Catalytic Conversion of Syngas to Higher Alcohols over Cu-Fe Based Catalysts

Yongwu Lu

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Catalytic conversion of syngas to higher alcohols over Cu-Fe based catalysts

By

Yongwu Lu

A Dissertation
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Mississippi State University
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in Biological Engineering
in the Department of Agricultural and Biological Engineering

Mississippi State, Mississippi

December 2014
Catalytic conversion of syngas to higher alcohols over Cu-Fe based catalysts

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Higher alcohol synthesis (HAS) from syngas or biomass-derived syngas is an important process for the production of oxygenate fuels, fuel additives and other intermediates for value-added chemical feedstock to produce medicine, cosmetics, lubricants, detergents, and polyesters.

Chapter I reviews biomass to liquid fuels technology, higher alcohols being used as alternative fuels and fuel additives, the historical perspective and commercial status of higher alcohols, the catalyst system and the reaction mechanism for HAS from syngas.

Chapter II discusses the Zn-Mn promoted Cu-Fe based catalyst that was synthesized by the co-precipitation method. The reaction temperature has been tested to study the influence on the catalytic performance. The maximal CO conversion rate was 72%, and the yield of alcohol and hydrocarbon was also very high. Cu was the active site for alcohol synthesis, iron carbide was the active site for olefin and paraffin synthesis. The reaction mechanism of HAS from syngas over Zn-Mn promoted Cu-Fe based catalyst was proposed.
Chapter III documents the three-dimensionally ordered macroporous (3DOM) Cu-Fe catalyst developed using a glyoxylate route colloidal crystal template method. The high intrinsic activity was ascribed to three factors. First, the unique ordered structure has a large pore size and interconnected macroporous tunnels of the catalyst with a large accessible surface area to improve the catalytic activity. Second, a high density of uniformly distributed defective Cu$^0$ and Fe$_5$C$_2$ nanoparticles derived from the glyoxylate route helps to provide abundant, active, and stable dual sites. Third, atomic steps on the Cu surface, induced by planar defects and lattice strain, serve as high-activity oxygenation sites. Active Fe$_5$C$_2$ chain-growth sites intimately surround the defective and strained form of the Cu surface, which results in a synergetic effect between the active and stable Cu–Fe$_5$C$_2$ dual site for HAS.

In Chapter IV, in situ ambient pressure x-ray photoelectron spectroscopy and in situ synchrotron powder diffraction were applied to identify the active site of 3DOM Cu-Fe catalyst for HAS. The results show that after syngas pretreatment of the 3DOM Cu-Fe catalyst, Cu$^0$ is the active oxygenation site for alcohol synthesis, and Fe$_5$C$_2$ is the active site for carbon chain growth.

Key words: higher alcohol synthesis, syngas, copper-iron catalyst, co-precipitation, three-dimensionally ordered macroporous, active site, defect, structure-activity relationship, in situ AP–XPS, in situ synchrotron powder diffraction
DEDICATION

I would like to dedicate this dissertation to my beloved parents, Mr. Baishi Lu and Mrs. Shaofeng Huang. Thank you very much for your love, support and encouragement all these years.
ACKNOWLEDGEMENTS

I wish to express my profound gratitude to Dr. Fei Yu, my major professor for his immeasurable support, consistent encouragement throughout my graduate study and this project. Without his valued guidance, perseverance, and patience, I would have not completed this work.

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Office of Basic Energy Sciences, through contract No.DE-AC02-06CH11357. The use of Field Emission–Scanning Electron Microscope (FE–SEM), X-ray Diffractometer (XRD), Transmission Electron Microscope (TEM) at Institute for Imaging and Analytical Technologies (I²AT) at Mississippi State University (MSU) were supported by National Science Foundation under NSF-MRI Grant # DBI-1126743, “Acquisition of a multi-user, analytical transmission electron microscope (TEM) for multi-disciplinary research and training”, NSF-MRI Grant # DMR-0619773, “Acquisition of a Multi User, High Resolution, Research Grade X-ray Diffractometer”, and NSF-IMR Grant # DMR-0216703 and 02070615, “Acquisition of a Multi User Analytical FE–SEM for Education and Research”.
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<tr>
<td>ADM</td>
<td>Alkaline-doped MoS$_2$</td>
</tr>
<tr>
<td>ASF</td>
<td>Anderson–Schultz–Flory</td>
</tr>
<tr>
<td>BE</td>
<td>Binding energy</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer–Emmett–Teller</td>
</tr>
<tr>
<td>BTL</td>
<td>Biomass to liquid</td>
</tr>
<tr>
<td>BTX</td>
<td>Benzene, toluene, xylene</td>
</tr>
<tr>
<td>CCT</td>
<td>Colloidal crystal template</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>DME</td>
<td>Dimethyl ether</td>
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<tr>
<td>EDS</td>
<td>Energy diffusive x-ray spectroscopy</td>
</tr>
<tr>
<td>EG</td>
<td>Ethylene glycol</td>
</tr>
<tr>
<td>EXAFS</td>
<td>Extended x-ray absorption fine structure</td>
</tr>
<tr>
<td>FE–SEM</td>
<td>Field emission–scanning electron microscopy</td>
</tr>
<tr>
<td>FFT</td>
<td>Fast Fourier Transform</td>
</tr>
<tr>
<td>FID</td>
<td>Flame ionization detector</td>
</tr>
<tr>
<td>FT</td>
<td>Fischer–Tropsch</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>FTS</td>
<td>Fischer–Tropsch synthesis</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>--------------</td>
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<tr>
<td>GC–MS</td>
<td>Gas chromatography–mass spectrometry</td>
</tr>
<tr>
<td>GHSV</td>
<td>Gas hourly space velocity</td>
</tr>
<tr>
<td>HAS</td>
<td>Higher alcohol synthesis</td>
</tr>
<tr>
<td>HDN</td>
<td>Hydrodenitrogenation</td>
</tr>
<tr>
<td>HDS</td>
<td>Hydrodesulfurization</td>
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<tr>
<td>H₂–TPR</td>
<td>Hydrogen–temperature programmed reduction</td>
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<td>HRTEM</td>
<td>High resolution transmission electron microscopy</td>
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<tr>
<td>In situ AP–XPS</td>
<td>In situ ambient pressure–x-ray photoelectron spectroscopy</td>
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<tr>
<td>ISO</td>
<td>Isomer shift</td>
</tr>
<tr>
<td>JCPDS</td>
<td>Joint Committee on Powder Diffraction Standards</td>
</tr>
<tr>
<td>KE</td>
<td>Kinetic energy</td>
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<tr>
<td>KMC</td>
<td>Kinetic Monte Carlo</td>
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<tr>
<td>LDHs</td>
<td>Layered double hydroxides</td>
</tr>
<tr>
<td>Mo₂C</td>
<td>Molybdenum carbide</td>
</tr>
<tr>
<td>MoS₂</td>
<td>Molybdenum sulfide</td>
</tr>
<tr>
<td>MMO</td>
<td>Mixed metal oxide</td>
</tr>
<tr>
<td>MTBE</td>
<td>Methyl tertiary butyl ether</td>
</tr>
<tr>
<td>NIST</td>
<td>National Institute of Standards and Technology</td>
</tr>
<tr>
<td>NPs</td>
<td>Nanoparticles</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
</tr>
<tr>
<td>QS</td>
<td>Quadrupole splitting</td>
</tr>
<tr>
<td>REO</td>
<td>Rare earth oxides</td>
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<tr>
<td>Abbreviation</td>
<td>Description</td>
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<td>------------------------------------------------</td>
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<tr>
<td>SAED</td>
<td>Selected area electron diffraction</td>
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<td>SEM</td>
<td>Scanning electron microscopy</td>
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<td>STEM</td>
<td>Scanning transmission electron microscopy</td>
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<tr>
<td>STY</td>
<td>Space time yield</td>
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<tr>
<td>TCD</td>
<td>Thermal conductivity detector</td>
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<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
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<tr>
<td>TOPAS</td>
<td>Total pattern analysis</td>
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<tr>
<td>TPR</td>
<td>Temperature programmed reduction</td>
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<td>UV-vis</td>
<td>Ultraviolet-visible spectroscopy</td>
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<td>WGS</td>
<td>Water gas shift</td>
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<td>XANES</td>
<td>X-ray absorption near edge structure</td>
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<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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<tr>
<td>XRD</td>
<td>X-ray diffraction/diffractometer</td>
</tr>
<tr>
<td>3DOM</td>
<td>Three-dimensionally ordered macroporous</td>
</tr>
</tbody>
</table>
CHAPTER I
HETEROGENEOUS CATALYTIC CONVERSION OF SYNGAS TO HIGHER ALCOHOLS: LITERATURE REVIEW

1.1 Introduction

Increasing concerns about global climate change, high local and global environmental pollution, high depletion of non-renewable energy resources, and rising crude oil prices have pushed the topic of energy to the center stage. According to the U.S. Energy Information Administration, world liquid fuel consumption is projected to increase by about one-third (28 million barrels per day), from almost 87 million barrels per day in 2010 to 115 million barrels per day in 2040 in the Reference case. The Reference case represents current judgment regarding exploration and development costs and accessibility of oil resources. It also assumes that countries in the Organization of the Petroleum Exploring Countries (OPEC) will invest in incremental production capacity in order to maintain a 39–43 percent share of total world liquid fuels production through 2040, consistent with their share over the past 15 years. These liquids include petroleum-derived fuels and nonpetroleum-derived fuels, such as ethanol, biodiesel, gas to liquids and coal to liquids, petroleum coke, natural gas liquids, crude oil consumed as a fuel, and liquid hydrogen. In order to meet the increased world liquid fuels consumption demand, world liquid fuels production (both conventional and unconventional) will be increased by about 28 million barrels per day from 2010 to 2040 in the Reference case.
In addition, world oil prices are increasing, which is shown in Figure 1.1. In the Reference case, the average world oil price is forecasted to increase from $81/barrel in 2010 to $117/barrel in 2025 and $163/barrel in 2040.

![Figure 1.1](image)

Figure 1.1 World oil prices in three cases (Dollars per barrel), 1990–2040

Note: Sources from Energy Information Administration

The unconventional fuels, such as biofuels, oil sands, extra-heavy oil, coal-to-liquids, gas-to-liquids, and shale oil are being explored. According to the International Energy Outlook 2013, for the period 2010–2040, the unconventional liquid fuels production, such as coal-to-liquids, gas-to-liquids, biofuels etc. will increase annually on average by ~5.5%, due to high oil prices. For example, the world production of biofuels is expected to increase from 1.3 million barrels per day in 2010 to 2.8 million barrels per day in 2040 in the Reference case.
Biomass contains various amounts of components, such as cellulose, hemicellulose, and lignin. The cellulose is a biopolymer of glucose, a 6-carbon sugar (hexose), the hemicellulose is mainly pentosans or polymeric pentose mostly xylose, and lignin is polymeric phenyl-propane. Biomass can be converted into a wide range of liquid fuels, called “biofuels”, such as bioethanol, biodiesel, liquid alkanes, and furfural and its derivatives for future transportation fuel demands. Among them, bioethanol has been received with great interest to use in automobiles, either as an additive or as a potential substitute for gasoline. Ethanol is already used as a gasoline additive in the United States (U.S.) and other countries such as Canada, Brazil, and Sweden. Ethanol is contained in about 10 vol. % of all gasoline sold in the United States. The additive of ethanol or higher alcohols to gasoline in automobiles can not only enhance octane quality, but also reduce the greenhouse gas emissions and other environmental pollutants such as NOx.

In addition to its potential application as a transportation fuel, bioethanol has been considered as a feedstock for the synthesis of variety of chemicals such as butadiene, hydrogen, acetaldehyde, and 1-butanol. Bioethanol also can be used to chemically transport hydrogen as a liquid by incorporating hydrogen atoms in the alcohol molecule, which can be transported and reformed to a hydrogen-rich gas used in a fuel cell. Therefore, the worldwide interest is growing in the production of ethanol and higher alcohols from biomass and possibly from other readily available carbonaceous sources such as coal without CO2 emissions.

According to 2013 Ethanol Industry Outlook from Renewable Fuels Association, global ethanol production in 2012 exceeded 21.8 billion gallons, with United
States and Brazil being the largest producers in the world, contributing 13.3 and 5.58 billion gallons. A major portion of the ethanol produced in the United States was used for blending with gasoline, but this mixture replaced only about 2% of all gasoline sold. 12 The Energy Independence and Security Act (EISA) of 2007 from the United States of Environmental Protection Agency (EPA) requires 36 billion gallons of U.S. renewable fuel to be blended into transportation fuel by 2022. 23 This has prompted a significant increase in the research and development effort dedicated to this challenge. Therefore, it is very urgent and significant to research the unconventional fuels and chemicals as alternatives to petroleum-derived fuels to meet the worldwide energy demand, reduce greenhouse gas emissions, improve the air quality, as well as increase national energy security.

Figure 1.2  Biomass-to-Liquid (BTL) technology
1.2 Biomass to liquid fuels

Figure 1.2 illustrates the Biomass to Liquid (BTL) technology that mainly includes three steps: biomass gasification to yield biomass-derived syngas, biomass-derived syngas cleaning to remove impurities, and catalytic conversion of syngas to liquid fuels and chemicals.

1.2.1 Synthesis gas derived from biomass gasification

Biomass gasification is a thermo-chemical process that uses partial oxidation to convert carbonaceous feedstock (such as woodchip, switchgrass, corn stover and so on) into a gaseous product known as synthesis gas. Synthesis gas (syngas) is mainly composed of carbon monoxide and hydrogen, with lesser amounts of carbon dioxide, methane, light hydrocarbons, water, and nitrogen. The reactions are carried out by using a gasifying agent (also called an oxidizing agent) such as air, oxygen, steam or a mixture of these gases at high temperatures (500–1400 °C), and at atmospheric or higher pressure conditions up to 480 psig. In the presence of a gasifying agent at elevated temperature, the large polymeric molecules of biomass including such as cellulose, hemicelluloses, lignin compounds decompose into lighter molecules and finally into gases (CO, H₂, CH₄, and light hydrocarbons), ash, char and small amount of contaminants. Char and tar result from the incomplete conversion of biomass. The overall reaction in an air and/or steam gasification can be expressed by Reaction (1.1) in Table 1.1, which proceeds with multiple reactions and pathways. The major reactions involved in the gasification process are expressed by Reactions (1.2–1.7) in Table 1.1.
Table 1.1  The reactions taking place in gasifier

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Reaction equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1.1) Overall reaction:</td>
<td>( \text{CH}_x \text{O}_y ) (biomass) + O(_2) (21 % \text{ from air}) + H(_2)O (steam) \rightarrow CO + H(_2) + CO(_2) + CH(_4) + H(_2)O + C ) (char) + tar</td>
</tr>
<tr>
<td>(1.2) Partial oxidation:</td>
<td>( \text{C} + \frac{1}{2} \text{O}_2 \leftrightarrow \text{CO} )</td>
</tr>
<tr>
<td>(1.3) Complete oxidation:</td>
<td>( \text{C} + \text{O}_2 \leftrightarrow \text{CO}_2 )</td>
</tr>
<tr>
<td>(1.4) Water-gas shift reaction:</td>
<td>( \text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 )</td>
</tr>
<tr>
<td>(1.5) Boudouard reaction:</td>
<td>( \text{C} + \text{CO}_2 \leftrightarrow 2\text{CO} )</td>
</tr>
<tr>
<td>(1.6) Methane reaction:</td>
<td>( \text{C} + 2\text{H}_2 \leftrightarrow \text{CH}_4 )</td>
</tr>
<tr>
<td>(1.7) Steam reforming reaction:</td>
<td>( \text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2 )</td>
</tr>
</tbody>
</table>

Three types of producer gas can be produced from gasification by using different gasifying agents. Low heating value gas (about 4–6 MJ/m\(^3\)) can be used directly in combustion or it can be used as fuel for gas engines and gas turbines. Medium/high heating value gases can be utilized as a feedstock to synthesize liquid fuels such as higher alcohols and Fischer–Tropsch gasoline, diesel, and jet fuels. Table 1.2 shows the three types of producer gas with their calorific values and gasifying agents.

Table 1.2  Types of producer gases, their calorific values and gasifying agents

<table>
<thead>
<tr>
<th>Producer gases</th>
<th>Calorific value</th>
<th>Gasifying agent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low calorific value</td>
<td>4–6 MJ/m(^3)</td>
<td>air and steam/air</td>
</tr>
<tr>
<td>Medium calorific value</td>
<td>12–18 MJ/m(^3)</td>
<td>oxygen and steam</td>
</tr>
<tr>
<td>High calorific value</td>
<td>40 MJ/m(^3)</td>
<td>hydrogen and hydrogenation</td>
</tr>
</tbody>
</table>

1.2.2  Biomass-derived syngas cleaning

The raw syngas obtained from biomass gasification usually contains some impurities. Impurities include sulfur, nitrogen, chlorine, and ash, can interfere with downstream applications. These impurities would result in the decrease of the process
efficiencies such as corrosion and pipe blockages as well as catastrophic failures such as rapid and permanent deactivation of catalysts. \(^{28}\) Incomplete gasification can also form undesirable products in the raw syngas in the form of tar and particulate char. \(^{28}\) In general, the impurity in the raw syngas from gasification can be classified into three types: (1) organic impurities, such as tars, benzene, toluene, and xylenes; (2) inorganic impurities, such as \(O_2\), \(NH_3\), HCN, \(H_2S\), COS, and HCl; (3) other impurities, such as dust and soot. \(^{29}\) The removal of contaminants or impurities is known as syngas cleaning. These contaminants should be removed to acceptable levels before the syngas can be further used for the Fischer–Tropsch synthesis reaction. The requirements of syngas cleaning for Fischer–Tropsch synthesis is shown in Table 1.3. \(^{29}\)

Table 1.3  The requirements of syngas cleaning for Fischer–Tropsch synthesis \(^{29}\)

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H_2S + COS + CS_2)</td>
<td>&lt; 1ppmv (^a)</td>
</tr>
<tr>
<td>(NH_3 + HCN)</td>
<td>&lt; 1ppmv</td>
</tr>
<tr>
<td>(HCl + HBr + HF)</td>
<td>&lt; 10 ppbv (^b)</td>
</tr>
<tr>
<td>Alkali metals (Na + K)</td>
<td>&lt; 10 ppbv</td>
</tr>
<tr>
<td>Particles (soot, ash)</td>
<td>“almost removed”</td>
</tr>
<tr>
<td>Organic components (tar)</td>
<td>Below dew point</td>
</tr>
<tr>
<td>Hetero-organic components (S, N, O)</td>
<td>&lt; 1ppmv</td>
</tr>
</tbody>
</table>

Note: \(^a\)ppmv: Parts per million by volume; \(^b\)ppbv: parts per billion by volume
12.3 Catalytic conversion of syngas to liquid fuels and chemicals

After syngas cleaning, the syngas can be catalytically converted into a wide range of liquid fuels and chemicals such as methanol, higher alcohols, gasoline, olefins, diesel, wax, and dimethyl ether (DME) as illustrated in Figure 1.3. 12

1.3 Higher alcohols as alternative fuels and fuel additives

Higher alcohols (alcohols higher than methanol) such as ethanol have replaced other additives (lead, aromatics, methyl tertiary butyl ethers (MTBE)) as an octane enhancer in automotive fuels. 30 The concern of the leaded gasoline emissions encouraged the environmental protection agency (EPA) to call for reduced lead in gasoline. Aromatics, such as benzene and toluene, have high octane qualities, but the
presence of these compounds produces more smoke and smog. Benzene is a well-known carcinogenic compound. MTBE has the adverse health and environmental effects on groundwater. The reasons that higher alcohols can be used as alternative fuels or fuel additives in transportation are as follows: reduction of greenhouse gas emissions, reduction of toxic exhaust emissions, enhancement of overall energy efficiency, and reduction of fuels costs. The difference between gasoline and diesel hydrocarbon and alcohols is that alcohols contain oxygen. Adding alcohols to petroleum oil allows the fuel to combust more completely because of the presence of oxygen, which increases the combustion efficiency and reduces air pollution. Blending 10% ethanol into gasoline can reduce greenhouse gas emissions. Table 1.4 compares the properties of alcohols including their boiling point, latent heat, vapor pressure and solubility in water, with those of octane and hexadecane. Compared to traditional fuels, alcohols possess less combustion energy. However, the lowest stoichiometric air to fuel ratio helps alcohol fuels to yield more power inside an engine when burning these fuels.

Table 1.4  Characteristics of chemically pure fuels

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Chemical weight (lb/mol)</th>
<th>Specific gravity</th>
<th>Boiling point (°C)</th>
<th>Latent heat (Btu/lb)</th>
<th>Combustion energy (Btu/lb)</th>
<th>Vapor pressure @ 100F (psig)</th>
<th>Solubility part in 100 parts H₂O</th>
<th>Stoichiometric air-fuel ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>32</td>
<td>0.79</td>
<td>65</td>
<td>503</td>
<td>10,260</td>
<td>4.6</td>
<td>infinite</td>
<td>6.5</td>
</tr>
<tr>
<td>Ethanol</td>
<td>46.1</td>
<td>0.79</td>
<td>78</td>
<td>396</td>
<td>13,160</td>
<td>2.2</td>
<td>infinite</td>
<td>9</td>
</tr>
<tr>
<td>Butanol</td>
<td>74.1</td>
<td>0.81</td>
<td>117</td>
<td>186</td>
<td>15,770</td>
<td>0.3</td>
<td>9</td>
<td>11.2</td>
</tr>
<tr>
<td>Octane</td>
<td>114</td>
<td>0.70</td>
<td>210</td>
<td>155</td>
<td>20,750</td>
<td>1.72</td>
<td>insoluble</td>
<td>15.2</td>
</tr>
<tr>
<td>Hexadecane</td>
<td>240</td>
<td>0.79</td>
<td>287</td>
<td>–</td>
<td>20,320</td>
<td>3.46</td>
<td>insoluble</td>
<td>15</td>
</tr>
</tbody>
</table>
1.4 Higher alcohols production from syngas via Fischer–Tropsch reaction

1.4.1 Historical perspective and commercial status

Alcohols were the products of early Fischer–Tropsch processes; however, the discovery of Co- and Fe-based Fischer–Tropsch catalysts that primarily synthesized nonoxygenated hydrocarbons for fuels diverted attention away from alcohols. The only commercial higher alcohol synthesis technology before 1950 was Farbenindustrie’s isobutyl oil process. After the discovery of the Arab oil fields in the late 1940s, the technology for higher alcohol synthesis based on petroleum came out. The oil crisis in the 1970s spurred on renewed interest in the production and utilization of higher alcohols as gasoline blends. Many companies discovered and patented their catalysts on ethanol synthesis and higher alcohol synthesis, such as Rh-based catalysts developed by Union Carbide and Sagami Chemical companies, Cu-ZnO-based catalysts developed by Süd-Chemie and MoS2-based catalysts developed by Dow Chemical.

After 1985, as the oil prices began to reduce, the interest in higher alcohol synthesis also declined. None of the higher alcohol synthesis catalysts developed to date have been adequately active and/or selective to propel industry for commercialization. As a consequence, no commercial higher alcohol synthesis plants are established today. Although there is no achieved commercialization, a few higher alcohol synthesis processes have advanced to the pilot-scale stage. Some examples are listed in Table 1.5.
Table 1.5  Current status of the selected processes for catalytic conversion of syngas to higher alcohols

<table>
<thead>
<tr>
<th>Process</th>
<th>Overall process scheme</th>
<th>Stage of development</th>
<th>Scale</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>IFP–Idemitsu</td>
<td>Reform natural gas to syngas; Pilot scale</td>
<td>Pilot scale</td>
<td>7000 bbl/y</td>
<td>Produced C&lt;sub&gt;1&lt;/sub&gt;–C&lt;sub&gt;7&lt;/sub&gt; linear alcohols; higher alcohols between 20 and 70%</td>
</tr>
<tr>
<td></td>
<td>Cu-Co-based modified FT synthesis catalysts; methanol distillation; extractive distillation with diethylene glycol (DEG); DEG recovery</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SEHT</td>
<td>Partial oxidation of natural gas to syngas; Pilot scale</td>
<td>Pilot scale</td>
<td>400 ton/d</td>
<td>Crude alcohol mixture contained 20% water; final water content &lt; 0.1%; blended (at 5%) to make premium gasoline.</td>
</tr>
<tr>
<td></td>
<td>Cu-Zn-based modified methanol synthesis catalysts; high pressure fixed-bed process; distillation of methanol and ethanol; water distillation; azeotropic distillation for C&lt;sub&gt;3+&lt;/sub&gt; alcohols.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lurgi–Octamix</td>
<td>Steam and autothermal natural gas reforming; Pilot plant</td>
<td>Pilot plant</td>
<td>2 ton/d</td>
<td>Process produced mixed alcohols containing 1–2 % water.</td>
</tr>
<tr>
<td></td>
<td>Cu-Zn-based modified methanol catalysts; low temperature, low pressure conversion to mixed alcohols; stabilizer column</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dow Chemical</td>
<td>MoS&lt;sub&gt;2&lt;/sub&gt;-based Syngas with sulfur converted to higher alcohols with nanosized improved MoS&lt;sub&gt;2&lt;/sub&gt;-based catalyst; 200–300 °C; 500–3000 psig.</td>
<td>Bench scale</td>
<td>Planned scale up to 500 gal/d</td>
<td>Higher alcohol yield of &gt; 0.4 g/(g cat. h)</td>
</tr>
<tr>
<td>Ecalene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
1.4.2 Reaction thermodynamics

The most favored thermodynamic product of syngas conversion is methane, and the important thermodynamic parameters for syngas conversion are summarized in Table 1.6.

Table 1.6 Selected thermodynamic data for syngas conversion reactions

<table>
<thead>
<tr>
<th>Process</th>
<th>Reaction</th>
<th>$\Delta G_{25^\circ C}$</th>
<th>$\Delta H_{25^\circ C}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol synthesis</td>
<td>CO + 2H₂ $\leftrightarrow$ CH₃OH</td>
<td>-25.06</td>
<td>-90.47</td>
</tr>
<tr>
<td>Ethanol synthesis</td>
<td>2CO + 4H₂ $\leftrightarrow$ C₂H₅OH + H₂O</td>
<td>-122.69</td>
<td>-256.09</td>
</tr>
<tr>
<td>Condensation/coupling</td>
<td>2CH₃OH $\leftrightarrow$ C₂H₅OH + H₂O</td>
<td>-71.64</td>
<td>-74.61</td>
</tr>
<tr>
<td>Methanation</td>
<td>CO + 3H₂ $\leftrightarrow$ CH₄ + H₂O</td>
<td>-141.85</td>
<td>-205.84</td>
</tr>
<tr>
<td>WGS reaction</td>
<td>CO + H₂O $\leftrightarrow$ CO₂ + H₂</td>
<td>-28.58</td>
<td>-41.09</td>
</tr>
<tr>
<td>Boudouard reaction</td>
<td>2CO $\leftrightarrow$ CO₂ + C</td>
<td>-120.02</td>
<td>-172.00</td>
</tr>
</tbody>
</table>

Alcohol synthesis from syngas can be described by the following stoichiometric Equation (1.1):

$$n\text{CO} + 2n\text{H}_2 \rightarrow C_n\text{H}_{2n+1}\text{OH} + (n-1)\text{H}_2\text{O} \quad n = 1, 2, 3...$$  \hspace{1cm} (1.1)

The hydrocarbons of alkane [Equation (1.2)] and alkene [Equation (1.3)] are formed by the Fischer–Tropsch reaction

$$n\text{CO} + (2n+1)\text{H}_2 \rightarrow C_n\text{H}_{2n+2} + n\text{H}_2\text{O} \quad n = 1, 2, 3...$$  \hspace{1cm} (1.2)

$$n\text{CO} + 2n\text{H}_2 \rightarrow C_n\text{H}_{2n} + n\text{H}_2\text{O} \quad n = 1, 2, 3...$$  \hspace{1cm} (1.3)

The side reactions, for example, the water–gas–shift (WGS) reaction [Equation (1.4)] and the Boudouard reaction [Equation (1.5)] may also happen during alcohol synthesis reactions.

$$\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$$  \hspace{1cm} (1.4)

$$2\text{CO} \leftrightarrow \text{C} + \text{CO}_2$$  \hspace{1cm} (1.5)
High pressure and low temperature will favor the formation of methanol, ethanol, and other oxygenated products because of the large reduction in moles and the high exothermicity of the syngas conversion reaction. Mawson et al. \textsuperscript{38} found that the equilibrium conversion of syngas to alcohols favors the formation of higher alcohols. The change of Gibbs free energy $\Delta G_{\text{rxn}}$ for methanol synthesis ($\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH}$) increases with temperature and is zero at approximately 137 °C; whereas for ethanol formation ($2\text{CO} + 4\text{H}_2 \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O}$), the change of Gibbs free energy $\Delta G_{\text{rxn}}$ also increases with temperature and is zero at approximately 280 °C. This is higher than the maximum operating temperature of most syngas conversion catalysts. \textsuperscript{12} Methane is the most favored species of conversion of syngas from a thermodynamic viewpoint as shown in Figure 1.4, \textsuperscript{12} and the selected catalysts must control or even suppress the formation of methane during higher alcohol synthesis reaction.
Zaman et al. \textsuperscript{37} compared the equilibrium mole fractions calculated as a function of temperature for the methanol synthesis reaction to those obtained for both the methanol synthesis and the ethanol synthesis reaction at $P = 3.0$ MPa with a $H_2/CO$ ratio of 2/1 (Figure 1.5). In these calculations, the formation of hydrocarbons was kinetically inhibited. In the case of the methanol synthesis (Figure 1.5a), the data illustrate that above 277 °C (550 K), the methanol mole fraction is low ($< 0.05$). In the case of both the methanol and ethanol synthesis (Figure 1.5b), no methanol is formed and the ethanol mole fraction is $< 0.05$ above 527 °C (800 K). Thus, the increase of higher alcohols selectivity often reported with the increase of temperature, which mostly results from the thermodynamics that decrease an equilibrium methanol yield with an increase of temperature. Since lower $H_2/CO$ ratio favor CO insertion and C–C chain growth, in order
to maximize higher alcohols formation, the H\textsubscript{2}/CO ratio should be close to the usage ratio, which is about 1.\textsuperscript{12, 37, 39, 40}

1.5 Catalysts system for higher alcohol synthesis

The heterogeneous catalysts used for ethanol and higher alcohol synthesis from syngas can be broadly classified into noble metals-based and non-noble metal-based catalysts.\textsuperscript{12, 30, 34, 39, 40} The major noble metal-based catalysts for the conversion of syngas to ethanol and other C\textsubscript{2+} oxygenates, usually contain Rh, Ru, and Re supported on various oxides, such as SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, CeO\textsubscript{2}, ZrO\textsubscript{2}, MgO, etc. The major non-noble metal-based catalysts for ethanol and higher alcohol synthesis from syngas are modified methanol catalysts, modified Mo-based catalysts, and modified Fischer–Tropsch synthesis catalysts. All these catalysts have been used for the synthesis of higher alcohols by at least two different pathways: (a) direct conversion of syngas to ethanol and higher alcohols, and (b) methanol homologation to ethanol. This literature review will only discuss the direct conversion of syngas to ethanol and higher alcohols over noble metal-based catalysts and non-noble metal based catalysts.

1.5.1 Rh-based catalysts

A wide range of noble metal-based catalysts have been used in the direct synthesis of ethanol and higher alcohols from syngas. Noble metals, such as Rh, Ru, and Re supported on various oxides, such as SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, TiO\textsubscript{2}, CeO\textsubscript{2}, ZrO\textsubscript{2}, and MgO, have been reported. Among them, Rh-supported catalysts have been studied extensively because of its production of C\textsubscript{2+} oxygenates with a high selectivity toward ethanol.
However, these noble catalysts are too expensive and seem unattractive for commercial application.

As early as 1975, the direct catalytic conversion of syngas to ethanol, higher alcohols and other oxygenate over Rh/SiO$_2$ catalysts promoted by metal ions, such as Fe, Mo, Mn, W, Th, and U in a stirred autoclave reactor were reported by the Union Carbide Company. Among them, a catalyst containing 2.5% Rh supported on SiO$_2$ and promoted by 0.05 wt.% Fe had the best catalytic performance. $^{36,41,42}$ The catalyst produced 49% methane, 2.8% methanol, 31.4% ethanol, and 9.1% acetic acid at T = 300 °C and P =1030 psig using syngas. However, the rates of methanol and ethanol production were about 50 g/L cat. h. Following this earlier work, several reports were published on the direct production of ethanol and C$_2$+ oxygenates from syngas by using a wide range of noble metal-based catalysts, including Rh, Ru, and Re supported on various oxides, such as SiO$_2$, Al$_2$O$_3$, CeO$_2$, ZrO$_2$, and MgO. $^{43-66}$ These studies aimed to investigate the effect of the nature of promoters and supports on the catalytic activity and selectivity for ethanol formation in a fixed-bed tubular reactor.

Holy et al. $^{44}$ reported an ethanol selectivity of about 30% at a CO conversion rate of about 6% at T = 278 °C, and P = 900 psig, using a H$_2$/CO =1 over Co-Fe-Rh/SiO$_2$ catalyst with a Co/Fe/Rh atomic ratio of 2.6/2.5/3.7. The reaction also produced a significant amount of methanol (25.3%) and propanol (24.9%).

Du et al. $^{49}$ investigated the promoter effect of rare earth oxides (REO), such as La$_2$O$_3$, CeO$_2$, Pr$_6$O$_{11}$, Nd$_2$O$_3$, and Sm$_2$O$_3$, on the catalytic performance of Rh/SiO$_2$ containing 2 wt.% Rh and 4.5 wt.% REO from syngas (H$_2$/CO = 1.69) in a fixed-bed reactor. The catalysts containing CeO$_2$ and Pr$_6$O$_{11}$ as promoters produced C$_2$ oxygenates
with a high selectivity (about 48%) toward ethanol at $T = 220 \, ^\circ\text{C}$ at atmospheric pressure. The authors explained that the additive promoters cover a part of the Rh metal, inhibiting the $\text{H}_2$ chemisorption activity of Rh and creating new active sites at the Rh-REO interface.\textsuperscript{12} During the catalyst pre-reduction, the $\text{H}_2$ chemisorbed on Rh particles spills over onto the promoter and partially reduces it, releasing a sub-oxide of the REO at the Rh-REO interface, which then wets the Rh particles through metal–metal bonding and oxide bridging and spreads out across the surface of Rh particles.\textsuperscript{12} The partially exposed cationic center or oxygen vacancy of the reduced REO acts as a Lewis acid center or an oxophilic center to coordinate or interact by charge–dipole interaction with the oxygen end of $\mu_2$-ligated CO adsorbed on the Rh active site for dissociation or insertion of CO to form $\text{C}_2\text{O}$-oxygenates.\textsuperscript{12}

Gronchi et al.\textsuperscript{51} studied the effect of Rh dispersion on $\text{V}_2\text{O}_5$ and ZrO$_2$ on the catalytic performance of syngas to ethanol at $220 \, ^\circ\text{C}$ and atmospheric pressure. The Rh loading (0.2–1.0 wt.%) on $\text{V}_2\text{O}_5$ and ZrO$_2$ support was used. They noticed that in the low-temperature range ($< 230 \, ^\circ\text{C}$), as the Rh particle size increases, the concentrations of active sites for CO insertion increases.\textsuperscript{12} Consequently, a high selectivity to ethanol rather than CO$_2$ is obtained. The 1wt.% Rh/$\text{V}_2\text{O}_5$ catalyst exhibited about 37% ethanol selectivity and a 4.5% CO conversion rate. Unfortunately, the reaction also produced undesirable C$_1$–C$_4$ hydrocarbons with high selectivity (> 50%).

Lin et al.\textsuperscript{52} have investigated the catalytic performance of Mn promoted 1% Rh/SiO$_2$ catalyst with a Rh/Mn weight ratio of 1 over syngas at $T = 310 \, ^\circ\text{C}$ at
P = 870 psig for about 1000 h on stream. The catalyst showed a high selectivity of 34.8% for ethanol, 30.7% for acetic acid, and 19.2% for acetaldehyde. However, the authors have not reported the CO conversion rate under the experimental conditions.

Burch et al. 53 investigated the direct ethanol synthesis from syngas over catalysts containing 2 wt.% Rh and 0–10 wt.% Fe$_2$O$_3$ supported on Al$_2$O$_3$ catalyst in a fixed-bed reactor at T = 270 °C at P = 145 psig. They found that the added Fe$_2$O$_3$ significantly inhibit CH$_4$ formation and increase the ethanol selectivity. 12 The catalyst composed of 2 wt.% Rh and 10 wt.% Fe demonstrated a maximum ethanol selectivity of about 50%. The authors remarked that the intimate interaction between metal and promoter results in an increased Rh-promoter interface, which accommodates chemisorbed CO that is carbon-bound to the Rh atom and oxygen-bound to the promoter ion. 12 Accordingly, this mode of CO adsorption is primary in the catalytic production of higher alcohols or oxygenates from syngas.

Ojeda et al. 57 studied the catalytic performance of Mn (0–3.2 wt.%) promoted 3 wt.% Rh/Al$_2$O$_3$ catalysts from syngas at T = 260 °C at P = 290 psig. The oxygenate selectivity was about 50%, and ethanol was the major oxygenate. The authors note that the amount of Mn promoter may partially block the Rh surface, and the addition of Mn decreased the relative surface carbon coverage over the Rh particles, thus enhancing the catalytic activity. The authors also note that the presence of oxidized Rh sites near the Rh-MnO interface, which favors the CO insertion reaction.

Haider et al. 60 investigated Fe-promotion of supported Rh catalysts for direct conversion of syngas to ethanol. They found that Rh/SiO$_2$ was ineffective for catalytic conversion of syngas to ethanol under the standard conditions while Rh/TiO$_2$ produced
some ethanol and oxygenates, with methane being the major undesirable hydrocarbon product. Fe promotion of Rh/SiO$_2$ and Rh/TiO$_2$ significantly improved the activity of the catalysts and their selectivity to ethanol and other oxygenates.

Gao et al. $^{61}$ investigated La and/or V promoted Rh/SiO$_2$ catalyst for higher alcohol synthesis from syngas. They found that La-V promoted Rh/SiO$_2$ catalyst exhibited higher activity and better selectivity towards ethanol formation compared with the La promoted or V promoted Rh/SiO$_2$ catalyst. The high performance of the La-V promoted Rh/SiO$_2$ catalyst seems to be due to a synergistic promoting effect of La and V, by modifying both chemisorption and catalytic properties.

Subramanian et al. $^{62}$ found that the La-V promoted Rh/SiO$_2$ catalyst was the most active/selective catalyst for higher alcohol synthesis from syngas compared with non-promoted Rh/SiO$_2$, La promoted Rh/SiO$_2$, and V promoted Rh/SiO$_2$. They found that the formation of undesired methane can be suppressed under conditions of relatively high temperature, low pressure, and low H$_2$/CO ratio. For the most active La-V promoted Rh/SiO$_2$ catalyst, the highest ethanol selectivity achieved was 51.8 % under the reaction conditions at $T = 270$ °C and at $P = 14$ bar using H$_2$/CO = 2.

Mo et al. $^{63}$ studied non-promoted, single, double and triple promoted Rh/SiO$_2$ catalysts containing different combinations of Fe, La, and V as promoters for higher alcohol synthesis from syngas. They found that the addition of promoters hindered the reduction of Rh and changed CO and H$_2$ adsorption behaviors on the catalyst surface. The addition of 0.8 wt.% Fe, 2.6 wt.% La, and 1.5 wt.% V to 1.5 wt.% Rh/SiO$_2$ resulted in the highest selectivity to ethanol (34.6%) and a moderate activity, comparing to other promoted catalysts at the reaction conditions of $T = 230$ °C and $P = 1.8$ atm. Based on the
synergetic effects of multiple promoters, they suggested that the key to the effective catalyst design for ethanol synthesis from syngas is a balance among CO dissociation, hydrogenation, and CO insertion.

Mei et al. \textsuperscript{64} investigated the reaction kinetics of ethanol synthesis from syngas over SiO\textsubscript{2}-supported Rh/Mn alloy catalysts by combining experimental measurements with first-principles-based kinetics modeling. They found that a Mn promoter can exist in a binary alloy with Rh and play a critical role in lowering the CO insertion reaction [CO + CH\textsubscript{x} (x = 1–3)] barriers. This improves the selectivity toward ethanol and other C\textsubscript{2+} oxygenates, and the barrier toward methane formation is unaffected. This postulation of supported Rh/Mn alloy nanoparticles being the active phase is supported by their experimental characterization using X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and X-ray diffraction (XRD) of used Rh/Mn/SiO\textsubscript{2} catalysts. First-principles density functional theory (DFT) calculations further confirmed that the binary Rh/Mn alloy is thermodynamically more stable than the mixed metal/metal oxides under the reducing reaction condition. The reaction kinetics of higher alcohol synthesis from syngas on the three-dimensional Rh/Mn nanoparticles under experimental operating conditions were studied by using kinetic Monte Carlo (KMC) simulations. The simulated reaction kinetics is in qualitative agreement with experimental observations. They also used DFT calculations to study the effects of various promoters (M = Ir, Ga, V, Ti, Sc, Ca, and Li) on the CO insertion reaction over Rh/M alloy nanoparticles, and they found that alloying the promoters with the electronegativity difference (\Delta \chi) between the promoter (M) and Rh being 0.7 is the most
effective in lowering the barriers of CO insertion reaction, which results in higher selectivity to ethanol.

Prieto et al. investigated the role of electronic properties of oxide promoters in Rh-catalyzed selective synthesis of oxygenates from synthesis gas. They prepared a series of model Rh/M@Al₂O₃ catalysts composing a common mesoporous γ-Al₂O₃ carrier having its surface covered by a monolayer of a MOₓ promoter (M = Fe, V, Nb, Ta, Ti, Y, Pr, Nd, and Sm) so as to shed light on the promotion effects during the higher alcohol synthesis from syngas. The series of supported transition metal and lanthanide oxide promoters (MOₓ) demonstrated a wide range of electron-withdrawing/electron-donating capacity (Lewis acidity/basicity) as ascertained by Ultraviolet-visible (UV-vis) spectroscopy coupled with alizarine adsorption. Interestingly, they observed that both the specific catalytic activity and the selectivity pattern (as described by the defined selectivity parameter (Φ)) were correlated with the electronic properties of the MOₓ oxidic promoters. Therefore, the electron-donating oxides promoted CO dissociation, leading to catalysts possessing higher activity and hydrocarbons selectivity, and the electron-donating promoters favored associative CO insertion events, producing more oxygenated products. Low-temperature and at-work CO-FTIR (Carbon monoxide–Fourier Transform Infrared Spectroscopy) experiments suggested that the high activity and hydrocarbon selectivity showed by catalysts promoted by more electron-withdrawing (acidic) oxide promoters (e.g., TaOₓ) were related to a higher proportion of bridged Rh₂(CO)₆ adsorption sites and to a higher electron density (i.e., a higher electron back-donation ability) of the Rh⁰ surface sites, both factors promoting CO dissociation events. In contrast, linear CO adsorption on Rh⁰ sites exhibiting electron back-donation in
catalysts promoted by electron-donating (basic) oxides (e.g., PrOₓ, SmOₓ) was likely related to associative CO activation and thus to the selective formation of oxygenates.

Schwartz et al. 66 studied the effect of Li and Mn promoters on Rh/TiO₂ catalysts by Fourier Transform Infrared Spectroscopy (FTIR) and Extended X-ray Absorption Fine Structure (EXAFS) for higher alcohol synthesis from syngas. They correlated the structural characteristics with activity and selectivity during higher alcohol synthesis from syngas over unpromoted Rh/TiO₂ and three promoted Rh catalysts: Li promoted Rh/TiO₂, Mn promoted Rh/TiO₂, and Li-Mn promoted Rh/TiO₂. They found that the presence of a promoter slightly decreases the Rh cluster size. However, no evidence was found for an electronic effect induced by the presence of Li and Mn. Higher turnover frequency (TOF) were found for the promoted catalysts, which also showed the lower dispersion. The Li promoter introduces a weakened CO adsorption site that appears to increase the selectivity to C₂⁺ oxygenates. The selectivity to C₂⁺ oxygenates varies inversely with the reducibility of Rh metal, so the lower the Rh reducibility, the higher the selectivity.

1.5.2 Modified methanol synthesis catalysts

The modified methanol synthesis catalysts can be divided into two groups: 34, 67–72 high pressure/high temperature Alkali-promoted Cu/ZnO/Cr₂O₃ catalysts (Process conditions: T = 300–425 °C, P = 12.5–30 MPa; Major product: branched primary alcohols), and low pressure/low temperature Alkali-promoted Cu/ZnO(Al₂O₃) catalysts (Process conditions: T = 275–310 °C, P = 5–10 MPa; Major product: primary alcohols). 34
1.5.2.1 Alkali/ZnO/Cr₂O₃ catalysts

For non-alkalized catalysts containing Cu-Zn-Cr oxides, higher alcohol synthesis yields were optimized for low Cr levels (15–21 wt.% Cr). Cr₂O₃ does not provide an active catalytic site but it is beneficial in small amounts because it acts as a structural promoter that increases the surface area of the catalyst and helps inhibit Cu sintering. Methanol synthesis is fast compared to higher alcohol synthesis over a 3% K₂O/ZnCr catalyst, but it is still equilibrium limited, even at high space velocities. CO₂-rich feeds have been shown to inhibit higher alcohol synthesis; a 3-fold decrease in C₂+ alcohol production was measured for higher alcohol synthesis at 400 °C with 6% CO₂. The production of primary alcohols was maximized over these alkali metal promoted high-temperature methanol synthesis catalysts with a CO₂-free feed with H₂/CO = 1 and CO conversion rate of ~5–20%. ³⁴

1.5.2.2 Alkali/Cu/ZnO(Al₂O₃) catalysts

Many of the early commercial processes for higher alcohol synthesis were based on alkali-promoted, low temperature methanol synthesis catalysts. ³⁴ Lurgi developed the Octamix process in collaboration with Süd Chemie, who provided the catalyst for the process. The Octamix catalyst contained 25–40 wt.% CuO, 10–18 wt.% Al₂O₃, 30–45 wt.% ZnO, and 1.7–2.5 wt.% K₂O with a Cu:Zn ratio of 0.4–1.9 with 3–18 wt.% of a variety of oxidic promoters (Cr, Ce, La, Mn, or Th). With a starting gas composition of 25–30% CO, 0–8% N₂, 0–5% CO₂, 0–5% CH₄, and a balance of H₂; CO conversions were between 21–29% with 29–45% selectivity for C₂+ alcohols and 17–25% CO₂ selectivity at T = 250–400 °C, P = 10 MPa, and a gas hourly space velocity (GHSV) of 1000–10,000 h⁻¹. Methanol is the most abundant oxygenated product (~80%).
1.5.3 Mo-based catalysts (Mo$_2$C, MoS$_2$)

Molybdenum (Mo) has relatively low activity for syngas conversion and forms primarily hydrocarbons. $^{37}$ Most studies of Mo catalysts have focused on compounds in which Mo is bound to the ligands C or S. In most cases the Mo-based catalyst is promoted with other elements, especially alkali metals and Group VIII metals.

1.5.3.1 Mo$_2$C-based catalysts

Levy et al. $^{73}$ was the first to report that Group VIB metal carbides have unique physical and chemical properties, which are similar to those of the Pt Group noble metals. Since then, metal carbides as a new catalytic material have attracted considerable attention. $^{74}$ Molybdenum carbide (Mo$_2$C) has long been recognized as a quasi-platinum catalyst with unique properties. Furthermore, Mo$_2$C also has the advantages of being inexpensive, sulfur tolerant, and carbon deposition resistant.

Mo$_2$C is known to be active for syngas conversion, forming light hydrocarbons at atmospheric pressure. $^{75}$ At elevated pressure, alkali metal oxide-promoted Mo$_2$C improves the selectivity to alcohols, especially methanol and ethanol.$^{37, 76-80}$ Woo et al. $^{76}$ and Xiang et al. $^{77}$ reported that unsupported Mo$_2$C produced CO$_2$ and hydrocarbons from syngas. The addition of K to the Mo$_2$C decreased CO conversion rate and increased the selectivity to alcohols, especially methanol and ethanol. Accordingly to Woo et al. $^{76}$, a loading of K/Mo = 0.2 gave maximum C$_{2+}$ alcohol selectivity. Xiang et al. $^{78}$ reported similar results. Similar data have recently been reported for the Rb-promoted Mo$_2$C catalyst supported on basic MgO. $^{79}$ The authors reported a total alcohol selectivity of 61.5 C atom % (CO$_2$-free analysis) over a 5 wt.% Mo$_2$C/MgO catalyst promoted with
15% Rb$_2$O$_3$, whereas without the Rb, the selectivity was 22% at $T = 300 \, ^\circ C$, $P = 3 \, MPa$, and using $H_2/CO = 1$. \textsuperscript{79}

Several studies evaluated the effect of addition of Group VIII metals to Mo$_2$C for syngas conversion. Xiang et al. \textsuperscript{80} compared the addition of Fe, Co, or Ni to unsupported K-Mo$_2$C catalysts, at $T = 300 \, ^\circ C$, $P = 8 \, MPa$, $H_2/CO = 1$, and a GHSV = 2000 h$^{-1}$. The selectivity to hydrocarbons (on a CO$_2$-free basis) was $> 47\%$ in each case, and the hydrocarbon selectivity decreased in the order Fe $>$ Co $>$ Ni. The space time yield (STY) of the higher alcohols was increased significantly by the addition of Ni to the K-Mo$_2$C, but decreased with the addition of Fe. \textsuperscript{80} The amount of Group VIII metal added to the K-Mo$_2$C also had an impact on the product distribution and in most cases, there was an optimum content of the metal relative to the Mo$_2$C. Xiang et al. \textsuperscript{77,81} reported that for the unsupported K-Ni-Mo$_2$C and K-Co-Mo$_2$C catalysts, a maximum in alcohol space time yield (STY) occurred at a Ni/Mo or Co/Mo mole ratio of 0.125. Both catalysts with Ni or Co added showed a lower alcohol selectivity than the K-Mo$_2$C catalyst. For the addition Fe to the K-Mo$_2$C, both the CO conversion and the selectivity to alcohols increased with the Fe/Mo ratio. \textsuperscript{82} The alcohol product distribution obtained over the K-M-Mo$_2$C catalysts ($M =$ Fe, Co, Ni) typically includes C$_1$–C$_6$ alcohols distributed according to the Anderson–Schulz–Flory (ASF) distribution. Thus, methanol is the most abundant alcohol in the product. \textsuperscript{81,82} Alcohols up to a carbon number of six are observed and the hydrocarbon product distribution also follows the ASF distribution. \textsuperscript{82}

Wu et al. \textsuperscript{83} reported Mo$_2$C supported on active carbon and promoted by K$_2$CO$_3$ for higher alcohol synthesis from syngas. They found that at optimal conditions, the activity and selectivity to alcohols over supported Mo$_2$C are significantly higher
compared to the bulk carbide. The CO conversion reaches a maximum when approximately 20 wt.% Mo$_2$C is loaded on active carbon. The selectivity to higher alcohols increases when increasing Mo$_2$C loading on active carbon. The effect of Mo$_2$C loading on the alcohol selectivity at a fixed K/Mo molar ratio of 0.14 could be related to the amount of K$_2$CO$_3$ actually on the active Mo$_2$C phase and the size, structure and composition of the supported carbide clusters. Un-promoted active carbon supported Mo$_2$C exhibits a high activity for CO conversion with hydrocarbons as the dominant products. They found that the K$_2$CO$_3$ promoter plays an essential role in directing the selectivity to alcohols rather than to hydrocarbons. The optimum selectivity toward higher alcohols and total alcohols was obtained at a K/Mo molar ratio of 0.21 over the active carbon supported Mo$_2$C (20 wt.%). 83

1.5.3.2 MoS$_2$-based catalysts

Molybdenum sulfide (MoS$_2$) based catalysts show good hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) performance, and are widely used in the petroleum industry. In 1984, Dow Chemical and the Union Carbide Corporation independently patented alkaline-doped MoS$_2$ (ADM) catalysts for higher alcohol synthesis from syngas. Work has been devoted to these types of catalysts by researchers because of their excellent sulfur tolerance. 84–88 ADM catalysts have the unique properties of being extremely resistant to sulfur poisoning. The sulfur tolerance of ADM catalysts will reduce the risk of sulfur poisons and will probably reduce the expensive cost of deeply removing sulfur compounds from the feed gas stream.

The role of alkali metal has two aspects in higher alcohol synthesis from syngas. First, the alkali metal can suppress the hydrogenation activity of the Mo active site.
Second, the alkali metal can provide additional active sites for the formation of higher alcohols. Cesium (Cs) is the most effective alkali promoter, although the K promoter has been extensively studied. These catalysts have 75–90% selectivity to higher alcohols from syngas with a H₂/CO = 1 and ~ 10% CO conversion efficiency. Both higher alcohols and hydrocarbons formed over MoS₂ catalysts follow similar ASF distribution. Toyoda et al. studied higher alcohol synthesis over Al₂O₃-supported MoS₂-based catalysts. They found that the addition of K improved the activity for higher alcohol synthesis because of the increasing proportion of selectivity for higher alcohols to the ratio of K/Mo at a maximum of higher alcohol selectivity with a K/Mo ratio of 0.6. The addition of K could favor the associative CO adsorption by the proposed formation pathway for the hydrogenation of CO. The higher alcohol selectivity and the chain growth probability of alcohols with potassium carbonate were higher than those with nitrate.

Morrill et al. studied the Mg/Al hydrotalcite-derived mixed-metal oxide (MMO) supported potassium promoted molybdenum sulfide (MoS₂) catalyst for higher alcohol synthesis from syngas at T = 310 °C and P = 1500 psig. The catalyst was shown to be more selective for C₂–C₄ linear alcohols than for methanol and demonstrated good alcohol to hydrocarbon selectivity. Morrill et al. found that alcohol selectivities varied greatly when the Mo is loaded on the support at 5 wt.% compared with 15 wt.% Mo samples, all with a Mo/K atomic ratio of 1/1. The most striking difference between these two catalysts is the comparatively low methanol and high C₃+ alcohol selectivities and productivities achieved with the 5% Mo catalyst, which was shown to be associated with ethanol dehydration and hydrogenation over residual acid sites on this catalyst with lower
K content. Preparing a series of catalysts with common composition (5% Mo and 3% K supported on MMO) in different manners all yield similar catalytic selectivities, thus indicating that selectivity is primarily controlled by the MMO-to-Mo ratio rather than the synthesis method. When the Mo loading is the same, catalytic higher alcohol productivity shows some correlation to the degree of stacking of the MoS$_2$ layers, as analyzed by X-ray diffraction (XRD) and scanning transmission electron microscopy (STEM). They also proposed that higher–alcohol–forming pathways occurred via CO insertion pathways or via coupling of adsorbed reaction intermediates at or near MoS$_2$ domains. No evidence was observed for significant alcohol-coupling pathways by adsorption of alcohols over downstream, bare MMO supports.  

1.5.4 Modified Cu-based Fischer–Tropsch catalysts (Cu-Co, Cu-Fe)

1.5.4.1 Cu-Co based catalysts

Because of the high selectivity to total alcohol and higher alcohols (C$_2$+OH), modified Fischer–Tropsch catalysts developed by the Institute Francais du Pétrol (IFP) have attracted much attention.  

The IFP catalyst was a homogeneous mixed-oxide formulation containing Cu and Co on an alumina support as the active components for higher alcohol synthesis, which was modified with Zn and alkali metals. The catalysts were designed for higher alcohol synthesis process conditions similar to low temperature methanol synthesis process conditions (P = 5–15 MPa, T = 220–350 °C, H$_2$/CO = 0.5–4 with CO$_2$ also as a reactant). Patented IFP catalyst formulations have the following composition, on an element basis: 10–50 wt.% Cu, 5–25 wt.% Co, 5–30 wt.% Al; 10–70 wt.% Zn; alkali/Al = 0–0.2; Zn/Al = 0.4–2.0; Co/Al = 0.2–0.75; Cu/Al = 0.1–3.0. The homogeneity of the catalyst correlates with good catalytic performance.
The IFP process yields mainly saturated, straight-chained terminal alcohols that follow an Anderson–Schultz–Flory (ASF) distribution for chain growth. At optimal conditions, carbon conversion rate of CO and CO$_2$ is between 5 and 30% and produces a liquid product containing 30–50% higher alcohols with hydrocarbons being the primary byproducts. However, the lack of long-term stability and low activity of these catalysts hinders the commercial application of this catalyst. Catalyst lifetimes have been quoted as long as 8000 h at the pilot-scale with little deactivation, caused mainly by coke formation and sintering that decreases the homogeneity of the catalyst.

Subramanian et al. investigate the Cu-Co nanoparticles catalysts for higher alcohol synthesis from syngas. They found that mixed Cu-Co nanoparticles are more selective to ethanol and higher oxygenates than that of Co core–Cu shell catalysts, whereas the latter are more active but not selective to ethanol. The mixed Cu-Co nanoparticle catalysts are not active because hydrocarbon formation, which typically accompanies high catalytic activity, is suppressed. To get high yield of ethanol, the catalyst design should properly balance between CO dissociation and CO insertion for the higher alcohol synthesis from syngas.

Wang et al. studied the structure and catalytic performance of higher alcohol synthesis from syngas over Cu-Co/$\gamma$-Al$_2$O$_3$ catalysts. The catalysts were prepared by incipient co-impregnation and were characterized by a combination of various techniques including in situ X-ray Diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), Temperature Programmed Reduction (TPR), X-ray Absorption Near Edge Structure / Extended X-ray Absorption Fine Structure (XANES/EXAFS), in situ magnetic method, and Transmission Electron Microscopy (TEM). They found that a much higher dispersion
of Cu than Co on $\gamma$-Al$_2$O$_3$ and a stronger interaction between cobalt and copper oxide particles, leading to the formation of mixed Cu-Co oxides in the calcined catalysts. Co oxide reduction was significantly enhanced in the presence of Cu. They found that the presence of Cu increased the selectivity to alcohols by an order of magnitude and decreased the overall CO conversion. The formation of bimetallic Cu-Co particles was found in the reduced catalysts and enrichment of the surface of bimetallic particles with Cu. These bimetallic Cu-Co particles could be involved in the higher alcohol synthesis over the supported Cu-Co catalysts.

Xiang et al. $^{98,99}$ studied long-chain higher alcohol synthesis from syngas over Co-Cu-Mn nanosized core-shell (Co-rich core structure and Cu-dominated CoCuMn mixed shell) particles prepared by using co-precipitation of metal salts into oxalate precursors and a subsequent thermal decomposition method. They found that using stoichiometric CO/H$_2$ feeds, the selectivities to 1-alcohols or combined 1-alcohols/1-alkanes were usually higher than 60% and occasionally as high as 95%. The Anderson–Schulz–Flory (ASF) chain growth probabilities for these products are higher than 0.6, but usually below 0.9 so as to optimize the C$_8$–C$_{14}$ slate as feedstock for plasticizers, lubricants, or detergents.

1.5.4.2 Cu-Fe based catalysts

Compared with Cu-Co based catalysts, Cu-Fe based catalysts show higher activity and C$_2$+OH selectivity. $^{100}$ In addition, Cu-Fe based catalysts also exhibit higher WGS activity, which makes them suitable for hydrogen-lean and CO$_2$ containing syngas derived from coal or biomass. $^{101}$ Studies on Cu-Fe based catalysts have increased in recent years. A series of CuFeMnZr catalysts developed by Sun’s Group showed > 50%
total alcohol selectivity and > 50% C$_2$OH selectivity. In a 3000 h stability test, no significant decrease in activity or selectivity was observed. In addition, their CuFeMnZr catalysts were successfully scaled-up and have passed the single tube reactor test.

Bao et al. studied higher alcohol synthesis from syngas over Cu-Fe composite oxides. The Cu-Fe composite oxides were prepared by co-precipitation methods. They found that the selectivity to C$_2$OH and C$_6$OH alcohol distribution was very high while the methane product fraction in the hydrocarbon distribution was rather low, displaying a promising potential in higher alcohol synthesis from syngas. They observed that the distribution of alcohols and hydrocarbons approximately obeyed Anderson–Schulz–Flory distribution with similar chain growth probability, indicating alcohols and hydrocarbons derived from the same intermediates. Higher reaction temperature accelerated the water–gas–shift (WGS) reaction and led to lower total alcohol selectivity. Gas hourly space velocity (GHSV) had great effect on catalytic performance and higher GHSV increased the total alcohol selectivity, indicating there existed a visible dehydration reaction of alcohols into hydrocarbons.

Xiao et al. reported Cu-Fe bimetallic nanoparticles had good alcohol selectivity and very high C$_6$OH in alcohol distribution, suggesting that Cu-Fe bimetallic nanoparticles are promising catalyst candidates for direct C$_6$OH synthesis from syngas. Cu and Fe species have contact with each other through forms of Cu-Fe alloy, CuFe$_2$O$_4$ and Cu(Fe)–CuFe$_2$O$_4$ in fresh Cu-Fe, while the forms Cu-Fe$_3$O$_4$ and Cu-FeC$_x$ are found in activated samples. As Cu–FeC$_x$ center benefits alcohol formation, Cu-Fe showed higher total alcohol selectivity than Fe or physical mixture of Cu and Fe. In addition, they
observed that total alcohol selectivity is more affected by Cu–FeCₓ synergism, while C₂₊OH and C₆₊OH selectivity was more affected by the nature of FeCₓ active sites.

Gao et al. 107 reported higher alcohol synthesis from syngas over CuFe-based catalysts derived from layered double hydroxides. The uniform and highly dispersed CuFe-based catalysts were prepared by a calcination-reduction process of CuFeMg-layered double hydroxides (LDHs) precursor, which exhibits good activity and selectivity towards higher alcohol synthesis from syngas. They observed that the sample of S₂-CuFeMg-Cat exhibited rather high CO conversion (56.89%), high selectivity towards higher alcohols (49.07%) as well as the total alcohol yield (0.28 g mL⁻¹(cat.) h⁻¹), which is better than that of the Cu-Fe based catalyst prepared by the co-precipitation method. They attributed the high catalytic performance to two factors. First, a homogeneous and high distribution of Cu and Fe active sites which provides more unsaturated coordination centers for H₂ and CO adsorption. Second, a strong synergistic effect between the Fe and Cu species contributes to the enhancement of selectivity towards alcohols.

Ding et al. 108 investigated the Mn promoter effect on Cu-Fe catalyst for higher alcohol synthesis from syngas. They found that the addition of Mn into the co-precipitated Fe-Cu catalysts had significant influence on the microstructure and the performance for higher alcohol synthesis. Adding Mn facilitated the formation of Fe–Mn–O solid solution and promoted the dispersion of both the Fe and Cu species, resulting in the increase of Brunauer–Emmett–Teller (BET) surface area and an increase in the active sites for CO hydrogenation. The increase in Mn content promoted the catalytic activity for higher alcohol synthesis and improved the selectivities of C₂₊OH and hydrocarbons, which may be attributed to the enhancement of synergistic effect.
between the Fe and Cu species in higher Mn concentration. The optimum temperature and pressure for the production of higher alcohols over the Mn-modified Cu-Fe based catalyst were determined as $T = 270 \, ^\circ\text{C}$ and $P = 6.0 \, \text{MPa}$.

1.6 Reaction mechanism for higher alcohol synthesis from synthesis gas

1.6.1 Rh-based catalysts

The reaction mechanism of ethanol formation over Rh-based catalysts includes adsorption of CO, which is carbon-bound to the Rh atom and oxygen-bound to a promoter ion.\textsuperscript{12,53,55} The adsorbed CO is then hydrogenated to form an adsorbed $-$CH$_x$– species, which is then inserted into adsorbed CO. The geometrical structure of the active site has been proposed to be $(\text{Rh}_x \text{Rh}_y^+) \text{O} \text{M}^+$, in which a part of Rh is formed as Rh$^+$ and the promoter ion (M$^+$) is in intimate contact with these Rh species. Figure 1.6 shows the hydrogenation of the adsorbed species results in the production of ethanol.\textsuperscript{12}

![Figure 1.6](image)

Figure 1.6 The simplified mechanism for the conversion of syngas to ethanol over Rh-based catalysts\textsuperscript{12}

Another mechanism for the synthesis of ethanol over Rh-based catalysts promoted by Mn is an acetate mechanism (formation of acetaldehyde followed by reduction).\textsuperscript{12,55} The formation of ethanol is proposed by the direct hydrogenation of the tilt-adsorbed CO molecules, followed by CH$_2$ insertion into the surface CH$_2$–O species to form an
adsorbed (ethylene oxide-type) intermediate. Subsequent hydrogenation of the CH$_2$–O intermediate species forms ethanol. On the other hand, acetaldehyde is formed through CO insertion into the surface CH$_3$–Rh species followed by hydrogenation. The promoters play an important role in stabilizing the intermediate of the surface acetyl species. Based on these mechanisms, it appears that tailoring Rh metal and a promoter ion to achieve a better Rh–promoter ion interaction is the key to increase ethanol selectivity by the insertion of adsorbed –CH$_2$– species rather than acetate formation.

Choi et al. used density functional theory (DFT) calculations and microkinetic modeling to study C$_2$H$_5$OH synthesis from syngas on Rh (111). The results showed that the main products involved in this process are CH$_4$, CH$_3$OH, and C$_2$H$_5$OH, where the ethanol productivity is low and Rh (111) is highly selective to methane rather than ethanol or methanol. The rate-limiting step of the overall reaction is the hydrogenation of CO to formyl species (HCO). The strong Rh–CO interaction is an obstacle to CO hydrogenation and therefore slows down the overall reaction; however, its high affinity to methyl (CH$_3$), oxygen (O), and acetyl species (CH$_3$CO) helps with the C–O bond cleavage of the methoxy species (CH$_3$O) and makes direct ethanol synthesis occur via CO insertion. The productivity and selectivity for C$_2$H$_5$OH are only controlled by CH$_4$ formation and C–C bond formation between CH$_3$ and CO. The results showed that to achieve the high C$_2$H$_5$OH productivity and selectivity, Rh has to get help from promoters and/or supports to suppress or minimize CH$_4$ production and/or boost chain growth from C$_1$ oxygenates to C$_2$ oxygenates.
1.6.2 Mo2C-based catalysts

It is proposed that the dual site on Mo2C based catalysts involve two types of Mo species, the low valence Mo (Mo-I, Mo\((0-2)\)) and the high valence Mo (Mo-II, Mo\((4-5)\)) species, as shown in Figure 1.7.\(^{101,102}\) The Mo-I site species serves the active site for CO dissociation, hydrogenation and chain growth to form surface alkyl species, while the Mo-II species serves the site for CO associative insertion and alcohol synthesis. The increase of the concentration of the Mo-II species would result in the increase of the total alcohol selectivity. The decrease of the Mo-I species would result in the decrease of chain propagation ability and lead to a lower selectivity to higher alcohols. Therefore, it is important to balance these two species in order to obtain a high selectivity of both total alcohols and higher alcohols (C\(_2\)-OH).\(^ {102}\)

![Figure 1.7](image)

**Figure 1.7** The reaction mechanism and network of higher alcohol synthesis from syngas over Mo2C-based catalysts.\(^ {102}\)

1.6.3 MoS\(_2\)-based catalysts

Alkali-doped MoS\(_2\)-based (ADM) catalysts produce mainly C\(_1\)–C\(_5\) linear primary alcohols, and the alcohols obey the ASF distribution, suggesting the sequential addition
of the monomers. However, the chain growth on ADM catalysts proceeds over CO insertion rather than methylene (CH₂) insertion. The reaction mechanism and reaction network of higher alcohol synthesis from syngas over M-KMoSₓ catalysts is presented in Figure 1.8. In general, at least two kinds of transition metal promoters exist simultaneously in ADM-based catalysts, the transition metal sulfide (MSₓ, M = Fe, Co, Ni) and the Mo containing mixed sulfide (M-KMoSₓ). The MSₓ site is active for the dissociation of CO and H₂ for the chain initiation, while M-KMoSₓ is the site for CO insertion, chain growth and alcohol formation. The synergetic effect of the dual site (MSₓ-M-KMoSₓ) increases the alcohol selectivity, and also enhances the chain growth ability. Furthermore, activated H* species on MSₓ that spillover onto M-KMoSₓ can improve the catalytic activity.

The formation of the M-KMoSₓ active site on the promoter M increases the alcohol selectivity of ADM-based catalysts. Additionally, the selectivity to higher alcohols also increases with the proper addition of promoter M because of the better CO
insertion and chain growth activities of M-KMoS\(_x\). However, the excess of M would result in the excessive MS\(_x\) sites existed on the surface, and the selectivity to hydrocarbons would increase due to the hydrogenation activity of MS\(_x\) sites, leading to the decrease of alcohol selectivity.\(^{102}\)

![Diagram of CO insertion mechanism on Cu-modified Fischer–Tropsch catalysts](image)

**Figure 1.9** CO insertion mechanism on Cu-modified Fischer–Tropsch catalysts\(^{102}\)

### 1.6.4 Modified Cu-based catalysts (Cu-Co, Cu-Fe)

The CO insertion mechanism for higher alcohol synthesis proposed by Xu et al.\(^{34}\) is widely accepted for Cu-modified Fischer–Tropsch catalysts, as shown in Figure 1.9. In the CO insertion mechanism, higher alcohol synthesis is regarded as a combination of
Fischer–Tropsch synthesis (FTS) and methanol synthesis, or as a process between FTS and methanol synthesis. The chain dissociation \( (k_d) \), chain initiation \( (k_I) \), and chain propagation \( (k_p) \) proceed similarly to the Fischer–Tropsch reaction to form surface alkyl species \( (C_nH_z^*) \), and the termination reaction of the alkyl species determines the products formation. The termination by CO insertion \( (k_{CO}) \) forms alcohols through surface acyl species \( (C_nH_2CO^*) \) followed by hydrogenation \( (k_H') \), while the termination by dehydrogenation or hydrogenation \( (k_H) \) forms olefins and paraffins, respectively. Thus the terminal alcohol formation competes with the hydrocarbon formation. The CO insertion mechanism elucidates why Cu-modified Fischer–Tropsch catalysts mainly produced linear 1-alcohols and the alcohols obey the ASF distribution with a similar chain growth probability as for hydrocarbons.\(^{34,102}\)

The CO insertion mechanism provides the reaction routes of the surface species. However, the specific structure of the dual site on Cu-modified Fischer–Tropsch catalysts is not clear. The Cu–M (M = Co, Fe etc.) center is the dual site for higher alcohol formation was proposed by Xu et al.\(^{34}\) On the Cu–M dual site, CO is dissociated on the Fischer–Tropsch element (Fe, Co etc.) and hydrogenated to form a methylene species, which initiates chain growth to generate a surface alkyl species, while CO molecularly adsorbs on Cu and inserts into the alkyl-metal bond to oxygenate the carbon chain. As presented in Figure 1.10,\(^ {102}\) either the molecularly adsorbed CO on Cu surface migrates to the surface of the Fischer–Tropsch element followed by CO insertion into the C–M bond, or the surface alkyl group on the Fischer–Tropsch element surface migrates to the Cu surface followed by CO insertion to form surface acyl species. Hydrogenation of the acyl groups yields alcohols. Both reaction routes require the synergism between the Cu
active site and Fischer–Tropsch elements active site. The loss of this synergism would decrease alcohol selectivity. 102

Figure 1.10 The reaction mechanism and network of higher alcohol synthesis from syngas over modified Cu-M based catalysts 102

1.7 Three-dimensionally ordered macroporous (3DOM) catalysts

Recently, 3DOM materials has been attractive because of their applications in catalysis, photonic crystal, and separation. 110–113 Sadakane et al. 114 reported a facile one-pot procedure to prepare 3DOM perovskite-type mixed metal oxide, La$_{1-x}$Sr$_x$FeO$_3$ ($x = 0–0.4$), which does not need any alkoxide precursor preparation. The strategy is to use an ethylene glycol (EG) solution of metal nitrate salts, which converts to a mixed metal glyoxylate salt by an in situ nitrate oxidation at low temperature before burning the template. Further calcination converts the glyoxylate salt to mixed metal oxide and removes the polymer template, resulting in the desired 3DOM materials. 114
Sadakane et al.\textsuperscript{115} reported a facile method to synthesize 3DOM alumina, iron oxide, manganese oxide, chromium oxide, and their mixed-metal oxides. An ethylene glycol (EG)–methanol mixed solution of metal nitrates was infiltrated into the void of the colloidal crystal template of a monodispersed poly(methyl methacrylate) (PMMA) sphere. Heating the initiated nitrate oxidation of the EG to yield metal glyoxylate salt. Further heating converted the glyoxylate salt to metal oxide and decomposed PMMA which produced the desired 3DOM metal oxides. There are two important parameters of this method that were classified in order to produce the desired 3DOM structure in high yield: (1) the nitrate oxidation temperature should be lower than the glass transition temperature of the PMMA, and (2) the heat produced by oxidative decomposition of the
PMMA should effectively be removed. The ordered (“inverse opals”) structures synthesized by using this method consist of a skeleton surrounding uniform close-packed macropores (Figure 1.11, insets).

The macropores are interconnected through windows which are formed as a result of the contact between the template spheres prior to infiltration of the precursor solution. Furthermore, the 3DOM materials have high porosity (theoretically ca. 74%). Connected macropores with high porosity can permit facile transport of guest molecules and particles in potential catalysis.

1.8 Research gap

Based on the literature review, the research gaps in the synthesis of higher alcohols from synthesis gas are identified as follows: there is no open literature on the 3DOM Cu-Fe catalysts for higher alcohol synthesis from syngas; the nature of the active site of Cu-Fe catalysts for higher alcohol synthesis from syngas is not thoroughly understood; the reaction mechanism for higher alcohol synthesis from syngas is not clear.

1.9 Research objectives

The primary objective of the research is to develop a catalyst system that is capable of producing higher alcohols with high yield and high selectivity from syngas. The objectives are as follows: (1) to develop novel 3DOM Cu-Fe catalysts with high intrinsic activity, high stability and high selectivity for higher alcohol synthesis from syngas; (2) to conduct in situ/ex situ investigations and understand the nature of the active site of 3DOM Cu-Fe catalysts for higher alcohol synthesis from syngas; (3) to
study the reaction mechanism of higher alcohol synthesis from syngas over 3DOM Cu-Fe catalysts.

The proposed research will explore the following hypotheses: (1) the unique 3DOM structure, which has a big pore size and interconnected macroporous tunnels with a large accessible surface area, can help to guarantee sufficient exposure to the reactant gas and is capable of enhancing the catalytic activity and selectivity; (2) higher alcohol synthesis inevitably competes with methanol synthesis and hydrocarbon synthesis in the presence of Cu-modified Fischer–Tropsch catalysts, a uniform high density and the stable distribution of active Cu-Fe dual sites derived from glyoxylate route with a poly(methyl methacrylate) (PMMA) colloidal crystal template method would favor higher alcohol synthesis, which requires an intimate and stable interfacial contact between the Cu oxygenate site and the Fe chain growth site to work together; (3) the self-supported 3DOM Cu-Fe catalysts will avoid the metal support interaction effect for studying the active sites and its synergetic effect.
1.10 References


CHAPTER II
CATALYTIC CONVERSION OF SYNGAS TO HIGHER ALCOHOLS OVER ZN-MN PROMOTED CU-FE BASED CATALYST


Abstract: The Zn-Mn promoted Cu-Fe based catalyst was synthesized by the co-precipitation method. Higher alcohol synthesis from syngas was studied in a half-inch tubular reactor system after the catalyst was reduced. The Zn-Mn promoted Cu-Fe based catalyst was characterized by SEM–EDS, TEM, XRD, and XPS. The liquid phase products (alcohol phase and hydrocarbon phase) were analyzed by GC–MS and the gas phase products were analyzed by GC. The results showed that the Zn-Mn promoted Cu-Fe based catalyst had high catalytic activity and high alcohol selectivity. The maximum CO conversion rate was 72%, and the yield of alcohol and hydrocarbon was also very high. Cu was the active site for higher alcohol synthesis, iron carbide was the active site for olefin and paraffin synthesis. The reaction mechanism of higher alcohol synthesis from syngas over a Zn-Mn promoted Cu-Fe based catalyst was proposed. The Zn-Mn promoted Cu-Fe based catalyst can be regarded as a potential candidate for catalytic conversion of biomass-derived syngas to higher alcohols.
2.1 Introduction

The world today largely relies on fossil fuel for energy demand. The petroleum energy sources are finite and will be depleted one day. Currently, several important problems need to be resolved worldwide, such as high need for energy, high depletion of non-renewable energy resources, and high local and global environmental pollution. Biofuels \(^1\) (biomass-derived fuels, including gasoline, diesel, jet fuel, higher alcohols etc.) produced from renewable resources or lignocellulosic biomass (such as woodchip, switchgrass, corn stover, etc.) can be used as an alternative to fossil fuel. The utilization of biofuels can mitigate global warming, and minimize fossil fuel burning and CO\(_2\) production. The two main utilization options of lignocellulosic biomass to produce useful and high-value fuel products are biochemical processes (biocatalytic hydrolysis) and thermochemical processes. The thermochemical processes mainly consist of gasifying biomass through gasification technology (thermal treatment), liquefying biomass (chemocatalytic hydrolysis), and pyrolysis technology. \(^2, 3\)

Higher alcohol synthesis from syngas (synthesis gas: CO + H\(_2\)) or biomass-derived syngas \(^3\) (producing gas from a gasifier that consists of CO, H\(_2\), CO\(_2\), N\(_2\), CH\(_4\) and some small alkanes) is an important process for the production of oxygenates fuels, fuel additives and other intermediates for value-added chemical feedstock such as medicine, cosmetic, lubricants, detergents, and polyester. \(^4, 5\) There are two types of heterogeneous catalysts used for higher alcohol synthesis from syngas: \(^5\) noble metal-based and non-noble metal-based catalysts. The noble metal-based catalysts, mainly Rh-based catalysts, show good catalytic performance but are too expensive for commercial applications. \(^6-9\) The major non-noble metal-based catalysts available for higher alcohol
synthesis from syngas include Cu-based catalysts and Mo-based catalysts. Mo-based catalysts (such as MoS$_2$, Mo$_2$C, etc)\textsuperscript{10-12} are sulfur resistant and less sensitive to CO$_2$, but these catalysts must be used at high pressures and temperatures to produce the desired products. Above all, Cu-based catalysts containing metal active toward Fischer–Tropsch synthesis (Fe, Co), such as Cu-Fe\textsuperscript{4,13} or Cu-Co\textsuperscript{14-18} based catalysts, are considered the most promising catalysts for higher alcohol synthesis from syngas. However, Cu-Co based catalysts are not available for large-scale industrial applications due to the poor stabilization of long-term runs and the low total alcohol selectivity.\textsuperscript{5} Cu-Fe based catalysts can be regarded as one of the best potential candidate catalysts for higher alcohol synthesis via catalytic conversion of biomass-derived syngas.

Lin et al.\textsuperscript{4} found that in co-precipitated Cu-Fe catalysts, Zn could be used as electrical/chemical promoter, and Mn could be used as structural promoter. Lin et al.\textsuperscript{4} also observed that there is an obvious synergism between Zn and Mn over co-modified Cu-Fe based catalysts, which led to a rise in the overall performance with high CO conversion rate and high selectivity of higher alcohols. Thus, Zn-Mn promoted Cu-Fe based catalysts could have good catalytic activity for the production of higher alcohols using syngas or biomass-derived syngas. However, there are still many problems that are unresolved. For example, what is the active site structure and what is the reaction mechanism of Zn-Mn promoted Cu-Fe based catalyst to yield higher alcohols? Therefore, it is significant to investigate and understand the active site structures of the Zn-Mn promoted Cu-Fe based catalyst after it was reduced. Before using biomass-derived syngas to produce higher alcohols via Zn-Mn promoted Cu-Fe based catalyst, it is very important to first use pure model syngas to evaluate the catalytic performance of the Zn-Mn
promoted Cu-Fe based catalyst and study the reaction mechanism of Zn-Mn promoted Cu-Fe based catalyst to produce higher alcohols. In this work, the crystalline structure and catalytic performance of the Zn-Mn promoted Cu-Fe based catalyst were investigated using model syngas and some significant results were obtained after the catalyst was reduced. The reaction mechanism was also proposed for the formation of higher alcohols based on the active site structures detected.

2.2 Experimental section

2.2.1 Catalyst preparation

A Zn-Mn promoted Cu-Fe based catalyst (Cu/Fe/Mn/Zn=1/0.5/0.2/0.2, atom ratio) was prepared by co-precipitation method, using sodium carbonate as a precipitant. In this process, the metal nitrates of Cu(NO$_3$)$_2$·3H$_2$O, Fe(NO$_3$)$_3$·9H$_2$O, Mn(NO$_3$)$_2$·4H$_2$O and Zn(NO$_3$)$_2$·6H$_2$O were mixed together and dissolved in distillate water in a beaker. Then the sodium carbonate solution was added to the aqueous solution of mixed metallic nitrates with strong stirring at room temperature until a pH of 7.0 was reached. After aging for 4 h, the resulting precipitate was washed thoroughly with distilled water, filtered off and dried at 120 °C for 12 h, and finally calcined at 450 °C in air for 5 h. All chemicals (analytical reagent) were purchased from Fischer Scientific (Pittsburgh, PA).

2.2.2 Catalytic pretreatment and test

Figure 2.1 shows the flowchart of the half-inch tubular reactor system used in this experiment. Fresh Zn-Mn promoted Cu-Fe based catalyst was reduced using syngas (H$_2$/CO = 1) at ambient pressure in the half-inch tubular reactor, heating the catalyst to

56
200 °C at 1 °C/min. The temperature was held at that temperature for 1 h, and then the catalyst was heated from 200 °C to 300 °C at 1 °C/min and held at 300 °C overnight. A gas flow rate of 50 mL min⁻¹ was maintained through the reducing process.

![Flowchart of half-inch tubular reactor system](image)

**Figure 2.1** The flowchart of half-inch tubular reactor system

The catalytic test was directly carried out in the half-inch tubular reactor using syngas (H₂/CO = 1) after the reduced process. After the pretreatment of the fresh catalyst, the temperature was decreased to 25 °C, and the syngas (H₂/CO = 1) pressure was gradually increased to 700 psig. Then the reaction temperature was gradually increased to the reacted temperature, for example 260 °C. The gas hourly space velocity (GHSV) was set to 2000 h⁻¹. The reaction period was set to 120 h at 220 °C, 240 °C, 260 °C and 280 °C
under the syngas (H$_2$/CO = 1) pressure of 700 psig. The outlet gas CO, H$_2$, CH$_4$, CO$_2$ and C$_1$–C$_3$ hydrocarbons were on-line analyzed by Shimazu GC (Columbia, MD) with packed columns of molecule sieve, TCD and FID detectors. 6% N$_2$ in the syngas (H$_2$/CO = 1) was used as an internal standard. The liquid hydrocarbon products and alcohol products were off-line analyzed by Agilent 5890 GC–MS (Santa Clara, CA) with capillary columns and TCD detector after being carefully separated by condensation. The test run was repeated three times, and the average value was used as the experimental result.

CO conversion rate is the mole percentage of carbon monoxide converted to products:

\[
\text{CO conversion rate (mol\%) } = \frac{\text{CO}_{\text{in}} - \text{CO}_{\text{out}}}{\text{CO}_{\text{in}}} \times 100
\]  

(2.1)

Space time yield (STY) is defined as weight of desired products (such as alcohols, hydrocarbons, etc.) produced per unit volume catalyst and per unit time:

\[
\text{STY (g mL$^{-1}$ (cat.) h$^{-1}$) } = \frac{\text{Weight of Alcohols produced (g)}}{\text{Volume of Catalyst (mL)}} \times (\text{h})
\]  

(2.2)

Selectivity is defined as the combined mole percentage of carbon present in both liquid and gas streams:

\[
\text{Selectivity (mol\%) } = \frac{\text{Number of CO converted to given product}}{\text{Total number of CO converted}} \times 100
\]  

(2.3)

If the alcohol chain is formed step-wise by insertion or addition of C$_1$ intermediates with constant growth probability ($\alpha$), then the chain length distribution is given by the Anderson–Schulz–Flory (ASF) distribution.\textsuperscript{19,20} Assuming that $\alpha$ to be independent from alcohol chain length, an equation may be derived as follows:

\[
\frac{W_n}{n} = (1 - \alpha)^2 \alpha^{n-1} \quad \text{or} \quad \ln \left( \frac{W_n}{n} \right) = n \ln \alpha + \text{const.}
\]  

(2.4)
where $W_n$ is the mass fraction of the species with carbon number $n$. From the slope of the plot of $\ln (W_n/n)$ against $n$, the value of $\alpha$ is obtained.

### 2.2.3 Catalyst characterization

#### 2.2.3.1 Scanning electron microscopy–energy diffusive x-ray spectroscopy (SEM–EDS)

SEM–EDS (Carl Zeiss Microscopy, Peabody, MA) were used to characterize the morphology and elemental compositions of Zn-Mn promoted Cu-Fe based catalyst. The silver conductive adhesive was brushed on the aluminum alloy stub, and then the catalyst sample was put on the silver conductive adhesive for SEM–EDS test. The EDS analysis was run without standard calibration.

#### 2.2.3.2 X-ray diffraction (XRD)

The phase composition and crystalline structure of fresh, reduced and reacted Zn-Mn promoted Cu-Fe based catalyst were characterized by X-ray diffraction (Ultima III XRD, Rigaku Americas, The Woodlands, TX) using Cu Kα ($\lambda = 0.15418$ nm) radiation, operated at 40 kV and 44 mA at a rate of $0.12^\circ$ min$^{-1}$, 2$\theta$ from 20$^\circ$ to 70$^\circ$.

The particle size, $t$ is calculated for the most intense peak using the Scherrer formula according to Equation (2.5):  

$$t = \left( \frac{0.9 \lambda}{B \cos \theta_B} \right) \times \frac{180}{\pi}$$  

(2.5)

where $t$ is the thickness of the crystal, $\lambda = 1.540$ Å is the wavelength of the target Cu Kα, $\theta_B$ is the Bragg angle. $B$ is the line broadening by reference to a standard so that $B^2 = B_M^2 - B_S^2$, where $B_M$ is the full width at half maximum (FWHM) of the diffracted plane of
the most intense peak at $2\theta$ degree, and $B_S$ is the full width at half maximum (FWHM: $0.1^\circ 2\theta$) of the standard material in radians.

### 2.2.3.3 Transmission electron microscopy (TEM)

Fresh and reacted Zn-Mn promoted Cu-Fe based catalysts were observed in a JEOL JEM-100CX II TEM (JEOL USA Inc., Peabody, MA) operated at 100 keV. The camera length for doing selected area electron diffraction (SAED) was 60 cm. The samples were dispersed in ethanol and sonicated for 20 min and then deposited over a Formvar copper grid to be observed in the microscope.

In order to analyze the particle size distribution quantitatively, the particle size distribution was fitted by using a log-normal function:  

$$P(D) = \frac{A}{D \sigma_D \sqrt{2\pi}} \exp\left(-\frac{1}{2\sigma_D^2} \ln\left(\frac{D}{D_0}\right)^2\right)$$  

(2.6)

where $\sigma_D$ is the standard deviation of the diameter and $D_0$ is the mean diameter.

### 2.2.3.4 X-ray photoelectron spectroscopy (XPS)

A PHI 1600 XPS surface Analysis System (Physical Electronics, Eden Prairie, MN) was employed to obtain XPS data. The instrument used a PHI 10-360 spherical capacitor energy analyzer and an Omni Focus II small-area lens to focus the incident source to an 800 µm diameter surface analysis area, using an achromatic Mg Kα X-ray source operating at 300W and 15 kV. Survey spectra were gathered using an average of 10 scans with a pass energy of 26.95 eV and ran from 1100 to 0 eV. High-resolution spectra were gathered using an average of 15 scans with a pass energy of 23.5 eV and a step size of 0.1 eV. The incident sample angle was held constant at 45°. The XPS data
was collected and averaged using PHI Surface Analysis software, Version 3.0 (Physical Electronics, Eden Prairie, MN). The XPS data was analyzed using Casa XPS software.

![SEM image](image1)

**Figure 2.2** SEM–EDS analysis of fresh Zn-Mn promoted Cu-Fe based catalyst

Note: (a) SEM image, (b) EDS spectrum, and (c) EDS mapping images of O, Zn, Cu, Fe, Mn elements, respectively

### 2.3 Results

#### 2.3.1 Scanning electron microscopy–energy diffusive X-ray spectroscopy (SEM–EDS)

Figure 2.2a shows the SEM image of fresh Zn-Mn promoted Cu-Fe based catalyst. Figure 2.2b exhibits the corresponding EDS spectrum analysis to Figure 2.2a. The weight percentage of Cu, Fe, Mn, Zn, and O elements were 44.99, 18.58, 11.19,
11.46, and 13.78, respectively; and the atom percentage of Cu, Fe, Mn, Zn, and O elements were 31.04, 14.59, 8.93, 7.68 and 37.77, respectively. The EDS elemental mapping images are shown in Figure 2.2c, which indicates that the Cu, Fe, Mn, Zn, and O elements were homogeneously distributed in the individual particle of the fresh Zn-Mn promoted Cu-Fe based catalyst.

![SEM-EDS analysis](image)

**Figure 2.3** SEM–EDS analysis of reduced Zn-Mn promoted Cu-Fe based catalyst after reaction at 260 °C

Note: (a) SEM image, (b) EDS spectrum, and (c) EDS mapping images of C, O, Cu, Zn, Fe, Mn elements, respectively

Figure 2.3a shows the SEM image of reduced Zn-Mn promoted Cu-Fe based catalyst after the reaction occurred at 260 °C. Figure 2.3b exhibits the corresponding EDS
spectrum analysis of Figure 2.3a. The weight percentage of Cu, Fe, Mn, Zn, O and C elements were 21.78, 15.68, 5.60, 2.55, 6.79 and 47.60, respectively; and the atom percentage of Cu, Fe, Mn, Zn, O and C elements were 11.72, 9.60, 3.49, 1.34, 14.52 and 59.34, respectively. The EDS elemental mapping images in Figure 2.3c show that Cu, Fe, Mn, Zn, O and C elements were homogeneously distributed in the individual particle catalyst. The carbon deposited on the surface of Zn-Mn promoted Cu-Fe based catalyst was observed. This may be due to the graphite deposition on the surface of Zn-Mn promoted Cu-Fe based catalyst and the formation of iron carbide.

2.3.2 X-ray diffraction (XRD)

The XRD pattern of fresh Zn-Mn promoted Cu-Fe based catalyst is shown in Figure 2.4a. The diffraction peaks corresponding to the planes (220), (311), (400), (422), (511) and (440) at 2θ of 30.041, 35.421, 43.137, 53.235, 57.078 and 62.681, respectively, confirmed the formation of the ZnFe₂O₄ spinel phase, which agreed with previous literature references 22–24 and (JCPDS 077-0011). The diffraction peaks corresponding to the planes (111), (−202), (−311) and (113) at 2θ of 38.841, 48.682, 66.290 and 68.205, respectively, showed the formation of the CuO phase, which agreed with previous research 21 and (JCPDS 009-2364). Lin et al 4, 25, 26 reported that FeMn mixed oxide catalyst was highly dispersed, and there were no obvious peaks in the XRD pattern. The XRD pattern only showed CuO diffraction peaks when testing the CuMn mixed oxide catalyst. Therefore, only the ZnFe₂O₄ and CuO phases were observed in the XRD pattern of fresh Zn-Mn promoted Cu-Fe based catalyst. The average particle size of the fresh Zn-Mn promoted Cu-Fe based catalyst was 13.3 nm, which was determined by using
Scherrer formula, where $B_M$ is the full width at half maximum (FWHM: 0.614° 2θ) of ZnFe$_2$O$_4$ (311) diffracted plane at 35.421° 2θ.

Figure 2.4  XRD patterns of fresh Zn-Mn promoted Cu-Fe based catalyst, reduced catalyst and after reaction at 220 °C, 240 °C, 260 °C, 280 °C

XRD pattern of reduced Zn-Mn promoted Cu-Fe based catalyst is shown in Figure 2.4b. The diffraction peak corresponding to the plane (200) at the 2θ of 21.599 confirmed the formation of Chaoite (or graphite) phase, which was consistent with (JCPDS 024-0734). The diffraction peaks corresponding to the plane (100), (002), (101), (102), (110), (103) and (112) at the 2θ of 31.769, 34.434, 36.099, 47.552, 56.610, 62.875 and 67.967, respectively, confirmed the formation of the ZnO phase, which was in accordance with (JCPDS 089-0511). The diffraction peaks corresponding to the planes
(111), (200) at the 2θ of 43.379 and 50.541 confirmed the formation of the Cu phase, which agreed with (JCPDS 006-4699). The diffraction peaks corresponding to the plane (012), (104), (113), (202) and (116) at the 2θ of 24.347, 31.500, 41.566, 45.360 and 51.915, respectively confirmed the formation of MnCO₃ phase, which showed agreement with (JCPDS 008-0868). The diffraction peaks corresponding to the plane (100), (002), (101) at the 2θ of 37.700, 41.566 and 43.231 confirmed the formation of iron carbide (Fe₂C) phase, which was consistent with (JCPDS 036-1249).

The XRD pattern of reduced Zn-Mn promoted Cu-Fe based catalyst after reaction at 260°C for 120 h is shown in Figure 2.4c. The diffraction peak corresponding to the plane (200) at the 2θ of 21.601 confirmed the formation of the Chaoite (or graphite) phase, which showed agreement with (JCPDS 022-1069). Compared with reduced Zn-Mn promoted Cu-Fe based catalyst, the intensity of the graphite peak in the reacted catalyst significantly increased (Figure 2.4d). This result may be because the graphite deposition gradually increased as the process of the CO hydrogenation reaction occurred.

The diffraction peaks corresponding to the plane (111), (200) at the 2θ of 43.400, 50.519 confirmed the formation of the Cu phase, which showed agreement with (JCPDS 006-4699). The diffraction peaks corresponding to the planes (012), (110), (202), (116), (122) and (214) at the 2θ of 24.901, 38.421, 46.361, 52.961, 61.621 and 65.517, respectively, confirmed the formation of the FeCO₃ phase, which was in accordance with (JCPDS 029-0696). The diffraction peaks corresponding to the plane (012), (104) at the 2θ of 24.342, 31.500 confirmed the formation of the MnCO₃ phase, which agreed with (JCPDS 008-0868).
In summary, ZnFe$_2$O$_4$ and CuO phases were observed in the XRD pattern of fresh Zn-Mn promoted Cu-Fe based catalyst. Cu, Fe$_2$C, ZnO, graphite and MnCO$_3$ existed in the XRD pattern of reduced Zn-Mn promoted Cu-Fe based catalyst. Cu, FeCO$_3$, graphite and MnCO$_3$ phases were shown in the XRD pattern of reduced Zn-Mn promoted Cu-Fe based catalyst after reaction at 260 °C for 120 h.

![Figure 2.5](image)

**Figure 2.5**  TEM analysis of fresh Zn-Mn promoted Cu-Fe based catalyst

Note: (a) TEM image, (b) the corresponding selected area electron diffraction (SAED) pattern, and (c) the particle distribution curve for fresh Zn-Mn promoted Cu-Fe based catalyst in part (a)

### 2.3.3 Transmission electron microscopy (TEM)

The crystalline structure, particle size, and morphology of catalyst were investigated by TEM. The TEM image of fresh Zn-Mn promoted Cu-Fe based catalyst is
presented in Figure 2.5a. The particles were approximately spherical in shape and their diameters were found to be in the range of 5–35 nm. The corresponding SAED pattern of fresh Zn-Mn promoted Cu-Fe based catalyst shown in Figure 2.5b depicted well-defined rings, which was attributed to the polycrystalline nature of the synthesized co-precipitated Zn-Mn promoted Cu-Fe based catalyst with fine grains. The index of the diffraction pattern is also shown in Figure 2.5b. Several polycrystalline complex oxides were formed, which was consistent with the XRD analysis in Figure 2.4.

The distribution of the particle size of fresh Zn-Mn promoted Cu-Fe based catalyst is shown in Figure 2.5c. A mean diameter ($D_0$) with a value of $14.29 \pm 7.38$ was obtained from the TEM image by using Equation (2.6), which showed agreement with the particle size calculated based on the XRD pattern in Figure 2.4a using Scherrer formula.

The TEM image of reduced Zn-Mn promoted Cu-Fe based catalyst after reaction at 260 °C is presented in Figure 2.6a. After reaction at 260 °C under model syngas, the graphite cluster was observed on the surface of the reacted Zn-Mn promoted Cu-Fe based catalyst, which agreed with SEM–EDS mapping of graphite (carbon) in Figure 2.3c, XRD analysis in Figure 2.4, and later XPS analysis. The corresponding SAED pattern of reduced catalyst after reaction at 260 °C shown in Figure 2.6b depicted rings, which indicated polycrystalline nature of reduced Zn-Mn promoted Cu-Fe based catalyst after reaction at 260 °C. Spots are also observed on the diffraction pattern because the grain size of the catalyst was increased after reaction at 260 °C. This is because graphite deposition and iron carbide formation on the surface of the Zn-Mn promoted Cu-Fe based
catalyst occurred. The index of the diffraction pattern is also shown in Figure 2.6b, which was consistent with the XRD analysis in Figure 2.4.

![TEM analysis of reduced Zn-Mn promoted Cu-Fe based catalyst after reaction at 260 °C](image)

**Figure 2.6** TEM analysis of reduced Zn-Mn promoted Cu-Fe based catalyst after reaction at 260 °C

Note: (a) TEM image of reduced Zn-Mn promoted Cu-Fe based catalyst after reaction at 260 °C, (b) the corresponding selected area electron diffraction (SAED) pattern

### 2.3.4 X-ray photoelectron spectroscopy (XPS)

XPS spectra of the high resolution scan for Cu 2p, Fe 2p, Mn 2p, Zn 2p, and O 1s in fresh Zn-Mn promoted Cu-Fe based catalyst are shown in Figures 2.7a–e. For high resolution scan of Cu 2p, two peaks at 933.6 eV and 953.6 eV attributing to the spin-orbit doublet of Cu 2p were assigned to the bonding energies of Cu (2p3/2) and Cu (2p1/2) in CuO, respectively. The two other peaks on the higher binding energy side of both Cu (2p3/2) and Cu (2p1/2) were satellite structures. These satellites can be attributed to shake-up transitions by ligand-to-metal 3d charge transfer. This charge transfer can occur for copper present in the Cu2+ form (3d⁹ configuration) but the transfer can not take place
if it is present as a metallic or in a Cu$^+$ state (3d$^{10}$ configuration) because of their completely filled 3d shells.

![XPS spectra of Zn-Mn promoted Cu-Fe based catalyst](image)

**Figure 2.7** XPS spectra of Zn-Mn promoted Cu-Fe based catalyst

Note: (a) Cu 2p, (b) Fe 2p, (c) Mn 2p, (d) Zn 2p, (e) O 1s of fresh Zn-Mn promoted Cu-Fe based catalyst, (f) Cu 2p of reduced Zn-Mn promoted Cu-Fe based catalyst and reduced catalyst after reaction at 260 °C

The binding energy of Fe (2p$_{3/2}$) was 710.7 eV and Fe (2p$_{1/2}$) was 724.3 eV, which corresponded to Fe$_2$O$_3$. The binding energy of Mn (2p$_{3/2}$) was 642.2 eV and...
Mn (2p_{1/2}) was 653.9 eV for Mn 2p spectra, which was the characteristic of Mn^{4+} ions and was in accordance with the binding energy of MnO$_2$. The binding energy of Zn (2p$_{3/2}$) was 1021.7 eV and Zn (2p$_{1/2}$) was 1044.7 eV for Zn 2p spectra, which was the characteristic of ZnO. The binding energy 530.0 eV of O1s was attributed to metal oxide of CuO, Fe$_2$O$_3$, MnO$_2$ and ZnO for O1s high resolution scan, which agreed with XPS database of NIST; and the binding energy 531.7 eV of O1s was due to surface hydration of the Zn-Mn promoted Cu-Fe based catalyst.

Figure 2.7f presents the XPS spectra of the high resolution scan for Cu 2p of reduced Zn-Mn promoted Cu-Fe based catalyst and reduced catalyst after reaction at 260 °C. The binding energy of Cu (2p$_{3/2}$) was 932.4 eV and the binding energy of Cu (2p$_{1/2}$) was 952.2 eV, which was the characteristic of pure Cu. The pure Cu phase characterized by XPS presented on the surface of reduced catalyst and reacted catalyst (260 °C), which showed agreement with the XRD analysis (Figures 2.4b and 2.4c) that pure Cu phase presented in reduced catalyst and also in the catalyst after reaction at 260 °C.

Table 2.1 lists surface composition analysis of fresh Zn-Mn promoted Cu-Fe based catalyst, reduced catalyst, and reduced catalyst after reaction at 260 °C by XPS. Compared with fresh Zn-Mn promoted Cu-Fe based catalyst, the carbon (graphite) content was high on the surface of reduced catalyst and reduced catalyst after reaction at 260 °C. This result may be attributed to the formation of iron carbide (Fe$_2$C) as active site for olefin and paraffin synthesis, and also the graphite deposition on the surface of Zn-Mn promoted Cu-Fe based catalyst, which agreed with EDS mapping analysis in Figure 2.3c and XRD analysis in Figure 2.4.
Table 2.1  Surface composition analysis of fresh Zn-Mn promoted Cu-Fe based catalyst, reduced catalyst, and reduced catalyst after reaction at 260 °C by XPS

<table>
<thead>
<tr>
<th>Elements</th>
<th>Fresh catalyst at.% (atomic ratios)</th>
<th>Reduced catalyst at.% (atomic ratios)</th>
<th>Reacted catalyst (260 °C at.% (atomic ratios)</th>
<th>Theoretic atom ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>6.19% (1.000)</td>
<td>2.24% (1.000)</td>
<td>1.71% (1.000)</td>
<td>1.0</td>
</tr>
<tr>
<td>Fe</td>
<td>5.71% (0.922)</td>
<td>1.95% (0.871)</td>
<td>1.41% (0.825)</td>
<td>0.5</td>
</tr>
<tr>
<td>Mn</td>
<td>4.70% (0.759)</td>
<td>1.41% (0.629)</td>
<td>1.28% (0.749)</td>
<td>0.2</td>
</tr>
<tr>
<td>Zn</td>
<td>4.45% (0.719)</td>
<td>1.50% (0.670)</td>
<td>1.34% (0.784)</td>
<td>0.2</td>
</tr>
<tr>
<td>O</td>
<td>39.59% (6.396)</td>
<td>9.76% (4.357)</td>
<td>6.30% (3.684)</td>
<td>–</td>
</tr>
<tr>
<td>C</td>
<td>39.35% (6.357)</td>
<td>83.14% (37.12)</td>
<td>87.97% (51.44)</td>
<td>–</td>
</tr>
</tbody>
</table>

Figure 2.8  Time on stream of CO conversion, CO₂ selectivity, alcohol selectivity, hydrocarbon selectivity and distribution on Zn-Mn promoted Cu-Fe based catalyst

Note: The reaction condition is P = 700 psig, T = 260 °C, GHSV of 2000 h⁻¹, H₂/CO = 1
2.3.5 Catalytic performance results

Figure 2.8 presents data concerning the time on stream of CO conversion, CO$_2$ selectivity, alcohol selectivity, hydrocarbon selectivity and the distribution on Zn-Mn promoted Cu-Fe based catalyst at the reaction conditions of $P = 700$ psig, $T = 260$ °C, GHSV = 2000 h$^{-1}$ with syngas mole ratio of $n$(H$_2$)/$n$(CO) = 1 after running 120 h. The CO conversion rate was approximately 67.43 %, the CO$_2$ selectivity was approximately 13.79 %, and the alcohol selectivity was approximately 32.54 %.

Table 2.2 Catalytic performance of Zn-Mn promoted Cu-Fe based catalyst

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>CO conversion (%)</th>
<th>STY (g mL$^{-1}$(cat.) h$^{-1}$)</th>
<th>Selectivity (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>ROH$^a$</td>
<td>HC$^a$</td>
</tr>
<tr>
<td>220</td>
<td>45.37</td>
<td>0.12</td>
<td>0.21</td>
</tr>
<tr>
<td>240</td>
<td>53.82</td>
<td>0.17</td>
<td>0.26</td>
</tr>
<tr>
<td>260</td>
<td>67.43</td>
<td>0.22</td>
<td>0.32</td>
</tr>
<tr>
<td>280</td>
<td>72.56</td>
<td>0.24</td>
<td>0.38</td>
</tr>
</tbody>
</table>

Note: Reaction condition: $P = 700$ psig, GHSV = 2000 h$^{-1}$, $H_2/CO = 1.0$. $^a$ROH for alcohol, and HC for hydrocarbon; $^b$Selectivity based on number of atom per gram carbon = [number of CO converted to given product/total number of CO converted] × 100%

The overall performance of the Zn-Mn promoted Cu-Fe based catalyst after being reduced with syngas for higher alcohols synthesis appeared to be related to a function of temperature (Tables 2.2 and 2.3). Table 2.2 shows that the alcohol yield was fairly high at a relatively mild operation conditions, i.e. 0.22 g mL$^{-1}$(cat.) h$^{-1}$ of total alcohols at 260 °C. The product distributions are listed in Table 2.3. The alcohol products were composed of C$_1$–C$_6$ mixed linear α-alcohols. Furthermore, the C$_2$OH selectivity was 39.22 % in total alcohols at 220 °C and reached 48.53 % at 280 °C.
Table 2.3  Product distributions of Zn-Mn promoted Cu-Fe based catalyst

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>ROH a (Wt.%)</th>
<th>HC a (Wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C₁</td>
<td>C₂</td>
</tr>
<tr>
<td>220</td>
<td>60.78</td>
<td>27.16</td>
</tr>
<tr>
<td>240</td>
<td>58.72</td>
<td>26.03</td>
</tr>
<tr>
<td>260</td>
<td>54.20</td>
<td>25.31</td>
</tr>
<tr>
<td>280</td>
<td>51.47</td>
<td>24.03</td>
</tr>
</tbody>
</table>

Note: Reaction condition: P = 700 psig, GHSV = 2000 h⁻¹, H₂/CO = 1.0. aROH for alcohol, and HC for hydrocarbon.

Figure 2.9  A–S–F plot for the distribution of alcohols over reduced Zn-Mn promoted Cu-Fe based catalyst at different temperatures

Note: (a) 220 °C, (b) 240 °C, (c) 260 °C, and (d) 280 °C. The reaction condition is P = 700 psig, GHSV = 2000 h⁻¹, and H₂/CO = 1.
Alcohol and hydrocarbon distributions of the Zn-Mn promoted Cu-Fe based catalyst are presented in Table 2.3. The chain growth probability ($\alpha$) is larger than zero but it is lower than one because a part of intermediate desorbed from the catalyst’s surface in each step of the growth of carbon chain. Therefore, the yield of each alcohol in the product decreased with an increase of the length of carbon chain according to the A–S–F distribution. Similarly to Cu-Co based catalyst, the carbon number distribution of alcohols over the Zn-Mn promoted Cu-Fe based catalyst obeyed excellent Anderson–Schulz–Flory (A–S–F) plots (Figure 2.9), because the mass fraction of each alcohol product was in the order of CH$_3$OH > C$_2$H$_5$OH > C$_3$H$_7$OH > C$_4$H$_9$OH > C$_5$H$_{11}$OH. The chain growth probability ($\alpha$) over the Zn-Mn promoted Cu-Fe based catalyst could be calculated as 0.188, 0.224, 0.262, 0.313, respectively, at 220 °C, 240 °C, 260 °C, 280 °C using the slope of the imitation straight line of mixed alcohols.

![Figure 2.10](image)

**Figure 2.10** The chain growth probability ($\alpha$) of alcohols over Zn-Mn promoted Cu-Fe based catalyst as a function of reaction temperature
The chain growth probability ($\alpha$) of alcohols over the Zn-Mn promoted Cu-Fe based catalyst was close to a positively linear function of reaction temperature (Figure 2.10). The higher the temperature, the larger the chain growth probability of alcohols. The main hydrocarbon products were olefins and paraffins (GC–MS analysis), and the CH$_4$ selectivity was relatively low (GC analysis).

2.4 Discussion

In the process of higher alcohol synthesis from syngas over the Zn-Mn promoted Cu-Fe based catalyst, the major reaction is the alcohol formation, while hydrocarbon formation and water-gas-shift reactions are the side reactions:  

- Alcohol formation:
  \[ n\text{CO} + 2n\text{H}_2 = \text{C}_n\text{H}_{2n+1}\text{OH} + (n - 1)\text{H}_2\text{O}; \]

- Hydrocarbon formation:
  \[ n\text{CO} + 2n\text{H}_2 = \text{C}_n\text{H}_{2n} + n\text{H}_2\text{O}; \]

- Water-gas-shift (WGS) reaction equilibrium:
  \[ \text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2. \]

Lin et al. 4 evaluated the catalytic performance of Cu-Fe based catalyst by using a Zn or Mn promoter in order to investigate their promotional effect upon Cu-Fe based catalysts. Cu-Fe based catalysts showed the reaction behavior of F–T synthesis rather than higher alcohols synthesis derived from the strong activation tendency of Fe towards CO dissociation. The addition of the Zn promoter into the Cu-Fe based catalyst promoted the formation of spinel oxide ZnFe$_2$O$_4$ to enhance the stabilization of the catalyst, 4, 35 which dramatically improved the catalytic performance of catalyst, increased CO conversion rate and decreased in higher alcohol selectivity. In contrast, the addition of the Mn promoter into Cu-Fe based catalyst hardly improved the CO conversion rate such that the effect of CO conversion rate was lower than the non-promoted Cu-Fe based catalyst.
However, the addition of Mn promoter increased the BET surface area of catalyst and improved the dispersion of Cu and Fe. It promoted the synergistic effect between Cu and Fe, resulting in the higher selectivity to total alcohols despite a decrease in higher alcohol selectivity due to its dilution effect. Therefore, Zn and Mn promoted the catalytic performance of Cu-Fe based catalyst in different ways. Zinc oxide can be regarded as an electrical/chemical promoter, while manganese is a structural promoter. The synergistic effect of Zn and Mn existed over Cu-Fe based catalyst, which largely improved the overall catalytic performance, and is shown in Figure 2.8 and Table 2.3.

Based on XRD and XPS analysis, the reduction of fresh Zn-Mn promoted Cu-Fe based catalyst under syngas (H\textsubscript{2}/CO = 1) at 300 °C can be described as follows

[Equations (2.7)–(2.9)]: The spinel oxide phase ZnFe\textsubscript{2}O\textsubscript{4} was reduced to form iron carbide (Fe\textsubscript{2}C), CuO was reduced to form Cu, and MnO\textsubscript{2} was reduced to form MnCO\textsubscript{3}.

\[
\text{ZnFe}_2\text{O}_4 + 4\text{H}_2 + \text{CO} \rightarrow \text{Fe}_2\text{C} + \text{ZnO} + 4\text{H}_2\text{O}\uparrow \tag{2.7}
\]

\[
2\text{CuO} + \text{H}_2 + \text{CO} \rightarrow 2\text{Cu} + \text{CO}_2\uparrow + \text{H}_2\text{O}\uparrow \tag{2.8}
\]

\[
\text{MnO}_2 + 2\text{CO} + \text{H}_2\text{O} \rightarrow \text{MnCO}_3 + \text{CO}_2\uparrow + \text{H}_2\uparrow \tag{2.9}
\]

The reaction process of the reduced Zn-Mn promoted Cu-Fe based catalyst under syngas (H\textsubscript{2}/CO = 1) at 220 °C, 240 °C, 260 °C, and 280 °C can be described as follows: Cu was the active site for mixed alcohols synthesis, and Fe\textsubscript{2}C was the active site for olefin and paraffin synthesis. The Zn-Mn promoted Cu-Fe based catalyst was gradually deactivated by graphite deposition on the surface of the catalyst and FeCO\textsubscript{3} formation due to iron carbide (Fe\textsubscript{2}C) deactivation [Equation (2.10)]. The graphite deposition was observed via XRD, EDS and XPS spectra.

\[
\text{Fe}_2\text{C} + 7\text{CO} + \text{H}_2 \rightarrow 2\text{FeCO}_3 + 6\text{C (graphite)} + \text{H}_2\text{O}\uparrow \tag{2.10}
\]
Figure 2.11 The proposed reaction mechanism for higher alcohol synthesis from syngas over Zn-Mn promoted Cu-Fe based catalyst

Zinc promoted the formation of the spinel oxide phase ZnFe$_2$O$_4$, but did not have significant role in carbide or metal formation. The reaction mechanism for CO hydrogenation to higher alcohols over Cu-Fe based catalysts is assumed to be similar to La promoted Co based catalysts $^{36}$ and Rh-based catalysts. $^{7,37,38}$ For Zn-Mn promoted Cu-Fe based catalyst, Cu was the active site for alcohol synthesis, serving as the dissociative adsorption of H$_2$ and associative adsorption of CO. $^{36,37}$ Iron carbide (Fe$_2$C) was the active site of the F–T function of dissociative adsorption of CO (carbon-chain growth) and associative adsorption of H$_2$. $^{38}$ The production of higher alcohols required the synergetic functioning of Fe and Cu. $^5$ The proposed reaction mechanism for higher alcohol synthesis from syngas over Zn-Mn promoted Cu-Fe based catalyst can be outlined in Figure 2.11, where * represents a vacant site and *R or R* indicates a molecule adsorbed on a site. The reaction mechanism for CO hydrogenation to higher alcohols over Zn-Mn promoted Cu-Fe based catalyst involved Cu surface association of
CO* and dissociation of H₂, Fe₂C surface dissociation of CO* and association of H₂, carbon species hydrogenation into CHₓ, CO* insertion into adsorbed CHₓ to form acyl species (CHₓCO*), 7, 36–38 carbon-chain growth of alkyl group (*CₙH₂) via *CHₓ addition, 7, 36–38 *CₙHₓ hydrogenation into olefin, paraffin products, and CO* insertion of *CₙHₓ species and further hydrogenation into higher alcohol products.

The active iron carbide Fe₂C surface acted as site for CO* dissociative adsorption, carbon-chain growth and for hydrogenation, while active copper site Cu surface adsorbed CO* molecularly. CO* molecular moved to an adsorbed *CHₓ alky group and inserted between iron carbide (Fe₂C) site and the *CHₓ alky group via surface migration over a short distance between Cu and Fe₂C sites, which was further hydrogenated to form ethanol. The carbon-chain growth of the alkyl group (*CₙHₓ) was propagated through *CHₓ addition. 38 Then the direct hydrogenation of *CₙHₓ species led to the olefin and paraffin products (which is consistent with GC–MS results). The CO* insertion of *CₙHₓ species and further hydrogenation resulted in higher alcohol synthesis. 7, 36–38

2.5 Conclusions

The Zn-Mn promoted Cu-Fe based catalyst had high catalytic activity, high yield of alcohols and hydrocarbons, and high alcohol selectivity at mild conditions. The production of alcohols over the Zn-Mn promoted Cu-Fe based catalyst followed A–S–F distributions. The chain growth probability (α) of alcohols over Zn-Mn promoted Cu-Fe based catalyst was a function of reaction temperature. The main hydrocarbon products were olefins and paraffins, and the CH₄ selectivity was relatively low. The Zn-Mn promoted Cu-Fe based catalyst could be regarded as a potential candidate for catalytic conversion of biomass-derived syngas to higher alcohols.
Cu was the active site for alcohol synthesis, and Fe₂C was the active site for olefin and paraffin synthesis. The reaction mechanism for CO hydrogenation to higher alcohols over Zn-Mn promoted Cu-Fe based catalyst involved Cu surface association of CO* and dissociation of H₂, Fe₂C surface dissociation of CO* and association of H₂, carbon species hydrogenation into CHₓ, CO* insertion into adsorbed CHₓ to form acyl species (CHₓCO*), carbon-chain growth of alkyl group (*CₙH₂) via *CHₓ addition, *CₙHₓ hydrogenation into olefin, paraffin product, and CO* insertion of *CₙHₓ species and further hydrogenation into higher alcohol products.

2.6 Acknowledgements

This work is supported by the Department of Energy under Awards (DE-FG3606GO86025, DE-FC2608NT01923), US Department of Agriculture under Award (AB567370MSU), NSFC (21173270), CNPC project (2011D-4604-0101), NCET-10-0811, and China University of Petroleum Theory Research Fund (LLYJ-2011-39). This material is based upon work performed through the Sustainable Energy Research Center at Mississippi State University. Y. Lu would like to thank Dr. Judith A. Schneider for the instructions and help of data analysis on TEM and XRD, Ms. Amanda Lawrence for the help of running TEM and SEM-EDS, and Dr. Erick Vasquez for the help of running XPS and data analysis.
2.7 Supporting information

Figure 2.12  Lab scale half-inch tubular reactor in MSU Pace Seed

Figure 2.13  Mixed alcohols and hydrocarbons made in MSU
Figure 2.14  Gas chromatography–mass spectrometry (GC–MS) analysis of mixed alcohols made in MSU

Figure 2.15  GC–MS analysis of hydrocarbons made in MSU and compared with 93# gasoline, and diesel
2.8 References


CHAPTER III
HIGH SELECTIVITY HIGHER ALCOHOL SYNTHESIS FROM SYNGAS OVER
THREE-DIMENSIONALLY ORDERED MACROPOROUS CU-FE CATALYSTS

This section was published in ChemCatChem journal in 2014. See the following:
Lu, Y., Cao, B., Yu, F., Liu, J., Bao, Z., Gao, J. High selectivity higher alcohols synthesis from syngas over three-dimensionally ordered macroporous Cu-Fe catalysts.

Abstract: Higher alcohols can be produced with high selectivity from syngas over three-dimensionally ordered macroporous (3DOM) Cu-Fe catalysts. The catalyst was developed by using a glyoxylate route colloidal crystal template method. The high intrinsic activity was ascribed to three factors. First, the unique ordered structure has a large pore size and interconnected macroporous tunnels of the catalyst with a large accessible surface area to improve the catalytic activity. Second, a high density of uniformly distributed defective Cu⁰ and χ-Fe₅C₂ nanoparticles derived from the glyoxylate route helps to provide abundant, active and stable dual sites. Third, atomic steps on the Cu surface, induced by planar defects and lattice strain, serve as high-activity oxygenation sites. Active χ-Fe₅C₂ chain-growth sites intimately surround the defective and strained form of the Cu surface, which results in a synergetic effect between the active and stable Cu–Fe₅C₂ dual sites for higher alcohol synthesis.
3.1 Introduction

Long-chain 1-alcohols are key intermediates used in chemical industries for the manufacture of plasticizers, detergents, lubricants.\(^1\) Currently, the large-scale industrial synthesis of 1-alcohols employs homogeneous catalysis, hydroformylation of 1-alkenes to give a mixture of \(n\)- and \(i\)-aldehydes, followed by separation of \(n\)-aldehydes and hydrogenation to \(n\)-alcohols.\(^2\) Alternatively, 1-alkenes can be directly hydrated and catalyzed to 1-alcohols by using acids, metal oxides, zeolites, or clays.\(^3\) However, according to Markovnikov’s rule, the proton bonds attached to the least substituted carbon,\(^4\) and 1-alcohols are difficult to obtain because of their limited regional selectivity.

Recently, many approaches have been dedicated to develop a one-pot tandem strategy for 1-alcohols synthesis from 1-alkenes. Nozaki et al.\(^5\) reported one-pot hydroformylation/ hydrogenation with one- and two-catalyst systems, which produced 1-alcohols with high selectivity and yields. Breit et al.\(^6\) developed a multifunctional Rh catalyst system that enables the simultaneous catalysis of two distinct transformations in a highly selective manner controlled by two cooperative ligands, with high yields and excellent selectivity of 1-alcohols. Grubbs et al.\(^7\) reported a direct catalytic anti-Markovnikov alkene hydration approach by using a triple relay catalysis system by coupling Pd oxidation, acid hydrolysis, and Ru reduction cycles, with good yield and regional selectivity. However, the further development of high-performance catalysts that fight the Markovnikov rule and recycle expensive noble metal are still two challenging issues. From this background, it is worthwhile to exploit a research protocol using heterogeneous Fischer–Tropsch (FT) catalysis to strictly produce 1-alcohols from syngas,
which can be derived from natural gas, coal, biomass, shale gas, and other carbonaceous materials.

The first report on the production of oxygenates from syngas dates back to the pioneering work of Fischer and Tropsch. Later, Roelen discovered the oxo-synthesis, commonly regarded as hydroformylation. He found that the propionaldehyde was formed if ethylene reacted with CO and H₂ in the presence of Co-Th catalysts. After a detailed study, Roelen put forward the idea to recycle the olefin to increase the chain growth during FT synthesis, although it escaped his notice that the hydroformylation reaction was actually a homogeneous rather than heterogeneous reaction.

To date, a large number of C₂⁺ oxygenates are synthesized with high selectivity from syngas by modified FT synthesis. Nevertheless, most of the research on C₂⁺ slate 1-alcohol synthesis is still focused on optimizing the C₂–C₅ rather than the C₆⁺ slate (Table 3.1 in Supporting Information), and few papers deal with direct C₆⁺ slate 1-alcohol synthesis. Xiang et al. reported that long-chain 1-alcohols can be produced by CO hydrogenation over Co-Cu-Mn core-shell nanoparticles, although more efforts are needed to further maximize the yield for potential large-scale industrial application.

3.2 Experimental section

Herein, we report on higher alcohol synthesis based on heterogeneous catalysis, and that Cu-Fe-modified FT catalysts can be tuned to strongly favor higher alcohol production. In particular, three-dimensionally ordered macroporous (3DOM) Cu-Fe catalysts are synthesized by using a facile glyoxylate route with poly(methyl methacrylate) (PMMA) colloidal crystal template method (Figures 3.7, 3.9 and 3.10 in Supporting Information).
One of the reasons to use this method of catalyst preparation is that the unique ordered structure, which has a big pore size and interconnected macroporous tunnels with a large accessible surface area, can help to guarantee sufficient exposure to the reactant gas and improve the catalytic activity.  

The other reason for using the glyoxylate route method of catalyst preparation is that the glyoxylate dianion ([HC(OH)O–COO]$^2^-$) is capable of coordinating with a number of metals to create polymeric structures. $^{13,14}$ The glyoxylate dianion functions as a double-bridge ligand to make an isomorphous substitution of cations in the heteropolynuclear structure (Figure 3.8 in Supporting Information). $^{14}$  

As 1-alcohol synthesis inevitably competes with methanol and hydrocarbons synthesis in the presence of Cu-modified FT catalysts during CO hydrogenation, $^{11,15}$ a uniform high density and the stable distribution of active Cu-Fe dual sites would favor higher alcohol synthesis, which requires an intimate and stable interfacial contact between the Cu oxygenation site and the Fe chain growth site to work together.

We hope that the glyoxylate route will result in the formation of a uniform high density and stable distribution of Cu-Fe-glyoxylate units as building blocks of a framework structure. Cu-Fe-glyoxylates were obtained from the in situ reaction of ethylene glycol with mixed Cu-Fe-nitrate precursors (Figure 3.8 in Supporting Information). On calcination, the glyoxylate salt was converted to Cu-Fe-oxide and PMMA was decomposed to produce 3DOM Cu-Fe oxide catalyst.
Figure 3.1  Characterization of fresh 3DOM Cu$_2$Fe$_1$ catalyst

Note: (a) SEM, (b) TEM images, (c) The indexed SAED pattern of the area shown in (b), (d) High resolution TEM image of CuO, inset FFT, (e) High resolution TEM image of Fe$_3$O$_4$, inset FFT, (f) XRD and (g) XPS
3.3 Results and discussion

Typical scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of fresh 3DOM Cu$_2$Fe$_1$ catalysts are shown in Figure 3.1a and b, respectively. The data shows the hierarchically macroporous structure that contains periodic voids with an average diameter of 200 $\pm$ 10 nm and a wall thickness of 50 $\pm$ 5 nm. In contrast to the coprecipitated Cu$_2$Fe$_1$ catalyst, the 3DOM Cu$_2$Fe$_1$ catalyst has larger accessible Brunauer–Emmet–Teller (BET) surface area (Table 3.2 in Supporting Information). The indexed selected-area electron diffraction (SAED) ring pattern in Figure 3.1b is shown in Figure 3.1c, which verifies that the catalyst is composed of polycrystalline CuO and Fe$_3$O$_4$ in agreement with x-ray diffraction (XRD) analysis (CuO: JCPDS no. 48-1548; Fe$_3$O$_4$: JCPDS no. 65-3107) shown in Figure 3.1f.

The high-resolution TEM (HRTEM) image of CuO is displayed in Figure 3.1d, and inset the fast Fourier transform (FFT) shows that CuO is aligned along the [011] zone axis. The HRTEM image of Fe$_3$O$_4$ is presented in Figure 3.1e, and inset the FFT indicates Fe$_3$O$_4$ is aligned along the [211] zone axis. The scanning TEM (STEM) image, elemental maps based on energy-dispersive X-ray spectroscopy (EDS; Figure 3.11 in Supporting Information) and HRTEM images of the fresh 3DOM Cu$_2$Fe$_1$ catalyst (Figure 3.12 in Supporting Information) indicate that a uniform high density and stable distribution of nanoparticles of Cu-Fe oxide catalysts were obtained from the glyoxylate route. X-ray photoelectron spectroscopy (XPS) spectra at the Cu 2p and Fe 2p levels (Figure 1g) gives further evidence to suggest that CuO$^{16}$ and Fe$_3$O$_4$$^{17}$ exist on the catalyst surface.
Figure 3.2  Catalytic performances of coprecipitated Cu$_2$Fe$_1$ and 3DOM Cu$_2$Fe$_1$ catalysts

Note: P = 700 psig, gas hourly space velocity (GHSV) = 2000 h$^{-1}$, H$_2$/CO = 1.0, time-on-stream = 120 h. The chain growth probability ($\alpha$) is calculated according to Equation (3.1),$^{16a}$ in which $n$ is the number of carbon atoms in 1-alcohols and $W_n$ is the weight fraction of 1-alcohols that contain $n$ carbon atoms

$$\ln \left( \frac{W_n}{n} \right) = n \ln \alpha + \ln \left( 1 - \alpha \right)^2 / \alpha$$  \hspace{1cm} (3.1)

The catalytic performance of the 3DOM Cu$_2$Fe$_1$ catalyst was compared with that of the coprecipitated Cu$_2$Fe$_1$ catalyst. This comparison is made according to activity, selectivity and Anderson–Schulz–Flory (ASF) $\alpha$-chain-growth probability (Figure 3.2). Both catalysts are active in 1-alcohol synthesis, and the total 1-alcohols selectivity increases with decreasing reaction temperatures. A total 1-alcohols selectivity value close to 48 % at low CO conversion was obtained for 3DOM Cu$_2$Fe$_1$ at 200 $^\circ$C, whereas for coprecipitated Cu$_2$Fe$_1$ the maximum is lower and reaches approximately 29 % at most.
In addition, the C_{2+} and C_{6+} slate 1-alcohols selectivity in the total 1-alcohols distribution for 3DOM Cu_{2}Fe_{1} at 200 °C are approximately 95 and 63 %, respectively, which is much higher than that of coprecipitated Cu_{2}Fe_{1}. These results indicate that the unique ordered macroporous structure derived from the glyoxylate route definitely improves the catalytic activity. In addition, the CO_{2} selectivity is quite low for 3DOM Cu_{2}Fe_{1} over a range of temperatures. As the CO conversion rate increases, an increase of CO_{2} production is generally related to the occurrence of the water–gas–shift (WGS) reaction [Equation (3.2)].

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2
\] (3.2)

The most intriguing observation from Figure 3.2 is the high \(\alpha\)-chain-growth probability for 1-alcohols formation in the presence of 3DOM Cu_{2}Fe_{1} catalyst. The \(\alpha\) values from 0.70–0.81 between 280–200 °C help to maximize the contribution from C_{6+} slate 1-alcohols. The ASF chain-growth distributions are linear for both the 3DOM Cu_{2}Fe_{1} and coprecipitated Cu_{2}Fe_{1} catalysts (Figure 3.13 in Supporting Information).

The 3DOM Cu_{2}Fe_{1} case study is encouraging in terms of a possible industrial application. A detailed catalytic performance study of this binary system was carried out by changing the relative amounts of Cu and Fe (Figure 3.14 in Supporting Information). The general trend appears to be that \(\alpha\) values increase for 1-alcohols and hydrocarbons with decreasing temperature. Notably, the correlated \(\alpha\) values for 1-alcohols and hydrocarbons (Figure 3.14, Tables 3.3 and 3.4 in Supporting Information) on varying the catalyst compositions and reaction conditions are consistent with a common chain-growth mechanism by CO insertion into the same type of intermediate, and then late kinetic branching to n-alkanes, 1-alcohols, and 1-alkenes.\(^{11,18}\)
Figure 3.3 Attempts to correlate the Cu intrinsic activities with the Cu stacking fault probability

Note: (a) Catalytic activities (column) and Cu surface area (scatter), (b) intrinsic activities per Cu surface area, (c) deviation of \(d_{111}/d_{200}\) (column) observed in XRD and the Cu stacking fault probability (scatter), and (d) relation of Cu intrinsic activity to the stacking fault probability. \(P = 700\) psig, \(T = 260^\circ C\), GHSV = 2000 h\(^{-1}\), \(H_2/CO = 1.0\), time on stream of 120 h, normalized to the most active sample. Rel. Act. S\(_{ACu}^{-1}\) : Relative activity per Cu surface area.

The CO insertion mechanism (Figure 3.15 in Supporting Information) elucidates why Cu-modified FT catalysts mainly produced linear 1-alcohols and why the alcohols obey the ASF distribution with a similar chain-growth probability as hydrocarbons. \(^{18}\)

Accordingly, we can assume that the associative CO insertion kinetic step is the rate-limiting elementary step and that Cu serves as the oxygenate site for 1-alcohol synthesis,
which is an essential prerequisite to correlate Cu defects or Cu lattice strain with intrinsic activities. If we consider the catalytic activity of the various catalysts, the total 1-alcohols yields of the six samples are shown in Figure 3.3a, normalized to the most active sample. The Cu sample exhibited little activity. If we divide the total 1-alcohols yield by the Cu surface area (Table 3.5 in Supporting Information), we can obtain the intrinsic activities (Figure 3.3b).

To find a structure–activity relationship for the observed intrinsic activity, XRD experiments were performed on the reduced catalysts. All the reduced catalysts display broad peaks of the metallic Cu face-centered cubic phase (Figure 3.16 in Supporting Information). The inactive Cu sample exhibits sharper peaks.

The characteristic underestimation of the intensity near the maximum of the 200 peak at approximately $2\theta = 50.4^\circ$ in the XRD patterns (Figure 3.4e and Figure 3.16 in Supporting Information) can be explained by the presence of twin boundaries and stacking faults that result in a broadening of this reflection, which usually causes a shift of the 111 and 200 peaks towards each other. This effect originates from the generation of thin hexagonal domains in the cubic lattice with the change in stacking sequence of the hexagonally close-packed (111) layers at the stacking fault (ideal is A-B-C-A; stacking fault, A-B-C-B-C-A; twin boundaries, A-B-C-B-A).$^{19a,b}$

The ratio of the distances between the (111) and (200) lattice planes ($d_{111}/d_{200}$) is constant at $2/\sqrt{3} = 1.1547$ for an ideal defect-free Cu face-centered cubic structure (Figure 3.3c). The inactive Cu sample has a ratio that is close to the ideal value, whereas the active 3DOM Cu-Fe catalysts showed a lower $d_{111}/d_{200}$ ratio.
Figure 3.4  Characterization of 3DOM Cu$_2$Fe$_1$ catalyst after reduction

Note: (a) HRTEM, inset FFT, (b) magnification of the area shown in part a, (c) and (d) magnifications of (b) that show stacking fault and twin boundary, (e) XRD, (f) Mössbauer spectrum. The syngas of H$_2$/CO = 1.0 was used for reduction
The peak positions of the Cu reflections and the corresponding \( d \) spacing from the XRD patterns using pattern deconvolution obtained by using TOPAS 5.0 software is presented in Table 3.8 and 3.9 in Supporting Information, respectively. Quantitative analysis was performed by using the \( d \) spacing of the 111 and 200 peaks. The stacking fault probability \( \delta \) is calculated according to Equation (3.3):\(^{21b,c}\)

\[
\delta = 8.3 \times \left[ \frac{\sin \theta(200)}{\sin \theta(111)} \right]_{\text{theo.}} - \left[ \frac{\sin \theta(200)}{\sin \theta(111)} \right]_{\text{meas.}} = 8.3 \times \left[ \frac{2}{\sqrt{3}} - \left( \frac{d(111)}{d(200)} \right)_{\text{meas.}} \right] = 8.3 \times \left[ \frac{2}{\sqrt{3}} - \left( \frac{d(111)}{d(200)} \right)_{\text{meas.}} \right]
\]

(3.3)

The resulting \( \delta \) in the Cu nanoparticles of the catalyst correlates linearly with the intrinsic activity (Figure 3.3d).

![HRTEM image of 3DOM Cu\(_2\)Fe\(_1\) catalyst after reduction](image)

**Figure 3.5** HRTEM image of 3DOM Cu\(_2\)Fe\(_1\) catalyst after reduction

Note: (a) Cu nanoparticle involving an abundance of twin boundaries, (b) typical Cu twins, (c) and (d) atomic Cu steps

The syngas of \( H_2/CO = 1.0 \) was used for reduction.

The highly active Cu is a defective form of a Cu-rich nanoparticle with planar defects. HRTEM observations provide further evidence that these types of planar defects...
are stacking faults (Figure 3.4c) and twin boundaries (Figure 3.4d and 3.5b). The Cu particle consists of a high density of twin boundaries (dark lines in Figure 3.5a). A magnification of the marked area in Figure 3.5a is shown in Figure 3.5b, which shows typical Cu twins (the dash line is the twin plane). The inset shows the two sets of spot diffraction patterns that are highlighted in green and orange, which correspond to the two sides of the twin plane, respectively. In addition, the nature of the Cu active site is also exhibited as microstrain that results from lattice defects. The essential role of strain for Cu/ZnO methanol synthesis catalysts has been highlighted before.20b, 21b, d

Typically, defects present as a mechanism of strain relaxation, and some residual strain is concentrated around them.21b Thus, defects can be regarded as coupled to strain. Accordingly, the microstrain shows a coarse trend with the intrinsic activity (Figure 3.17 in Supporting Information). This observation is in accordance with the defect-activity correlation (Figure 3.3d). Behrens et al.21b suggests the main role of the bulk defects for catalysis is that an extended defect induces a line defect at the exposed surface, which is typically a step. The HRTEM image in Figure 3.5 shows stepped surface facets such as (100) and (111). These atomic steps will intrinsically serve as high-activity oxygenation sites for 1-alcohol synthesis.

Generally speaking, the Fe active site is critical for the carbon-chain growth in FT synthesis. It has been found that the iron carbide (Fe₅C₇) particle size affects the carbon-chain growth ability in FT synthesis significantly.22a Thus, long-chain product selectivity also depends on the nature of Fe₅C₇ sites. The HRTEM image of the reduced 3DOM Cu₂Fe₁ catalysts is illustrated in Figure 3.4a (inset is shown the FFT of Cu [011] zone axis), in which the Cu particle that contains planar defects is surrounded intimately by
several Hägg carbide $\chi$-Fe$_5$C$_2$ nanoparticles. STEM–EDS mapping (Figure 3.18 in Supporting Information) further evidences that the reduced 3DOM Cu$_2$Fe$_1$ catalysts possess uniform high density and stable distributions of active Cu and Fe$_x$Cy nanoparticles. The phase components of Cu (JCPDS no. 004-0836) and $\chi$-Fe$_5$C$_2$ (JCPDS no. 051-0997; Figure 3.19 in Supporting Information) were further characterized by XRD (Figure 3.4e). The fitted Mössbauer spectrum (Figure 3.4f; Table 3.10 in Supporting Information), which displays three sextets, further confirms the existence of a $\chi$-Fe$_5$C$_2$ phase. 22 Our results are consistent with previous reports that $\chi$-Fe$_5$C$_2$ is the active site for CO dissociation and carbon-chain propagation for Fe-based catalysts for Fischer–Tropsch synthesis. 22,23 Hence, a high density of defective Cu oxygenation sites in intimate contact with active $\chi$-Fe$_5$C$_2$ nanoparticle chain-propagation sites results in the synergetic function between the active and stable Cu–Fe$_x$Cy dual sites for higher alcohol synthesis from syngas.

Figure 3.6 XPS spectra of fresh, reduced, post-reaction of 3DOM Cu$_2$Fe$_1$ catalyst
Note: (a) Cu 2p XPS spectra and (b) Cu (LMM) Auger spectra
The actual chemical state of the Cu active site for alcohols synthesis remains under debate with intrinsic activity ascribed to both Cu\(^{0}\) and Cu\(^{+}\) species.\(^{24}\) It is crucial to shed light on which Cu state is responsible for the intrinsic activity. XPS experiments on the catalyst surface were performed after three different treatments. The fresh 3DOM Cu\(_2\)Fe\(_1\) sample (Figure 3.6), the Cu 2p\(_{3/2}\) and Cu 2p\(_{1/2}\) peaks are accompanied by distinct shakeup satellites at binding energies (BEs) of 942 and 962 eV. These characteristic satellites can be attributed to the charge transfer between the transition metal 3d and surrounding ligand oxygen 2p orbitals\(^{16c}\) and they do not occur in Cu\(_2\)O and Cu\(^{0}\) because of their completely filled 3d orbitals. Hence, the Cu 2p\(_{3/2}\) peak BE of 933.6 eV is indicative of CuO.\(^{16}\) After reduction, the Cu 2p\(_{3/2}\) peak shifts to a lower BE at 932.4 eV. The disappearance of the satellite peaks confirms that no Cu\(^{2+}\) species remains on the surface after reduction.\(^{16b}\) However, it is hard to distinguish between Cu\(^{0}\) and Cu\(^{+}\) species based on their similar Cu 2p BEs. The Cu 2p\(_{3/2}\) BE is 932.2 eV for Cu\(_2\)O and is 932.4 eV for Cu\(^{0}\).\(^{24}\) Generally, the kinetic energies of the Cu (LMM) Auger peaks are applied to differentiate Cu\(^{0}\) from Cu\(^{+}\) species (Figure 3.20 and Table 3.11 in Supporting Information). The line position in Cu (LMM) Auger of the reduced 3DOM Cu\(_2\)Fe\(_1\) catalysts shows that Cu\(^{0}\) is the main Cu species detected on the surface. After reaction, the surface Cu species are not re-oxidized to Cu\(^{+}\) species and remain in the Cu\(^{0}\) state. Overall, Cu\(^{0}\) is the predominant Cu species detected on the samples after reduction and reaction, and Cu\(^{+}\) species do not contribute to the activity.

### 3.4 Conclusions

In summary, we have demonstrated that higher alcohols can be produced from syngas over heterogeneous catalysis with high selectivity. This breakthrough is achieved
through the targeted design of three-dimensionally ordered macroporous Cu-Fe catalysts by using a facile glyoxylate route poly(methyl methacrylate) colloidal crystal template method. The highest selectivity to 1-alcohols was approximately 48%. The highest distribution of C$_2^+$ and C$_6^+$ slate in total 1-alcohols was approximately 95 and 63 $\%$, respectively. The chain-growth probabilities for 1-alcohols higher than 0.7 and values below 0.8 usually help to maximize the contribution of C$_6^+$ slate 1-alcohols as a feedstock for plasticizers, detergents, lubricants.

The high intrinsic activity was ascribed to three factors. First, the unique ordered structure has a large pore size and interconnected macroporous tunnels of the catalyst with a large accessible surface area which improves the catalytic activity. Second, a high density of uniformly distributed defective Cu$^0$ and Hägg carbide $\chi$-Fe$_5$C$_2$ nanoparticles derived from the glyoxylate route helps to provide abundant, active, stable dual sites. Third, atomic steps on the Cu surface, induced by planar defects and lattice strain, serve as high-activity oxygenation sites. Active $\chi$-Fe$_5$C$_2$ chain-growth sites surround the defective and strained form of Cu surface intimately, which results in a synergetic effect between the active and stable Cu–Fe$_x$C$_y$ dual site for higher alcohol synthesis.

3.5 Acknowledgements

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### 3.6 Supporting information

Table 3.1  Compilation of catalytic performance data for a variety of catalysts active in 1-alcohol synthesis

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>H\textsubscript{2}/CO Ratio</th>
<th>T (°C)</th>
<th>P (psig)</th>
<th>GHSV</th>
<th>CO Conv. (%)</th>
<th>Total Alcohol STY</th>
<th>Total Alcohol Select. (%)</th>
<th>C\textsubscript{2}OH Select. in total Alcohol (%)</th>
<th>C\textsubscript{3}OH Select. in total Alcohol (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3DOM Cu\textsubscript{3}Fe\textsubscript{2}</td>
<td>1</td>
<td>200</td>
<td>700</td>
<td>2000</td>
<td>12.9</td>
<td>0.23</td>
<td>47.6</td>
<td>74.6</td>
<td>62.4</td>
<td>This work</td>
</tr>
<tr>
<td>Co\textsubscript{2}Fe\textsubscript{0.2}Mn\textsubscript{0.1}</td>
<td>2</td>
<td>240</td>
<td>870</td>
<td>2000</td>
<td>18</td>
<td>0.24</td>
<td>37.0</td>
<td>NA</td>
<td>NA</td>
<td>11</td>
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<tr>
<td>Zn\textsubscript{0.3}Mg\textsubscript{0.2}Cu\textsubscript{0.3}</td>
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<td>260</td>
<td>700</td>
<td>2000</td>
<td>67.4</td>
<td>0.22</td>
<td>32.5</td>
<td>45.8</td>
<td>1.0</td>
<td>16a</td>
</tr>
<tr>
<td>Cu\textsubscript{2}Co\textsubscript{3}Al\textsubscript{2}O\textsubscript{2}</td>
<td>2</td>
<td>250</td>
<td>290</td>
<td>3600</td>
<td>16.5</td>
<td>0.21</td>
<td>17.1</td>
<td>64.3</td>
<td>&lt; 20.5</td>
<td>16b</td>
</tr>
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<td>Co\textsubscript{1.6}Mo\textsubscript{0.4}K\textsubscript{0.4} (4.2% Co/MWCNT)</td>
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<td>290</td>
<td>725</td>
<td>8000</td>
<td>21.1</td>
<td>0.33</td>
<td>85.0</td>
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<td>NA</td>
<td>25</td>
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<td>580</td>
<td>6000</td>
<td>52.6</td>
<td>0.24</td>
<td>35.3</td>
<td>53.3</td>
<td>2.0</td>
<td>26</td>
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<td>CuFeMgO (LDH)</td>
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<td>300</td>
<td>580</td>
<td>2000</td>
<td>56.9</td>
<td>0.28</td>
<td>49.1</td>
<td>66.9</td>
<td>11.3</td>
<td>27</td>
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<tr>
<td>Cu-Co/FeO\textsubscript{3}</td>
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<td>3900</td>
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<td>NA</td>
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<td>1500</td>
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<td>34.2</td>
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<td>2400</td>
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<td>82.5</td>
<td>11.5</td>
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<td>1450</td>
<td>5000</td>
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<td>3410</td>
<td>4.94</td>
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<td>35</td>
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<td>1%K/Co/FeO\textsubscript{3}</td>
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<td>300</td>
<td>870</td>
<td>10000</td>
<td>37.5</td>
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<td>435</td>
<td>12000</td>
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<td>42.7</td>
<td>39.6</td>
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<tr>
<td>5%Co/40%Mn/2ZrO\textsubscript{2}</td>
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<td>280</td>
<td>870</td>
<td>4000</td>
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<td>36.0</td>
<td>51.6</td>
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<td>1015</td>
<td>4000</td>
<td>50.2</td>
<td>0.14</td>
<td>22.7</td>
<td>71.3</td>
<td>&lt; 0.62</td>
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<td>Fe-Cu/Al\textsubscript{2}O\textsubscript{3} (Al\textsubscript{2}O\textsubscript{3} loading : 89.3%)</td>
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<td>0.01</td>
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<td>203</td>
<td>9000</td>
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<td>91.2</td>
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<td>580</td>
<td>6000</td>
<td>55.4</td>
<td>0.10</td>
<td>23.0</td>
<td>75.6</td>
<td>NA</td>
<td>47</td>
</tr>
<tr>
<td>2.0wt.%Rh-5wt%Mo/Al\textsubscript{2}O\textsubscript{3}</td>
<td>1</td>
<td>300</td>
<td>435</td>
<td>20</td>
<td>2.6</td>
<td>0.12</td>
<td>64.0</td>
<td>71.9</td>
<td>&lt; 4.3</td>
<td>48</td>
</tr>
<tr>
<td>K\textsubscript{2}Co/CoMo/Al\textsubscript{2}O</td>
<td>1</td>
<td>310</td>
<td>1500</td>
<td>1377</td>
<td>8</td>
<td>0.23</td>
<td>60.0</td>
<td>55.5</td>
<td>NA</td>
<td>49</td>
</tr>
</tbody>
</table>

Note: \textsuperscript{a} no mention of CO\textsubscript{2} selectivity; \textsuperscript{b} h\textsuperscript{-1}; \textsuperscript{c} g ml\textsuperscript{-1} cat h\textsuperscript{-1}; \textsuperscript{d} LL d\textsuperscript{-1} h\textsuperscript{-1}; \textsuperscript{e} carbon atom %; \textsuperscript{f} estimated from the data reported in the literature; \textsuperscript{g} g ml\textsuperscript{-1} cat h\textsuperscript{-1}; \textsuperscript{h} g g\textsuperscript{-1} (cat) h\textsuperscript{-1}; \textsuperscript{i} cm\textsuperscript{3} (STP) min\textsuperscript{-1}; 3DOM= three-dimensionally ordered macroporous; CPT = co-precipitation; LDH = layered double hydroxide; NPs = nanoparticles; C/S = core/shell; STY = space time yield; T = Reaction temperature; P = Reaction pressure.
So far, most of the present-day research on C$_2$+ slate 1-alcohols synthesis is still focused on optimizing the C$_2$–C$_5$ rather than C$_{6+}$ slate, and few papers deal with the direct long-chain 1-alcohol synthesis via heterogeneous CO hydrogenation. Thus, there is an urgency to develop heterogeneous catalysts with high catalytic activity and high selectivity of direct C$_{6+}$ slate long-chain 1-alcohol synthesis via CO hydrogenation. In this study, we demonstrate that modified FT Cu-Fe binary catalysts can be tuned so as to strongly favor 1-alcohols production. In particular, 3DOM Cu-Fe binary catalysts are synthesized by using a facile glyoxylate route poly(methyl methacrylate) (PMMA) colloidal crystal template (CCT) method so as to help to maximize the yield of C$_{6+}$ slate 1-alcohols as feedstock for plasticizers, detergents, lubricants, and so on.

3.6.1 Experimental section

3.6.1.1 Sample preparation

3.6.1.1.1 Synthesis of 3DOM Cu-Fe oxide catalysts

3DOM Cu-Fe oxide catalysts were prepared by a poly(methyl methacrylate) (PMMA) colloidal crystal template (CCT) method, using ethylene glycol (EG)–methanol solution of metal nitrates Cu(NO$_3$)$_2$·6H$_2$O and Fe(NO$_3$)$_3$·9H$_2$O as precursors, which is shown in Figure 3.7. First, the mono-disperse PMMA micro-spheres were synthesized by using an emulsion technique (Figure 3.9). Second, the obtained latex PMMA was centrifuged to form CCT. Third, the stoichiometric amount of mixed Cu-Fe nitrates were dissolved with 15 ml of EG by stirring in a 100 ml beaker at room temperature for 2 h, and the mixed solution was poured into a 50 ml volumetric flask. Methanol (6 ml) and EG were added to achieve the solution with desired concentration of methanol (the final concentration of methanol was 12 vol.%). Then the mixed Cu-Fe
precursors were added to the CCT, permeated the voids between the close-packed spheres, and condensed into a hard inorganic framework upon frying. Excessive liquid was removed from the impregnated microspheres template via a Buchner funnel connected to vacuum. The infiltered template was dried in a desiccator by using anhydrous calcium chloride at room temperature overnight. Finally, the dried sample was mixed with γ-alumina spheres (diameter: 0.125 inch) and heated in a quartz tube at the rate of 1 °C/min from room temperature to 450 °C in air for 5 h. EG was oxidized to the glyoxylate dianion in solution at about 120 °C. The mixed Cu-Fe glyoxylate was converted to mixed Cu-Fe oxide at nearly 400 °C. The 3DOM Cu-Fe oxide catalyst was obtained by further calcination at 450 °C (Figure 3.10).

Figure 3.7  Scheme of the preparation of 3DOM Cu-Fe catalyst using a facile glyoxylate route of poly(methyl methacrylate) (PMMA) colloidal crystal template (CCT) method
The glyoxylate route method \(^{14}\) has the advantages that the complexes are obtained in a short time, in a yield of practically 100\%. The in situ redox reaction may be written in Figure 3.8.

![Scheme of the glyoxylate route method and Cu-Fe glyoxylates heteropolynuclear structure](image)

Figure 3.8  Scheme of the glyoxylate route method and Cu-Fe glyoxylates heteropolynuclear structure

Note: (a) the glyoxylate route method and (b) 2Fe(III)–Cu(II) glyoxylates heteropolynuclear structure

### 3.6.1.1.2 Synthesis of the precipitated Cu and the coprecipitated Cu-Fe catalyst

The precipitated Cu and the coprecipitated Cu-Fe catalysts were prepared using traditional precipitation method \(^{16a}\) using sodium carbonate as precipitating agent, for a comparison with 3DOM Cu-Fe catalysts.

### 3.6.1.2 Catalyst characterization

#### 3.6.1.2.1 X-ray diffraction (XRD)

XRD measurements were carried out by using an Ultima III X-ray diffractometer (Rigaku Americas, The Woodlands, TX) with Cu K\(\alpha\) radiation (\(\lambda = 0.154\) nm) operated at 40 kW and 44 mA at a rate of 0.08 \(^{\circ}\) min\(^{-1}\). Before transferring for XRD measurement, the selected catalysts sample after reduction were carefully protected using inert nitrogen gas to avoid being re-oxidized by air. Rietveld refinements fit of the X-ray diffraction patterns of selected catalysts sample after reduction (include Cu Ref. catalyst sample)
were performed in the range 10–100° 2θ using the software package TOPAS (A. A. Coelho, Topas, General Profile and Structure Analysis Software for Powder Diffraction Data, Version 5.0, 2012). The background was modeled using a five order Chebychev polynomial. Some technical details are listed in Table 3.6, selected results are reported in Table 3.7 and graphical representations of the Rietveld fits are shown in Figure 3.16. Plots of the intrinsic catalytic activity versus the Rietveld fits are shown in Figure 3.17.

The X-ray diffraction patterns were fitted using TOPAS software with a background function (Chebychev polynomial), five pseudo-Voigt functions to simulate the Cu phase without structural model and a simultaneous pattern for Hägg carbide \( \chi \)-Fe\(_5\)C\(_2\) based on the contribution of \( \chi \)-Fe\(_5\)C\(_2\) to the Rietveld fit for those samples with a significant contribution of crystalline \( \chi \)-Fe\(_5\)C\(_2\). The errors of the peak positions were estimated to be smaller than \( \pm 0.04° 2θ \). The zero-shift values determined from the full pattern Rietveld analysis (Table 3.7) were used to correct the raw position of the Cu peaks. The stacking fault probability \( δ \) was determined from the measurements of interval between the adjacent peaks Cu (111) and Cu (200), which are known to shift in opposite direction as \( δ \) increases, and comparing them to the corresponding interval in a “perfect” material. The Equation (3.3)\(^{21b,c}\) was used to calculate the stacking fault probability \( δ \).

### 3.6.1.2.2 Scanning electron microscopy (SEM)

JEOL JSM-6500F Field Emission–Scanning electron microscopy (FE–SEM) was used to characterize the morphology of the PMMA, colloidal crystal template, and 3DOM Cu-Fe catalyst. The operating voltage was 5 kV.
3.6.1.2.3 **High resolution transmission electron microscopy (HRTEM)**

HRTEM and scanning TEM (STEM) images were obtained on a JEOL 2100 electron microscope (JEOL, Japan) operated at 200 kV. The composition and elemental distribution of the catalysts were mapped through X-ray energy dispersive spectrometer (EDS) by displaying the integrated intensity of respective elemental signals as a function of the beam position when operating the TEM in scanning mode (STEM). STEM images were digitally processed through Gatan Digi-Scan. The catalyst samples were dispersed in ethanol and sonicated for 20 min and then deposited over a Formvar Nickel grid.

3.6.1.2.4 **Mössbauer spectrum**

Mössbauer spectrum experiments were carried out using a $^{57}$Co/Rh source in a constant acceleration transmission spectrometer. The spectra were recorded at 27 °C. The spectrometer was calibrated using a standard α-Fe foil and the reported isomer shifts (ISO) are relative to the center of the α-Fe spectrum. The WinNormos-for-Igor 3.0 program was used to determine the Mössbauer parameters. A nonlinear least-squares fitting procedure with a set of independent Lorentzian lines that models the spectra as a combination of singlet, quadruple doublets and/or magnetic sextets was used for data analysis. The spectra components were identified according to their isomer shift, quadruple splitting, and magnetic hyperfine field. Magnetic hyperfine fields were calibrated with the 330 kOe field of α-Fe at room temperature (27 °C). Before transferring for Mössbauer measurement, the selected catalyst samples after reduction were carefully protected using inert nitrogen gas to avoid being re-oxidized by air.
3.6.1.2.5 X-ray photoelectron spectroscopy (XPS)

XPS was recorded with a PHI 1600 XPS surface Analysis System (Physical Electronics, Eden Prairie, MN). The instrument used a PHI 10-360 spherical capacitor energy analyzer and an Omni Focus II small-area lens to focus the incident source to an 800 µm diameter surface analysis area, using an achromatic Mg Kα X-ray source \( (h\nu = 1253.6 \text{ eV}) \) operating at 300 W and 15 kV. Survey spectra were gathered using an average of 10 scans with a pass energy of 26.95 eV and ran from 1100 to 0 eV. High resolution spectra were gathered using an average of 15 scans with a pass energy of 23.5 eV and a step size of 0.1 eV. The incident sample angle was held constant at 45°. XPS data was collected and averaged using PHI Surface Analysis software, Version 3.0 (Physical Electronics, Eden Prairie, MN). XPS data was then analyzed by using Casa XPS software. The C1s peak of adventitious carbon (284.5 eV) was used as a reference for estimating the binding energy. The binding energies were given with an accuracy of ±0.1 eV. Before transferring for XPS measurement, the catalyst samples after reduction were carefully protected using inert nitrogen gas to avoid being re-oxidized by air.

3.6.1.2.6 Brunauer–Emmett–Teller (BET) measurement

The textural properties (BET specific surface areas, pore volume, pore size) of catalysts were measured with linear parts of the BET plot of the N₂ isotherms. Nitrogen adsorption/desorption isotherms at −196 °C were recorded using a Micromeritics ASAP 2010 porosimeter. The samples were outgassed in a N₂ flow at 250 °C for 4 h before the measurement.
3.6.1.2.7 N₂O chemisorption to determine Cu surface area

The Cu surface area was measured by a nitrous oxide decomposition method \(^{24,52}\) by using Micromeritics Autochem 2920. N₂O chemisorption process consists of three sequential steps:

Step 1: \( \text{CuO} + \text{H}_2 \rightarrow \text{Cu} + \text{H}_2\text{O} \)  

Step 2: \( 2\text{Cu} + \text{N}_2\text{O} \rightarrow \text{Cu}_2\text{O} + \text{N}_2 \)  

Step 3: \( \text{Cu}_2\text{O} + \text{H}_2 \rightarrow 2\text{Cu} + \text{H}_2\text{O} \)

First, the catalysts (100 mg) were reduced with 5 % H₂/Ar at 300 °C for 3 h followed by purging with He for 30 min and afterwards cooling to 60 °C. Then the catalysts were exposed to 5 % N₂O/Ar for 1 h to oxidize surface Cu atoms to Cu₂O, and the decomposition of N₂O to N₂ was monitored by using mass spectrometer. Finally, the samples were cooled down to room temperature, and the temperature-programmed reduction (TPR) was performed under a 5 % H₂/Ar flow to reduce Cu₂O back to metallic Cu using a ramp rate of 10 °C/min to 300 °C. The Cu surface area was calculated from the amount of H₂ consumed during the TPR step by assuming that Cu crystallites are spherical. The following Equation (3.7) is used to calculate Cu surface area:

\[
\text{Cu S. A.} \left( \frac{\text{m}^2}{\text{g}_{\text{Cu}}} \right) = \frac{100 \times (\text{Mol H}_2) \times (\text{SF}) \times (N_A)}{(\text{SD}_{\text{Cu}}) \times W_{\text{Cu}}} 
\]

where Mol H₂ = amount of H₂ consumed during the TPR step per unit mass of the catalyst (mol H₂/g_{cat}), SF = stoichiometric factor = 2, \( N_A = \) Avogadro’s number = 6.022×10\(^{23}\) atoms/mol, SD\(_{\text{Cu}}\) = Cu surface density = 1.46×10\(^{19}\) atoms/m², \( W_{\text{Cu}} \) = Cu content of the catalyst determined from elemental analysis (wt.%).
3.6.1.3 The catalytic performance

The catalytic performance of the catalysts was tested in a stainless steel fixed-bed reactor (half-inch diameter). 1 gram catalyst was loaded into the reactor for every reaction test. The remaining volume of the reactor tube was filled with quartz bead in a size of 2 mm. All the catalysts were reduced and activated with syngas (H₂/CO =1.0) at T = 300 °C, P = 10 psig, and 2000 h⁻¹ of GHSV for 48 h. The reaction conditions were maintained at T = 200~280 °C, P = 700 psig, 2000 h⁻¹ of GHSV, and syngas (H₂/CO =1.0, 6% N₂ as internal standard), time-on-stream 120 h.

3.6.1.4 Product analysis

The product and reactant in the gas phase were detected online by using Agilent 7890 gas chromatograph provided with two thermal conductivity detectors (TCD) and a flame ionization detector (FID). Helium and nitrogen were used as the carrier gases. C₁–C₄-ranged alkanes and alkenes were analyzed using a HP Plot capillary column with a flame ionization detector (FID); CO, CO₂, CH₄, and N₂ were analyzed by using molecular sieve-packed column with a thermal conductivity detector. The 6% N₂ in the syngas was used as an internal standard for the calculation of CO conversion.

The liquid products were collected by using a condenser kept at −5 °C. Alcohols and hydrocarbons were analyzed by using an Agilent 7683B Series Injector coupled to an Agilent 6890 Series gas chromatograph system and a 5973 Mass Selective Detector, i.e., a quadrupole type GC–MS, as well as a FID detector. An Agilent DB-WAXetr (50 m × 0.32 mm I.D., 1.0μm) capillary column was used for analyzing oxygenated compounds and HP-5 capillary column was used for analyzing hydrocarbons.
3.6.2 Results and discussion

Figure 3.9 SEM images of PMMA microspheres and PMMA colloidal crystal template (CCT)

Note: (a) PMMA microspheres, and (b) PMMA colloidal crystal template (CCT)

Figure 3.10 SEM images of 3DOM Cu-Fe catalysts

Note: (a) 3DOM Cu$_1$Fe$_1$, (b) 3DOM Cu$_2$Fe$_1$, (c) 3DOM Cu$_3$Fe$_1$, and (d) 3DOM Cu$_1$Fe$_2$
Figure 3.11  STEM-EDS mapping images of the fresh 3DOM Cu$_2$Fe$_1$ catalyst

Note: STEM-EDS mapping images demonstrate a uniform high density and a stable distribution of 3DOM Cu-Fe oxide derived from the glyoxylate route method.

Figure 3.12  HRTEM image of the fresh 3DOM Cu$_2$Fe$_1$ catalyst

Note: HRTEM image indicates a uniform high density and a stable distribution of CuO and Fe$_3$O$_4$ mixed oxide nanoparticles derived from the glyoxylate route method.

Table 3.2  The physicochemical properties and the catalytic performance $^a$

<table>
<thead>
<tr>
<th>Fresh catalysts (by molar)</th>
<th>$^a$S$_{BET}$</th>
<th>$^b$V$_{pore}$</th>
<th>$^c$d$_{pore}$</th>
<th>$^d$d$_{MT}$</th>
<th>$^e$CO Conv.</th>
<th>$^f$STY</th>
<th>Selectivity</th>
<th>Alcohols Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>/ m$^2$ g$^{-1}$</td>
<td>/ cm$^3$ g$^{-1}$</td>
<td>/ nm</td>
<td>/ nm</td>
<td>/ %</td>
<td>/ g g$^{-1}$ (cat.) h$^{-1}$</td>
<td>/ wt. %</td>
<td>/ wt.%</td>
</tr>
<tr>
<td>3DOM Cu$_2$Fe$_1$</td>
<td>37.0</td>
<td>0.088</td>
<td>9.5</td>
<td>14.6</td>
<td>31.2</td>
<td>0.09</td>
<td>0.15</td>
<td>10.5</td>
</tr>
<tr>
<td>3DOM Cu$_2$Fe$_1$</td>
<td>27.7</td>
<td>0.076</td>
<td>10.9</td>
<td>14.5</td>
<td>44.3</td>
<td>0.11</td>
<td>0.13</td>
<td>19.8</td>
</tr>
<tr>
<td>3DOM Cu$_2$Fe$_1$</td>
<td>43.3</td>
<td>0.089</td>
<td>8.2</td>
<td>14.3</td>
<td>58.4</td>
<td>0.19</td>
<td>0.26</td>
<td>31.3</td>
</tr>
<tr>
<td>3DOM Cu$_2$Fe$_1$</td>
<td>28.5</td>
<td>0.082</td>
<td>11.5</td>
<td>16.5</td>
<td>38.9</td>
<td>0.13</td>
<td>0.18</td>
<td>25.8</td>
</tr>
<tr>
<td>CPT $^a$Cu$_2$Fe$_1$</td>
<td>10.7</td>
<td>0.063</td>
<td>23.4</td>
<td>18.9</td>
<td>27.5</td>
<td>0.07</td>
<td>0.10</td>
<td>22.9</td>
</tr>
</tbody>
</table>

Note: $^a$ Reaction conditions: P = 700 psig, T = 260 °C, GHSV = 2000 h$^{-1}$, H$_2$/CO = 1.0, time-on-stream 120 h. $^b$CPT: Coprecipitated. $^a$BET specific surface areas evaluated in P/P$_0$ from 0.05 to 0.9, ±2 m$^2$ g$^{-1}$. $^b$Total pore volumes estimated based on the volume adsorbed at P/P$_0$ of 0.989, ±0.005 (cm$^3$ g$^{-1}$). $^c$Pore sizes derived from the adsorption branches of the isotherms by using the BJH method, ±0.5 nm. $^d$Average crystallite size estimated by the Scherrer equation from XRD pattern, ±0.3 nm. $^e$CO conversion rate (mol%) = $\frac{CO_{in}-CO_{out}}{CO_{in}} \times 100$, ±3%. $^f$STY (g g$^{-1}$ (cat.) h$^{-1}$) = $\frac{\text{Weight of product produced (g)}}{\text{Weight of Catalyst (g) x h}}$ ±0.01 (g g$^{-1}$ (cat.) h$^{-1}$).

$^a$ROH for alcohols and $^b$HC for hydrocarbons.
The ASF plots are based on the 1-ahols distribution were obtained when performing the CO hydrogenation reaction at the condition of $P = 700$ psig, $T = 200$ °C, GHSV = 2000 h$^{-1}$, $H_2/CO = 1.0$, time-on-stream of 120 h. Errors for chain growth are calculated from the deviations of $\ln (W_n/n)$ versus $n$ from linearity. The Anderson–Schulz–Flory (ASF) chain growth probability $\alpha$ of products are calculated according to Equation (3.1),\textsuperscript{16a} where $n$ is the number of carbon atoms in products, $W_n$ is the weight fraction of products containing $n$ carbon atoms, and $1 - \alpha$ is the probability of chain termination.
Figure 3.14  The catalytic activity and selectivity performance for 3DOM Cu-Fe catalysts with varying relative amounts of metal atoms

Note: The reaction condition is $P = 700$ psig, GHSV = $2000$ h$^{-1}$, and $H_2/CO = 1.0$

The Anderson–Schulz–Flory (ASF) chain growth probability $\alpha$ of products are calculated according to Equation (3.1), where $n$ is the number of carbon atoms in products, $W_n$ is the weight fraction of products containing $n$ carbon atoms, and $1-\alpha$ is the probability of chain termination.

The observation of the correlated $\alpha$-values for 1-alcohols and hydrocarbons (Tables 3.3 and 3.4) for varying catalyst compositions and reaction conditions are in agreement with a common chain growth mechanism by CO insertion into the same type of intermediate, and then late kinetic branching to $n$-alkanes, 1-alcohols, and 1-alkenes. $^{11}$
Accordingly, we can assume the associative CO insertion kinetic step as the rate-limiting elementary step and that Cu serves as the oxygenate site for 1-alcohol synthesis, which is an essential prerequisite to correlate Cu defects or Cu lattice strain with intrinsic activities. The CO insertion mechanism on the Cu-modified FTS catalysts for 1-alcohol synthesis is shown in Figure 3.15.

Table 3.3  The chain growth probability ($\alpha$) of 1-alcohols and hydrocarbons over various catalysts at 200 °C

<table>
<thead>
<tr>
<th>Chain growth probability ($\alpha$) for various catalysts</th>
<th>3DOM Cu$_2$Fe$_2$</th>
<th>3DOM Cu$_1$Fe$_1$</th>
<th>3DOM Cu$_2$Fe$_1$</th>
<th>Coprecipitated Cu$_2$Fe$_1$</th>
<th>3DOM Cu$_3$Fe$_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-alcohols</td>
<td>0.75</td>
<td>0.78</td>
<td>0.81</td>
<td>0.71</td>
<td>0.76</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>0.80</td>
<td>0.82</td>
<td>0.83</td>
<td>0.74</td>
<td>0.81</td>
</tr>
</tbody>
</table>

Note: Hydrocarbons include olefins and paraffins

Table 3.4  The chain growth probability ($\alpha$) of 1-alcohols and hydrocarbons over 3DOM Cu$_2$Fe$_1$ catalyst at different temperatures

<table>
<thead>
<tr>
<th>Chain growth probability ($\alpha$) for 3DOM Cu$_2$Fe$_1$ catalysts</th>
<th>200 °C</th>
<th>220 °C</th>
<th>240 °C</th>
<th>260 °C</th>
<th>280 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-alcohols</td>
<td>0.81</td>
<td>0.78</td>
<td>0.74</td>
<td>0.71</td>
<td>0.70</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>0.83</td>
<td>0.80</td>
<td>0.78</td>
<td>0.75</td>
<td>0.73</td>
</tr>
</tbody>
</table>

Note: Hydrocarbons include olefins and paraffins
The CO insertion mechanism for higher alcohol synthesis proposed by Xu et al. is widely accepted for modified FT catalysts (Figure 3.15). In the CO insertion mechanism, higher alcohol synthesis is regarded as a combination of Fischer–Tropsch synthesis (FTS) and methanol synthesis, or as a process between FTS and methanol synthesis. The CO dissociation \( (k_d) \), chain initiation \( (k_i) \) and chain propagation \( (k_p) \) proceed similarly to the FT reaction to form surface alkyl species \( (C_nH_z^*) \), and the termination reaction of the alkyl species determines the products formation. The termination by CO insertion \( (k_{co}) \) forms alcohols through surface acyl species \( (C_nH_zCO^*) \) followed by hydrogenation \( (k_{H^*}) \), while the termination by dehydrogenation or hydrogenation \( (k_{III}) \) forms olefins and paraffins, respectively. The 1-alcohols formation
competes with the hydrocarbon formation. The CO insertion mechanism elucidates why modified FT catalysts mainly produced linear 1-alcohols and the alcohols obey the ASF distribution with a similar chain growth probability as for hydrocarbons.

Table 3.5  The selected characteristics of the catalysts samples after reduction using syngas

<table>
<thead>
<tr>
<th>Sample after reduction</th>
<th>$^a$S_{BET} / m$^2$ g$^{-1}$</th>
<th>$^b$V$_{pore}$/ cm$^3$ g$^{-1}$</th>
<th>$^c$d$_{pore}$/ nm</th>
<th>$^d$N$_2$O Cu Surface Area / m$^2$ g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu Ref.</td>
<td>8.69</td>
<td>0.025</td>
<td>11.5</td>
<td>1.6</td>
</tr>
<tr>
<td>3DOM Cu$_1$Fe$_2$</td>
<td>74.7</td>
<td>0.358</td>
<td>19.2</td>
<td>13.0</td>
</tr>
<tr>
<td>3DOM Cu$_1$Fe$_1$</td>
<td>88.6</td>
<td>0.393</td>
<td>17.7</td>
<td>29.9</td>
</tr>
<tr>
<td>3DOM Cu$_2$Fe$_1$</td>
<td>86.2</td>
<td>0.483</td>
<td>22.4</td>
<td>14.3</td>
</tr>
<tr>
<td>Coprecipitated Cu$_2$Fe$_1$</td>
<td>39.3</td>
<td>0.308</td>
<td>31.3</td>
<td>12.8</td>
</tr>
<tr>
<td>3DOM Cu$_3$Fe$_1$</td>
<td>74.3</td>
<td>0.450</td>
<td>24.2</td>
<td>11.8</td>
</tr>
</tbody>
</table>

Note: $^a$BET specific surface areas evaluated in $P/P_0$ from 0.05 to 0.99, ± 2.0 (m$^2$ g$^{-1}$). $^b$Total pore volumes estimated based on the volume adsorbed at $P/P_0$ of 0.989, ± 0.005 (cm$^3$ g$^{-1}$). $^c$Pore sizes derived from the adsorption branches of the isotherms by using the BJH method, ± 0.5 nm. $^d$Cu surface area determined from N$_2$O chemisorption, ± 0.5 (m$^2$ g$^{-1}$)
Figure 3.16  Graphical representation of the Rietveld refinement fits (Cu and $\chi$-Fe$_2$C$_2$) for the selected reduced catalyst samples and the pure Cu reference sample.
The quality of the fits is representative for all patterns (Figure 3.16). The characteristic underestimation of the intensity near the maximum of the 200 peak at approximately $2\theta = 50.4^\circ$ in the XRD pattern can be explained by the presence of twin boundaries and stacking faults that result in a broadening of this reflection.  

Figure 3.17 Attempts to correlate the intrinsic catalytic activities of the catalysts with the results obtained by Rietveld refinement.

Note: (a) Cu lattice parameter, (b) Cu lattice strain, (c) the isotropic disorder parameter for Cu, and (d) the crystallite domain size of Cu.

The refined Cu lattice parameter $a$ (fcc, Fm3m, $a = 3.6150$ Å) shows some significant variation indicating that compressive strain for most samples. This compressive strain is most likely induced by the Gibbs-Thomson effect that can lead to a
decrease in the bulk lattice constant for small particles.\textsuperscript{21b} This kind of strain is localized in the body of particles and should be irrelevant to catalytic activity. However, it can be partially compensated by surface “outward” relaxation and both effects are very hard to separate for small particles in the nanometer-range on basis of diffraction data.\textsuperscript{21b} The maximal detected lattice parameter deviation is less than $-0.1\%$.

The Rietveld software extracts a Gaussian distribution of lattice spacing around a mean value, to which the above mentioned effects, but in particular also the presence of defects contribute. The amount of this indirect micro-strain is also relatively low ($< 0.3\%$), but shows a coarse trend with the intrinsic activity. This observation is in accordance with the defect-activity correlation. Typically, defects appear as a mechanism of strain relaxation, and some residual strain is concentrated around them.\textsuperscript{21b} Thus, defects can be considered as coupled to strain and planar defects should also have some contribution to the measured strain.

The equivalent isotropic temperature factor or disorder parameter $B_{eq}$ (the thermal motion and static disorder of the atoms in the lattice) does not correlate with the intrinsic activity. The crystallite domain size as determined from the peak widths (and separated from the strain contribution by the different $hkl$-dependence of both effects by the Rietveld software) does not show a clear trend with intrinsic activity.
Table 3.6  The details of Rietveld analysis of the XRD results of the reduced catalysts samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>(R_{\text{Bragg}})</th>
<th>(R_{\text{wp}}/R_{\text{wp}}')</th>
<th>No. of parameters</th>
<th>GOF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu Ref.</td>
<td>1.94</td>
<td>5.20/16.85</td>
<td>28</td>
<td>1.13</td>
</tr>
<tr>
<td>3DOM Cu,Fe₂</td>
<td>2.09</td>
<td>11.73/38.50</td>
<td>31</td>
<td>1.18</td>
</tr>
<tr>
<td>3DOM Cu,Fe₁</td>
<td>4.26</td>
<td>7.26/32.76</td>
<td>28</td>
<td>1.11</td>
</tr>
<tr>
<td>3DOM Cu₂Fe₁</td>
<td>4.79</td>
<td>6.76/31.86</td>
<td>43</td>
<td>1.13</td>
</tr>
<tr>
<td>Coprecipitated Cu₂Fe₁</td>
<td>2.36</td>
<td>6.62/29.22</td>
<td>40</td>
<td>1.08</td>
</tr>
<tr>
<td>3DOM Cu₃Fe₁</td>
<td>3.85</td>
<td>6.35/28.91</td>
<td>35</td>
<td>1.18</td>
</tr>
</tbody>
</table>

Note: Criteria of fit (see Young 1995 for details). 53 “R-Bragg”, \(R_{\text{Bragg}} = \frac{\sum |I_o,k - I_c,k|}{\sum I_o,k}\), “R-weighted pattern”, \(R_{\text{wp}} = \sqrt{\sum w_m (Y_o,m - Y_c,m)^2 / \sum w_m Y_o,m^2}\); \(R_{\text{wp}}'\) (background corrected) = \(\sqrt{\sum w_m (Y_o,m - Y_c,m - Bkg,m)^2 / \sum w_m (Y_o,m - Bkg,m)^2}\); “Goodness of fit”, GOF = \(\text{chi} = \sqrt{\sum w_m (Y_o,m - Y_c,m)^2 / M - P}\). \(w_m\) the weighting given to data point \(m\) which for counting statistics is given by \(w_m = 1/\sigma(Y_o,m)^2\) where \(\sigma(Y_o,m)\) is the error in \(Y_o,m\), and \(I_o,\alpha,\kappa\) and \(I_c,\kappa\) the “observed” and calculated intensities of the \(k\)th reflection.

Table 3.7  The selected results of the Rietveld refinement

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice Parameter (a) / Å</th>
<th>Lattice strain (\varepsilon_0) / %</th>
<th>B_sq / Å²</th>
<th>L_voxel-IB /nm</th>
<th>Zero shift / °2θ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu Ref.</td>
<td>3.61571±0.00090</td>
<td>0.03±0.01</td>
<td>0.34±0.03</td>
<td>50.1±10.0</td>
<td>0.03±0.01</td>
</tr>
<tr>
<td>3DOM Cu₁,Fe₂</td>
<td>3.60549±0.00140</td>
<td>0.24±0.08</td>
<td>0.54±0.13</td>
<td>14.6±1.3</td>
<td>0.08±0.03</td>
</tr>
<tr>
<td>3DOM Cu₁,Fe₁</td>
<td>3.61217±0.00120</td>
<td>0.13±0.06</td>
<td>0.48±0.11</td>
<td>14.5±0.6</td>
<td>0.13±0.04</td>
</tr>
<tr>
<td>3DOM Cu₂Fe₁</td>
<td>3.61447±0.00150</td>
<td>0.29±0.03</td>
<td>0.45±0.09</td>
<td>14.3±0.9</td>
<td>0.07±0.02</td>
</tr>
<tr>
<td>Coprecipitated Cu₁,Fe₁</td>
<td>3.61247±0.00180</td>
<td>0.15±0.05</td>
<td>0.39±0.06</td>
<td>16.5±1.4</td>
<td>0.04±0.02</td>
</tr>
<tr>
<td>3DOM Cu₃Fe₁</td>
<td>3.61425±0.00130</td>
<td>0.19±0.04</td>
<td>0.31±0.08</td>
<td>18.9±1.9</td>
<td>0.05±0.02</td>
</tr>
</tbody>
</table>

Note: The crystallite domain size in form of volume-weighted column length based on the integral breadths of the reflections.
Table 3.8  Peak positions in $2\theta^\circ$ of Cu reflections from pattern deconvolution of the selected reduced catalysts samples

<table>
<thead>
<tr>
<th>Peak</th>
<th>Cu Ref.</th>
<th>3DOM Cu1Fe2</th>
<th>3DOM Cu1Fe1</th>
<th>3DOM Cu2Fe1</th>
<th>Coprecipitated Cu2Fe1</th>
<th>3DOM Cu3Fe1</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>43.359</td>
<td>43.321</td>
<td>43.278</td>
<td>43.361</td>
<td>43.332</td>
<td>43.344</td>
</tr>
<tr>
<td>200</td>
<td>50.480</td>
<td>50.406</td>
<td>50.360</td>
<td>50.415</td>
<td>50.421</td>
<td>50.410</td>
</tr>
<tr>
<td>220</td>
<td>74.141</td>
<td>74.339</td>
<td>74.138</td>
<td>74.220</td>
<td>74.138</td>
<td>74.100</td>
</tr>
<tr>
<td>311</td>
<td>89.940</td>
<td>89.860</td>
<td>89.720</td>
<td>89.819</td>
<td>90.018</td>
<td>89.921</td>
</tr>
<tr>
<td>222</td>
<td>95.160</td>
<td>95.134</td>
<td>95.126</td>
<td>95.161</td>
<td>95.175</td>
<td>95.262</td>
</tr>
</tbody>
</table>

Table 3.9  $d$ spacing (Å) of Cu reflections from pattern deconvolution of the selected reduced catalysts samples

<table>
<thead>
<tr>
<th>Peak</th>
<th>Cu Ref.</th>
<th>3DOM Cu1Fe2</th>
<th>3DOM Cu1Fe1</th>
<th>3DOM Cu2Fe1</th>
<th>Coprecipitated Cu2Fe1</th>
<th>3DOM Cu3Fe1</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>2.0851</td>
<td>2.0869</td>
<td>2.0889</td>
<td>2.0850</td>
<td>2.0864</td>
<td>2.0858</td>
</tr>
<tr>
<td>200</td>
<td>1.8064</td>
<td>1.8089</td>
<td>1.8104</td>
<td>1.8086</td>
<td>1.8084</td>
<td>1.8088</td>
</tr>
<tr>
<td>220</td>
<td>1.2778</td>
<td>1.2749</td>
<td>1.2779</td>
<td>1.2767</td>
<td>1.2779</td>
<td>1.2784</td>
</tr>
<tr>
<td>311</td>
<td>1.0899</td>
<td>1.0907</td>
<td>1.0920</td>
<td>1.0911</td>
<td>1.0892</td>
<td>1.0901</td>
</tr>
<tr>
<td>222</td>
<td>1.0434</td>
<td>1.0436</td>
<td>1.0437</td>
<td>1.0434</td>
<td>1.0433</td>
<td>1.0426</td>
</tr>
</tbody>
</table>

Figure 3.18  STEM-EDS mapping image of the 3DOM Cu2Fe1 catalyst after reduction

Note: The syngas of $H_2/CO = 1$ was used for reduction. STEM-EDS mapping images demonstrate a uniform high density and a stable distribution of Cu, Fe, and C elements in the reduced catalysts.
Table 3.10  Mössbauer parameters of the reduced 3DOM Cu$_2$Fe$_1$ catalyst measured at 27 °C

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>IS / mm s$^{-1}$</th>
<th>QS / mm s$^{-1}$</th>
<th>Hyperfine field / T</th>
<th>Phase</th>
<th>Spectra contribution / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>3DOM Cu$_2$Fe$_1$</td>
<td>0.26</td>
<td>0.05</td>
<td>22.1</td>
<td>χ-Fe$_5$C$_2$(II)</td>
<td>27.0</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>0.05</td>
<td>18.1</td>
<td>χ-Fe$_5$C$_2$(I)</td>
<td>31.1</td>
</tr>
<tr>
<td></td>
<td>0.21</td>
<td>0.07</td>
<td>10.5</td>
<td>χ-Fe$_5$C$_2$(III)</td>
<td>20.4</td>
</tr>
<tr>
<td></td>
<td>0.32</td>
<td>1.07</td>
<td></td>
<td>spm phase</td>
<td>21.5</td>
</tr>
</tbody>
</table>

Note: The result was obtained from Figure 3.4f, which agrees with the report by the reference paper. Experimental uncertainties: Isomer shift: IS±0.01mm s$^{-1}$; Quadrupole splitting: QS±0.01mm s$^{-1}$; Hyperfine field: ±0.1T; Spectra contribution: ±3.0%. (Reducing conditions: T = 300 °C, P = 10 psig, H$_2$/CO = 1.0, GHSV = 2000 h$^{-1}$) (spm: super-paramagnetic)

Figure 3.19  XRD pattern of the reduced 3DOM Fe catalyst

Note: The result represents Hägg carbide χ-Fe$_5$C$_2$ species, which is in agreement with JCPDS no. 051-0997 and the report by the reference paper.
Figure 3.20  Cu 2p XPS spectra and Cu (LMM) Auger of the fresh, reduced and post-reacted 3DOM Cu-Fe catalysts

Note: (a) Cu 2p XPS spectra and (b) Cu (LMM) Auger of the fresh, reduced, and post-reacted 3DOM Cu$_3$Fe$_1$ catalyst, (c) Cu 2p XPS spectra and (d) Cu (LMM) Auger of the fresh, reduced, and post-reacted 3DOM Cu$_1$Fe$_1$ catalyst, (e) Cu 2p XPS spectra and (f) Cu (LMM) Auger of the fresh, reduced, post-reacted 3DOM Cu$_1$Fe$_2$ catalyst
Table 3.11 The Cu 2p\textsubscript{3/2} binding energies (BE) and Cu (LMM) kinetic energies (KE) for various catalysts

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Treatment</th>
<th>Cu 2p\textsubscript{3/2} BE / eV</th>
<th>Cu (LMM) KE / eV</th>
<th>α\textsubscript{Cu} / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>3DOM Cu\textsubscript{1}Fe\textsubscript{1}</td>
<td>Fresh</td>
<td>933.4</td>
<td>918.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Reduced</td>
<td>932.3</td>
<td>918.7</td>
<td>1851.0</td>
</tr>
<tr>
<td></td>
<td>Post-reacted</td>
<td>932.3</td>
<td>918.8</td>
<td>1851.1</td>
</tr>
<tr>
<td>3DOM Cu\textsubscript{2}Fe\textsubscript{1}</td>
<td>Fresh</td>
<td>933.6</td>
<td>917.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Reduced</td>
<td>932.4</td>
<td>918.9</td>
<td>1851.3</td>
</tr>
<tr>
<td></td>
<td>Post-reacted</td>
<td>932.4</td>
<td>918.8</td>
<td>1851.2</td>
</tr>
<tr>
<td>3DOM Cu\textsubscript{3}Fe\textsubscript{1}</td>
<td>Fresh</td>
<td>933.5</td>
<td>917.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Reduced</td>
<td>932.5</td>
<td>918.6</td>
<td>1851.1</td>
</tr>
<tr>
<td></td>
<td>Post-reacted</td>
<td>932.5</td>
<td>918.8</td>
<td>1851.1</td>
</tr>
<tr>
<td>3DOM Cu\textsubscript{1}Fe\textsubscript{2}</td>
<td>Fresh</td>
<td>933.2</td>
<td>917.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Reduced</td>
<td>932.2</td>
<td>918.9</td>
<td>1851.1</td>
</tr>
<tr>
<td></td>
<td>Post-reacted</td>
<td>932.2</td>
<td>919.1</td>
<td>1851.3</td>
</tr>
</tbody>
</table>

Note: The results were obtained from Figure 3.6 and Figure 3.20. Experimental uncertainties: BE ± 0.1 eV, KE ± 0.1 eV

Table 3.11 summarizes the Cu 2p\textsubscript{3/2} binding energies (BE) and Cu (LMM) kinetic energies (KE) for the various catalysts (Figure 3.6 and Figure 3.20). The Cu 2p\textsubscript{3/2} BE of the fresh samples is in the range of 933.2–933.6 eV and decreases to 932.2–932.5 eV after reduction and reaction. On the other hand, the Cu (LMM) KE for the reduced catalysts increases to 918.6–918.9 eV compared to the values of the fresh samples.

After exposure to syngas (H\textsubscript{2}/CO =1), the KE of the Cu (LMM) peak has a small change. The KE values agree well with those reported for Cu\textsuperscript{0} species on the surface of Cu-containing catalysts.\textsuperscript{24,56} The modified Auger parameter α\textsubscript{Cu} can be employed to differentiate Cu\textsuperscript{0} (1850.6–1851.6 eV) from Cu\textsuperscript{+} species (1848.6–1849.5 eV) according to Equation (3.8).\textsuperscript{57}

\[
\alpha_{\text{Cu}} = h\nu + \text{KE(Cu}_{\text{LMM}}) - \text{KE(Cu } 2p_{3/2}) = \text{KE(Cu}_{\text{LMM}}) + \text{BE(Cu } 2p_{3/2}) \quad (3.8)
\]
As also shown in Table 3.11, the values of the modified Auger parameter for the reduced and post-reacted catalysts are 1851.0–1851.3 eV, which again corresponds to Cu$^0$ species.
3.7 References


CHAPTER IV

IN SITU AMBIENT PRESSURE X-RAY PHOTOELECTRON SPECTROSCOPY AND SYNCHROTRON POWDER DIFFRACTION STUDIES OF THREE-DIMENSIONALLY ORDERED MACROPOROUS CU-FE CATALYSTS FOR HIGHER ALCOHOL SYNTHESIS FROM SYNGAS

Abstract: In situ ambient pressure x-ray photoelectron spectroscopy (AP–XPS) and in situ synchrotron powder diffraction were applied to identify the active site of three-dimensionally ordered macroporous (3DOM) Cu-Fe catalysts for higher alcohol synthesis from syngas. The results show that after syngas pretreatment of the 3DOM Cu-Fe catalysts, Cu\(^0\) is the active oxygenation site for alcohol synthesis, and \(\chi\)-Fe\(_5\)C\(_2\) is the active site for carbon chain growth.

4.1 Introduction

Higher alcohols (C\(_2\)OH), \(^1\) commonly referred to alcohols higher than methanol, have drawn considerable interest as value-added chemicals, oxygenates fuels or fuel additives. \(^2\) Adding higher alcohols to fuel causes combustion to take place more completely because of the presence of oxygen, which increases the combustion efficiency and reduces air pollution. \(^2\) One promising method of higher alcohol production, is the catalytic conversion of mixtures of carbon monoxide and hydrogen (syngas) derived from coal, biomass, natural gas, or shale gas. \(^3\) Although Rh-based catalysts offer high
selectivity (C₂,OH), their prohibitive cost has urged research on comparable and less expensive Cu-based alternatives, \(^4\) mainly modified Fischer–Tropsch (FT) catalysts such as Cu-Co \(^5\)–\(^7\) and Cu-Fe \(^8\)–\(^10\) based catalysts. Compared with Cu-Co based catalysts, Cu-Fe based catalysts exhibit higher intrinsic activity and selectivity. \(^5\)–\(^10\)

Higher alcohol synthesis (HAS) via modified FT catalysts share some common reactions with methanol synthesis and FT synthesis (FTS). \(^2\)–\(^4\) Methanol synthesis only requires oxygenation, in which an associative C–O bond introduces oxygen into the carbon chain. FTS only involves chain propagation, which needs C–O breaking and then hydrogenation into alkenes and alkanes. However, HAS requires a dual site, involving both oxygenation and chain propagation, \(^11\) as illustrated in Figure 4.1. Xu et al. \(^12\) first proposed that the Cu-M (M = Fe, Co, etc.) center is the dual site of modified FT catalysts for HAS, where CO dissociative adsorption on the FT element (such as Fe, Co etc.) sites and hydrogenated to form methylene species, which initiates carbon chain propagation to form surface alkyl species, while CO associative adsorption occurs on the Cu sites and inserts into the alkyl-metal bond to oxygenate the carbon chain. For such insertion to happen, FT element sites and Cu sites must be very close to permit the CO* species surface migration. \(^11\) Subramanian et al. \(^13\) reported that Cu-Co alloy nanoparticles (NPs) displayed higher C₂,OH selectivity than Co@Cu core-shell NPs, indicating that a homogeneous distribution of the Cu-M dual site is required for HAS. Xiao et al. \(^11\) observed that the physical mixture of monometallic Cu-Fe nanoparticles exhibited very little C₂,OH selectivity, evidencing that any agglomeration of one type of site and separation of different types of sites from each other will destroy the dual site synergism.
The Cu active site for methanol synthesis \textsuperscript{14,15} and the Fe active site for FTS \textsuperscript{16,17} were deliberately investigated. Natesakhawat et al. \textsuperscript{14} reported that only Cu\textsuperscript{0} species were responsible for the activity of methanol synthesis. Behrens et al. \textsuperscript{15} showed that the active site of methanol synthesis consisted of Cu steps decorated with Zn atoms. Shroff et al. \textsuperscript{16} observed that ħägg carbide (\(\chi\)-Fe\textsubscript{5}C\textsubscript{2}) is the active site of iron based FT catalysts via syngas or CO activation. Yang et al. \textsuperscript{17} directly synthesized high active \(\chi\)-Fe\textsubscript{5}C\textsubscript{2} NPs and further confirmed that \(\chi\)-Fe\textsubscript{5}C\textsubscript{2} is the active site for FTS. However, detailed insights into the active Cu-Fe dual site for HAS is rare. \textsuperscript{2-4,8-10} Thus, it is essential to unravel the Cu-Fe dual site, in order to gain a fundamental understanding of their intrinsic activity.

The in situ and operando studies are prospective and essential to understand the catalytic reaction mechanisms. These experiments can help to correlate catalytic intrinsic activity with the molecular structure of active sites in approximate (in situ) or real catalytic conditions (operando). \textsuperscript{18} Generally, the active state of a catalyst on the surface is instantly generated in reaction conditions and can be changed after being removed from the reactor. \textsuperscript{18} For example, Zhu et al. \textsuperscript{19} investigated the methane partial oxidation
for the production of syngas over ceria doped with Rh catalyst, and found that without in situ studies of surface chemistry of catalysts during catalysis, the different surface chemistries of Rh-CeO$_2$-air and Rh-CeO$_2$-H$_2$ before catalysis identified with ex situ studies contradict the same catalytic performance of methane partial oxidation on Rh-CeO$_2$-air and Rh-CeO$_2$-H$_2$ during catalysis. Yurieva et al. $^{20}$ performed in situ XRD and HRTEM studies on the copper-zinc methanol synthesis catalyst during its reduction and re-oxidation, and found that the copper-zinc catalyst undergoes the reversible structural and phase transitions. Barrio et al. $^{21}$ conducted the in situ study of Cu-Ce catalyst after it underwent the water–gas–shift (WGS) reaction, and discovered Cu$^0$ closely interacting with oxygen vacancies of CeO$_x$ and was an active site in WGS. Therefore, a Cu-containing system (include Cu-Fe catalysts in this study) should be studied by using in situ methods due to its high sensitivity to redox conditions.

The utilization of 3DOM materials have received growing attention because their pores size is in the sub-micrometer range. These materials have significant applications in photonic crystals, separation and catalysis. $^{22-25}$ In comparison with traditional coprecipitated catalysts, 3DOM catalysts can homogeneously combine multiple catalytic components together at the atomic level by using the composite precursors. $^{22,23}$ This is beneficial for developing high selectivity HAS catalysts, which requires the dual site to have intimate contact so that no separation can occur. Moreover, connected macro-pores with high porosity can increase the surface area, permit facile mass transport of guest molecules, provides less resistance to active sites, and thus enhance the intrinsic catalytic activity and selectivity. $^{23,24}$ Herein, to design high-performance HAS catalysts and better elucidate the dual site structure, as well as to avoid strong metal support interaction, a
series of unsupported 3DOM Cu-Fe catalysts were prepared by using poly(methyl methacrylate) (PMMA) colloidal crystal template (CCT) method. The 3DOM Cu-Fe catalysts were used for HAS and in situ catalysis characterization.

4.2 Experimental section

4.2.1 Catalyst preparation

3DOM Cu-Fe catalysts were prepared by using poly(methyl methacrylate) (PMMA) colloidal crystal template (CCT) method, using ethylene glycol (EG)–methanol solution of metal nitrates Cu(NO$_3$)$_2$·6H$_2$O and Fe(NO$_3$)$_3$·9H$_2$O as precursors. Monodispersed PMMA micro-spheres were synthesized by using an emulsion technique. The obtained latex PMMA was centrifuged to form CCT. The stoichiometric amount of mixed metal nitrates were dissolved with 15 ml of EG by stirring in a 100 ml beaker at room temperature for 2 h, and the mixed solution was poured into a 50 ml volumetric flask. Methanol (6 ml) and EG were added to achieve the solution with desired concentration of methanol (the final concentration of methanol was 12 vol.%). Then the mixed precursors of copper and iron were added to the CCT, permeated the voids between the close-packed spheres, and condensed into a hard inorganic framework upon frying. Excessive liquid was removed from the impregnated microspheres template via a Buchner funnel connected to vacuum. The infiltered template was dried in a desiccator by using anhydrous calcium chloride at room temperature overnight. Finally, the dried sample was mixed with γ-alumina sphere (0.125 inch) and heated in a quartz tube at the rate of 1 °C/min from room temperature to 450 °C in air for 5 h. EG was oxidized to the glyoxylate dianion in aqueous solution at about 120 °C. The metal glyoxylate converted
to their metal oxide at nearly 400 °C. The 3DOM Cu-Fe catalyst was obtained by further calcination at 450 °C.

4.2.2 Catalyst handling and samples prepared for ex situ characterization

The reduced catalysts samples used for ex situ XRD, Mössbauer spectra, and HRTEM characterizations were prepared by reducing the fresh catalysts in a fixed-bed reactor with syngas (H₂/CO = 1) at P = 10 psig, T = 300 °C, and GHSV = 2000 h⁻¹ for 48 h.

4.2.3 Catalyst characterization

4.2.3.1 Specific surface area

The textural properties (BET specific surface areas, pore volume, pore size) of fresh catalysts were measured with linear parts of the BET plot of the N₂ isotherms. Nitrogen adsorption/desorption isotherms at –196 °C were recorded using a Micromeritics ASAP 2010 porosimeter. The samples were outgassed in N₂ flow at 300 °C for 4 h before the measurement.

4.2.3.2 Hydrogen–temperature programmed reduction (H₂–TPR)

H₂–TPR was carried out using a ChemBET PULSAR TPR/TPD instrument (Quantachrome, Boynton Beach, Florida). About 10 mg of catalyst was treated in 4% H₂/Ar with a flow rate of 70 mL/min, and the reduction temperature was increased from room temperature to 1000 °C at a rate of 10 °C/min. The hydrogen consumption was calibrated using the H₂–TPR of CuO (Aldrich, 99.99%) as the standard sample under the same conditions.
4.2.3.3 Transmission electron microscopy (TEM)

High resolution transmission electronic microscopy (HRTEM) images were obtained on a JEOL 2100 electron microscope (JEOL, Japan) operated at 200 kV. The catalyst samples were dispersed in ethanol and sonicated for 20 min and then deposited over a formvar Nickel grid.

4.2.3.4 Mössbauer spectra

Mössbauer experiments were carried out using a $^{57}$Co/Rh source in a constant acceleration transmission spectrometer. The spectra were recorded at 27 °C. The spectrometer was calibrated using a standard $\alpha$-Fe foil and the reported isomer shifts (ISO) are relative to the center of the $\alpha$-Fe spectrum. The WinNormos-for-Igor 3.0 program was used to determine the Mössbauer parameters. A nonlinear least-squares fitting procedure with a set of independent Lorentzian lines that models the spectra as a combination of singlet, quadruple doublets and/or magnetic sextets was used for data analysis. The spectra components were identified according to their isomer shift, quadruple splitting, and magnetic hyperfine field. Magnetic hyperfine fields were calibrated with the 330 kOe field of $\alpha$-Fe at room temperature (27 °C). Before transferring for Mössbauer spectra measurement, the catalyst samples after reduction were carefully protected using inert nitrogen gas to avoid being re-oxidized by air.

4.2.3.5 X-ray diffraction (XRD)

XRD measurements were carried out by using an Ultima III X-ray diffractometer (Rigaku Americas, The Woodlands, TX) with Cu Kα radiation ($\lambda = 0.154$ nm) operated at 40 kV and 44 mA at a rate of 0.08 ° min$^{-1}$. The crystal phase compositions of the samples
were determined by comparing the measured \( d \)-spacings with standard JCPDS values. Before transferring for XRD measurement, the catalyst samples after reduction were carefully protected using inert nitrogen gas to avoid being re-oxidized by air.

4.2.3.6 In situ synchrotron powder diffraction

In situ synchrotron powder diffraction was performed at Beamline 17-BM of the Advanced Photon Source (APS) at Argonne National Laboratory. X-rays of wavelength \( \lambda = 0.72775 \) Å (17 KeV) and a 0.3 mm diameter beam size was used to obtain two-dimensional (2D) diffraction patterns in the transmission geometry using a Perkin-Elmer flat panel area detector positioned 200 mm downstream of the sample. The sample heating apparatus was developed by Chupas et al.\textsuperscript{27} The experimental setup is shown in Figure 4.2. Lanthanum hexaboride (LaB\(_6\)) standard reference material (SRM 660a) was used to calibrate the detector orientation, and 2D images were processed by using the GSAS-II software.\textsuperscript{28}

The catalyst was homogeneously diluted with amorphous SiO\(_2\) (catalyst/amorphous SiO\(_2\) = 0.5, by volume), and then the diluted catalyst sample (about 50 mg) was loaded into a glass capillary cell (i.d. = 0.8 mm), which was attached to a flow system. The small resistance heating coils were installed directly above and below the capillary, and the temperature was monitored with a 0.5 mm chromel-alumel thermocouple that was placed in the capillary near the sample.

Diffraction data (2\( \theta \) from 5 to 45°) were collected continuously during reduction (3.5 % H\(_2\)/He) under a ramping mode with a heating rate of 3 °C/min, with 60 s collection time for each diffraction pattern. The sample was heated up to 500 °C.
Figure 4.2  Scheme of in situ synchrotron powder diffraction experimental setup

Note: Beamline 17-BM of the Advanced Photon Source (APS) at Argonne National Laboratory

4.2.3.7 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was recorded with a PHI 1600 XPS surface Analysis System (Physical Electronics, Eden Prairie, MN). The instrument used a PHI 10-360 spherical capacitor energy analyzer and an Omni Focus II small-area lens to focus the incident source to an 800 µm diameter surface analysis area, using an achromatic Mg Kα X-ray source (hv = 1253.6 eV) operating at 300 W and 15 kV. Survey spectra were gathered using an average of 10 scans with a pass energy of 26.95 eV and ran from 1100 to 0 eV. High-resolution spectra were gathered using an average of 15 scans with a pass energy of 23.5 eV and a step size of 0.1 eV. The incident sample angle was held constant at 45°. XPS data was collected and averaged using PHI Surface...
Analysis software, Version 3.0 (Physical Electronics, Eden Prairie, MN). XPS data was then analyzed by using Casa XPS software. The C1s peak of adventitious carbon (284.5 eV) was used as a reference for estimating the binding energy. The binding energies were given with an accuracy of ±0.1 eV.

4.2.3.8 In situ ambient pressure x-ray photoelectron spectroscopy (In situ AP–XPS)

In situ AP–XPS constitutes an initial step in bridging the so-called pressure gap between surface science (traditionally ultrahigh vacuum) and heterogeneous catalysis (1–200 bar) by using mbar pressures, and provides special insights into the surface structure of the active site of a catalyst.

Unlike in vacuum studies, the reactant gases are introduced to flow through the catalyst at a certain temperature in the reactor of AP–XPS while acquiring data. The gas flows through the reactor and exits through the exit port and an aperture interfaces the gaseous environment of the pre-lens. The flow rate in the reactor was measured by using a mass flow meter installed between each gas source and the entrance of the flow reaction cell. In this study, the flow rate of pure gas is in the range of 3–5 mL pure gas per minute (mL min\(^{-1}\)). The total pressure of the mixture gas of the reactor is measured with a capacitance gauge installed at the entrance. The pressure at the exit is measured by using another capacitance gauge. An average of the pressures at entrance and exit is used as the pressure in the catalytic reactor. The x-ray source is a monochromated Al K\(\alpha\) (\(h\nu = 1486.7\) eV). The catalyst is heated through heating the vacuum side of a sample stage using e-beaming heater installed in the vacuum section between the external wall of the
catalytic reactor and the internal wall of the UHV chamber. The gaseous side is the internal wall of the reactor.

Au thin film (0.4 mm thick, 99.99%, VWR) was used as a substrate to load a catalyst. Au foil was deliberately roughened using a SiC knife to increase adhesion. A certain amount of 3DOM Cu$_2$Fe$_1$ catalyst was suspended in ethanol (100%) and deposited on pre-cleaned Au foil. The deposition was repeated until the Au foil was completely covered in sample. Ethanol left in the sample on the Au foil was vaporized by placing the Au foil in a vacuum oven at 60 °C, and the dry sample was ready for XPS studies. Any residual carbonaceous surface species were removed by treating the sample in 1 mbar O$_2$ at 300 °C.

The in situ reaction medium was syngas with a ratio of H$_2$/CO = 1. The reaction pressure was 1 mbar. The temperature was varied from room temperature to 400 °C, and each target temperature was held for 1 h before spectrum collection. High resolution spectra (Cu 2p, Cu (LMM), Fe 2p, C 1s) were gathered by using an average of 35 scans with a pass energy of 23.5 eV and a step size of 0.1 eV. All spectra are calibrated to their corresponding Au4f$_{7/2}$ binding energy value which is 84.0 eV.

4.3 Results and discussion

4.3.1 Fresh catalysts

4.3.1.1 Specific surface area

Table 4.1 gives the results of N$_2$ physisorption for the fresh catalysts. The 3DOM Cu$_2$Fe$_1$ catalyst possessed the largest BET surface area, which was 43.3 m$^2$/g, and its pore volume was approximately 0.089 cm$^3$/g, and the average pore size was 8.2 nm.
### Table 4.1  The textural properties of the fresh 3DOM catalysts

<table>
<thead>
<tr>
<th>Fresh catalysts (by molar)</th>
<th>BET Surface area (m²/g)</th>
<th>Pore Volume (cm³/g)</th>
<th>Average Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3DOM Cu</td>
<td>7.4</td>
<td>0.048</td>
<td>26.3</td>
</tr>
<tr>
<td>3DOM Fe</td>
<td>42.0</td>
<td>0.118</td>
<td>11.2</td>
</tr>
<tr>
<td>3DOM Cu₁Fe₂</td>
<td>37.0</td>
<td>0.088</td>
<td>9.5</td>
</tr>
<tr>
<td>3DOM Cu₁Fe₁</td>
<td>27.7</td>
<td>0.076</td>
<td>10.9</td>
</tr>
<tr>
<td>3DOM Cu₂Fe₁</td>
<td>43.3</td>
<td>0.089</td>
<td>8.2</td>
</tr>
<tr>
<td>3DOM Cu₃Fe₁</td>
<td>28.5</td>
<td>0.082</td>
<td>11.5</td>
</tr>
</tbody>
</table>

### 4.3.1.2  Crystalline structure of fresh 3DOM catalysts

Figure 4.3 shows the XRD pattern of fresh 3DOM Cu-Fe catalyst. The diffraction peaks of catalysts are in agreement with the standard file JCPDS 48-1548 (CuO) and JCPDS 65-3107 (Fe₃O₄). The characteristic diffraction peaks with 2θ values at 32.51°, 35.42°, 35.54°, 38.71°, 38.90°, 48.72°, 58.26°, 61.52°, 66.22°, 68.12°, 72.37°, and 74.98° correspond to (110), (002), (11–1), (111), (200), (20–2), (202), (11–3), (31–1), (220), (311), and (004) lattice faces of monoclinic CuO. The characteristic diffraction peaks with 2θ values at 18.30°, 30.10°, 35.45°, 37.09°, 43.09°, 53.46°, 56.98°, and 62.57° correspond to (111), (220), (311), (222), (400), (422), (511), and (440) lattice faces of magnetite Fe₃O₄. It should be noted that as the Cu/Fe molar ratio of the 3DOM catalysts increased from 0 to 3, the peak intensity gradually increased. Therefore, only CuO and Fe₃O₄ phases were observed in the XRD pattern of fresh 3DOM Cu-Fe catalysts.
Figure 4.3 XRD pattern of fresh 3DOM Cu-Fe catalysts

Note: (a) 3DOM Cu₁Fe₂, (b) 3DOM Cu₁Fe₁, (c) 3DOM Cu₂Fe₁, and (d) 3DOM Cu₃Fe₁

4.3.1.3 XPS study of fresh 3DOM catalysts

Figure 4.4 shows Cu 2p and Fe 2p X-ray photoelectron spectroscopy (XPS) spectra of fresh 3DOM Cu-Fe catalysts. Taking the 3DOM Cu₂Fe₁ catalyst as an example, the high resolution scan of Cu 2p, two peaks at 933.6 eV and 953.6 eV attributed to the spin-orbit doublet of Cu 2p were assigned to the bonding energies of Cu (2p₃/₂) and Cu (2p₁/₂) in CuO, respectively. ³¹, ³²

The two other peaks on the higher binding energy side of both Cu (2p₃/₂) and Cu (2p₁/₂) were satellite structures. These satellites can be attributed to shake-up transitions by ligand-to-metal 3d charge transfer. ³³, ³⁴ This charge transfer can occur for copper present in the Cu²⁺ form (3d⁰ configuration) but can not take place if it is present as a metallic or in a Cu⁺ state (3d¹⁰ configuration) because of their completely filled 3d shells.
For the high resolution scan of Fe 2p, the broad Fe 2p signals are contributed from the coexistence of Fe$^{3+}$ and Fe$^{2+}$ states, and in addition, no satellites can be identified, indicating only Fe$_3$O$_4$ phase existed in the catalyst. \textsuperscript{35-37}

Figure 4.4 Cu 2p and Fe 2p XPS spectra of fresh 3DOM Cu-Fe catalyst

Note: (a) Cu 2p and (b) Fe 2p XPS spectra of fresh 3DOM Cu$_1$Fe$_2$, 3DOM Cu$_1$Fe$_1$, 3DOM Cu$_2$Fe$_1$ and 3DOM Cu$_3$Fe$_1$ catalysts

4.3.2 The 3DOM Cu-Fe catalysts after reduction

4.3.2.1 Reduction behavior of the 3DOM catalysts

Temperature programmed reduction (TPR) is a technique for the characterization of solid materials and is often used in the area of heterogeneous catalysis to find the most efficient reduction conditions. For metal oxide catalysts, H$_2$–TPR measurement can
reflect the reducibility of metallic ions with high valence to ions with low valence or metal atoms, and the potential to remove or take up oxygen, i.e. the mobility of the lattice oxygen. Thus, it reflects the redox ability of the catalysts. In this work, the temperature of the reduction peak is taken as a measure to evaluate the redox ability of the catalysts.

Figure 4.5 shows the H$_2$-TPR profiles of 3DOM Cu-Fe catalysts. The two reduction peaks of 3DOM Cu$_2$Fe$_1$ catalyst indicate that two reduction stages occurred. The first peak at 301 °C could be due to the contributions from both the reduction of CuO to metallic copper and the reduction of Fe$_3$O$_4$ to FeO. The second peak at 498 °C is ascribed to the reduction of FeO to metallic Fe.

As the Cu/Fe molar ratio of the 3DOM catalysts increased from 0.5 to 3, the first reduction region gradually shifted to higher temperatures, and the second reduction region gradually shifted to lower temperatures, indicating the presence of Cu in catalysts facilitates the reduction of FeO to metallic Fe. CuO is reduced to Cu between 100 °C and 220 °C, and Cu crystallites nucleate and offer active sites for H$_2$ dissociative adsorption. Consequently, the reactive hydrogen atoms can reduce Fe$_3$O$_4$ at lower temperature with higher Cu content in the catalyst. Table 4.2 shows the temperatures and area ratio of reduction peaks in the H$_2$–TPR of 3DOM Cu-Fe catalysts.
Figure 4.5  The H$_2$–TPR profiles of 3DOM Cu-Fe catalysts

Table 4.2  The temperatures and area ratio of the reduction peaks in the H$_2$–TPR of 3DOM Cu-Fe catalysts

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Low-temperature stage</th>
<th>High-temperature stage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{\text{red}}$ ($^\circ$C)$^a$</td>
<td>Area ratio (%)</td>
</tr>
<tr>
<td>3DOM Cu$_1$Fe$_2$</td>
<td>256</td>
<td>23.0</td>
</tr>
<tr>
<td>3DOM Cu$_1$Fe$_1$</td>
<td>296</td>
<td>49.3</td>
</tr>
<tr>
<td>3DOM Cu$_2$Fe$_1$</td>
<td>301</td>
<td>64.9</td>
</tr>
<tr>
<td>3DOM Cu$_3$Fe$_1$</td>
<td>331</td>
<td>72.8</td>
</tr>
</tbody>
</table>

Note: $^a$ The temperature of the reduction peak
4.3.2.2 Crystallite structure of 3DOM catalysts after reduction

Figure 4.6 shows the XRD pattern of 3DOM catalysts after reduction by using syngas ($H_2/CO = 1$). After the reduction by syngas, CuO was reduced to Cu$^0$, which is in agreement with JCPDS no. 004-0836, and Fe$_3$O$_4$ was transformed to Hägg iron carbide ($\chi$-Fe$_5$C$_2$), which is in accordance with JCPDS no. 051-0997. As the Cu/Fe molar ratio of the 3DOM catalysts increased from 0 to 3, the peak intensity gradually increased.

![XRD pattern of 3DOM catalysts after reduction](image)

Figure 4.6 XRD pattern of 3DOM catalysts after reduction

Note: (a) 3DOM Fe, (b) 3DOM Cu$_1$Fe$_2$, (c) 3DOM Cu$_1$Fe$_1$, (d) 3DOM Cu$_2$Fe$_1$, and (e) 3DOM Cu$_3$Fe$_1$. The syngas of $H_2/CO = 1$ was used for reduction.

4.3.2.3 Mössbauer spectra of 3DOM catalysts after reduction

Figure 4.7 presents the Mössbauer spectra of the reduced 3DOM catalysts measured at 27 °C. All the Mössbauer spectra can be fitted with three sextets and one
doublet, representing hägg iron carbide \( \chi-\text{Fe}_3\text{C}_2 \) with different hyperfine parameters. \(^{38-40}\)

The fitting results are summarized in Table 4.3. The increase in Cu loading led to an increase in \( \chi-\text{Fe}_3\text{C}_2 \) content, indicating that Cu enhanced the reduction and carburization ability of catalyst, which is in agreement with previous \( \text{H}_2\)-TPR test.

![Mössbauer spectra of the reduced 3DOM catalysts at 27 °C](image)

**Figure 4.7** Mössbauer spectra of the reduced 3DOM catalysts at 27 °C

Note: (a) 3DOM Fe, (b) 3DOM Cu\(_1\)Fe\(_2\), (c) 3DOM Cu\(_1\)Fe\(_1\), (d) 3DOM Cu\(_2\)Fe\(_1\), and (e) 3DOM Cu\(_3\)Fe\(_1\). The syngas of \( \text{H}_2/\text{CO} = 1 \) was used for reduction.
Table 4.3 Mössbauer parameters of the reduced 3DOM Cu-Fe catalysts measured at 27 °C

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>IS (mm s⁻¹)</th>
<th>QS (mm s⁻¹)</th>
<th>Hyperfine field (T)</th>
<th>Phase</th>
<th>Spectral contribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3DOM Fe</td>
<td>0.25</td>
<td>0.09</td>
<td>22.0</td>
<td>χ-Fe₅C₂(II)</td>
<td>32.9</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>0.10</td>
<td>18.8</td>
<td>χ-Fe₅C₂(I)</td>
<td>24.1</td>
</tr>
<tr>
<td></td>
<td>0.23</td>
<td>0.08</td>
<td>10.9</td>
<td>χ-Fe₅C₂(III)</td>
<td>24.1</td>
</tr>
<tr>
<td></td>
<td>0.33</td>
<td>1.06</td>
<td></td>
<td>spm phase</td>
<td>18.9</td>
</tr>
<tr>
<td>3DOM Cu₁Fe₂</td>
<td>0.26</td>
<td>0.08</td>
<td>22.2</td>
<td>χ-Fe₅C₂(II)</td>
<td>29.3</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>0.12</td>
<td>18.7</td>
<td>χ-Fe₅C₂(I)</td>
<td>24.5</td>
</tr>
<tr>
<td></td>
<td>0.22</td>
<td>0.10</td>
<td>10.6</td>
<td>χ-Fe₅C₂(III)</td>
<td>25.8</td>
</tr>
<tr>
<td></td>
<td>0.31</td>
<td>1.06</td>
<td></td>
<td>spm phase</td>
<td>20.4</td>
</tr>
<tr>
<td>3DOM Cu₁Fe₁</td>
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<td>0.04</td>
<td>22.2</td>
<td>χ-Fe₅C₂(II)</td>
<td>29.5</td>
</tr>
<tr>
<td></td>
<td>0.16</td>
<td>0.12</td>
<td>18.5</td>
<td>χ-Fe₅C₂(I)</td>
<td>24.3</td>
</tr>
<tr>
<td></td>
<td>0.23</td>
<td>0.11</td>
<td>10.7</td>
<td>χ-Fe₅C₂(III)</td>
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</tr>
<tr>
<td></td>
<td>0.31</td>
<td>1.06</td>
<td></td>
<td>spm phase</td>
<td>20.7</td>
</tr>
<tr>
<td>3DOM Cu₂Fe₁</td>
<td>0.26</td>
<td>0.05</td>
<td>22.1</td>
<td>χ-Fe₅C₂(II)</td>
<td>27.0</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>0.05</td>
<td>18.1</td>
<td>χ-Fe₅C₂(I)</td>
<td>31.1</td>
</tr>
<tr>
<td></td>
<td>0.21</td>
<td>0.07</td>
<td>10.5</td>
<td>χ-Fe₅C₂(III)</td>
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</tr>
<tr>
<td></td>
<td>0.32</td>
<td>1.07</td>
<td></td>
<td>spm phase</td>
<td>21.5</td>
</tr>
<tr>
<td>3DOM Cu₃Fe₁</td>
<td>0.28</td>
<td>0.04</td>
<td>22.0</td>
<td>χ-Fe₅C₂(II)</td>
<td>26.2</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>0.11</td>
<td>18.1</td>
<td>χ-Fe₅C₂(I)</td>
<td>24.9</td>
</tr>
<tr>
<td></td>
<td>0.22</td>
<td>0.12</td>
<td>10.5</td>
<td>χ-Fe₅C₂(III)</td>
<td>24.5</td>
</tr>
<tr>
<td></td>
<td>0.31</td>
<td>1.07</td>
<td></td>
<td>spm phase</td>
<td>24.4</td>
</tr>
</tbody>
</table>

Note: The reduction condition is T = 300 °C, P =10 psig, H₂/CO =1.0 and GHSV = 2000 h⁻¹. Experimental uncertainties: Isomer shift: IS±0.01mm s⁻¹; Quadrupole splitting: QS±0.01mm s⁻¹; Hyperfine field: ±0.1T; Spectra contribution: ±3.0%. [Note: super-paramagnetic (spm)]
4.3.2.4 HRTEM images of 3DOM Cu$_2$Fe$_1$ catalysts before and after reduction

HRTEM image of the fresh 3DOM Cu$_2$Fe$_1$ catalyst is shown in Figure 4.8a. The interplanar spacing $d$ was measured to be 0.484 nm and 0.297 nm, which was characteristic of Fe$_3$O$_4$ (111), Fe$_3$O$_4$ (200), respectively. The interplanar spacing $d$ was measured to be 0.232 nm, which was characteristic of CuO (111). Figure 4.8b shows the corresponding indexed selected area electron diffraction (SAED) pattern of Figure 4.8a, confirming the existence of CuO and Fe$_3$O$_4$ in the fresh 3DOM Cu$_2$Fe$_1$ catalyst, which agrees with the previous XRD and XPS analysis in Figure 4.3 and Figure 4.4, respectively.

Figure 4.8c shows the HRTEM image of the 3DOM Cu$_2$Fe$_1$ catalyst after reduction using syngas. The interplanar spacing $d$ was measured to be 0.209 nm, which was characteristic of Cu (111). The interplanar spacing $d$ was measured to be 0.250 nm and 0.211 nm, which was characteristic of Hägg carbide $\chi$-Fe$_5$C$_2$ (002), and (112), respectively. Figure 4.8d shows the corresponding indexed SAED pattern of Figure 4.8c, confirming the existence of Cu$^0$ and $\chi$-Fe$_5$C$_2$, which agrees with the previous XRD and Mössbauer spectra analysis in Figure 4.6 and Figure 4.7, respectively. Therefore, HRTEM confirms that, after reduction using syngas, CuO reduces to the Cu$^0$ species, and Fe$_3$O$_4$ reduces and carburizes to $\chi$-Fe$_5$C$_2$.

Generally, Cu$^0$ is active oxygenate site for alcohol synthesis, and $\chi$-Fe$_5$C$_2$ is the active site for carbon chain growth. The synergetic effect between Cu$^0$ and $\chi$-Fe$_5$C$_2$ play an important role for high selectivity higher alcohol synthesis from syngas, which require these two active sites intimately contact and work together.
Note: (a) HRTEM image of fresh 3DOM Cu$_2$Fe$_1$ catalyst, (b) the corresponding selected area electron diffraction pattern (SAED) of part (a), (c) HRTEM image of 3DOM Cu$_2$Fe$_1$ catalyst after reduction, and (d) the corresponding SAED pattern of part (c)

4.3.2.5 In situ AP-XPS study of 3DOM Cu$_2$Fe$_1$ catalyst

The simultaneous analysis of Cu 2p and Cu LMM spectra allows distinguishing copper species at the surface reliably. As shown in Figure 4.9a, for the fresh 3DOM Cu$_2$Fe$_1$ catalyst (pretreated by 1.0 mbar O$_2$ at 300 °C), the Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$ peaks are accompanied by distinct shakeup satellites at binding energy of 942 and 962 eV. These characteristic satellites can be attributed to the charge transfer between the transition metal 3d and surrounding ligand oxygen 2p orbitals, and they do not occur in Cu$_2$O and
Cu\textsuperscript{0} due to their completely filled 3d orbitals. Hence, the Cu2p\textsubscript{3/2} peak B.E. of 933.6 eV is indicative of CuO.\textsuperscript{41}

The broadening of main Cu (LMM) peak at 918.0 eV to lower kinetic energies was found during syngas (0.5 mbar CO and 0.5 mbar H\textsubscript{2}) reduction up to 100 °C (Figure 4.9b), whereas some features in Cu 2p spectra can be observed: the drop of shakeup satellite intensity and the shift of Cu 2p\textsubscript{3/2} peak to lower binding energy side. It indicated the formation of monovalent copper (Cu\textsuperscript{+}) at the surface of CuO. As the increase of temperature to 150, 200, 250, 300, 350, and 400 °C, the appearance of Cu LMM peaks at 918.6 and 921.3 eV attributed to metallic copper (Cu\textsuperscript{0}), whereas no shakeup satellite of Cu\textsuperscript{2+} species was detected in Cu 2p spectra.

Under the temperature of 100 and 150°C in syngas reduction, there was negligible carbon species found on the surface (Figure 4.9d). Upon heating to 200 °C, the iron phase is partially carburized and converted into iron carbide, as shown by the appearance of a peak at 283.5 eV in the C1s spectra.\textsuperscript{42} Figure 4.9c further confirms that the formed iron carbide is Hägg carbide \(\chi\)-Fe\textsubscript{5}C\textsubscript{2},\textsuperscript{43} which agrees with previous Mössbauer spectra analysis. Upon heating to 250 °C, the carbide peak is associated with a shoulder at 284.6 eV. Upon heating to 300 °C, the contribution of the shoulder peak at 284.6 eV became larger, which is assigned to the occurrence of generic non-oxygenated surface carbon species. In general, the deposited carbon species on the catalyst surface may have deactivated the catalyst. Therefore, the reaction temperature for HAS from syngas over 3DOM Cu-Fe based catalysts should be less than 300 °C in order to suppress or avoid the carbon species being deposited on the surface of the catalyst.
Figure 4.9  In situ AP-XPS study of 3DOM Cu$_2$Fe$_1$ catalyst using syngas at various temperatures

Note: (a) Cu 2p, (b) Cu LMM, (c) Fe 2p and (d) C 1s spectra. The syngas is a mixture of 0.5 mbar H$_2$ and 0.5 mbar CO for in situ AP-XPS study
Figure 4.10  Temperature-resolved synchrotron powder diffraction patterns during the in situ reduction of 3DOM Cu$_2$Fe$_1$ catalyst

Note: The reduction gas was 3.5 % H$_2$/He. The reduction temperature ranged from room temperature to 500 ℃. (a) contour image and (b) the selected diffraction patterns
4.3.2.6 **In situ synchrotron powder diffraction study of 3DOM Cu$_2$Fe$_1$ catalyst**

An in situ synchrotron powder diffraction study of 3DOM Cu$_2$Fe$_1$ catalyst was performed under 3.5 % H$_2$/He from room temperature to 500 °C. Figure 4.10 shows that the phase transition occurred at about 200 °C indicating CuO reduces to Cu$^0$ species (JCPDS no. 48-1548) at 200 °C. As the temperature further increased up to 500 °C, the Cu$^0$ phase remained the same. Nevertheless, no diffractions for metallic Fe (α-Fe) were detected up to 500 °C, which is the maximum temperature studied. Therefore, in situ synchrotron powder diffraction study indicated that after reduction under H$_2$ flow, the Cu$^0$ was the active species for catalysis reaction.

4.4 **Conclusions**

In situ AP–XPS and in situ synchrotron powder diffraction were applied to identify the active site of 3DOM Cu-Fe catalysts for higher alcohol synthesis from syngas. The results show that after syngas pretreatment of the Cu-Fe catalysts, Cu$^0$ is the active oxygenation site for alcohol synthesis, and χ-Fe$_5$C$_2$ is the active site for carbon chain growth.

4.5 **Acknowledgements**

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4.6 References


