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Alkali Promoted Molybdenum (IV) Sulfide Based Catalysts, Development and Characterization for Alcohol Synthesis from Carbon Monoxide and Hydrogen

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ALKALI PROMOTED MOLYBDENUM (IV) SULFIDE BASED CATALYSTS,
DEVELOPMENT AND CHARACTERIZATION FOR ALCOHOL SYNTHESIS
FROM CARBON MONOXIDE AND HYDROGEN

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2013

Dedication

This thesis is dedicated to my hard working parents Edgar and Imelda L. Molina.

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DEVELOPMENT AND CHARACTERIZATION FOR ALCOHOL SYNTHESIS
FROM CARBON MONOXIDE AND HYDROGEN

By

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THESIS

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Abstract

For more than a century transition metal sulfides (TMS) have been the anchor of hydro-processing fuels and upgrading bitumen and coal in refineries worldwide. As oil supplies dwindle and environmental laws become more stringent, there is a greater need for cleaner alternative fuels and/or synthetic fuels. The depletion of oil reserves and a rapidly increasing energy demand worldwide, together with the interest to reduce dependence on foreign oil makes alcohol production for fuels and chemicals via the Fischer Tropsch synthesis (FTS) very attractive. The original Fischer-Tropsch (FT) reaction is the heart of all gas-to-liquid technologies; it creates higher alcohols and hydrocarbons from CO/H₂ using a metal catalyst. This research focuses on the development of alkali promoted MoS₂-based catalysts to investigate an optimal synthesis for their assistance in the production of long chain alcohols (via FTS) for their use as synthetic transportation liquid fuels. Properties of catalytic material are strongly affected by every step of the preparation together with the quality of the raw materials. The choice of a laboratory method for preparing a given catalyst depends on the physical and chemical characteristics desired in the final composition. Characterization methods of K_{0.3}/Cs_{0.3}-MoS₂ and K_{0.3}/Cs_{0.3}-Co_{0.5}MoS₂ catalysts have been carried out through Scanning Electron Microscopy (SEM), BET porosity and surface analysis, Transmission Electron Microscopy (TEM) and X-Ray Diffraction (XRD). Various characterization methods have been deployed to correlate FTS products versus crystal and morphological properties of these heterogeneous catalysts. A lab scale gas to liquid system has been developed to evaluate its efficiency in testing FT catalysts for their production of alcohols.

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Introduction

Fossil fuels have allowed technologies to advance modern transportation for over a century. Over 80 million barrels of petroleum are processed every day in refineries worldwide to meet the need for liquid transportation fuels such as gasoline, diesel fuel and jet fuel. Despite the advancement made in upgrading fuel economy of vehicles, world usage of transportation fuels has continued to increase and is assumed to remain high well into the next millennium.¹ Several realities have emerged in the 20th century; the potential risks associated with the human emissions into the environment, complex geopolitics, and energy security concerns such as the continuous availability of energy in varied forms, in sufficient quantities, and at reasonable prices and eventually the dwindling supply of this essential non-renewable resource.²

For an analysis that extends well into the 21st century and explores the long-term availability of the dominant fossil fuel, oil, the future production profile of unconventional oil and resources eases many of the concerns aforementioned. Unconventional oil and resources include, but are not limited to, oil shale, heavy crude oil, tar sands (natural bitumen), coal, natural gas, biomass, fuel cell, and oxygenated fuels. U.S. fuel improvement efforts have become focused on using alternative fuels to satisfy the sustainable development objectives of keeping fuels affordable, increasing energy security, and evolving towards near-zero emissions of both air pollutants and greenhouse gases.³

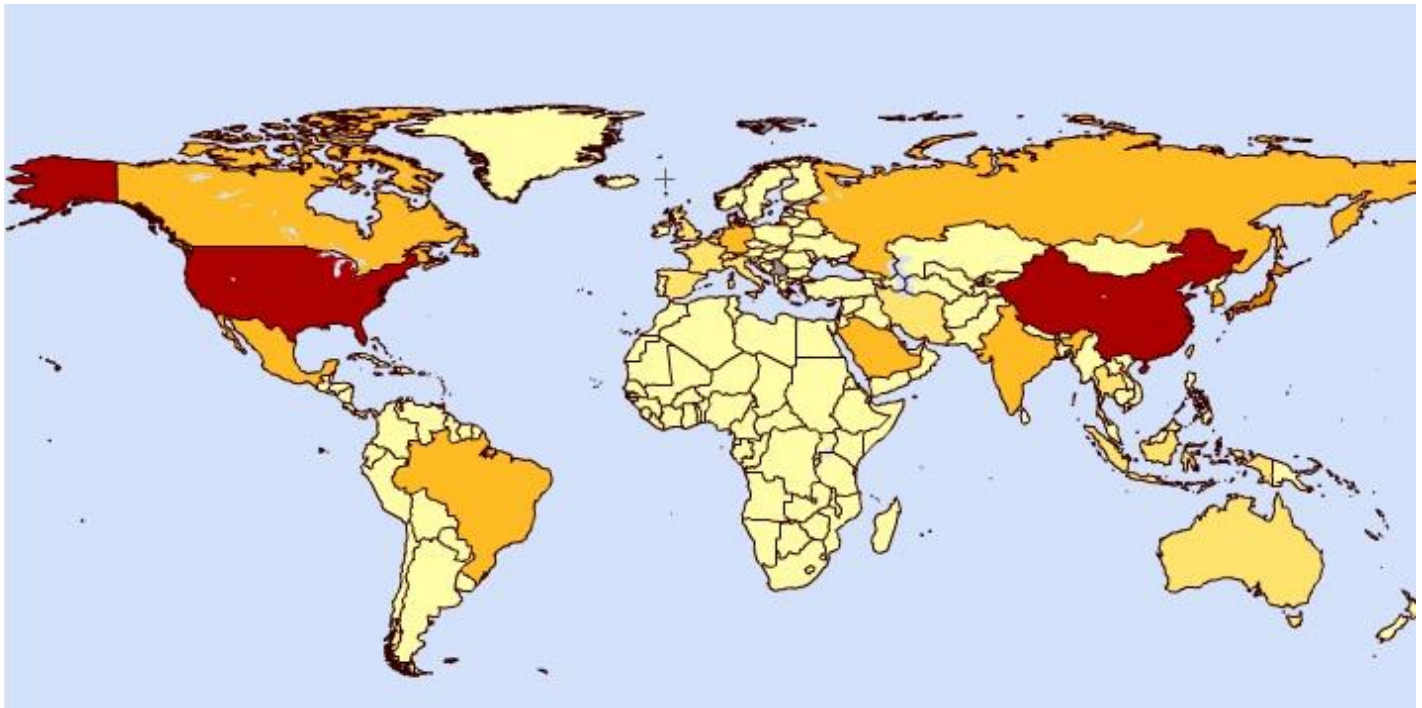
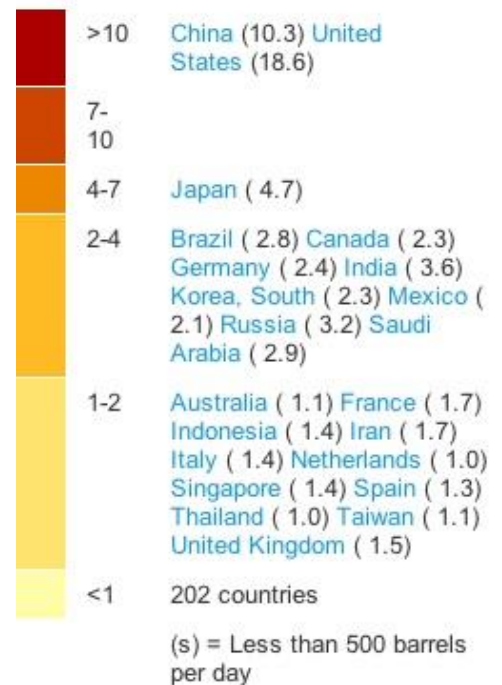


Figure 1: World Oil Consumption 2012.⁴ Provided by the Environmental Protection Agency (EPA)

2012 World Oil Consumption
(millions of barrels per day)

According to the EPA the United States was the lead consumer of oil, consuming 18,555 barrels of petroleum per day in 2012. Also, in 2012 the United States ranked 2nd for the consumption of coal at 890 million short tons.⁵

Within the last two decades the Fischer Tropsch Synthesis (FTS) has been the subject of renewed interest, especially in Brazil and the United States.⁶ FTS is a well-recognized process that creates higher alcohols and hydrocarbons (also known as FT products) from synthesis gas or syngas (CO and H₂) with the aid of a catalyst. The use of syngas-derived fuels is undoubtedly among the leading candidate fuel for addressing challenges posed by compression-ignition engines. Compression-ignition engines are a major player in transport, whether they are used for buses, trucks, trains, and in some



regions, automobiles as well.³ The Fischer Tropsch synthesis provides a promising advantage of an efficient, synthetic route to ethanol and/or other higher alcohols. Over the last century there has however been a continued search for the answers to this seemingly difficult task.

The objective of this research project was to develop scientific data for the catalytic process for the selective conversion of higher alcohols. This desired route would convert syngas to liquid alcohol that could be utilized as alternative transportation liquid fuels. To establish a basis for this process, the research involves the preparation, catalytic testing, and characterization of $K_{0.3}/Cs_{0.3}-MoS_2$ and $K_{0.3}/Cs_{0.3}-Co_{0.5}MoS_2$ catalysts.⁷

The four principal goals addressed are:

1. To synthesize an alkali/ MoS_2 -based catalyst that is selective in the formation of alcohols.
2. To understand which alkali/ MoS_2 - based catalyst functions with better activity, selectivity and stability for yields of higher alcohols from H_2/CO synthesis gas.
3. To test the alkali/ MoS_2 -series for the conversion of syngas (CO/H_2) to alcohol using a lab scale gas to liquid (GTL) technology.
4. To carry out characterization of fresh versus spent catalyst.

The chapters that follow will discuss a brief history of Fischer-Tropsch, explain the Fischer Tropsch Synthesis and advantages of FT use and products. They will provide the motive for utilizing the alkali promoter (potassium, lithium, cesium), cobalt promoter and molybdenum(IV) sulfide complex as a precursor to our catalytic series. They will discuss how a catalyst works and what makes a good catalyst. Furthermore, they will describe the benefits of the hydrothermal synthesis; a detailed schematic of the gas to liquid technology used for testing these catalysts will be presented. Final chapters will include experimental methods, characterization, results and discussion of the catalytic material and the conclusion.

Chapter 1: Franz Fischer and Hans Tropsch

Louis Jacques Thenard made the first apparent recognition of the function of a catalyst in 1813, he reported that ammonia was decomposed to give hydrogen and nitrogen when it was passed over red-hot metals. Ten years later Thenard discovered that the reaction occurred over iron, copper, silver, gold and platinum, the rate of the reaction decreasing in the corresponding order. Since then other notable scientists such as Paul Sabatier, J.J. Berzelius, Humphrey Davy, Michael Faraday and H.L. Le Chatelier made unique significant contributions to the field of catalysis. In 1918 Fritz Haber won the Nobel Prize for the catalytic synthesis of ammonia from the elements. In 1931 Carl Bosch and Friedrich Bergius shared the Nobel Prize for the hydrogenation of coal for the production of liquid hydrocarbons for use as synthetic fuel. The hydrogenation of coal became a crucial area of research for nations who were going through an emergence of industrialization.^{8,9}

Petroleum became essential to industrialized nations by the 1920's, the high production of automobiles, the introduction of airplanes and petroleum-powered ships, and the recognition of petroleum's high energy content compared to wood and coal required a shift from solid to liquid fuels as a major energy source. Nations that were at a time period of industrialization, reacted in various ways. Germany, Britain, Canada, France, Japan, Italy and other nations having little or no domestic petroleum continued to import petroleum. During the 1930s-1940s World War II caused Germany, Japan and Italy to acquire petroleum by force from other nations.

At the beginning of the twentieth century, Germany's fuel requirement began to change because they had virtually no petroleum deposits. First, Germany became increasingly dependent of gasoline and diesel oil engines to sustain transportation and military, and second, continuous industrialization and urbanization led to the replacement of coal with smokeless liquid fuels that not only were higher in energy content but cleaner burning and easier to handle. Petroleum was clearly the fuel of the future, and to assure that Germany would never lack a bountiful supply, German scientists and engineers invented and developed two processes that allowed them to produce petroleum from their country's abundant coal

supply. This would later become the world's first technologically successful synthetic transportation liquid fuel industry.⁹

1.1 A Brief History

One of the two processes was the Fischer-Tropsch Synthesis, named after the two German scientists, Hans Fischer and Franz Tropsch (Figure 2), who discovered that when coal and steam are reacted they give a gaseous mixture of carbon monoxide and hydrogen that under low pressure ($P=1-10$ atm) and temperature ($T=180-200^{\circ}\text{C}$) converted to petroleum-like liquids with the aid of a catalyst. Fischer and Tropsch later developed the cobalt catalysts that were critical to the F-T's success. With wartime coal investigations underway Fischer's experiments with synthesis gas continued. In 1923 Fischer and Tropsch showed that reacting the gas in a tubular, electrically heated converter at high temperature and pressure, $400-450^{\circ}\text{C}$ and $100-150$ atm, and with an alkali-iron instead of metallic oxide catalysts, gave a mixture of oxygen containing organic compounds such as alcohols, aldehydes, ketones, and fatty acids, termed as synthol. This reaction produced no hydrocarbons.¹⁰ Other studies conducted later by Fischer included using small combustion tubes 495 millimeters (mm) long, a gas heated horizontal aluminum block furnace, and different reaction conditions, cobalt-iron catalysts at $250-300^{\circ}\text{C}$ and 1 atm eliminated completely the oxygenated compounds. The products contained only hydrocarbon gases (ethane, propane, butane) and liquids (octane, nonane, isononene).¹¹



Figure 2: Franz Fischer (left) and Hans Tropsch (right).⁹

Ten years later Fischer's research moved to the next level with the construction of the first large pilot plant in 1934 in which he planned to solve the synthesis' three main problems; removing the large amount of heat released in the gas stream during the reaction, the catalyst's short lifetime, and the significant loss of catalytic metals during their recovery (regeneration) for reuse that persisted during the operation. At this time research resumed and the developmental work on synthetic motor fuel and lubricating oil at most of the FT-plants, constructed later in the 1930s, used the standardized cobalt catalysts.¹²

After the war, the main use of the process was in South Africa where Sasol produced synthetic fuels from coal using the FT technology. Through and through, time and again, the rise and fall of FT-pilot plants and technology has had its moments of high and low interest, this has been tied to the availability of cheap petroleum or to political considerations.¹³ Relatively recently, there has been a significant revival of interest in the process, largely for use as a step in the conversion of coal, natural gas, and biomass to fuels (GTL, gas to liquids), for example, using the Shell Middle Distillates (SMDS) Process, for use in regions of the world having large reserves of natural gas. The process is also now being used in China, a country that has large reserves of coal but few natural gas or oil resources.⁸ Other GTL plants utilizing FT-technology include Shell Pearl GTL, Sasol, PetroSA, United Paper Mills Ltd (UPM), Rentech, and the United States Air Force Research Laboratory.

1.2 The Fischer Tropsch Process

The FTS begins with the production of syngas from carbonaceous feedstock such as: natural gas through steam reforming or partial oxidation, or from coal through O₂-blown gasification and even from biomass through gasification.¹⁴ The FTS-based gas to liquids (GTL) technology includes the three processing steps namely syngas generation, syngas conversion and hydroprocessing.¹⁵ Common use of the term "synthetic fuel" is used to describe fuels manufactured via FT conversion. The feedstock is reacted at high temperatures or gasified. After an appropriate cleaning the syngas can then undergo FT conversion, followed by hydrocracking, the breakdown of compounds into simpler molecules, ending with the complete conversion to synthetic fuels, jet fuel and diesel (Figure 3).

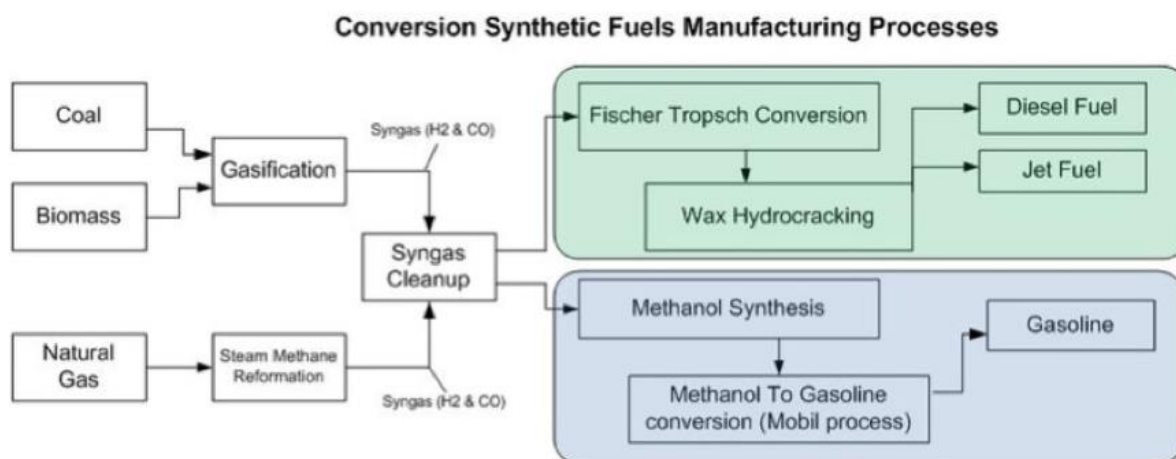


Figure 3: Coal, biomass, and natural gas are used in the manufacturing of diesel fuel, jet fuel and gasoline.¹⁶

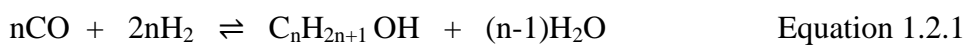
FT products are preferred for synthetic fuels because they are mainly linear thus the quality of the products is very high.¹⁷ With suitable conditions purified synthesis gas used in the FTS yields products that are free of sulfur and nitrogen, making them environmentally friendly. By virtue of their high octane numbered alcohols are interesting as gasoline additives or replacements.¹⁸⁻²⁰ Fuel alcohols have many good characteristics, for example outstanding anti-knock properties and good miscibility with gasoline, which make them attractive as octane boosters in gasoline. Mixtures of higher alcohols and methanol are preferred over pure methanol because of their higher freezing tolerance in automotive systems, reduced fuel volatility and lower vapor lock tendency and also because of their volumetric heating values are higher than for pure methanol.²¹

The conversion from carbonaceous feedstock to synthetic fuels is a lengthy process that cannot be completed without the aid of a metal catalyst. The field of catalysis is a key component in the petroleum refining industry. There is a continuing requirement for development of FTS-catalysts with improved properties to answer today's challenges for alternative fuel supplies.²²

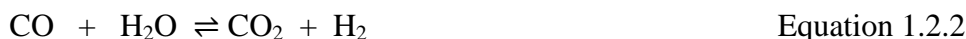
1.2.1 Fischer Tropsch Mechanism

The mechanism FT synthesis has been the subject of extensive study for over 80 years. The comprehension of the surface chemistry at the molecular level is seen by many scientists as crucial for scientific knowledge to improve the aspect involved in the black art of making catalysts.²³ There is no evidence that catalysts have been developed on the basis of a given mechanism. The mechanism has been the subject of long academic studies, and has been reviewed extensively. This is due primarily to the complexity of the CO chemistry and to the broad product range relating to the number of carbons involved and the chemical nature of the formed products.²⁴

The overall reaction of alcohols are synthesized from synthesis gas (CO + H₂) by the following reaction:



Occurring in tandem is the water gas shift (wgs) reaction



Alternate reactions produce light hydrocarbons according to reactions



Thermodynamic considerations of the above reactions, which have been discussed in detail by Natta²⁵ and Klier²⁶ are summarized in Figure 4, indicate that hydrocarbon formation is accompanied with a more negative free-energy change than for the formation of alcohols, as shown. To minimize or avoid the formation of hydrocarbons and allow the selective formation of alcohols, it is necessary to use a catalyst that will promote the formation of surface intermediates that give rise to the production of alcohols. In other words, the catalyst should be able to change the thermodynamically controlled process, which favors the production of hydrocarbons, to a kinetically controlled process, which would favor the production of alcohols.

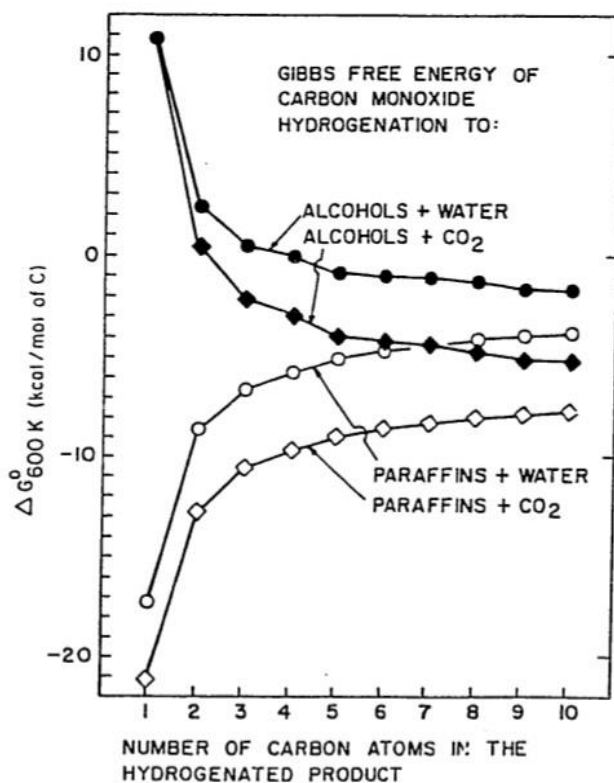
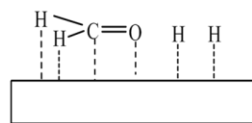
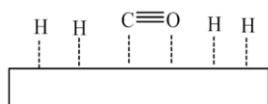


Figure 4: Gibbs free energies, ΔG° , at 600K (kcal/mol of carbon) for the formation of alcohols and hydrocarbons from synthesis gas.²⁷

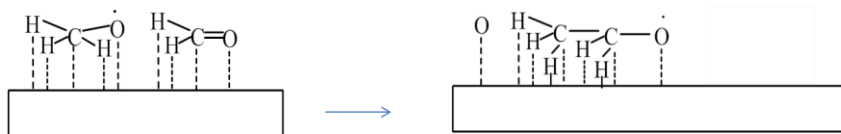
Linear and branched higher alcohols are obtained over the molybdenum based catalyst modified by methanol while mainly linear alcohols are produced over alkali promoted Group VIII metals. Both linear and branched chained formation of alcohols is indicative that at least two different mechanisms are operable in alcohol synthesis.²⁷⁻³⁰

Santiesteban et. Al.²⁷ postulated the reaction system for the production of mixed alcohols from syngas over alkali-modified MoS₂ catalysts based on a CO insertion mechanism. This reaction scheme can be presented in three steps, chain initiation, propagation, and termination as follows (NOTE: “S” denotes “Active Surface Site”):

Initiation



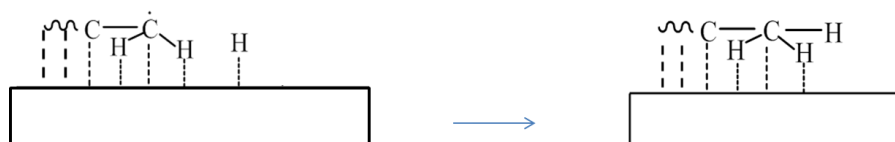
Propagation



Propagation



Termination



It should be evident that a discussion on the FT mechanism is beyond the scope of this thesis; however the interested reader is referred to several review papers on this topic.⁹²⁻¹⁰² In that regard, it is significant to mention catalysts and the overall advantages of precursor and synthesis methods.

Chapter 2: Catalysis

Catalysts can be divided into two main types –homogeneous and heterogeneous. A homogeneous catalytic process is one in which the catalyst is in the same phase as the reactants. In contrast, a heterogeneous catalyst exists in a different phase to that of the reactants; the catalyst is usually a solid and the reactants are either gases or liquids.³² This research is concerned solely with heterogeneous catalysis. When a reaction at a surface leads to a new surface entity that desorbs to give products and results in the regeneration of the surface, we have a catalytic process and are dealing with the phenomenon of the “heterogeneous catalysis”.³³

2.1 How a Heterogeneous Catalyst Works

Most industrial catalyzed reactions are of the heterogeneous type. The Fischer-Tropsch Synthesis involves CO and H₂ reacting on the surface of a heterogeneous catalyst. A heterogeneous catalyst is a substance that changes the rate of a chemical reaction due to its participation. It works when the reactants diffuse onto its surface and are adsorbed to it through formation of chemical bonds. After the reaction, the product desorbs from the surface of the catalyst and diffuses away, thus the surface area of the catalyst is very critical as it determines the catalytic site. This phenomenon is called adsorption. To understand heterogeneous catalysis, we should have an understanding of the phenomena of adsorption. Figure 5 below explains the route by which a heterogeneous catalyst works.

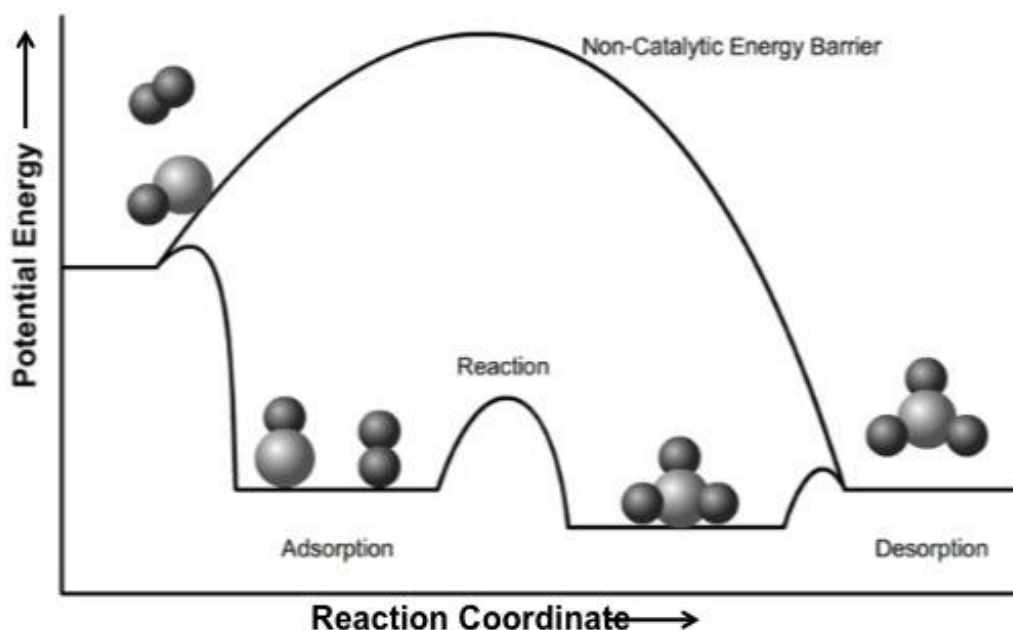


Figure 5: The route by which a heterogeneous catalyst functions.³⁴

First, the reactants are adsorbed on the surface of the catalyst. This is a chemical reaction and there is an interaction between the electrons of the reactants and the atoms on the surface of the catalyst. It is important to note that adsorption should not be confused with absorption; they are different. Adsorption is when a molecule binds to the surface of the material, while absorption means that it is taken into the body of the material. Second, the adsorbed reactants (mainly the lighter ones such as hydrogen) diffuse over and are free to migrate on the surface of the catalyst. Next, when the reactants meet they are free to react but are still bound to the surface. Last, the products of the reaction break free from the surface allowing them to desorb, meaning that the product molecules break away. This leaves the active site available for a new set of molecules to react.

An active catalyst needs to adsorb the reactant molecules strongly enough for them to react, but not so strongly that the product molecules stick more or less permanently to the surface. Silver, for example, isn't a good catalyst because it doesn't form strong enough attachments with reactant molecules. Tungsten, on the other hand, isn't a good catalyst because it adsorbs too strongly. Metals like

platinum and cobalt make active catalysts because they adsorb strongly enough to hold and activate the reactants, but not so strongly that the products can't break away.^{34,35}

The initial and final states for the uncatalyzed and catalyzed reactions are exactly the same: all that the catalyst has done is to change the all-over energetics, providing an alternative route from reactant to product. This is a fundamental principal of catalysis: a catalyst can bring about a change in the rate of a chemical reaction, but has no effect on the all-over thermodynamics of the reaction, that is, the equilibrium position.

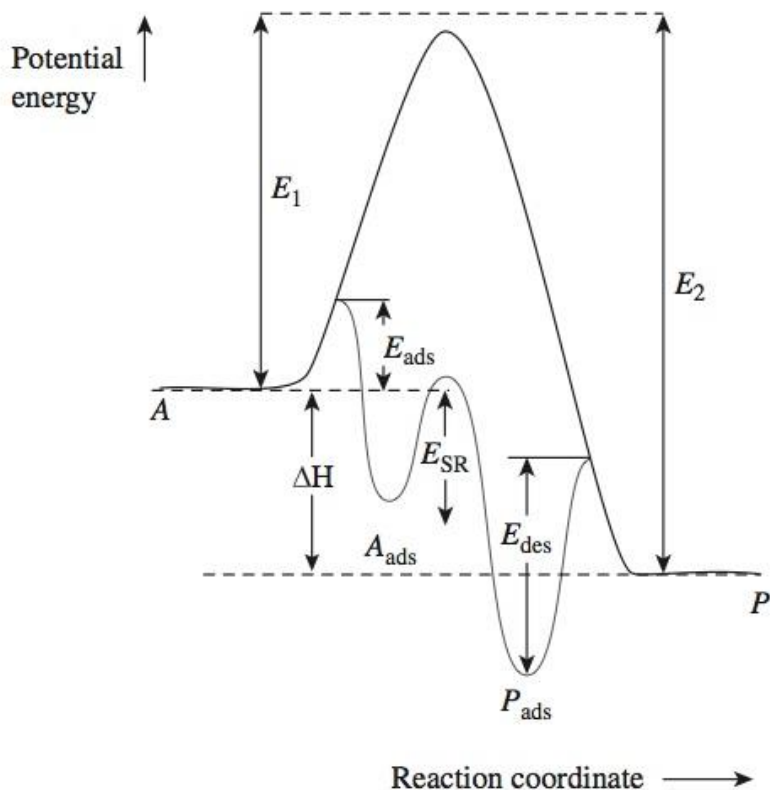


Figure 6: Schematic diagram of the energy profile for a reaction A to B without and with a catalyst.³⁶

Figure 6 shows the energetics of a simple model reaction, the decomposition of molecule A to give products P. The upper curve in Figure 6 represents the uncatalyzed reaction. For the reaction in the gas phase, the activation energy for the forward reaction is shown as E_1 and that for the reverse reaction is shown as E_2 . The enthalpy of the reaction ΔH is given by $E_1 - E_2$; in the figure as drawn, as E_2 is

greater than E_I , the value of ΔH is negative. When the reactant can adsorb on a surface, a new state is formed, A_{ads} , with a heat of adsorption, $\Delta H_{A(ads)}$. Depending on the system, there may or may not be an activation energy E_{ads} for this adsorption step. Once the species A is adsorbed, it may be transformed into P_{ads} by a surface reaction process with an activation energy E_{SR} . The product species P is shown as being adsorbed with an adsorption energy of ΔH_{Pads} . Finally, P is desorbed with an activation energy E_{des} .³⁶

2.1.1 What Makes an Effective Catalyst

The most crucial properties of a catalyst are its activity and selectivity under operating conditions. Therefore, an important feature of characterizing a newly synthesized catalyst is the determination of the catalytic properties of the new material.

As previously mentioned heterogeneous catalytic reactions occur on the surface of the catalytically active material by the making and breaking of bonds between the reacting species and the atoms of the catalyst surface. In order to optimize the rate of the reaction, the surface area of the catalyst must be high; if the surface area is non-uniform in composition, it must contain as many positions as possible at which the molecule involved in the process can be adsorbed. Thus all the available surfaces, external and internal, must be accessible to the reactant molecules approaching it from a gas phase, it must also be possible for the products to get away from the surface.

Consider the model reaction:



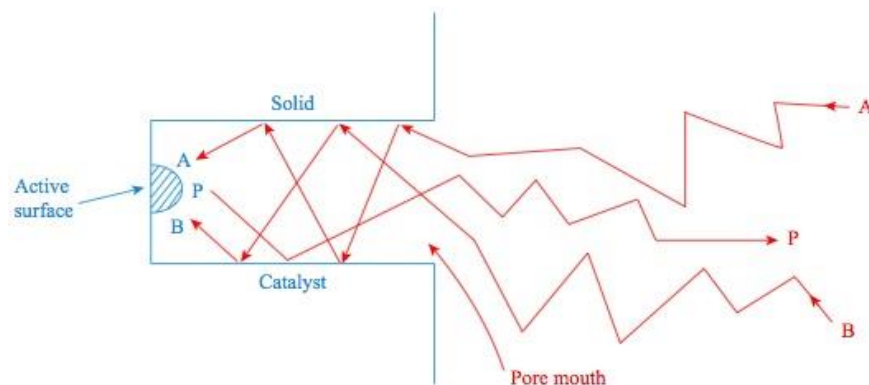


Figure 7: Schematic of molecules A and B approaching a pore, being adsorbed on the active surface within the pore, followed by the desorption and diffusion of product P out of the pore.³⁷

Each of the molecules A and B approach the solid catalyst material from the gas phase, making a series of gas-phase collisions on the way (Figure 7). These collisions can be with other A molecules or with the species B, the product P or even an added inert gas. Once the molecule A reaches the solid, it then has to get to the active surface, which might be, for example, a metal crystallite embedded within a pore. Therefore, A has to diffuse down the pore and will make collisions with the walls of the pore as well as with gas-phase molecules; the relative number of surface collisions relative to gas-phase collisions will then depend on the pore diameter as well as on the reaction conditions (pressure and temperature). Once adsorbed on the active surface, the adsorbed species derived from molecule A can react with an equivalent species resulting from the diffusion and adsorption of molecule B to give adsorbed product P; P then desorbs and has to diffuse out of the pore and away from the surface.

The rate of the reaction may still be determined by the rate of adsorption of A or B, by the surface reaction of A with B or by desorption of product P; however, the rate may also be affected by the rates of diffusion to or from the surface and also into or out of the pore. Hence, in addition to having a high active catalytic surface, the catalyst must have easily accessible outer and inner surfaces.³⁷

Although some catalytic materials are comprised of single substances, most catalysts have three types of easily distinguishable components: (1) active components, (2) a support or carrier, and (3) promoters. These three components are demonstrated below.

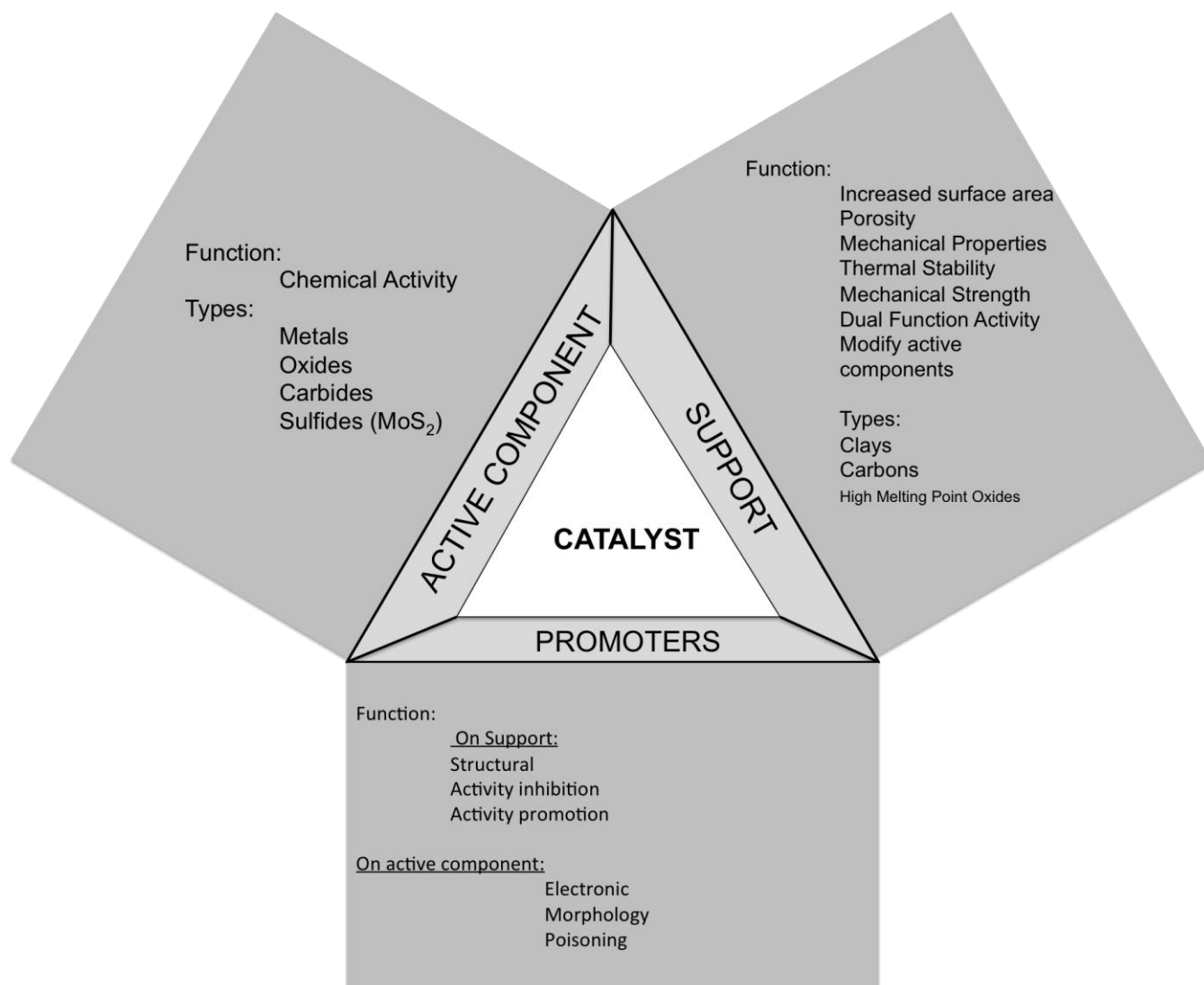


Figure 8: Catalyst Components.³⁸

Most commonly encountered active components are metals, oxides and sulfides. More recently carbides have gained special interest as well. An effective catalyst may have different types of active surface species and each will be capable of catalyzing either a single reaction or a whole range of related reactions.³⁸ (Figure 8) Typically metals species are used for reactions of hydrocarbons or long chain alcohol, such as the Fischer Tropsch Synthesis, and steam reforming of natural gas. Oxides are used for selective oxidation reactions, or reactions requiring either acids or bases. Sulfides can be used for reactions involving sulfur-containing molecules such as hydrodesulphurization.³⁹

A support's main purpose is to provide a high surface area for the active components. They are usually used when the active component involves an expensive metal, such as platinum; this is also to reduce the amount of platinum necessary for industrial sized reactions. Supports aid in preventing sintering. The support allows the melting point of the active component to increase, giving it thermal stability. They are also used to provide proper dispersion of the active component. Although supports may offer a wide range of benefits, unsupported catalysts also have their benefits. The catalysts involved in this thesis are without a support. As unsupported metal catalysts are often susceptible to sintering when using high temperatures, the metal particles have to be stabilized to give as high surface area as possible. As sintering often occurs, stabilization may be achieved by the addition of a “promoter” that helps anchor the metal atoms on the surface and prevent surface migration and/or particle coalescence.^{36, 40, 41}

Promoters are small agents that, when added (often in a small ratio) results in desirable activity, selectivity, or stability effects. They are designed to assist the active component or the supports. They give support in order to inhibit undesirable activity such example includes coke formation. Promoters can provide dual functional activity, such as extra acidity like in catalytic reforming; this is achieved by adding chloride ions to the surface. Promotion of the active substance may either be structural or electronic.³⁷

An effective catalyst is in large part, due to the precursor materials used for its preparation and synthesis. Aside from precursor materials it is also important to recognize the method in which to synthesize them based on what is desired for their final products.

2.2 Synthesis Method

The properties of a heterogeneous catalyst are strongly affected by every step of the preparation together with the quality of the raw materials. The choice of a laboratory method for preparing a given catalyst depends on the physical and chemical characteristics desired in the final composition. The

variety of possibilities may seem that catalyst preparation is a “black art”. However, some generalization can be made on catalyst preparation, and unit operation. Although there are many variations in preparation, a set of elementary steps, can be deduced and described in a general way.

1. The chemical and physical transformations that are implied.
2. The scientific laws which govern such transformations based on fundamental inorganic chemistry
3. The operation variables such as temperature, pressure, pH, time, and concentration.
4. The general characteristics of the products of the operation.
5. The type of the required apparatus.

Most catalyst formulations involve a combination of some or even all these operations. However, even though preparation procedures differ greatly from one catalyst to another, three broad categories can be used to classify preparation methods:

1. Bulk catalysts and supports
2. Impregnated catalysts
3. Mixed-agglomerated catalysts

The catalysts later described in this thesis are bulk catalysts. Bulk catalysts are mainly comprised of active components such as the substances mentioned in section 2.1.1. Table 1 below describes various unit operations in catalyst preparation.⁴²

Unit Operations in Catalyst Preparation			
1.)	Precipitation	7.)	Calcination
2.)	Gelation	8.)	Forming operation
3.)	Hydrothermal Transformation	9.)	Impregnation
4.)	Decantation, Filtration, centrifugation	10.)	Crushing and grinding
5.)	Washing	11.)	Mixing
6.)	Drying	12.)	Activation

Table 1: Various unit operations for the preparation of catalysts.⁴³

Consider unit operation three, hydrothermal transformations. For hydrothermal transformations we usually consider the modification of substances induced by temperature and pressure in the presence of a solvent, usually water. These transformations are usually executed at low temperatures (100-300°C).⁴² They involve textural or structural modifications of the solid; these modifications are compiled below:

1. Small crystals → large crystals
2. Small amorphous particles → large amorphous particles
3. Amorphous solid → crystalline solid
4. Crystal 1 → crystal 2
5. High porous gel → low porous gel

Only amorphous solid to crystalline solid will be considered for the purpose of importance regarding synthesis methods involved in this thesis. The active compound used to synthesize the alkali promoted MoS₂-based catalysts series involved in this research is the crystalline solid MoS₂, formed from the MoS₃ intermediate. MoS₃ is not readily available, as MoS₃ can only be prepared in the amorphous form. It is typically prepared from (NH₄)₂Mo^{VI}S₄, either by acidification of an aqueous solution or by thermal decomposition between 260-300°C. Above 310°C, MoS₃ decomposes to

hexagonal crystalline MoS_2 .⁴⁴ Hydrothermal transformations are achieved using specific reactors and this unit operation will be described in detail in the following section.

2.2.1 Hydrothermal Synthesis

The term *hydrothermal* usually refers to any heterogeneous reaction in the presence of aqueous solvents or mineralizers under high pressure and temperature conditions to dissolve and recrystallize (recover) materials that are relatively insoluble under ordinary conditions. Morey and Niggli (1913) defined hydrothermal synthesis as “...in the hydrothermal method the components are subjected to the action of water, at temperatures generally near though often considerably above the critical temperature of water ($\sim 370^\circ\text{C}$) in closed bombs, and therefore, under the corresponding high pressures developed by such solutions.”⁴⁵ In the last decade, the hydrothermal technique has offered several new advantages like homogeneous precipitation using metal chelates under hydrothermal conditions, decomposition of hazardous and/or refractory chemical substances, and a host of other environmental engineering and chemical engineering issues dealing with recycling of rubbers and plastics (instead of burning), and so forth. Other advantages of utilizing the hydrothermal technique include high reaction rate of powders, good dispersion in liquid, almost pollution free, does not require very expensive and highly sophisticated equipment, energy saving processing, and many times it produces new phases.

Following the successful development of ceramic processing during the 1970s, the hydrothermal technique became more attractive to ceramists and synthetic chemists because of enhanced kinetics. The duration of the experiment is reduced by two orders of magnitude, at least, which makes the technique more economic. Ceramics include the production of powdered material, in this case heterogeneous catalysts. Hydrothermal synthesis is the chosen method of synthesis for this research, not only because of the advantages aforementioned but because of its ability to decompose our precursor products, $(\text{NH}_4)_2\text{MoS}_4$, to MoS_2 crystalline solid.⁴⁶

The beginnings of hydrothermal research is associated with the study of the natural systems by earth scientists, who were interested in understanding the genesis of various rocks, minerals and ore deposits through laboratory simulations of the conditions existing in the earth's crust. Many of these natural formations contain the compounds selected to derive the alkali promoted MoS₂-based catalysts in this thesis. Early studies noted that the crystallization of various phases found in nature, and the stoichiometry's of the phases, depend mainly on the type and concentration of alkali metal; it was observed that the addition of alkali elements in natural hydrothermal systems play an important role in the formation of various phases. Conditions of hydrothermal synthesis are achieved using closed system high pressure/temperature reactors or "bomb reactors", more specifically, a high-pressure batch reactor parr model 4540 (Figure 9).



Figure 9: Hydrothermal Batch Reactor Autoclave Parr Model 4540.⁴⁷

These unique properties place the hydrothermal technique in a new light for the 21st century and one can foresee a slow emergence of a new branch of science and technology for sustained human development.⁴⁷

2.3 Precursor Selection

Although the use of hydrothermal technology was first utilized in the mid-1970s, there are minimal articles using hydrothermal methods to develop heterogeneous unsupported alkali-promoted transition metal sulfide FT catalysts for the production of alcohols. One major step in hydrothermal synthesis is the selection of compounds with promising properties and the development of methods providing the crystal and morphological formations for their practical use.⁴⁷ The selection of precursors has a direct impact on the cost and availability of the chemicals. The sulfides of transition metals have been used in the petroleum industry in hydrodesulphurization, hydrodenitrogenation and hydrogenation reactions for over 50 years. Molybdenum(IV) sulfide, when supported with an alkali can be used as a catalyst for alcohol production from syngas. The precursor selections are explained herein.

2.3.1 Alkali Promoter (K, Cs)

Molybdenum(IV) sulfide alone does not define an FT catalyst. Without an alkali promoter the sulfide produces essentially no alcohols in CO hydrogenation regardless of conversion levels. The addition of the alkali promoter to the sulfide causes a decrease in hydrotreating activity and a very significant decrease in the activity for both hydrogenation of ethene and methanation of CO.⁴⁸ Most importantly the addition of the alkali promoter shifts the product distribution at high pressure from hydrocarbons towards alcohols.⁴⁹ The behavior of the alkali promoter is studied in relation to the MoS₂ complex because of the speculations based on the promotional effects.

Several surface science studies have investigated the deposition of alkali metals on MoS₂. Low coverage deposition of an alkali metal on MoS₂ results in a disordered over layer of strongly ionized adspecies. At higher coverage the alkali adspecies begin to form 2D islands and further alkali deposition yields 3D structures.^{50,51} For alkali adsorption on the WS₂ surface, which has the same structure as MoS₂, it is observed that the alkali addition causes the largest attenuation of the W signal in ion scattering spectroscopy, and this has been interpreted in the way that the alkali adatoms occupy the hollow sites directly above the metal atoms.⁵² Density functional theory calculations have also observed

that this is the favored adsorption site on MoS₂.⁵³ It can be assumed that the decreased hydrogenation activity of the alkali promoted sulfide could very well be related to the position of the alkali adspecies at the edge of the sulfide. Other reports state that the adsorption capacities of both CO and H₂ (as well as O₂) are reduced with increasing alkali addition; however their experiments do not provide empirical data based on the relative coverage versus promotional effect.⁵⁴

Santiesteban reported that only hydrocarbons were produced over un-doped MoS₂, and that the selectivity is dramatically altered toward alcohols upon promotion of the MoS₂ with either potassium or cesium. Using identical molar concentrations, regardless of reaction temperature, the Cs-doped catalyst is more active for the synthesis of alcohols than the K-doped catalyst.²⁷ Santiesteban described the alkali effect as being twofold. One effect is aiding the activation of CO, although the effect mainly leads to hydrogenation without breakage of the C-O bond. The other effect of the alkali is as a suppressant of the hydrogenation ability of the catalyst through site blocking on the sulfide surface. This suggestion is in line with the abovementioned preference of the alkali adspecies for the rim sites associated with the hydrogenation activity.⁵⁴

It is generally reported that the heavier alkalis are preferred to Li or Na, but there are varying reports concerning the order amongst the alkalis. Kinkade reports the order of the promotion to be Cs > Rb > K > Na > Li as opposed to Iranmahboob et al. who found that K was a better promoter than Cs. Woo et al, found the order of promotion to be K > Rb > Cs. Various patents also mention that potassium is the preferable promoter. The variety in these results may be because the effects of K, Rb, and Cs are similar that the differences might easily be encountered by other uncontrolled factors.⁵⁵⁻⁶¹

2.3.2 Transition Metal (Cobalt)

Cobalt catalysts are known to promote a wide variety of reactions including the homologation of alcohols. Cobalt is also known to be an effective Fischer-Tropsch catalyst, used for alkane production. Cobalt is usually the catalyst of choice for many F-T commercial processes.^{27,62} Cobalt inclusion in

MoS₂ catalysts increases selectivity of higher alcohols and improves overall alcohol yields. It is well established that all Group VIII transition metals are active for F-T synthesis. However, the only F-T catalysts, which have sufficient CO hydrogenation activity for commercial applications, are Ni, Co, Fe, or Ru as the active metal phase. These metals are orders of magnitude more active than other group VIII metals and some characteristics are summarized on the Table 2 below.

<i>Active metal</i>	<i>Price</i>	<i>F–T activity</i>	<i>WGS activity</i>	<i>Hydrogenation activity</i>
Ni	++++	+	+/-	+++++
Fe	+	+	+++	+
Co	+++	+++	+/-	+++
Ru	+++++	+++++	+/-	+++

Table 2: Ni, Fe, Co, Ru characteristics favorable to catalytic industry.⁶³

As previously discussed, the water gas shift (WGS) simultaneously occurs during the FTS; however, the WGS is not a desirable reaction. Although cobalt is 3 times more active than Fe in F-T while its price is over 250 times more expensive, its activity is much less than that of iron, not to mention its hydrogenation ability is favorable.⁶³ Another advantage of using cobalt is that it is more resistant toward oxidation and more stable against deactivation by water, a Fischer Tropsch byproduct.⁶⁴ This leaves cobalt as the most appropriate element to prepare FT catalysts having a promising outlook for commercial applications.

According to Dow Chemical researchers, the addition of cobalt to the alkali-doped MoS₂ catalyst shifted the selectivity in favor of ethanol. Santiesteban also reported that cobalt on alkali-doped MoS₂ catalysts have the effect of changing the selectivity in favor of ethanol under certain operating conditions.²⁷

2.3.3 MoS₂- Complex

Transition metal sulfide catalysts have been a mainstay in important industrial processes. Originally used for the hydrogenation of coal and tar, MoS₂ catalysts have played an active role in the

field of petroleum hydro processing (hydrodesulfurization, hydrodenitrogenation, hydrorefining, hydrocracking, etc.). MoS₂ catalysts are effective because of their potential to be resistant to catalytic poisoning and sulfur poisoning.²⁷ One of the promising catalyst for higher alcohol synthesis is the molybdenum based catalyst modified by methanol and molybdenum sulfide based catalyst. A reactant stream incorporating a known quantity of methanol is passed through the “methanol modified catalyst” to determine if chain growth of higher alcohols occurred.⁶⁶⁻⁶⁹ Because ethanol and other higher chain linear alcohols are not attainable in sufficient quantities using methanol modified catalysts, the interest is shifted towards molybdenum (IV) sulfide based catalysts. Complications associated with reproducibility, lack of selectivity towards alcohols or the excessive price of starting materials is rarely encountered.

Performance of MoS₂ has been linked with its structure and morphology.⁶² Molybdenum(IV) sulfide exists in two crystalline forms of hexagonal and rhombohedral. The hexagonal form is to be the MoS₂ phase present in the catalytic system presented in this research.

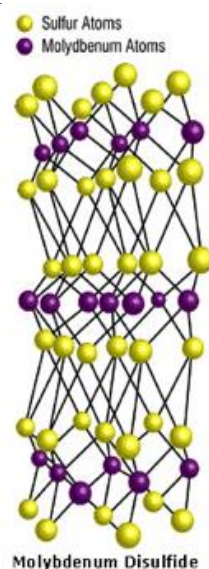


Figure10: Molybdenum Sulfide Structure.⁷⁰

It is a layered compound consisting of stacks S-Mo-S slabs held together by Van der Waals interactions. Each layer is comprised of two hexagonal planes of S atoms and an intermediate hexagonal plane of Mo atoms, which are trigonal prismatic coordinated to the S atoms (Figure 10). The active phase for hydrotreating catalysts has a MoS₂-like structure, and active sites are located at edge surface of

the MoS₂. Chianelli et al. developed the Rim-Edge Model that correlates stacking degree and selectivity properties for non-promoted and non-supported catalysts (Figure 11).⁷¹

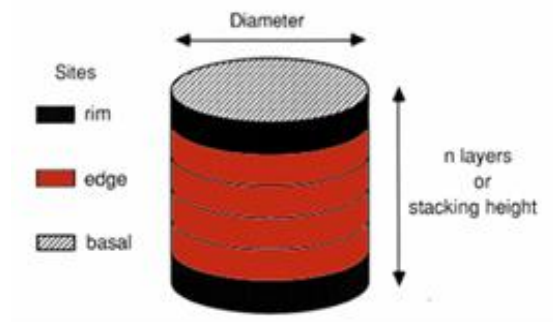


Figure 11: Rim Edge Model.⁷¹

The rim edge model postulated by Chianelli describes the active phase as MoS₂ stacks where the top and bottom is associated with rim sites active in hydrogenation. Basal planes are formed of completely coordinated sulfur atoms, making it almost inert. This model establishes that the stack height of MoS₂ slabs influences selectivity by varying the ratio of rim sites to edge sites.⁷² Oxygen enrichment at edge of MoS₂ single crystals has been shown to occur by scanning auger studies.⁷³ This preferential interaction between O₂ and edge planes was used by Chianelli to determine the edge plane area of MoS₂. In their study it was reported that the total surface areas of the MoS₂ catalysts gave no correlation with hydrodesulfurization activity.⁷⁴ However, a linear relationship was found when activities were plotted against O₂ chemisorption capacities. Chianelli and coworkers concluded that their results supported the hypothesis of Voorhoeve and Stuver.⁷⁵ They proposed that the edge planes in MoS₂ and WS₂ were the site of their catalytic activity.

Chapter 3: Experimental

This section provides a general description of the experimental work, the experimental setup and the catalysts used in the investigations. FT catalysts have been synthesized using the hydrothermal method. Two series of alkali promoted transition metal sulfide catalysts $K_{0.3}/Cs_{0.3}$ - MoS_2 and $K_{0.3}/Cs_{0.3}$ - $Co_{0.5}MoS_2$ have been synthesized and the catalyst promotional effects have been compared to that of MoS_2 and $Co_{0.5}MoS_2$ catalysts.

3.1 Gas to Liquid Technology

A laboratory scale gas to liquid system was developed to evaluate its efficiency in testing FT catalysts for their production of alcohols. Collaborators at Lamar University in Beaumont, Texas have the capability and the resources required to design such a system. Dr. Tracy Benson's expertise in chemical engineering and reactor design has enabled us to carry out testing of the alkali promoted transition metal sulfide catalysts. The GTL system was designed for continuous flow of reactants and products to mimic the type of reactor found in industry; it simulates coal conversion to synthetic liquid fuels.

This system uses a 1/4" 316 stainless steel tubing for the tubular reactor. It is flow controlled and backpressure regulated. The backpressure regulator allows one to change input and output flow rates (0.1-100L/min) while maintaining system pressure 1-500 psi. The reactor was heated using a tube furnace (Figure 12). Temperature range for the furnace was 25-700°C. However, our reactions were conducted at 300°C.

Catalyst packing can be from 0.25 to 100 grams but was kept at 0.25g for this work. The reactions were run for duration of 8 hours. Reaction conditions were pressure of 450 psi, temperature of 300°C, and H_2/CO ratio was 0.8/1.

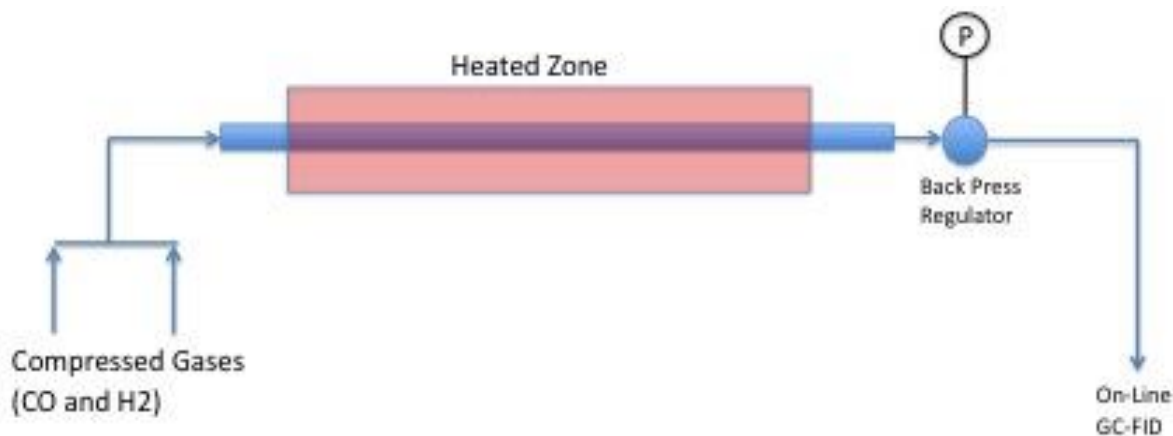


Figure 12: Gas to Liquid Schematic.

This laboratory packed bed reactor is coupled to a gas chromatograph that uses a FID (flame ionization detector) for analysis of alcohol products (Figure 13). An additional GC-TCD (thermal conductivity detector) is used for analysis of CO and H₂. Included in the reactor setup are temperature-programmed controls, pressure control devices (including back pressure regulator) and hand-operated needle valves for fine control of reactant gases and liquids. This type of reactor/analytical device will yield kinetics (changing of the gas hourly space velocities (GHSVs)) and catalyst robustness (time on stream analysis).



Figure 13: Actual representation of gas to liquid system assembled at Lamar University under Dr. Tracy Benson.

Chromatography was achieved via two independent columns. The GC-TCD uses a carboxen-1010 PLOT column for fixed gas analysis (i.e. CO and H₂). The FID uses an Rxi – 1 ms (Restek, Inc.) column used for analysis of product compounds (i.e. C1-C5 hydrocarbons and C1-C8 alcohols).

3.2 Alkali Promoted Transition Metal MoS₂-based Catalyst Series Preparation

FT catalysts have been synthesized using the hydrothermal method. Two series of alkali promoted transition metal sulfide catalysts K_{0.3}/Cs_{0.3}-MoS₂ and K_{0.3}/Cs_{0.3}-Co_{0.5}MoS₂ have been synthesized and the catalyst promotional effects have been compared to that of MoS₂ and Co_{0.5}MoS₂ catalysts.

The steps of synthesis are described herein.

Synthesis begins by preparing an ammonium tetrathiomolybdate (ATM) precursor. The synthesis of ammonium tetrathiomolybdate (ATM) was reported by Kruss in 1884. Later, Alonso et al. described an improved method for synthesis of ATM.^{76,77} Alonso's method is as follows: Ammonium

heptamolybdate (12.5 grams) was dissolved in 60 ml of deionized water, then 100 ml of ammonium sulfide was added to this solution. The solution was heated to 55°C, the temperature was maintained for 30 minutes and stirred on a hot plate. The products are a bright red ammonium salt that is sealed, kept in solution to prevent decomposition and stored in a refrigerator. The reaction is as follows:



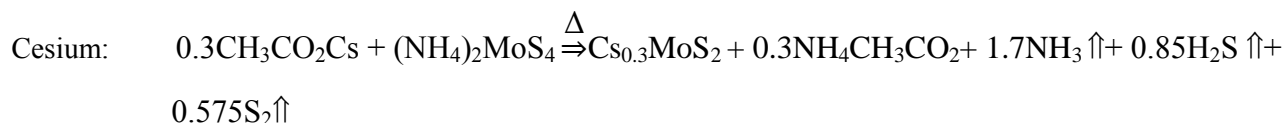
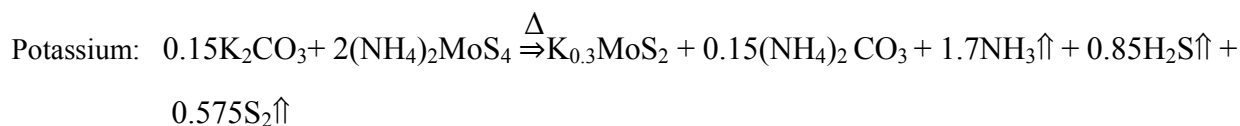
Synthesis for $\text{K}_{0.3}/\text{Cs}_{0.3}\text{-MoS}_2$ begins by calculating the mass of the alkali compounds (with a ratio of 0.3 mole of alkali metal to 1 mole of molybdenum at 5.00 grams of ATM). The ATM solution was filtered to collect 5.00 grams. The calculated masses of the alkali compounds are listed in Table 3 below.

Table 3: Mass of the alkali compounds on a 0.3 mol X to 1 mol Mo ratio at 5.00 grams of ATM.

(X=alkali metal)

Compound	Mass (grams)
Potassium Carbonate	0.40g
Cesium Acetate	1.10g
ATM	5.00g

All compounds were mixed in an aqueous solution. Five grams of ATM was dissolved in 50 mL of DI water, the alkali compound was dissolved separately in 10 mL of DI water then mixed together under stirring for 15 minutes. The proposed reactions are as follows:

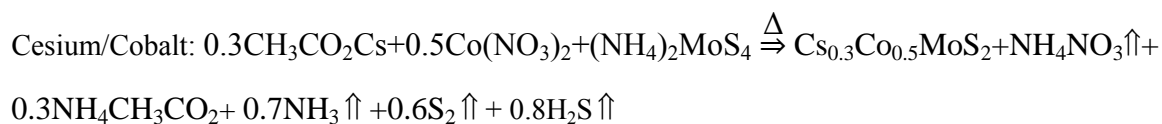
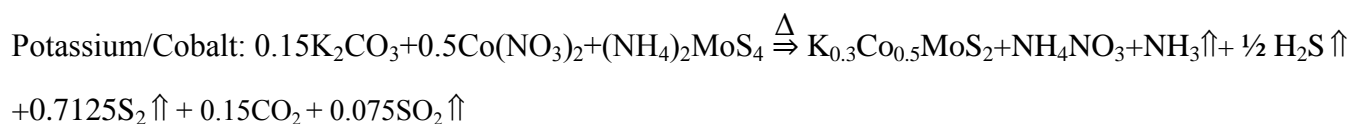


Synthesis for the $K_{0.3}/Cs_{0.3}-MoS_2$ series begins by calculating the mass of the alkali compounds and the cobalt nitrate hexahydrate (with a ratio of 0.3 mole of alkali metal to 1 mole of molybdenum at 5 grams of ATM and 0.5 mole of cobalt to 1 mole of molybdenum at 5 grams of ATM). The ATM solution was vacuum filtered to collect 5.00 grams. The calculated masses of the alkali compounds and the cobalt nitrate hexahydrate are listed in Table 4 below.

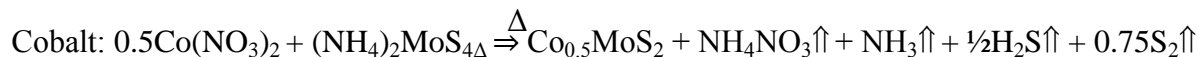
Table 4: Mass of the alkali compounds based on a 0.3 mol X and 0.5 mol Co to 1 mol Mo ratio at 5.00 grams of ATM. (X=alkali metal)

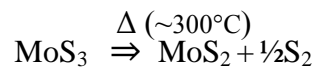
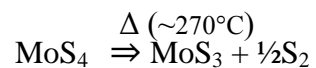
Compound	Mass (grams)
Potassium Carbonate	0.40g
Cesium Acetate	1.10g
Cobalt Nitrate Hexahydrate	2.80g
ATM	5.00g

All compounds were mixed in aqueous solution. Five grams of ATM was dissolved in 50 mL of DI water, each alkali compound was dissolved separately in 10 mL of DI water then mixed together, under stirring for 15 minutes. The cobalt nitrate hexahydrate was then dissolved in 10mL of DI water and added to the mixture last, under stirring for another 15 minutes. The proposed reactions are as follows:



The $Co_{0.5}MoS_2$ catalyst was synthesized in a similar method with the ratio of 0.5 mole of cobalt to 1 mole of molybdenum and the MoS_2 was synthesized at 5.00 grams of ATM. Proposed reactions are as follows:





For each reaction the mixed solution was then transferred to a 600 mL borosilicate liner and placed inside a high-pressure batch reactor parr model 4540 (see figure 9). The contents were reacted for 2 hours at 300°C reaching pressures of 1300psi.⁷² After the hydrothermal process took place each catalyst was vacuum filtered, washed using isopropanol and dried in a desiccator.

Chapter 4: Results and Discussion

This chapter aims at discussing the characterization performed on the alkali based MoS₂ series. It aims at describing structural features of their components through scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Crystal phase of the catalytic surface was evaluated using x-ray diffraction (XRD). Plausible identification of the structures active sites and influence on activity and selectivity will be compared to that found in catalytic literature. Fischer Tropsch products of each tested catalyst will be discussed along with a comparison to other researchers who have conducted FT experiments at lab scale.

4.1 Characterization

4.1.1 XRD

Powder diffraction patterns for the K_{0.3}/Cs_{0.3}-MoS₂ and K_{0.3}/Cs_{0.3}-Co_{0.5}MoS₂ catalysts were obtained with a Bruker D8 Discover. Scans were conducted with a step size of 0.02° in 2θ and a scan rate of 5.0°/min. XRD was utilized for phase identification and for identifying possible crystal phase changes.

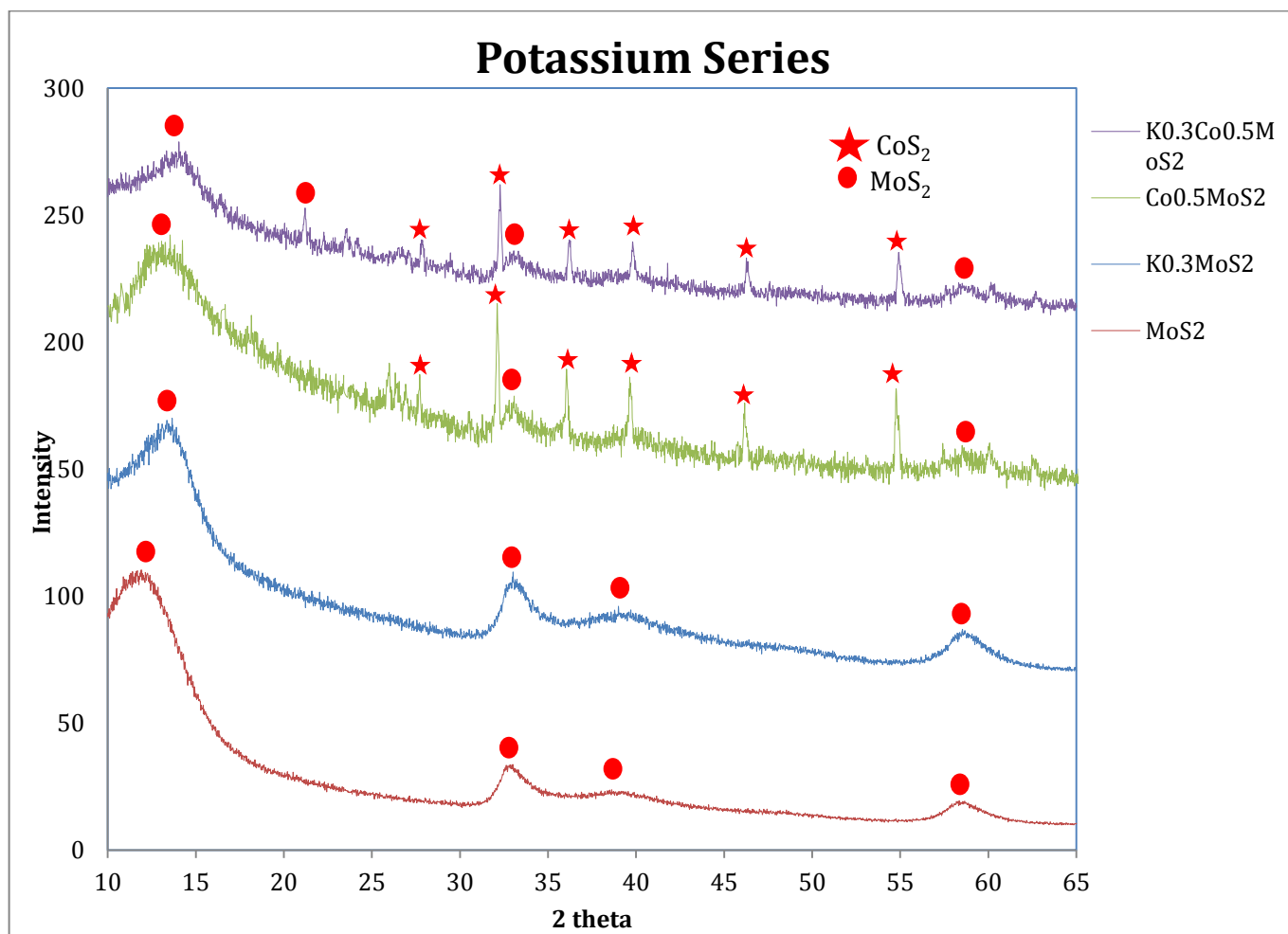


Figure 14: X-Ray diffraction pattern and peak identification of the potassium promoted series, $\text{Co}_{0.5}\text{MoS}_2$ and MoS_2 .

The MoS_2 diffraction pattern exhibits the properties of a poorly crystalline hexagonal MoS_2 . The initial peak to the left of the diffraction pattern (10° - 15° 2Theta) is the most predominant; this featured peak is consistent throughout the potassium series. Santiesteban et. al stated that this peak is broadly intense giving a strong indication that there is stacking of the MoS_2 layers. The shift of this peak to the right after adding a new component could be due to structural changes of intercalation which is not completely understood and is the subject of interest for future work. The next intense peak occurring at 33° 2theta provides evidence of these stacking faults indicated by its asymmetric shape.²⁷

There are two phases present throughout these diffraction patterns, disordered MoS_2 and crystalline CoS_2 . Chianelli mentioned that the broad intensity of the peak occurring at 38.7° 2theta for

the $K_{0.3}MoS_2$ and MoS_2 XRD patterns suggests that the two-layer MoS_2 stacking sequence is maintained for at least two stacks.⁷⁸ For the diffraction patterns of MoS_2 and $K_{0.3}MoS_2$ a broad MoS_2 peak is identified at 38.7 2theta with a d-spacing of 2.32nm. Occurring on the diffraction patterns where cobalt is present ($Co_{0.5}MoS_2$ and $K_{0.3}Co_{0.5}MoS_2$) a crystalline peak of CoS_2 occurs in proximity at 39.6 2theta with a d-spacing of 2.25nm. The broad peak occurring between 55°-60° 2theta is the last indicated peak shown for the MoS_2 phase (Figure 14).

All of the materials show disordered MoS_2 with crystalline cobalt sulfide. It was observed that the diffraction pattern for the potassium series indicated single peaks of CoS_2 and MoS_2 . A probable explanation can be that the addition of potassium to the precursor leads to segregated cobalt suggesting that thermally decomposed sulfide precursors may contain a mixture of molybdenum and cobalt sulfides instead of a dispersed Co-Mo-S type of material. The Co-Mo-S type phase was not present in these diffraction patterns. According to Chianelli et al. the structure and performance of the subsequent finished catalyst is understood to be dependent on the intensity of the thermal treatment. Chianelli showed that when various hydrodesulfurization catalysts were prepared by changing the annealing temperature; the conclusions were that there was a difference in catalyst morphology and selectivity to various HDS reactions. Studies on phase equilibria under hydrothermal conditions have found that this method of catalytic synthesis may in fact give rise to new phases that do not have natural analogues or have not been identified.⁴⁶

Between temperatures of 300-350°C materials develop a greater abundance of crystalline cobalt sulfides, and on salted samples, potassium sulfides are present. Using a software called “Find It” or the Eva software provided on the XRD analytical equipment, various literature references and an online data base MatNavi NIMS Materials Database, no peak identification of potassium compounds were found in these X-ray patterns. Possible reasons may be due to the high dispersion capability of hydrothermal synthesis preventing isolated peaks of the alkali promoter to form on the XRD diffraction pattern.^{27, 71, 79}

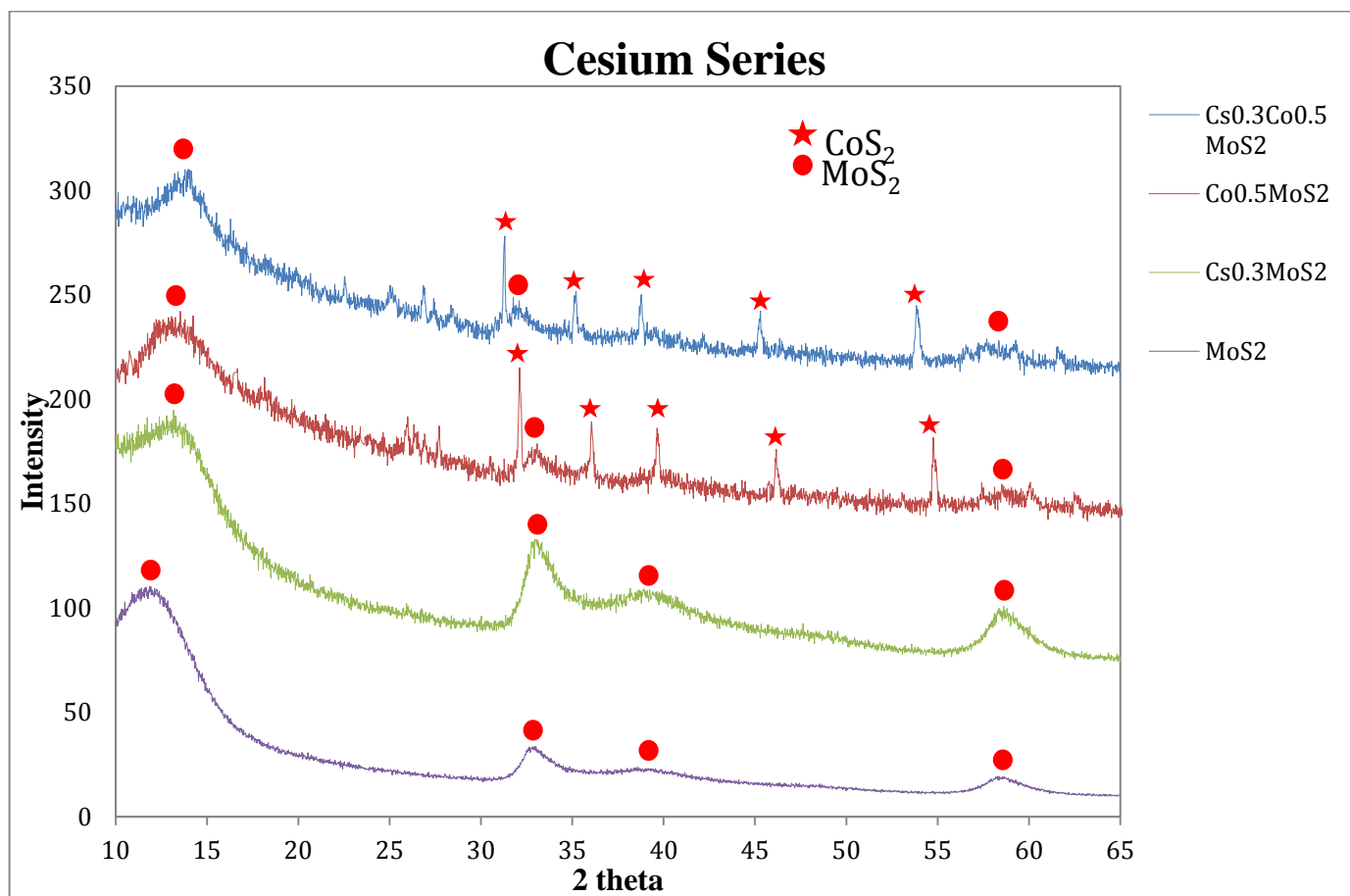


Figure 15: X-ray diffraction pattern of Cesium Promoted MoS₂-based series.

Similar characteristics from the potassium series were observed in the XRD pattern of the cesium promoted series. The hexagonal phase of MoS₂ is still predominant showing the same corresponding peaks for MoS₂ phase. Peaks of CoS₂ were also detected at the same 2theta range (Figure 15). Santiesteban, a researcher from Lehigh University, witnessed similar peaks occurring on Co_{0.5}MoS₂ and Cs_{0.3}Co_{0.5}MoS₂ between 20°-27° 2theta he attributed this to catalytic exposure to the atmosphere for long periods of time showing the agglomeration and crystallization of the cesium compound (Cs₂CO₃).²⁷ This phase was not recognized by the analytical methods by which peak identification was performed.

An interesting feature recognized in this diffraction pattern is the shifting to the left when Co_{0.5}MoS₂ is promoted with cesium. The shift to a lower diffraction angle is due to the insertion of

cesium between CoS_2 and MoS_2 sheets and the expansion of the interlayer spacing (d-spacing), the shift of the peaks after adding the alkali was also described by Takahashi.¹⁰³

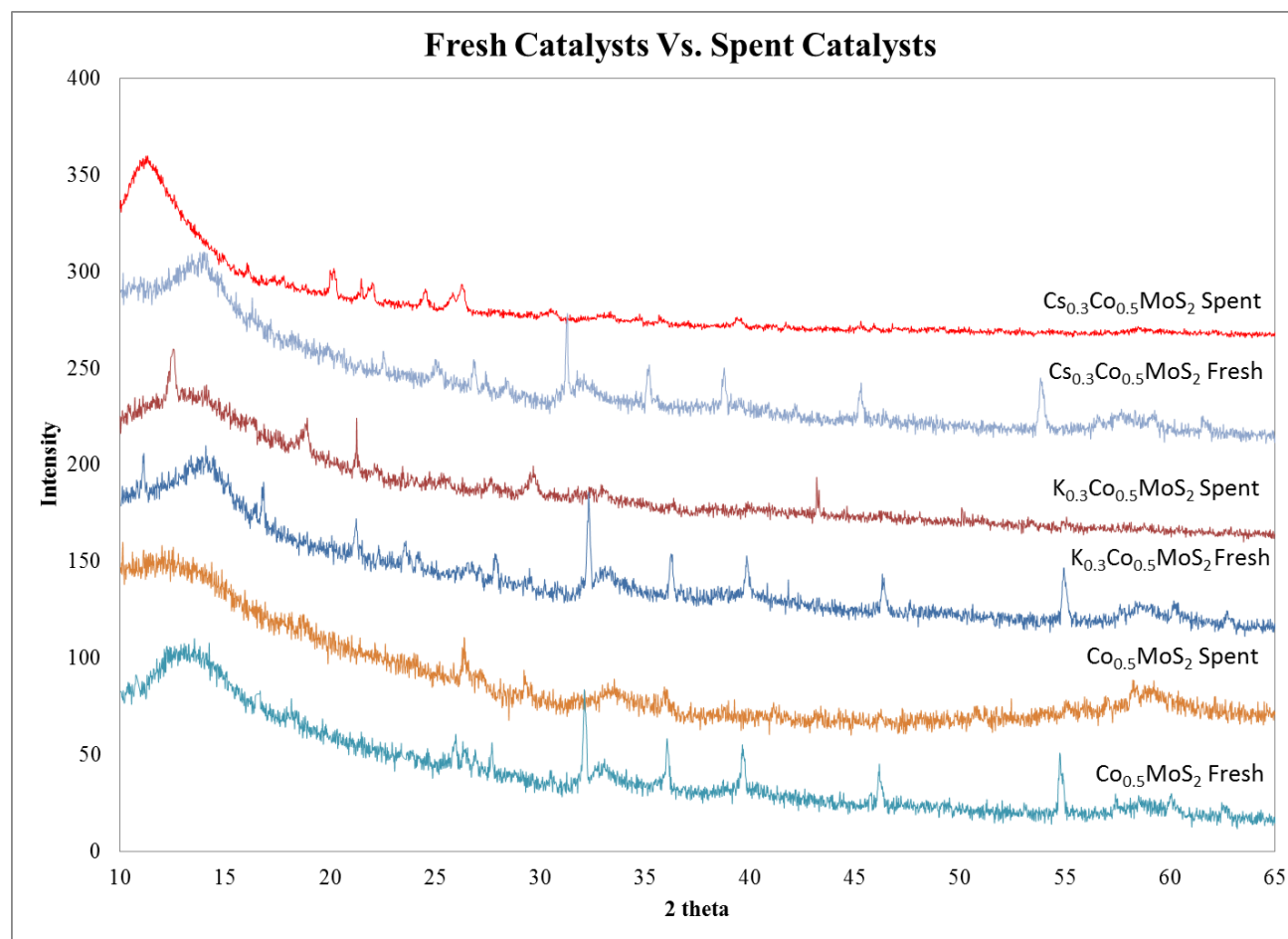


Figure 16: X-Ray Diffraction pattern of fresh vs. spent catalysts for the alkali promoted- Co_5MoS_2 Series.

Each catalyst was tested for FTS in the gas to liquid technology (Figure 16) at 300°C at pressures of 450 psi, for 8 hours at a ratio of $\text{H}_2:\text{CO}$ 0.8:1. General conclusions of the above diffractions are as follows:

1. MoS_2 broad peaks seem to disperse over the spent catalysts.
2. The small peaks occurring between 20°-30° 2theta on the $\text{Cs}_{0.3}\text{Co}_{0.5}\text{MoS}_2$ catalyst increased in intensity. It is possible that agglomeration of cesium occurred on the catalytic surface.

However, no cesium peaks were identified by the analytical methods by which peak identification was performed.

3. CoS₂ phase was dispersed and not detected in the spent catalysts. The X-ray diffraction patterns of the spent catalyst samples could support the notion of a change in the state of the cobalt promoter.⁸⁴

4.1.2 BET Porosity and Surface Analysis

The surface area of the fresh and spent catalytic series was determined using the conventional multi-point BET method. The measurements were performed in a Micromeritics TriStar 3000 BET Surface and Porosity Analyzer. Prior to analysis, the samples were evacuated overnight conducted by degassing with dry N₂ at 250°C for 1 hour.

Table 5: BET surface analysis for each catalyst (fresh vs. spent).

Name	Surface Area m ² /g Fresh	Surface Area m ² /g Spent
MoS ₂	169	
K _{0.3} MoS ₂	268	
Cs _{0.3} MoS ₂	444	41
Co _{0.5} MoS ₂	66.3	23
K _{0.3} Co _{0.5} MoS ₂	70.2	481
Cs _{0.3} Co _{0.5} MoS ₂	32.9	16

Addition of the alkali promoter upon MoS₂ led to a surface area increase. When potassium was added to MoS₂ it increased the surface area by nearly 100m²/g. However when cesium was added the surface area quadrupled. The alkali metal insertion into the MoS₂ expands the distance between MoS₂ stacking giving a higher surface area. Catalytic surface area varies with the ionic radius of the alkali metals.⁸⁹ XRD analysis did not observe peaks of alkali metal phases, due to the high dispersion of this alkali metal.

The surface area for $\text{Co}_{0.5}\text{MoS}_2$ is $66 \text{ m}^2/\text{g}$, upon addition of potassium surface area nearly stayed the same. Alkali metals occupy the surface porosity. Potassium's ionic radius is smaller than that of cesium so the potassium enters the pore but does not completely block it, hence the surface area nearly stayed the same. Cesium on the other hand, having a larger ionic radius, leads to a loss of surface area, this is proposed to be due to pore blockage by the cesium.

BET surface area measurements were also taken for the fresh vs. spent catalyst. The majority of the catalyst had a surface area decrease that is usual and has been previously reported for syngas exposed catalysts under high pressure and temperature. The loss of the surface area for the present catalyst was quite significant. One possible reason for this loss of surface area is that the alkali promoter could have agglomerated on the surface during testing. This agglomeration, in turn, could have blocked the pores of the catalyst, thus giving a lower surface area (Figure 22).⁹⁰

This is the case for all the catalysts except $\text{K}_{0.3}\text{Co}_{0.5}\text{MoS}_2$. This catalyst observed a dramatic increase in surface area after exposure to syngas. The figure 17 below shows the SEM images taken of this catalyst fresh vs. spent. Witnessed by SEM is the complete change in morphology from small particles to rod shape random orientated like morphology providing a higher surface area and porosity for the $\text{K}_{0.3}\text{Co}_{0.5}\text{MoS}_2$ catalyst.

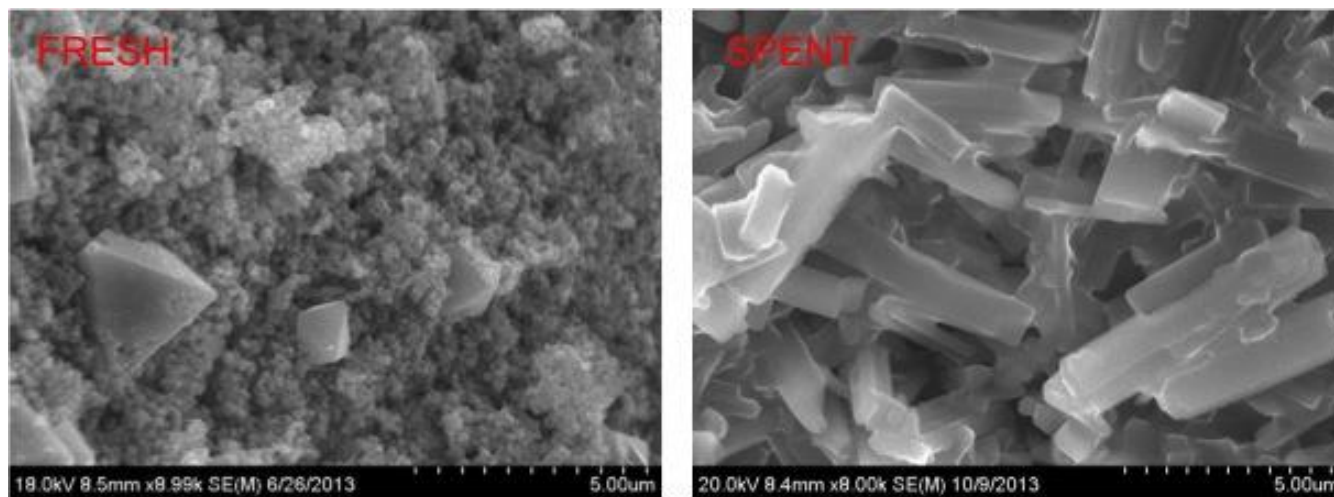


Figure 17: Fresh $\text{K}_{0.3}\text{Co}_{0.5}\text{MoS}_2$ catalyst on the left shows particle porous like material. Spent catalyst observes rod shaped random orientated type material providing higher surface area and porosity.

4.1.3 Scanning Electron Microscopy and Transmission Electron Microscopy

Scanning electron microscopy was taken using Hitachi SEM analytical instrument. Electron Microscopy is a useful tool for gathering chemical and microstructural information for heterogeneous catalysts. Two types of instruments that can be used to perform this analysis is a.) Scanning Electron Microscopy and b.) Transmission Electron Microscopy (model Zeiss EM10). Each catalyst was prepared on a carbon tape and placed on specified sample holder for analysis. Two features were observed using the SEM and TEM. They are depicted and described below.

A feature that was observed consistently in the alkali- $\text{Co}_{0.5}\text{MoS}_2$ series and alkali- MoS_2 series was MoS_2 stacking. Figure 18 SEM image was taken at an angle of a particle observing MoS_2 stacking on the surface as well as on its side angle. This has been observed as the “rag” structure consisting of several stacked and highly disordered S-Mo-S layers. XRD analysis confirms poorly crystalline structure of hexagonal MoS_2 .⁸²

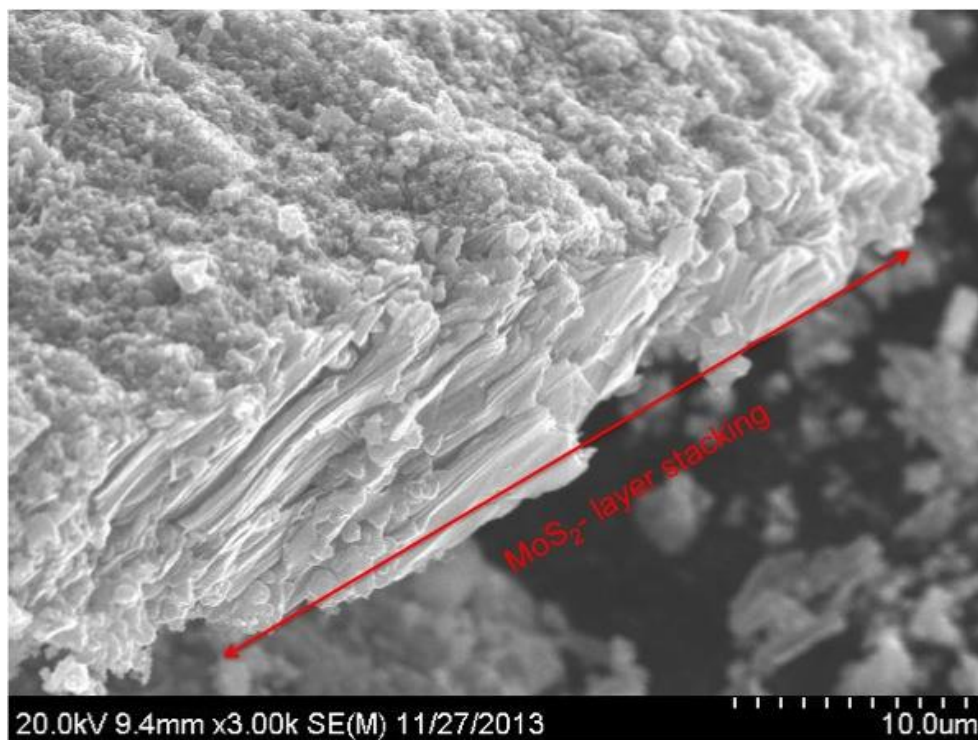


Figure 18: MoS_2 Stacking observed using SEM imaging at 10.0um.

TEM samples were prepared diluting a minimal amount of sample in isopropanol and sonicating for 30 minutes. A drop of the solution was placed on slot copper grid supported on formvar/carbon. TEM analysis depicts how hexagonal slabs of MoS₂ agglomerate together to form arbitrary shapes (Figure 19), this feature was also observed by Baksh.⁶²

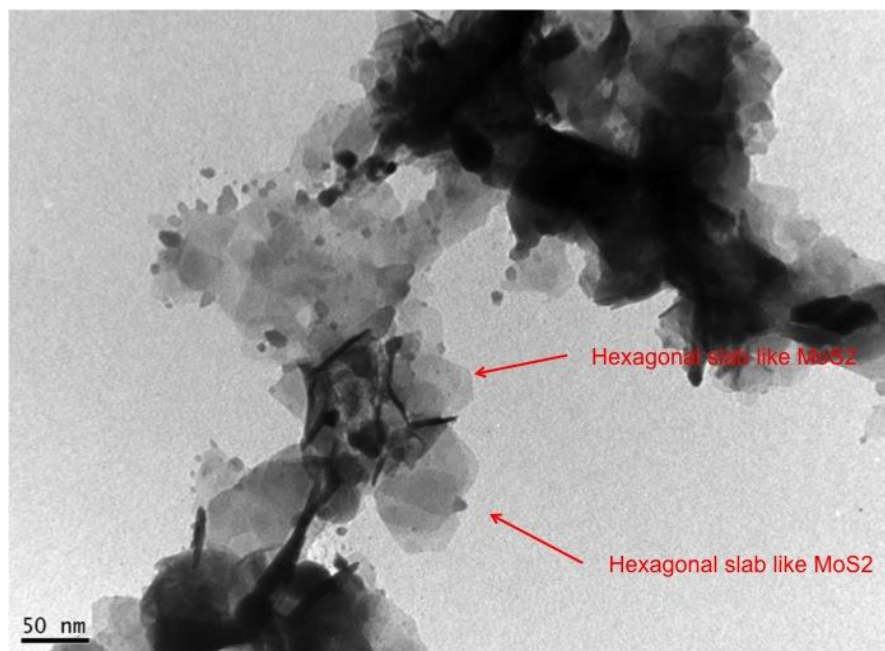


Figure 19: Slab like MoS₂ hexagonal structures present in TEM images from K_{0.3}Co_{0.5}MoS₂ catalyst.

The second feature observed was MoS₂-nano flower like morphology. The surface of the nano-flower like structure can be seen in the SEM image in Figure 20 below. Similar structural characteristics are shown in the TEM image in Figure 21. These nano-flower like structures were also observed by Qingfeng et. al.⁸³

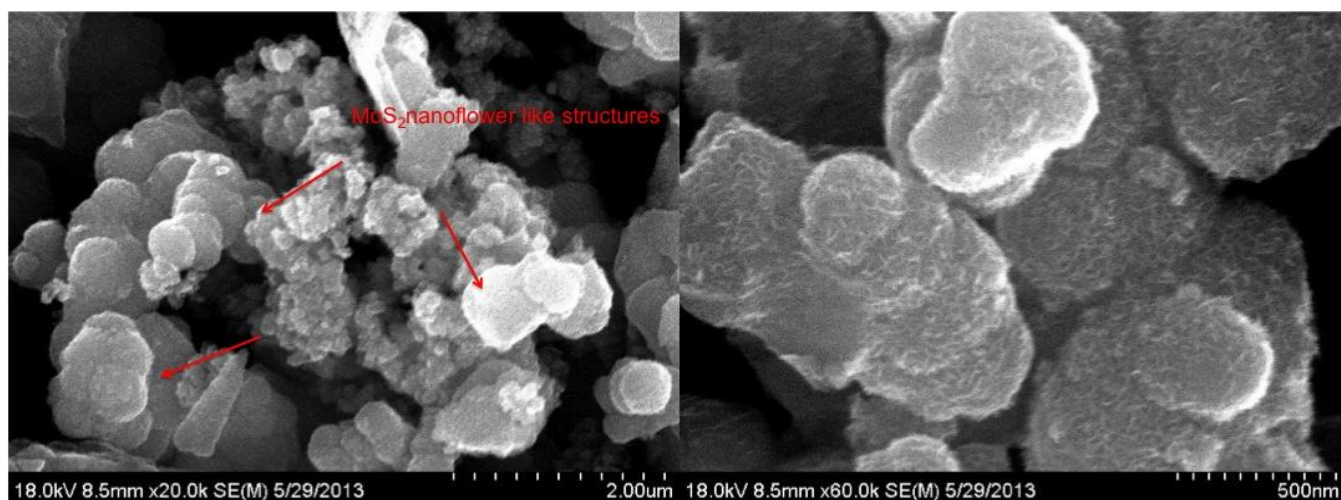


Figure 20: MoS₂ Nano flower like structure at 2.00 μm magnification (right) and at 500 nm magnification (left).

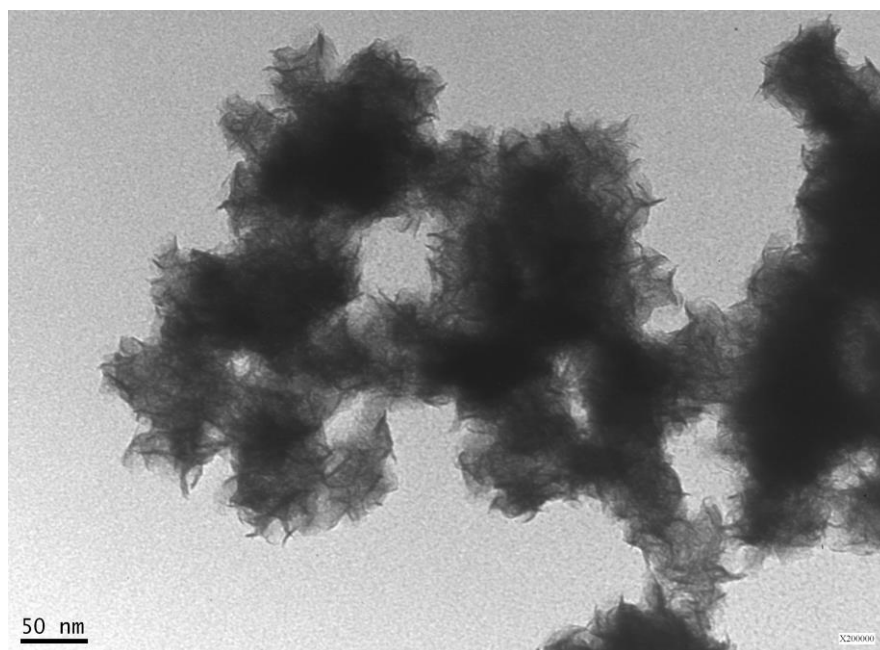


Figure 21: MoS₂ Nano flower like structure observed on TEM.

Lastly, it is important to compare the SEM images of the fresh versus spent catalyst to decipher if the morphological differences between them provide evidence that indicates morphological change on the surface of the catalyst (Figure 22).⁸⁴

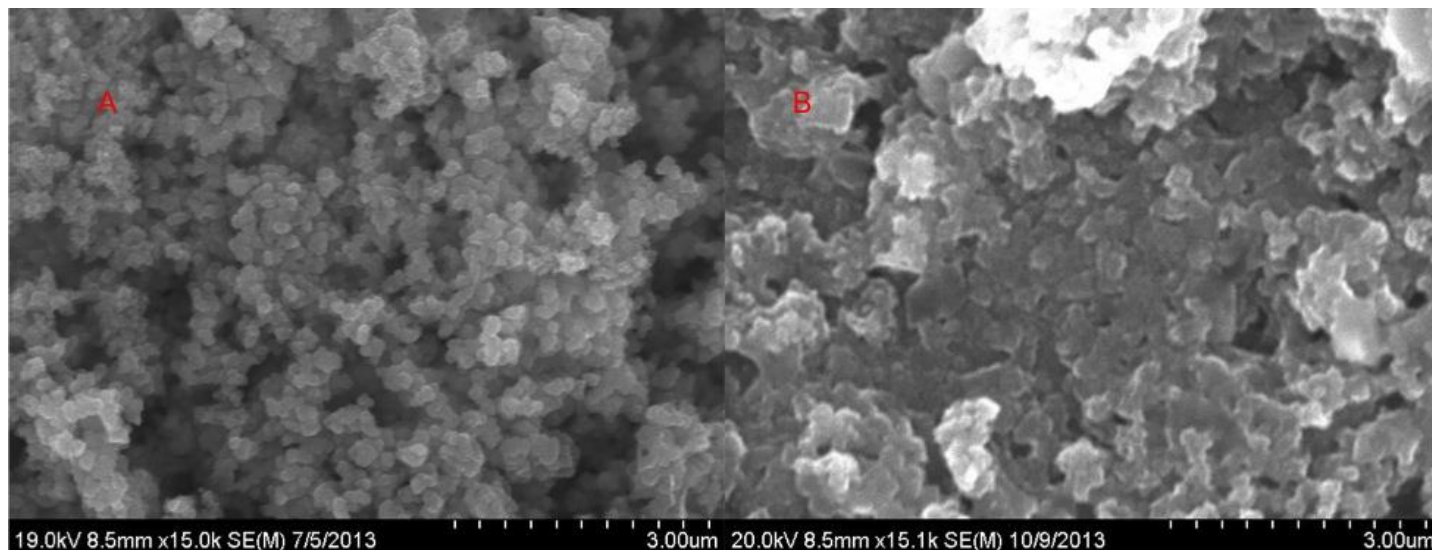


Figure 22: SEM images of fresh (A) versus spent catalyst (B) surface morphology change for catalyst $\text{Co}_{0.5}\text{MoS}_2$.

The figure above exemplifies the fresh vs. spent catalyst that can be attributed to loss of surface area. Image “A” observes particle and porous morphology while image “B” exhibits the agglomeration of the catalyst on the surface. The appearance of agglomerated morphology is associated with decrease in surface area.⁸⁵

4.2 Fischer-Tropsch Products

The ability for a catalyst to participate in the Fischer Tropsch synthesis and yield desired products depends on many factors. Among these factors are time, temperature, H_2/CO ratio, pressure, synthesis and to a deeper extent reactor design. The following section will discuss the FT products attained with the aforementioned gas-to-liquid technology. Selectivity, stability and activity of each catalyst in the $\text{Cs}_{0.3}\text{-MoS}_2/\text{Cs}_{0.3}\text{-Co}_{0.5}\text{MoS}_2$ were assessed.

The concentration (mol/mL) below were calculated using GC/FID. As the dependence of areas or heights on concentrations, or on mass is not known, it is necessary to find it by a calibration standard. A calibration standard was used to determine the peak area for each desired alcohol. Once the peak area from each desired alcohol was attained, it was multiplied by the response factor. The response factor is

used as a multiplication factor that will be applied to the peak area for the current compound to determine the concentration (ug/mL). Please refer to the example below.

Compound	Peak Area Determined by GC/FID	Multiplication Factor from Standard
-----------------	---------------------------------------	--

Ethanol	16830	2.48E-03
---------	-------	----------

Molecular Weight of Ethanol = 60g/mol EtOH

$16830 \times 2.48\text{E-}03 = 41.73\text{ug/mL}$ (concentration)

$41.73\text{ug/mL} >>>> 4.713\text{E-}05\text{g/mL}$

$4.713\text{E-}05 \text{ g/mL} \div 60\text{g/mol EtOH} = \underline{9.08\text{E-}07 \text{ mol/mL}}$

4.2.1 Cs-MoS₂ and Cs-CoMoS₂ Series

The cesium series (Cs_{0.3}MoS₂, Cs_{0.3}Co_{0.5}MoS₂), Co_{0.5}MoS₂, and MoS₂ are the catalytic materials for which FT products have been evaluated. The precursors used for synthesis of this series were chosen on the basis of the extensive literature and background knowledge providing evidence that the precursors chosen yield a favorable catalyst. Each catalyst was run in the GTL technology provided by Lamar University. Several experiments were initially conducted using the Co_{0.5}MoS₂-catalyst to design an optimal set of reaction conditions. The optimal reaction conditions that were observed are H₂/CO ratio 0.8/1.0, reaction pressure of 450 psi, and temperature of 300°C and samples were collected for a period of eight hours on the hour.

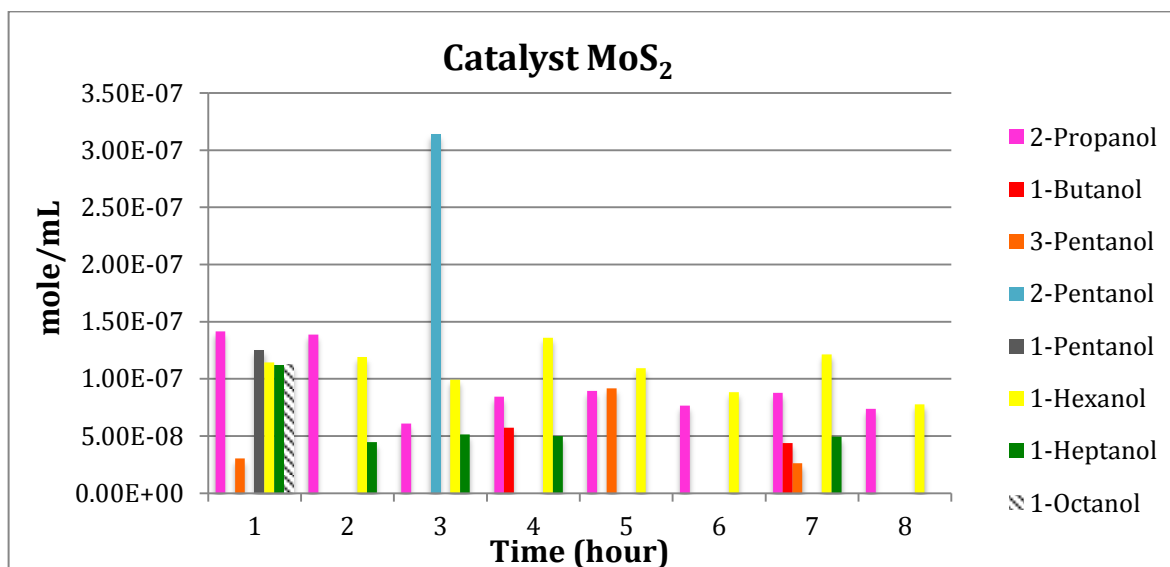


Figure 23: Catalyst MoS₂-Mole/mL of alcohols produced per hour over an eight hour FTS reaction period.

The alcohols that were consistently present during the eight-hour reaction were 2-propanol and 1-hexanol. The presence of these two alcohols at a consistent concentration (mol/mL) per hour, indicate that the MoS₂ catalyst is selective for the formation of these alcohols. 1-Heptanol is also featured in the eight-hour reaction, however it does not remain consistent in the fifth, sixth and eighth hour. This inconsistency is due to a shift in selectivity. Witnessed for the first time in this catalytic series is the production of 1-octanol, it appears in the first hour (Figure 23). MoS₂ is the catalyst selective for a more abundant group of alcohols. It is important to note that it is more favorable for a catalyst to be selective in the formation of 1 or 2 alcohols as opposed to three or more. At the industrial level, a high product range makes separation more difficult and costly. Another important trend to notice is the oscillation of the C5 alcohols, these are 3-pentanol, 2-pentanol and 1-pentanol. They appear every other hour; this transient behavior has not been reported for catalyst like this series, though it has been reported for FT synthesis.^{86,87} Based on literature for oscillatory behavior in FT-systems, this behavior can be due to: complex kinetics associated with changes in the active species, non-isothermal behavior, WGS reaction producing water, phase separation or onset of supercritical fluid phase, or adsorption on active sites.⁶²

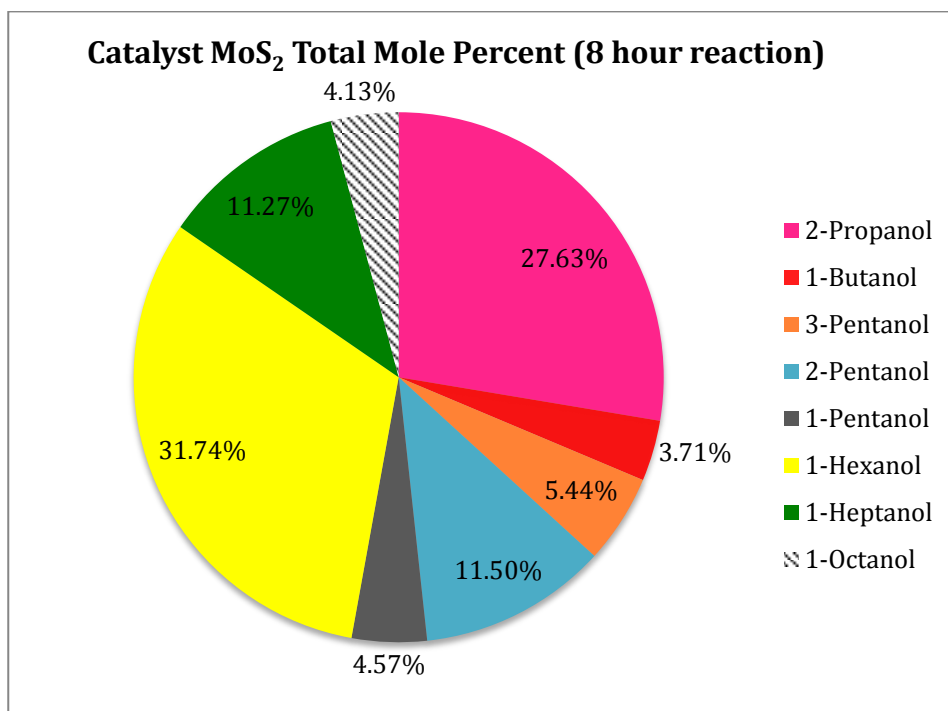


Figure 24: The total mole% of individual alcohols detected for an eight-hour duration over MoS₂-catalyst.

During the eight hour reaction period, MoS₂ was selective for four main alcohols, in order from highest to least: 1-hexanol (31.74%), 2-propanol (27.63%), 2-pentanol (11.50%) and 1-Heptanol (11.27%). Among this catalytic series, MoS₂ was the only catalyst that produced 2-propanol. 2-Propanol was not detected as a product for the other catalysts later described (Figure 24). The consistent presence of 2-propanol in the MoS₂ reaction indicates its selectivity for the production of this C3 alcohol.

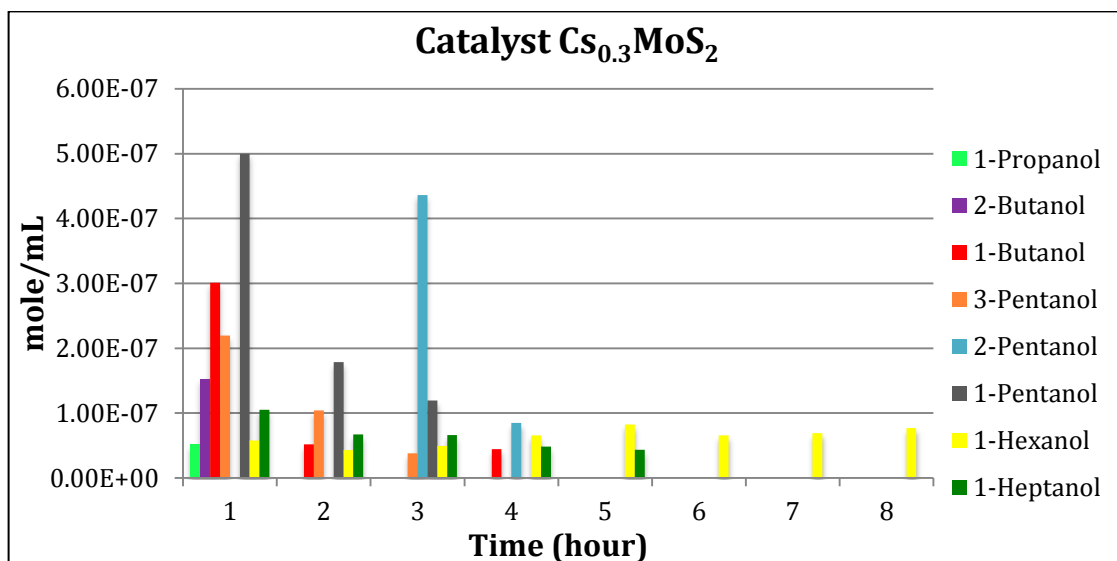


Figure 25: Catalyst $\text{Cs}_{0.3}\text{MoS}_2$ - Mole/mL of alcohols produced per hour over an eight-hour FTS reaction period.

The featured alcohol for the $\text{Cs}_{0.3}\text{MoS}_2$ catalyst was 1-hexanol. Although the quantity is not high it remains at a consistent concentration (mol/mL) through the duration of the reaction. 1-Heptanol is consistently present through the 1st-5th hour and then it becomes selective for only 1-hexanol. C2-C5 alcohols (1-propanol, 2-butanol, 1-butanol, 3-pentanol, 2-pentanol and 1-pentanol) have a slight presence during the 1st through 4th hour, but a shift in selectivity towards C6-C7 alcohols occur after the 4th hour.

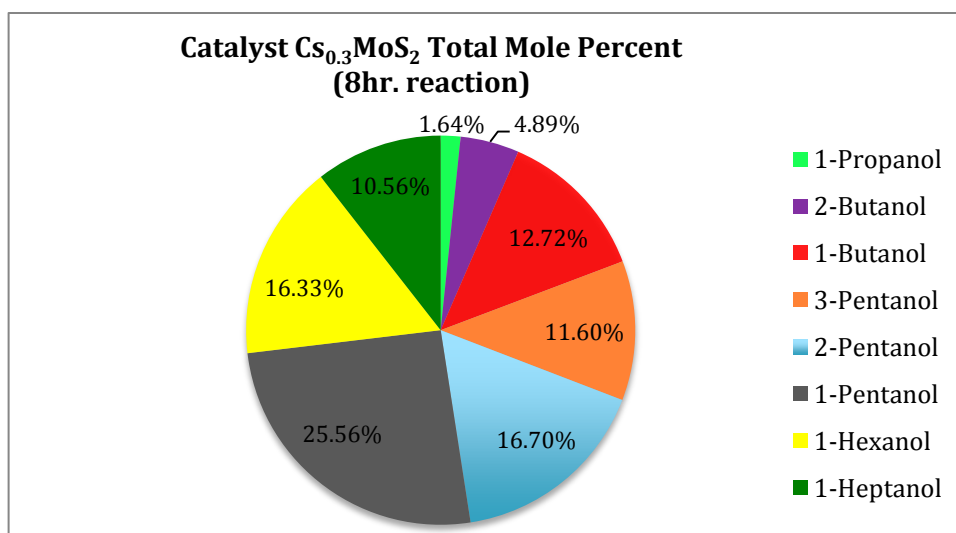


Figure 26: The total mole% of individual alcohols detected for an eight-hour duration over $\text{Cs}_{0.3}\text{MoS}_2$ -catalyst.

The alcohols produced for the $\text{Cs}_{0.3}\text{MoS}_2$ -catalyst from highest to lowest in mole% were 1-pentanol, 2-pentanol, 1-hexanol and 3-pentanol. Although the 1-hexanol was consistently predominant for the duration of the eight-hour reaction, the C5 alcohols had a greater mole%. The C5 alcohols were not selective for the duration of the eight-hour period; however their mole% was greater when their selectivity was present in the first four hours.

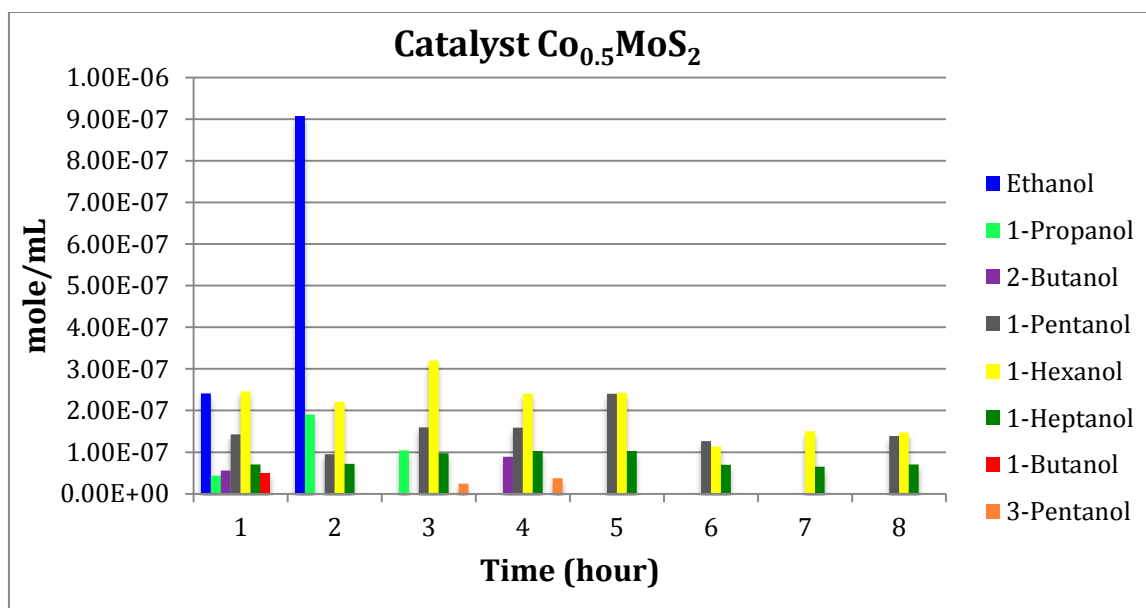


Figure 27: Catalyst $\text{Co}_{0.5}\text{MoS}_2$ - Mole/mL of alcohols produced per hour over an eight-hour FTS reaction period.

The graph above shows the alcohol production during an eight-hour period for the $\text{Co}_{0.5}\text{MoS}_2$ -catalyst. 1-Hexanol and 1-Heptanol alcohols were the most prevalent over this time span. A stability trend for 1-heptanol and 1-hexanol are featured indicating high catalytic stability for these alcohols. The concentration for 1-hexanol was above $2.00\text{E}-07$ mol/mL during the first 5 hours then decreased between the 6th to 8th hour (Figure 27). 1-Hexanol is present throughout the whole reaction as opposed to the C2-C4 alcohols that are present only in the first four hours. 1-Pentanol was present for the duration of the eight hours; however it was not detected in the 7th hour. An interesting feature is the high concentration (mol/mL) of ethanol at the second hour.

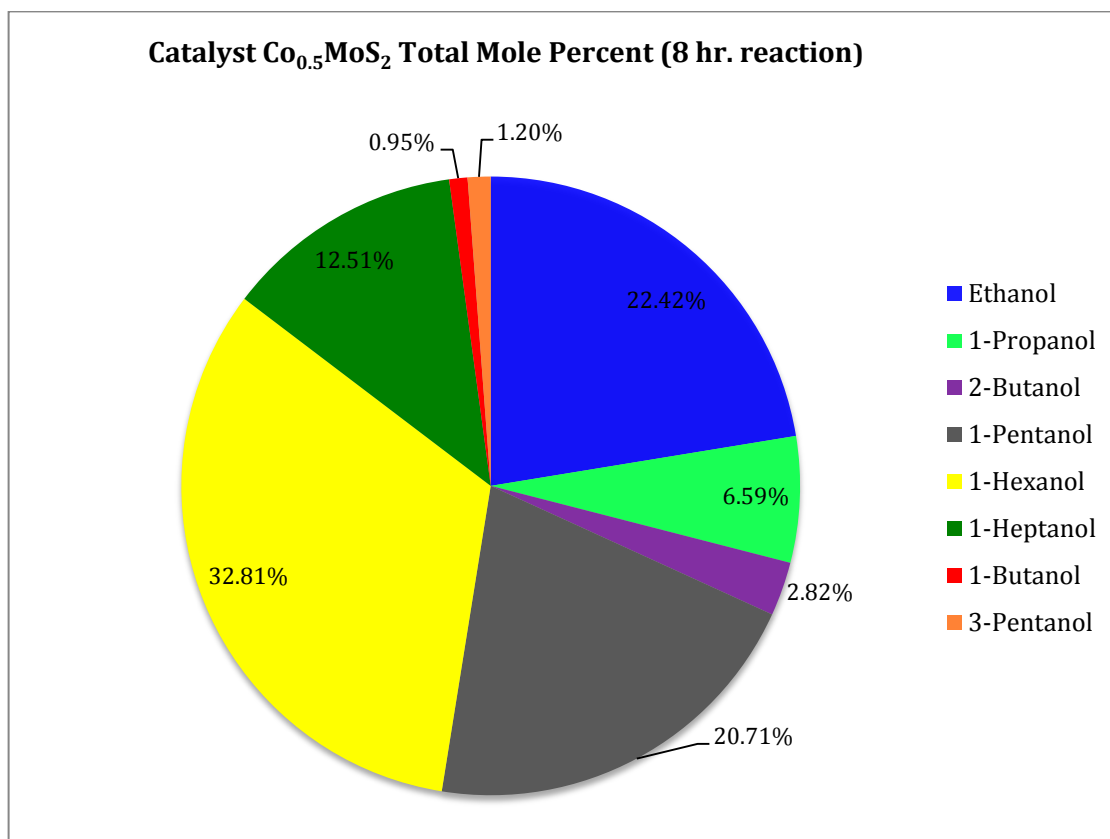


Figure 28: The total mole% of individual alcohols detected for an eight-hour duration over $\text{Co}_{0.5}\text{MoS}_2$ -catalyst.

The chart above shows the total mole percent for each alcohol detected over an eight-hour reaction time. The $\text{Co}_{0.5}\text{MoS}_2$ -catalyst gave the highest mole percent value of ethanol amongst the cesium catalytic series. A distinguishing component of this catalyst is the use of cobalt. Cobalt has a high activity for the Fischer-Tropsch reaction; it decreases the unfavorable reaction, the water gas shift, and pushes the products in the favor of alcohols.⁶³ Although ethanol was produced only the 1st and 2nd hour of the reaction it still gave the 2nd highest mole percent (22.42%), 1-hexanol gave the 1st highest mole percent (32.81%).

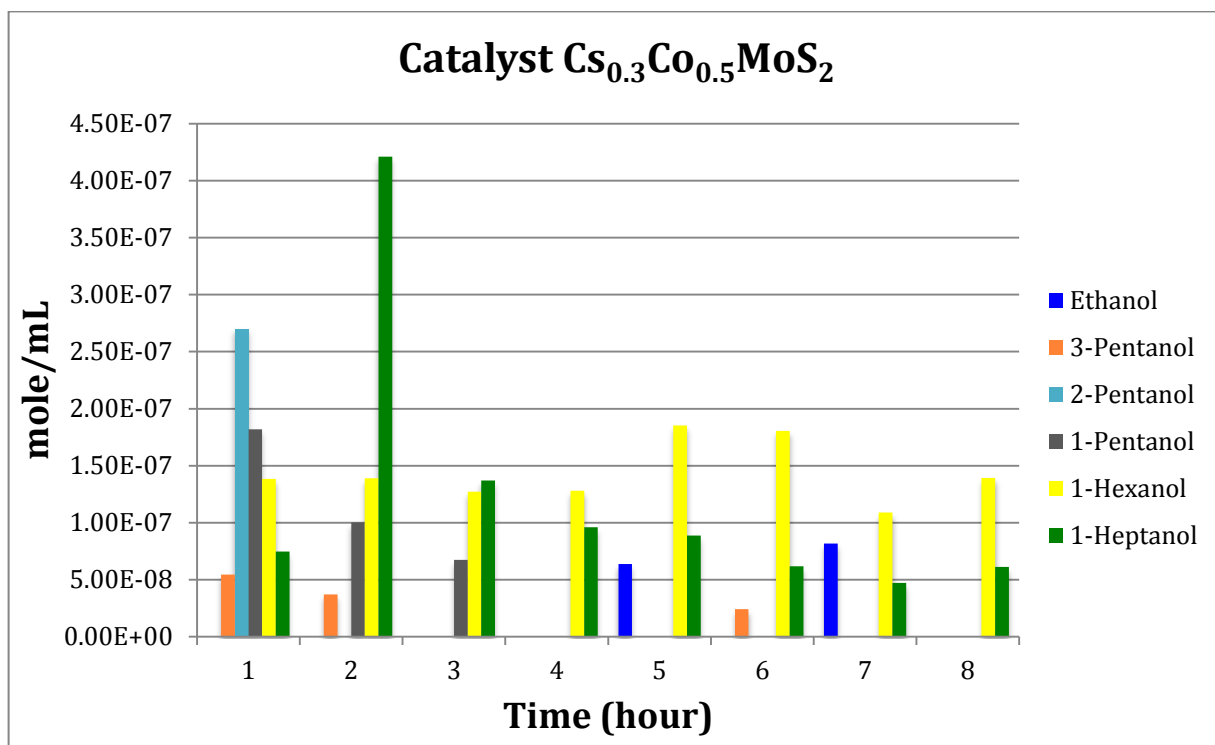


Figure 29: Catalyst $\text{Cs}_{0.3}\text{Co}_{0.5}\text{MoS}_2$ - Mole/mL of alcohols produced per hour over an eight-hour FTS reaction period.

Catalyst $\text{Cs}_{0.3}\text{Co}_{0.5}\text{MoS}_2$ is the catalyst that produced the least diversity of alcohol groups; it is selective for 1-hexanol and 1-heptanol. As previously mentioned, it is favorable for a catalyst to produce a specific group of alcohols as opposed to a diverse amount. Ethanol and 3-pentanol were the least produced appearing in the 5th and 7th hour at very low concentrations (mol/mL). C5 alcohols were detected for the first three hours but were not stable. 1-Hexanol and 1-heptanol were consistently observed for the complete eight-hour duration.

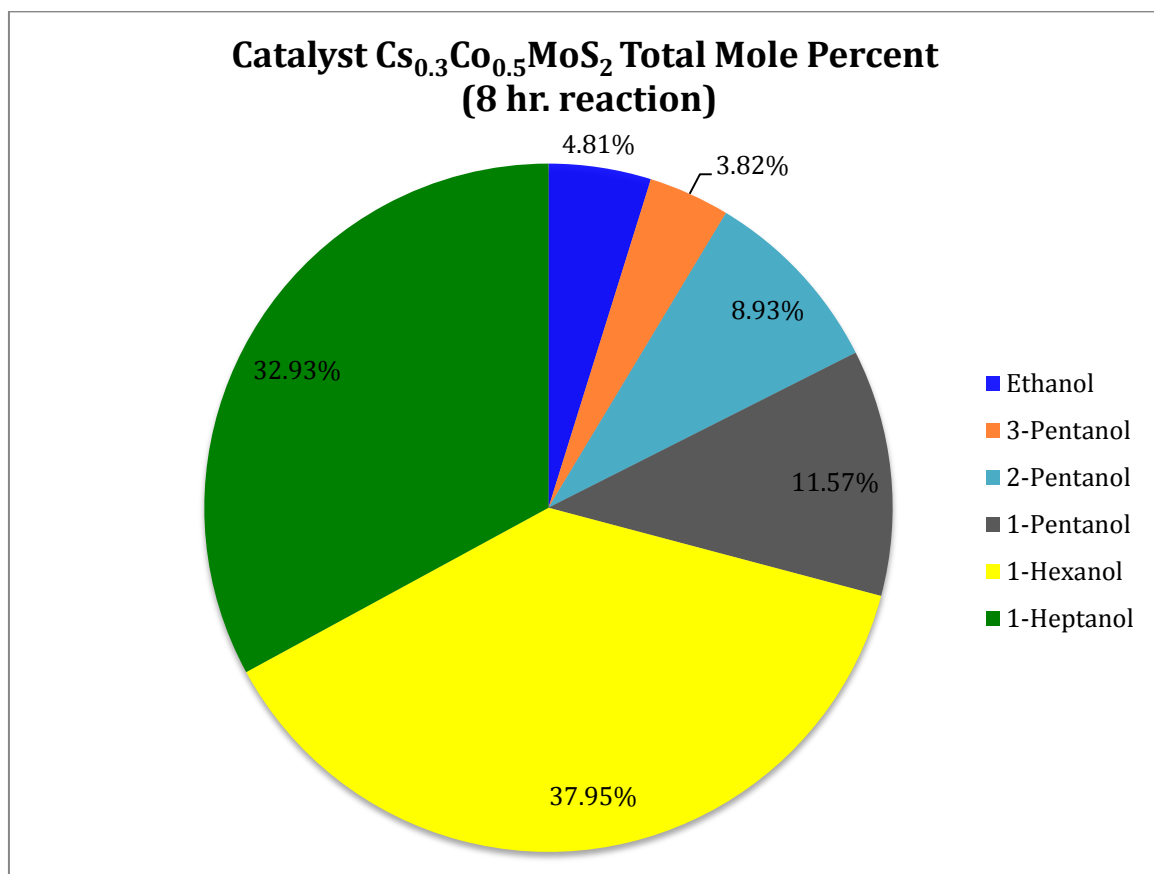


Figure 30: The total mole% of individual alcohols detected for an eight-hour duration over $\text{Cs}_{0.3}\text{Co}_{0.5}\text{MoS}_2$ -catalyst.

Catalyst $\text{Cs}_{0.3}\text{Co}_{0.5}\text{MoS}_2$, is the most selective of the four catalyst evaluated. It produced the least amount of alcohol diversity and the greatest concentrations for 1-hexanol and 1-heptanol alcohols (Figure 30). Similar to the $\text{Co}_{0.5}\text{MoS}_2$ catalyst, ethanol also appeared in the presence of cobalt. These were the only two catalysts that produce ethanol. This was observed by Dow Chemical researchers, the addition of cobalt to the alkali-doped MoS_2 catalyst shifts the selectivity in favor of ethanol.⁶⁵

Chapter 5: Conclusion

In a book by Satterfield, *Heterogeneous Catalysis in Practice*, he reminisces of the typical sentiments when he first encounters the world of heterogeneous catalysis, "...his first impression... is apt to be that of a vast and confusing field, replete with an enormous quantity of perhaps significant but empirical facts, interspersed with perhaps useful theories." ^{88,27} Nearly 30 years after this book was published and nearly a century after catalytic research was first recorded, heterogeneous catalysis is still a field of extensive research interest and theories. Conclusions from this research contribute to the understanding of hydrothermally synthesized unsupported alkali-promoted MoS₂- based catalysts; the main features are summarized below.

XRD patterns for the potassium and cesium series observed poorly crystalline phases of MoS₂ occurring approximately at 10°-15° 2theta, 33° 2theta, 37°-40° 2theta, and 55°-60° 2theta. These peaks were described to be attributed to MoS₂ stacking. CoS₂ peaks were also consistently observed in both the cesium and potassium phases. A probable explanation can be that the addition of the alkali to the precursor leads to segregated cobalt suggesting that the thermally decomposed sulfide precursors may contain a mixture of molybdenum and cobalt sulfides instead of dispersed Co-Mo-S type of material. Co-Mo-S type material was not detected. Shifting occurred on the diffraction patterns for the cesium and potassium series. The shift in the diffraction angle is due to the insertion of cesium between CoS₂ and MoS₂ sheets and the expansion of the interlayer spacing (d-spacing) or could be due to structural changes of intercalation which is not completely understood and is a subject of interest for future work. Alkali peak phases were also not detected, reasons maybe due to the high dispersion capability of hydrothermal synthesis preventing isolated peaks of the alkali promoter to form on the XRD diffraction pattern.

Fresh versus Spent x-ray diffraction patterns concluded that MoS₂ peaks dissipated over the syn-gas exposed catalysts. Small peaks occurring between 20°-27° 2theta on the Cs_{0.3}Co_{0.5}MoS₂ increased in intensity. It is possible that agglomeration of the cesium compound occurred on the catalytic surface. However, no cesium peaks were identified by which peak identification was performed. Phase equilibria

studies on hydrothermal conditions have found that this method of catalytic synthesis may in fact give rise to new phases that do not have natural analogues or have not been identified in literature.

BET porosity and surface analysis concluded that alkali addition to MoS₂ increased surface area. The increase in surface area corresponded to the size of ionic radius of the alkali metal $\text{Cs}^+ > \text{K}^+$. Upon potassium doping to Co_{0.5}MoS₂ catalyst surface area nearly stayed the same. Potassium's ionic radius is smaller than that of cesium, this potassium enters surface pores but does not completely block them. Cesium having a larger ionic radius, led to a loss of surface area attributed to pore blockage by the cesium.

Spent versus fresh surface areas determined the consistency reported in literature, a decrease in surface area for syngas exposed catalysts. One possible reason for this loss of surface area can be due to the agglomeration of catalytic surface during syngas exposure and FT testing under high temperature and pressure conditions. However, catalyst K_{0.3}Co_{0.5}MoS₂ showed an increase in surface area once it was exposed to syngas (70m²/g to 481m²/g). Witnessed by SEM imaging of K_{0.3}Co_{0.5}MoS₂ completely changed in morphology from small particles to rod shaped random orientated morphology providing higher surface area and porosity.

SEM and TEM electron spectroscopy confirmed two morphological features present on the catalytic surface; the “rag” structure consisting of several stacked and highly disordered S-Mo-S layers and MoS₂-nanoflower like material. SEM images of fresh versus spent catalyst provided evidence that indicated change in surface morphology of the catalyst exhibiting agglomeration once they were exposed to syngas.

The optimal reaction conditions that were observed are H₂/CO ratio 0.8/1.0, reaction pressure of 450 psi, and temperature of 300°C. Samples were collected for a period of eight hours on the hour. Fischer Tropsch reaction testing was carried out through the gas to liquid technology previously described.

General conclusions for the concentrations (mol/mL) of alcohols versus reaction time for the catalytic series are as follows:

1. Highest concentration (mol/mL) values belonged to the 1-hexanol and 1-heptanol alcohol group.
2. The alcohols produced from the MoS₂-catalyst versus reaction time gave the most diverse group of alcohols. This is not a favorable characteristic of an effective catalyst. It also had transient oscillating behavior possibly due to the water gas shift, complex kinetics, or changes in active species. MoS₂ was the only catalyst active for 2-propanol and 1-octanol.
3. Cs_{0.3}Co_{0.5}MoS₂ was the most stable, active and selective for alcohol formation. It produced the least diversity of alcohol groups indicating its high selectivity for 1-hexanol and 1-heptanol.

General conclusions for the total mole percent of the individual alcohols detected over the eight-hour period are as follows:

1. The catalyst with cobalt, Co_{0.5}MoS₂ and Cs_{0.3}Co_{0.5}MoS₂, were the only catalyst active for ethanol. According to Dow Chemical Company and other researchers cobalt promotes ethanol formation.
2. Highest mole percent detected for the majority of the cesium series were the 1-hexanol and 1-heptanol. However, Cs_{0.3}MoS₂ was the only catalyst to produce C5 alcohols in a greater mole percent than the C6-C7 group.
3. MoS₂ catalyst was the only catalyst to yield 1-octanol and 2-propanol.
4. Cs_{0.3}Co_{0.5}MoS₂ gave the highest mole percent values for 1-hexanol and 1-heptanol among this series.

5.1 Future Work

Further investigations of this research include testing K_{0.3}MoS₂ and K_{0.3}Co_{0.5}MoS₂ for the production of alcohols and characterization of the spent material for K_{0.3}MoS₂ and MoS₂ using BET, XRD, SEM and TEM. Future research with collaborators from Lamar University, Dr. Tracy Benson, include purchasing an already commercialized Fischer- Tropsch catalyst and testing it using the

assembled gas to liquid technology that was utilized to test the cesium catalytic series reported in this research. This will determine what optimization parameters are required for the improvement of the assembled gas to liquid technology. Other studies will include a thorough understanding of the shifting occurring on the XRD patterns.

Lamar and UTEP/MRTI will also perform kinetic evaluation for this catalytic series. Kinetic studies, in addition to yielding basic information about the process, provide practical information needed for rational design of reactor systems. $\text{Cs}_{0.3}\text{Co}_{0.5}\text{MoS}_2$ seemed to be the most active, selective and stable for C6-C8 alcohols at the reaction conditions. However, one cannot speculate that these conditions alone are optimal for each catalyst that was tested. Each specific catalyst behavior is highly dependent on reaction conditions and preparation.

The most reasonable kinetic interpretation to begin with is the calculation of alpha explained in terms of the Shultz-flory Diagram (Figure 31).⁹¹

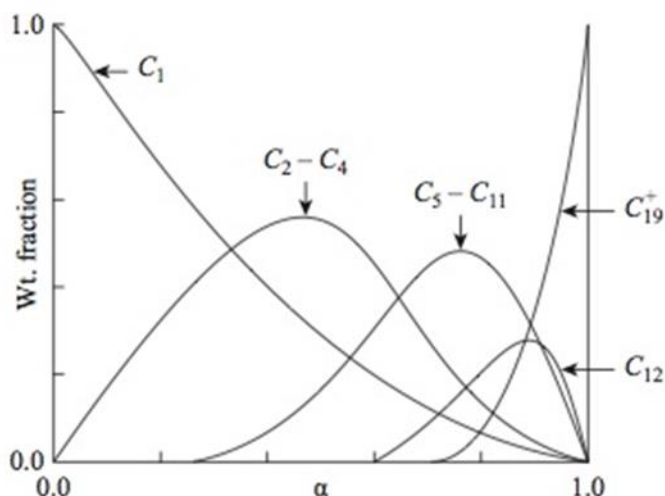


Figure 31: Weight fraction of FT products as a function of α , the chain growth probability.⁶⁵

Because the FTS yields various products with different molecular weights, a simplified plot of the weight fraction of any particular product range to be expected for any value of α can be determined. Alpha (α) can be defined by the following equation:

$$\alpha = k_p / k_p + k_t$$

where k_p is the propagation rate and k_t termination rate of the reactions. If an α value increases, it means that the propagation rate increases and the propagation cycle continues. For example, the figure above shows that when α value is minimal, only shorter chain carbon products are possible. When α is halfway between the 0.0 and 1.0, C5-C10 compounds are produced. At higher α values longer chain carbon products (e.g. C20) can be formed in the reaction. This is a simple model that will be used to provide valuable kinetic information for this family of catalysts.

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Vita

Belinda Molina was born in El Paso, Texas on August 1, 1985 to Imelda L. Molina and her husband, Master Sergeant Edgar Molina. The youngest of three daughters, Belinda enjoyed a happy and nourishing childhood typical for a middle-class, military family. A naturally inquisitive and energetic youth, Ms. Molina developed a fondness for math and science early in her education that allowed her to excel as a student. Early aspirations to become a medical professional prompted her to attend Maxine L. Silva Magnet High School for Health Care Professions, from which she graduated in 2003.

Deciding not to pursue a career in the medical field after High School, Belinda enrolled at the University of Texas at El Paso, where a strong math and science background led her to gravitate naturally towards the physical sciences. During the completion of her undergraduate studies, Belinda took advantage of internship opportunities at NASA's Johnson Space Center in 2008 and at the University of Arizona in 2009. These internships proved to be valuable learning experiences that allowed Ms. Molina to familiarize herself with the use of sophisticated scientific instruments and become comfortable working in research facilities. Additionally, Belinda was able to use her research at the University of Arizona to contribute to the publication of "Characterization of Diffraction gratings comprised of Core/Shell Nanocrystals," Photonics CMDITR Review for Undergraduate Research Volume 6, Number 1, Aug. 2009

Upon completion of her Bachelors Degree of Science in Chemistry in 2010, Belinda decided to continue her studies and enrolled in the Masters Program for Chemistry at the University of Texas at El Paso. As a graduate student, Ms. Molina was once again given the opportunity to work with NASA when she received a student research program fellowship at the Glenn Research Center in Cleveland, Ohio in the summers of 2011 and 2012. She is expected to graduate with a Masters Degree in Chemistry in December of 2013.

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