CH}_{n=1} species leads to hydrocarbon formation [10].

The catalysts that have been studied for this reaction include Rh-based catalysts and alkaline-promoted Cu-based catalysts [10]. Rh-based catalysts have been found so far, to the most selective catalysts for the synthesis of higher alcohols from CO hydrogenation [10]. The activity and selectivity of Rh catalysts has been attributed to their ability to catalyze both CO dissociation and CO insertion [11]. However, CO dissociation on surfaces such as for RnX(X=I) is almost impossible or very slow and the presence of steps/kinks is necessary to enhance the CO dissociation rate [12]. This is in agreement with the catalytic behavior of Rh in CO hydrogenation since it has been suggested that metals which adsorb CO strongly enough to activate the molecule but do not dissociate it readily are active catalysts for the formation of oxygenates [13]. However, the high cost and limited availability of the precious Rh metal catalysts [14] have led to the
La and/or V oxide promoted Rh/SiO₂ catalysts: Effect of temperature, H₂/CO ratio, space velocity, and pressure on ethanol selectivity from syngas

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CO hydrogenation to ethanol was carried out over Rh(La₅/SiO₂) promoted with La and/or V oxides. Recent results at 250 °C and 1.8 bar have shown 21% ethanol selectivity for the doubly promoted Rh-La₅/SiO₂ catalysts. Here, we extend this work to examine the effects of reaction conditions—temperature, H₂/CO ratio, space velocity, and pressure—on the activity and selectivity of these catalysts. An ethanol selectivity of 31% (close to the highest literature value) at a CO conversion of 73% was achieved with a corresponding methane selectivity of 15.4% at 270 °C, 14 bar and H₂/CO = 2 over the Rh-La₅/SiO₂ catalyst. Combined La-V promotion reduces methane selectivity and increases CO₂ oxygenate selectivity compared to the singly promoted catalysts by increasing the rate of CO insertion. Contrary to literature studies, higher pressures led to a dramatic increase in methane selectivity at the expense of ethanol, indicating increased CO dissociation activity at higher pressures, leaving fewer active CO molecules for insertion. The chain growth factor (x) for higher oxygenates differed significantly from that for hydrocarbons, suggesting that formation of these two types of products either proceeds by different mechanisms or at different active sites.

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1. Introduction

The catalytic hydrogenation of CO is one of the most promising technologies for the synthesis of ethanol and higher alcohols from syngas, which can be derived from coal, biomass, or natural gas. Among the potential end products of coal/biomass gasification, ethanol is particularly attractive since it serves as a clean alternative fuel, a gasoline blend, and a hydrogen carrier [1].

Supported Rh-based catalysts have the highest activity and selectivity for the formation of ethanol and other C₂ oxygenates due to their ability to catalyze both CO dissociation and CO insertion [2-6]. For example, He et al. recently reported 58% selectivity to ethanol on a 6% Rh-Mn/SiO₂ powdered catalyst [7]. The most relevant feature of Rh is its ability to adsorb reactive CO both associatively and dissociatively, allowing it to form both hydrocarbons and oxygenates. Novel materials such as carbon nanotube-based Rh catalysts [8], Cu-Co-based nanoparticles [9], electrodeposited Cu-Zn-based nanowires [10], and Rh catalysts in microchannel reactors [7] have also been reported recently for this reaction.

The general mechanism of C₂ oxygenate formation from syngas has been extensively studied [2,4,11-15]. CO dissociation is believed to be the first step in the synthesis of C₂ oxygenates from syngas. The resulting surface carbon is then hydrogenated to form a surface hydrocarbon species (CH₃)₂. This (CH₃)₂ species can then undergo (a) CO insertion to form oxygenates, or (b) hydrogenation to form methane, or (c) chain growth to form higher hydrocarbons. In a parallel reaction sequence, associatively adsorbed CO can be hydrogenated directly to form methanol [11,14,15]. Methane is the most thermodynamically favored product but is economically undesirable. Thus, hydrocarbon formation, which typically accompanies high catalyst activity, must be suppressed kinetically to maximize the ethanol selectivity.

The influence of various promoters on the catalytic activity of Rh has been extensively studied in recent years. It is proposed that the carbon atom of a CO molecule binds to the Rh atom and the oxygen atom binds to a neighboring promoter cation (tilt-adsorbed CO species) which can either weaken the C-O bond resulting in CO dissociation or promote CO insertion [16-22]. Lanthana and vanadia promoters have been reported to enhance the formation of C₂ oxygenates by assisting in CO dissociation and/or insertion [23,24]. Vanadia has also been found to improve the activity and selectivity toward ethanol by enhancing the hydrogenation of acyl intermediates [25,26].

Here, a series of La and/or V oxide promoted Rh/SiO₂ catalysts were tested for CO hydrogenation in a fixed bed microreactor system at various conditions. This present research is an extension of the work of Gao et al. [27] on these Rh/SiO₂ catalysts. The focus of
Vita

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