ABSTRACT

This research aimed at developing Fe-Zn-Ru based catalysts loaded on silica and γ-alumina supports. Four distinct Fischer-Tropsch catalysts were prepared through the incipient wetness technique. These catalysts were Fe-Zn-Ru/γ-alumina, Fe-Zn-Ru/K/γ-alumina, Fe-Zn-Ru/silica, and Fe-Zn-Ru/K/silica. The primary objective was to study the strong metal-support interaction (SMSI) effect on the catalyst activity and selectivity in the Fischer-Tropsch reaction. To achieve this goal, data from temperature programmed reduction (TPR) of the as-produced catalysts were correlated to the data obtained from bench-scale, fixed bed reactor studies. The TPR was conducted under dilute hydrogen and carbon monoxide atmospheres as well as under a dilute syngas atmosphere. The TPR data clearly showed the effect of support type as well as the presence of potassium on the activation behavior of the catalysts. The catalysts were tested in the bench-scale, fixed-bed reactor system in a temperature range of 300-400 °C, pressure of 350 psi, and a syngas flowrate of 30 mL/min. The bench-scale studies showed that the γ-alumina supported catalysts produced more hydrocarbons at lower temperatures, while the silica supported catalysts produced more hydrocarbons at higher temperatures. The ideal Fischer-Tropsch condition observed for each catalyst in this research was 350 psi and 350 °C.

The catalysts were fully characterized using temperature programmed reduction analysis in H₂, CO, and a H₂/CO mixture, particle size analysis, and BET methods. An investigation of the micro-structural properties of the catalysts and distribution of the active phases on the support together with surface composition and morphology was conducted via XRD and SEM/EDS techniques. Additionally, thermogravimetric analyses were carried out to evaluate the Fe conversion at each reduction step in correlation with the TPR results.

Lastly, density functional theory (DFT) calculations were used to determine the interaction of CO₂ with γ-Al₂O₃ supported transition dimers. This modeling approach found that CO₂ adsorbs on M₂/γ-Al₂O₃ negatively charged and in bent configuration, indicating a partial activation of CO₂. The most favorable adsorption site for CO₂ on M₂/γ-Al₂O₃ was the interface between the metal dimer and the support.
EXECUTIVE SUMMARY

This research addressed the issue of producing liquid fuels from syngas using a novel approach of developing catalysts based on active phase-support interaction to enhance the conversion of syngas to liquid fuels.

Synthesis of liquid fuels from coal has a two-fold advantage. With respect to Illinois, the state with the largest reserves of coal, the production of transportation fuels at a reasonable cost creates a new market segment with a niche for low sulfur liquid fuels. The coal industry has been severely hit in the wake of new environmental regulations. The coal to liquid fuels technology will provide significant impetus to this industry in the state. On a national level, the successful deployment of this technology will give United States independence from the few countries that contain petroleum reserves, especially since these regions are wrought with political instability making the steady supply of petroleum nearly impossible. One of the ways of converting coal to transportation fuels is the Fischer Tropsch Synthesis of coal-derived syngas. However, as with any technology, some fundamental scientific and engineering challenges have to be overcome to economically compete with liquid fuel reserves prior to commercialization.

Cobalt catalysts have been found to be very effective for the Fischer Tropsch synthesis, provided the H₂:CO ratio is 2:1. Syngas produced from sources such as coal results in low H₂:CO ratios (of the range of 0.67 – 1). In such cases, iron, which has a lower activity towards FT synthesis is often advocated particularly due to its activity towards the water gas shift reaction which can alter the H₂:CO ratio favorably towards the stoichiometric ratio for FT synthesis. Often, promoters such as Cu, to enhance the reducibility, Zn for catalyst dispersion on the support and K for promoting the FT synthesis are used. In spite of these promoters, iron based catalysts do not perform as well as their Co counterparts both in terms of their mechanical stability and FT activity. It is therefore desired that a catalyst be designed that would be able to utilize a coal derived syngas feed but would also show activity that is of a similar order of magnitude as cobalt. Such a catalyst that can operate effectively over a range of H₂:CO ratios would not only be useful from an operational point of view but also from the production cost aspect. The requirements for such a catalyst are superior activity towards both water gas shift reaction as well as the primary FT synthesis reactions. A significant number and combination of promoters have been researched in the past. However, the promoters have enhanced the activity of iron-based catalysts to a limited degree only. The investigators hypothesized that strong metal (FT active phase) – support interaction is a bottleneck towards achieving the full potential of the activity of iron based catalysts. The investigators thus focused on performing experimental and model-based research to understand the metal – support interaction and design a catalyst that is comparable to Co based catalysts in terms of their activity and with enhanced selectivity of the FT process towards liquid hydrocarbons.

The specific objectives of this project were to conduct fundamental studies, both experimental and model based, a) to understand the nature of metal – support interaction in FT catalysts and to study the effect of such an interaction on the FT process, b) to
evaluate the impact of Ru on the FT process in an iron based catalyst, c) to design an optimal catalyst with enhanced activity and selectivity for producing liquid transportation fuels from coal-derived syngas, and d) to evaluate the effect of process conditions on the FT product distribution, CO conversion, and selectivity towards liquid fuels. The work performed to complete these objectives can be outlined by the following primary tasks—catalyst preparation, physical characterization of the catalysts, temperature programmed reduction (TPR) studies, thermogravimetric analysis (TGA), bench scale studies of Fischer Tropsch synthesis, and molecular-level modeling.

Four catalysts (two on a γ-alumina support and two on a silica support) were produced and fully characterized. These catalysts were Fe-Zn-Ru/γ-alumina, Fe-Zn-Ru/K/γ-alumina, Fe-Zn-Ru/silica, and Fe-Zn-Ru/K/silica. Energy dispersive X-ray (EDS) and X-ray diffraction (XRD) both confirmed the presence of the catalyst components. BET analysis showed that the γ-alumina-supported catalysts possess a higher specific surface area than the silica-supported catalysts (Fe-Zn-Ru/γ-alumina=125.53, Fe-Zn-Ru/K/γ-alumina=116.14, Fe-Zn-Ru/silica=87.18, and Fe-Zn-Ru/K/silica=90.76 m²/g. The final characterization method was particle size analysis, which determined that the γ-alumina catalysts had a smaller average particle size than the silica-supported catalysts (Fe-Zn-Ru/γ-alumina=31.73, Fe-Zn-Ru/K/γ-alumina=31.56, Fe-Zn-Ru/silica=103.5, and Fe-Zn-Ru/K/silica=113.6 μm). The reason for the larger silica supported catalyst particles was likely due to agglomeration from the particle size analysis wet sample method.

Catalysts often must be activated by heating under a flow of a reducing gas. This activation prepares the metal surface for reaction with the analyzing gases. TPR is a method of monitoring the steps of reduction for metal oxides as a function of temperature. The reducible components of the prepared catalysts were Fe₂O₃ and RuO. In order to evaluate the effect of activation atmosphere and the corresponding mechanisms involved, TPR experiments were conducted in three atmospheres, namely, 5% H₂, 5% CO, or 2.5% H₂ + 2.5% CO in Ar. Notable results include a shift (temperature increase) observed of the reduction peaks upon the addition of a potassium promoter to the catalyst on both supports under hydrogen flow. This effect was not observed when CO was the reducing agent. In addition, the γ-alumina-supported catalysts displayed 2 reduction steps (reactions) during the TPR under H₂, while the silica-supported catalysts showed 3 reduction steps during the TPR under H₂. Both the γ-alumina-supported and silica-supported catalysts exhibited 2 reduction steps during the TPR under CO. This information indicates an active role by the support during catalyst activation.

The percentage of iron conversion at the reduction temperatures found during the TPR experiments were determined by TGA. Catalyst sample weight loss was monitored during reduction by hydrogen at temperatures corresponding to signal peak maxima in the TPR graphs. By comparing the sample weight losses with theoretical weight losses of iron oxides during the reduction process (Fe₂O₃→Fe₃O₄→FeO→Fe), the reduction mechanism at each TPR characteristic temperature was determined.

Fischer-Tropsch experiments were conducted in a lab-scale, fixed-bed reactor system in a temperature range of 300-400 °C, pressure of 350 psi, and a syngas (H₂:CO=2) flowrate
of 30 mL/min. The H₂ and CO conversions were calculated and the product distribution from each of these tests were analyzed and compared. The overall highest H₂ conversions for each catalyst were observed at 350 psi and 400 °C, the absolute highest was shown by Fe-Zn-Ru/K/silica at 80%. The highest CO conversion during the FT tests at 350 psi and 350 °C and 350 psi and 400 °C was exhibited by the Fe-Zn-Ru/K/silica catalyst. For both conditions, the conversion was 80%. The overall highest CO conversions for each catalyst were observed at 350 psi and 400 °C.

During the FT experiments at 350 psi and 300 °C, γ-alumina-supported catalysts produced the widest range of hydrocarbons and no oxygenates, while the silica-supported catalysts produced great amounts of oxygenates. For the FT tests conducted at 350 psi and 350 °C, the Fe-Zn-Ru/γ-alumina produced the widest range of hydrocarbons and no oxygenates, however the use of silica as support resulted in the formation of alcohols. At 350 psi and 400 °C, the silica-supported catalysts demonstrated the widest range of hydrocarbons. This shows that the use of silica as a support facilitates chain growth more than the γ-alumina-supported catalysts. The best FT experimental conditions in this research were identified as 350 psi and 350 °C for all catalysts. Further FT tests should be conducted at varying pressures to identify the catalyst activity at other conditions.

In order to model the catalyst-support behaviors, density functional theory (DFT) calculations were carried out using the Vienna ab-initio simulation package (VASP). The projector augmented wave method was employed to describe the ion-electron interactions and the generalized gradient approximation (GGA) was chosen for the exchange and correlation potential. Ab initio molecular dynamics simulation within the same framework of DFT and pseudopotential was performed for CO₂ adsorption on the γ-Al₂O₃ supported transition dimers. By this approach, CO₂ was determined to adsorb on M₂/γ-Al₂O₃ negatively charged and in bent configuration, indicating a partial activation of CO₂. Both the supported metal dimer and the γ-Al₂O₃ support contribute to the activation of CO₂ by donating their electronic charges to the adsorbed CO₂. The most favorable adsorption site for CO₂ on M₂/γ-Al₂O₃ was the interface between the metal dimer and the support. The electronic charges on the adsorbed CO₂ make CO₂ distort from its linear configuration in the gas phase. The presence of the metal dimer enhances the binding of CO₂ with the substrate, including both dry and partially hydroxylated γ-Al₂O₃. As such, the adsorption energy of CO₂ on M₂/γ-Al₂O₃ is much higher than that on the γ-Al₂O₃ surfaces without the supported metal dimer. It was also demonstrated that the binding strength of CO₂ with M₂/γ-Al₂O₃ correlates with the electron-donating ability of the substrate. The investigators recommend further examination of CO₂ interactions with γ-Al₂O₃-supported binary metal clusters with the rationale that the catalytic property of a supported metal catalyst can be tuned by introducing a second metal. The use of SiO₂ as a support for the metal clusters would also be of great interest for future work.
OBJECTIVES

This work addressed a novel approach for improving the activity and selectivity of iron-based FT catalysts towards a narrow product distribution. This was achieved by a simultaneous molecular modeling and experimental approach. In addition, the activity of the FT catalyst was further boosted by doping the iron-based catalyst with zinc, ruthenium, and potassium. The investigators adopted this approach in hopes to provide (a) a better understanding of the metal support interaction for designing FT catalysts, (b) enhanced Fe-based FT catalyst activity, (c) narrow distribution of the length of carbon chains in the product, (d) reduction of the capital cost of the FT plant due to elimination of hydro-cracking units, (e) simplification of the coal to liquid fuel production technology, (f) increased conversion of the syngas without increasing the formation of the long chain hydrocarbons or waxes (<1%). And finally, the investigators attempted to increase the attractiveness of Illinois coal as transportation fuel feedstock.

The specific objectives of this project were to conduct fundamental studies, both experimental and model based, a) to understand the nature of metal – support interaction in FT catalysts and to study the effect of such an interaction of the FT process, b) to evaluate the impact of Ru on the FT process in a iron based catalyst, c) to design an optimal catalyst with enhanced activity and selectivity for producing liquid transportation fuels from coal derived syngas, and d) to evaluate the effect of process conditions on the FT product distribution, CO conversion, selectivity towards liquid fuels and the kinetics of the reaction. The data obtained from these studies can be easily used for scaling up the process using the optimal catalyst.

The following primary tasks were completed to achieve the above objectives:

Task 1. Catalysts Preparation

Four distinct Fisher-Tropsch catalysts were prepared through the incipient wetness technique. These catalysts were Fe-Zn-Ru/γ-alumina, Fe-Zn-Ru/K/γ-alumina, Fe-Zn-Ru/silica, and Fe-Zn-Ru/K/silica.

Task 2. Physical Characterization of the Catalysts

SEM/EDS - The microstructural properties of the catalyst and the distribution of the active phases on the support were evaluated in the backscattering mode in a scanning electron microscope. Additionally, the surface morphology and composition of the catalysts were analyzed by Energy Dispersive X-ray (EDS).

BET - BET surface area, pore volume, pore size, and average pore size distribution of supports and catalysts were obtained from full-range N₂ sorption isotherms using an adsorption surface area model 2000 Quantachrome analyzer.
XRD- The powder X-ray diffraction technique was performed using a Rigaku Miniflex II XRD to identify the various crystalline phases present in the catalysts along with any amorphous phases.

Task 3. TPR Studies

TPR was performed using a Quantachrome ChemBET 3000 instrument coupled with a programmable furnace and a data acquisition system. Hydrogen, carbon monoxide, and a mixture of these gases were used individually as reducing agents.

Task 4. TGA Studies

TGA studies were performed to identify the reduction mechanism undergone by the as-produced catalyst at different activation temperatures and iron conversion at reduction temperatures identified during TPR studies.

Task 5. Bench Scale Studies of the Fischer Tropsch Synthesis

Fixed bed FT experiments were carried out at 350 psi, in a temperature range of 300-400 °C, and with a syngas flow rate of 30 mL/min. The syngas H\textsubscript{2}:CO ratio was set at 2:1. These experimental conditions were applied in the same experimental run for each catalyst sample in a fixed order. The catalyst activity was defined as moles CO converted per kilogram catalyst per second, and hence represents an average over the reaction regime. The selectivities of the various reaction products were calculated on the basis of the molar fraction of that hydrocarbon in the hydrocarbon mixture, as determined by mass spectrometry.

Task 6. Molecular-level Modeling

DFT calculations were performed using the Vienna ab-initio simulation package (VASP) to determine the interaction of CO\textsubscript{2} with γ-Al\textsubscript{2}O\textsubscript{3} supported transition dimers. CO\textsubscript{2} interactions with supported binary metal clusters, in particular, the γ-Al\textsubscript{2}O\textsubscript{3} supported Co-Cu and Fe-Zn clusters, were also examined.
INTRODUCTION AND BACKGROUND

In 1925, Professor Franz Fischer, founding director of the Kaiser-Wilhelm Institute of Coal Research in Mülheim an der Ruhr in Germany, and his head of department, Dr Hans Tropsch, applied for a patent describing a process to produce liquid hydrocarbons from carbon monoxide gas and hydrogen using metal catalysts. This process, referred to as Fischer Tropsch (FT) synthesis, was used to produce synthetic liquid fuels in Germany from 1938 to 1944, during WWII, using thoria and magnesia-promoted cobalt catalysts. They were also produced in South Africa from the mid 1950’s at Sasol plants in fixed and fluidized-bed reactors utilizing potassium-promoted iron catalysts; and the facilities there are still in operation. Today, an increasing demand for clean fuels and chemicals is expected to lead to an important shift from crude oil to natural gas as feedstock for chemical industries. This will certainly involve the use of FT technology. However, the successful application of FT processes requires intensive research on a new generation of active and selective catalysts. These catalysts are often loaded with small amounts of promoter elements that enhance their overall catalytic performances and catalyst lifetime. These beneficial effects are, however, only obtained if the promoter element is added in the appropriate manner and in a limited range of promoter loading. Although catalyst promotion is heavily studied in the field of heterogeneous catalysis, not so much is known about the physical and chemical origins of iron FT promotion effects. The catalysts are often loaded onto supports to disperse the active phase onto a larger surface, and these supports are generally considered to remain inert during the catalysis. Thus, supports have been selected based on their stability under reaction condition, surface area and ease of loading the active phase. Although the supports do not directly participate in the reactions, they do play an important role in the formation of active phases, reactant spillover and ultimately the activity of the catalysts depending on the active phase-support interaction. This research explored the impact of support on FT synthesis reactions on iron based catalysts with Zn, Ru, and K promoters for enhancing the catalyst activity and selectivity towards the desired product distribution from coal-derived syngas. A concurrent experimental and molecular modeling based approach was undertaken with internal information feedback to both activities to understand the role of metal-support interaction in the activity of the catalyst and for the design of the optimal catalyst.

Most of the previous studies have focused on synthesis and characterization of different FT catalysts, and provided essential information for catalyst development and industrial reactor design. However, an understanding of the processes at the atomic level, which is important to design more efficient catalysts, remains poor. The overall process of FT synthesis is comprised of a complex network of elementary bond-breaking and bond-forming steps. These steps include CO and H\textsubscript{2} activation, as well as, hydrogenation and chain growth over supported metals. The balance of the bond breaking and bond formation steps controls the reactivity and selectivity of the process. For example, transition metals to the left in the periodic table will readily activate CO but the products, i.e. surface carbon and oxygen, are too strongly bound to the surface, thus blocking subsequent hydrogenation and carbon coupling reactions. Transition metals to the right, on the other hand, are not active enough to dissociate CO. The ideal catalysts for FT synthesis would be those metals that can promote CO activation, along with a balanced
degree of surface hydrogenation and hydrocarbon coupling in order to produce longer chain hydrocarbon products. Fe and Co have been chosen as the main components in commercial FT catalysts, depending on the source of syngas.\(^2,3\) Therefore, analyses of the elementary steps involved in the reaction are important in the search of more effective catalysts.

Fe-based oxides have been used as commercial catalysts for FT synthesis to produce a large variety of paraffin and olefin products, ranging from methane to high molecular weight waxes\(^4\). During activation by synthesis gas and subsequent FTS reaction, several phases including metallic iron, iron carbides and iron oxides are known to co-exist at steady-state conditions\(^5,6,7\). The distribution and amounts of these phases depend on exposure to various activation and reaction conditions, leading to different catalytic performances in FTS. Some researchers\(^8\) have proposed that surface iron atoms are responsible for FTS activity, while some others considered surface carbides or a mixture of carbides\(^9,10\) and metallic iron\(^11\) to be the active phase. There are also some reports that suggest that magnetite Fe\(_3\)O\(_4\) is the active phase in FTS\(^12,13,14\). Davis\(^15\) reported that zinc promotes the catalytic properties of Fe oxides. Zinc oxide, as a non-reducible oxide in FTS conditions, appears to stabilize the surface area of Fe oxide. Ruthenium is a well known active component of FT catalysts, although Ru-based catalysts are not as commonly used as Fe- or Co-based catalysts, because of the high cost. As a result, investigations of the FT reaction over Ru-based catalysts have been limited. However, the role of Ru as an electronic promoter for Co-based catalysts has been investigated\(^16\). Ruthenium shows exceptionally high selectivities to C\(_5\) or higher products and higher turnover rates compared to unpromoted Co catalysts. The supports of Ru-based catalysts affect the CO/H\(_2\) reaction\(^17,18\). Although the main products are light hydrocarbons including CH\(_4\), Ru has higher turnover frequencies and better olefin selectivity. A strong metal-support interaction (SMSI) is presumably responsible for the epitaxial stabilization of preferred crystal faces, and/or transfer of electrons between the metal particles and the support\(^17,19\). Additionally, Ru promoted the Fe reduction significantly and supported the increase in the Fe metallic crystalline size. Therefore, CO adsorbs at bridge state, to form the active CO species on this Fe-Zn-Ru catalyst. The addition of potassium increases the olefin/paraffin ratio in the FT reaction\(^20\). Also, adding potassium should result in higher CO dissociation and hydrocarbon chain growth and a decrease in CH\(_4\) selectivity.

It is well known that for many metal-catalyzed reactions, the support influences the catalytic properties of the metal particles\(^21\). For example, it has been well established that the reaction rates of hydrogenation and hydrogenolysis reactions of hydrocarbons over supported Pt catalysts are improved when the Pt particles are supported on acidic supports. It has also been observed that the electronic properties of the supported Pt particles depend on the acid/base properties of the support. However, the nature of this interaction between metal and support that leads to altered electronic properties is poorly understood. Moreover, there is no understanding on how the support-induced changes in the electronic properties affect the catalytic properties. Filling the pores of the support with a solution of the catalytically active elements, after which solvent is removed by drying, is a straightforward way to load a support with active material. However, in this process various interactions are possible between the dissolved catalyst precursor and the
surface of the support, which can be used to obtain a good dispersion of the active components over the support.

Silica and alumina supports contain several types of hydroxyl groups: isolated, germinal or H-bonded for silica and linear or bridged for γ-alumina. Hydroxyl groups play a very important role in catalyst preparation, because they represent anchoring sites where catalyst precursors can be attached to the support. Although those of silica are chemically indistinguishable, the OH groups on alumina differ significantly in chemical character. The linear hydroxyls on alumina have anionic (basic) character. The hydroxyls react in water with both protons and OH⁻ groups, giving the surface ionic character. The following equilibrium reactions occur:

\[
\begin{align*}
\text{Basic sites} & \quad M-OH + H^+ = M-OH_2^+ \\
\text{Acidic sites} & \quad M-OH + OH^- = M-O^- + H_2O
\end{align*}
\]

Obviously, the charged state of the surface enables one to bind catalysts precursors to the ionic sites of the support.

Silica with surface areas up to 300 m²g⁻¹ consists of dense particles with diameters of 7 nm and above, and do not contain micropores. Though silica supports are amorphous, the surface may exhibit some local order, such as that of the mineral β-crystobalites. The surfaces of silica support contain OH groups at densities of between 4 and 5.5 OH per nm². Silica surfaces contain only terminal OH groups, i.e. bound to a single Si atom. In contrast, γ-alumina contains several hydroxyl, between 10 and 15 OH per nm², the linear one being Brønsted bases (H⁺ acceptors) and the bridged ones Brønsted acids (H⁺ donor). After dehydroxylation, the surface develops Lewis acidity, whereas silica contains only isolated OH groups¹⁹. These differences in the surface charge yields differences in the manner and quantity of catalysts loading as well as the chemical characteristics of the catalyst. These differences in turn affect the activity of the catalyst towards a particular reaction.

One of the goals of this investigation was to understand the nature of the support interaction and to relate the support-induced changes in catalytic properties to the yield and specific selectivity of the Fischer-Tropsch reaction. It is well known that nanosized clusters (active sites in catalysis) exhibit unique properties and play a role in many technical applications. Detailed structural information about their surfaces is critical to a deeper understanding of their physics and chemistry. Scanning tunneling microscopy (STM) allows atomic-scale investigation of the electronic and geometric structure of surfaces, but almost no atomically resolved STM results of nanosized clusters thicker than a few atomic layers are currently available²². This is due to the finite size of the STM tip that leads to convolution effects which, in turn, severely disturb measurements. One specific example for the lack of structural knowledge of nanosized cluster surfaces is the so-called “strong-metal support interaction” (SMSI) in heterogeneous catalysis. SMSI has been termed by Tauster et al.²² to account for the changes in catalytic activity when the group VIII metals Fe, Ni, Rh, Pt, Pd, and Ir, supported on oxides are reduced at elevated temperature. It was found that the adsorption of H₂ and CO is drastically
reduced, but competitive hydrogenation versus hydrogenolysis reactions is greatly favored in SMSI systems. For example, methanol production from CO or CO$_2$ and H$_2$ is enhanced by 3 orders of magnitude$^{23}$. Because SMSI allows one to tailor the selectivity of a catalyst, it has caused widespread interest. Berry et al$^{24}$ reported that iron in the silica-supported material is reduced more easily to Fe$^0$ when compared to alumina supported iron. They also observed that the amenability of iron to reduction in the multimetallic system is also dependent on the nature of the support, with more facile reduction to the zero-valent state being achieved on silica, where the metal-support interaction is weaker. Additionally, the authors claimed that dispersion of iron catalyst is better on silica when Ru is present as a promoter.

In addition to using standard analytical techniques to evaluate the activity of the catalysts, such as temperature programmed reduction, temperature programmed reaction and thermogravimetric analysis (at different FT pressures), the investigators evaluated the catalysts in a fixed-bed plug-flow reactor. The fixed bed catalytic reactor is one of the most widely used reactor types in the refining and petrochemical industry. In its simplest form, it is a tube filled with a solid catalyst, through which gaseous (or, less frequently, liquid) reactants flow and they are converted into products. One of the first questions that have to be addressed in designing a fixed bed reactor is whether and how heat will be added to or removed from the reactor. The simplest choice is to use an adiabatic reactor. When heat transfer is not an issue, the reactor can be a single vessel with a relatively large diameter, it will require no utilities during the steady-state operation, and only one single catalyst bed will be needed. Unfortunately, many important reactions cannot be successfully carried out in a single adiabatic reactor. If the reaction is adequately endothermic, then the temperature in the reactor will decrease as the reaction proceeds, and the reaction may become unacceptably slow before reaching the desired extent of reaction. In case of exothermic reactions, the temperature of adiabatic reaction may be higher than what a reactor fabricated with economically reasonable materials can withstand. In addition, high temperatures may lead to unfavorable equilibriums or the production of unwanted by-products (e.g. waxes in FT synthesis). Thus, it is desired to add heat to an endothermic reaction or to remove it from an exothermic reaction. This may be achieved in a configuration that has separate heat exchangers and reactors, or one with separate heat exchange and reaction sections within the same reactor. In addition, a reactor system may be used wherein continuous heat addition or removal through the wall of the fixed bed reactor may occur. However, the reactors in such a system will have fairly small diameter so that heat transfers in or out of it is fast enough to avoid unacceptable temperature gradients in the radial direction. Another problem in the last system is the formation of localized hot spots inside the catalytic bed. If the catalyst is exposed to too high a temperature, undesired products will be formed, which may damage the structural integrity of the catalyst (for example, carbon in Fischer–Tropsch synthesis). As a result, slurry phase reactors are preferred in FT processes. However, the slurry bubble reactors are three phase reactors reducing the diffusivities of the gases to the active sites, therefore limiting both heat and mass transfer. Thus, the investigators utilized the two-phase (gas-solid) reactor system that is easier to operate to evaluate these catalysts.
Concurrently with the fixed bed FT experiments, the investigators utilized modeling to understand the behavior of catalyst supports. Especially, SMSI was the subject of focus. DFT electronic structure calculations were used to study the CO$_2$ interaction with the $\gamma$-Al$_2$O$_3$ support metal catalyst at the atomic level. Periodic DFT calculations were carried out primarily using the Vienna Ab initio Simulation Package (VASP). VASP is a plane wave code with ultrasoft pseudopotential or projector augmented wave (PAW) to describe nuclei and core electrons. Gradient-corrected exchange-correlation functionals, PW91, PBE, and revPBE have been implemented in the package. An electronic smearing of 0.1 eV was found to improve convergence of electronic self-consistent cycles. For bulk and surface calculations, Monkhorst-Pack scheme was used to generate k-points for k-space sampling. A space of less than 0.05 Å$^{-1}$ between two adjacent k-points in any directions was found to be sufficient for most oxides. A geometry optimization is considered converged when the maximum force on the movable atoms reaches 0.05 eV/Å or smaller. The previous work of Dr. Ge and some test calculations using a cutoff energy up to 600 eV showed that the plane wave basis set is well converged at 400 eV for Al$_2$O$_3$, TiO$_2$, and BaO.

The technology explored in this work aimed at improving FT technology for the conversion of coal-derived syngas to liquid fuels. This was achieved by a novel approach for designing an optimal catalyst for FT synthesis. One of the main bottlenecks in commercializing the coal to liquid fuels is the catalyst activity and selectivity for liquid hydrocarbons. Applying FT technology requires prior coal gasification. Therefore, FT combined with advanced gasification technology (with regards to conditioning of coal gasification products) will overcome a number of problems currently faced by the industry. The gas conditioning technology previously developed by the investigators of this work funded by ICCI may also be used to effectively alter the CO/H$_2$ ratio amenable for narrow product distribution while removing impurities such as H$_2$S and CO$_2$ in a single reactor. Thus, the combination of these two technologies is especially crucial to the market for FT liquid fuels production utilizing Illinois coal.

Illinois coal is high in sulfur and chlorine and low in mercury. Therefore, the product stream should be cleaned before further applications. Gas treatment facilities refine the raw gas using available commercial technologies that are an integral part of the gasification plant. Trace elements or other impurities are removed from the syngas and are either re-circulated to the gasifier or recovered. Sulfur, for example, is recovered either in its elemental form or as sulfuric acid, both marketable commodities. This particular distribution of the impurities will also be useful in the reduction of mercury after the gasification stage, for example by combining the mercury with elemental sulfur to form non-toxic mercury sulfide. The high sulfur issue has plagued Illinois coal in the energy production sector (via combustion processes). Taking these technological opportunities into account, Illinois coal should play a key role in the energy sector. The emergence of the need for domestically produced liquid transportation fuels at costs comparable to that obtained from the refineries dependent on foreign sources will help develop new markets for Illinois. The researched technology will boost the acceptance of Illinois coal in the FT liquid fuels market primarily due to comparable costs with the added benefit of lower toxic impurities.
EXPERIMENTAL PROCEDURES

Task 1. Catalysts Preparation

Four distinct Fisher-Tropsch catalysts were prepared. These catalysts were Fe-Zn-Ru/γ-alumina, Fe-Zn-Ru/K/γ-alumina, Fe-Zn-Ru/silica, and Fe-Zn-Ru/K/silica. The γ-alumina powder support was obtained from Alfa Aesar (Ward Hill, MA) and the silica powder was obtained from Aldrich (Milwaukee, WI). These catalysts were prepared using the method of impregnating the supports via homogeneous deposition precipitation from the aqueous solution of Fe nitrate and Zn nitrates. This solution of Fe(NO₃)₃, (Aldrich, 99.9% 3.0 M) and/or Zn(NO₃)₂ (Aldrich, 99.9% 1.4 M) and, additionally, RuCl₃ · H₂O (Johnson Matthey, 41.83% Ru) were used for catalyst preparation. The solution containing the nitrates with a Zn/Fe atomic ratio of 0.1 and 0.5 mole % RuCl₃ was put into the beaker of de-ionized water and the support. Using incipient wetness impregnation, potassium was added to the Fe-Zn-Ru impregnated supports by means of K₂CO₃ (Aldrich, 99.9% 0.16 M).

The following is a description of the preparation of a Fe-Zn-Ru catalyst supported on γ-alumina. The first step was to prepare a 3 M solution of Fe(NO₃)₃. This was achieved using Fe(NO₃)₃ · 9H₂O. In order to prepare 3 M solution, 60.6 g of Fe(NO₃)₃ · 9H₂O was mixed with 50 ml distilled water. Next, a 1.4 M solution of Zn(NO₃)₂ was prepared using 20.8 g of Zn(NO₃)₂ · 6H₂O combined with 50 ml of distilled water. The next step in the catalyst preparation was to properly mix the two solutions to get a 0.1 atomic ratio of Zn/Fe. To attain the proper atomic ratio, 50 ml of the Fe(NO₃)₃ solution was mixed with 10.7 ml of the Zn(NO₃)₂. This solution was then mixed with the γ-alumina support. The support was then stirred for 10 h and subsequently filtered. After that, it was dried for 10 h at 100 °C and calcined for 15 h at 350 °C. The catalyst was then impregnated with Ru. 0.25 g of RuCl₃ was blended with 50 ml of distilled water in order to form a 0.5 mole % RuCl₃ solution. The catalyst was once again stirred for 10 h and filtered. The catalyst was then dried for 10 h at 100 °C and calcined for 6 h at 350 °C.

In order to add the potassium, 1.1057 g of K₂CO₃ was mixed with 50 ml of distilled water to create a 0.16 M solution of K₂CO₃. This solution was mixed with the catalyst solution and stirred for 15 min. After stirring, the catalyst was filtered, and then dried for 15 h at 100 °C and calcined for 4 h at 400 °C. Using this method, four catalysts were created.

Task 2. Physical Characterization of the Catalysts

After preparation, it was necessary to study the characteristics of the catalysts. The physical characterization of the catalysts included: SEM, EDS, BET, XRD, and particle size analysis.

Scanning Electron Microscopy (SEM) A Hitachi S570 was used to study the catalysts. In order to prepare the sample, a small portion of the catalyst was placed on an aluminum sample stub. The catalyst powder was then held onto the sample stub by means of double sided tape. After the sample stubs were prepared, they were placed in an oven and held
at 40 °C for 24 hours. Next, the sample stubs were removed from the oven and sputter coated. The sample stubs were then placed into the SEM. An accelerating voltage of 20 kV was used to examine the specimens. The SEM used in backscatter mode displayed distribution of the active phases on the support, as well as the microstructural properties of the catalysts.

Energy Dispersive X-Ray - EDS was used to establish the surface morphology and confirm the catalyst composition. Each catalyst was placed on a carbon stub using carbon adhesive tabs. Next, the EDS analysis was conducted at the following parameters: accelerating voltage = 30kV, spot size = 200, pressure = 100 Pa, and working distance = 14.

BET Analysis - Brunauer-Emmett-Teller (BET) analysis was conducted using a Quantachrome model 2000 analyzer. These experiments determined the surface area of the catalysts. Approximately 0.5 g of the catalyst was placed into the sample cell and then heated to 200 °C. The sample was then left for degassing overnight. After the degassing was completed, the samples were allowed to cool down to room temperature. The analysis was then conducted using liquid nitrogen as the coolant.

X-Ray Diffraction- X-ray diffraction (XRD) was conducted using a Rigaku MiniFlex II desktop X-ray diffractometer. XRD was used to identify the different crystalline phases and any amorphous phase present in the catalysts. Also, XRD was conducted in order to determine the dominating phase in the supports, as well as the catalyst composition.

Particle Size Analysis- A Microtrac Bluwave particle size analyzer was used to conduct experiments on the catalysts. These experiments determined the particle size distribution of the iron-based catalysts.

Task 3. TPR Studies

Catalysts are not generally stored in their useful form. Before any chemisorption studies can be conducted, the catalyst must be activated by heating it under a flow of reducing gas. This gas could be hydrogen or carbon monoxide. This activation prepares the metal surface for reaction with the analyzing gases. This is a crucial preparation step that can give very important information about the nature of the catalyst composition.

The reduction rate of metal oxide is a function of temperature; therefore the temperature at which the maximum rate is observed is a characteristic of the metal oxide, the metal, and its interaction with the support material. TPR is a method of monitoring the amount of reduction as a function of temperature. Temperature is increased in a linear fashion, so a characteristic reduction profile can be recorded for further analysis.

The catalysts that are being studied are both Fe-Zn-Ru and Fe-Zn-Ru/K on γ-alumina and silica. The main components of these catalysts are Fe₂O₃, ZnO, RuO, and K₂O, with the reducible components being Fe₂O₃ and RuO. The reduction of Fe₂O₃ follows the steps below:
\[ \begin{align*}
3\text{Fe}_2\text{O}_3 & \rightarrow 2\text{Fe}_3\text{O}_4 & 3.3\% \text{ reduction in initial weight} \\
\text{Fe}_3\text{O}_4 & \rightarrow 3\text{FeO} & 6.7\% \text{ reduction in initial weight} \\
\text{FeO} & \rightarrow \text{Fe} & 20\% \text{ reduction in initial weight}
\end{align*} \]

The combination of data from both the TPR and TGA provides more detailed information as to which mechanism occurs at any given temperature.

Temperature programmed reduction (TPR) was performed using a Quantachrome Chembet 3000 instrument coupled with a programmable furnace and a data acquisition system. The reducing agents used were hydrogen, carbon monoxide, and a mixture of hydrogen and carbon monoxide, with a H₂:CO ratio of 2:1. In the experiments, a 0.05 g sample of the catalyst was placed in the bottom of a U-type quartz tube cell with an inner diameter of 4 mm. This cell has a thermocouple that is in direct contact with the sample bed. The sample was placed into the degassing station of the machine and left for degassing over night at 150 °C for 12 hours. After the sample had been degassed, it was moved from the degassing station into the analysis station, which is inside the programmable furnace. Next, a gas mixture of 5% H₂, 5% CO, or 2.5% H₂ + 2.5% CO in Ar, respectively, was passed through the reference side of a thermal conductivity detector (TCD). This gas was then introduced into the reactor cell and an electronic mass flow meter controlled and measured the gas flow rate. While the gas was flowing, the temperature was increased up to 800 °C. The products that were in the gas phase then flowed through the TCD on the sample side. The Quantachrome software recorded and processed the difference in thermal conductivity signal between the two sides and the sample temperature.

Task 4. TGA Studies

The catalysts were also investigated using a pressurized thermogravimetric analyzer (TGA). The model used for these experiments was a Cahn TherMax 500. The TGA was used to conduct catalyst reduction tests at the temperatures established during the TPR tests for each respective catalyst. Two different forms of reduction tests were carried out. The first set of tests involved loading a catalyst sample into the TGA and heating the sample up to the first peak temperature under a flow of nitrogen. After both the weight and temperature stabilized at the first peak temperature, the flow was switched to hydrogen. The catalyst was left under hydrogen flow until the weight change became stable. Next, the flow was switched back to nitrogen, and the temperature was increased to the next peak temperature. Once again, after the weight and temperature stabilized at the next peak temperature, the flow was switched to hydrogen until the weight change stabilized and the flow was then switched back to nitrogen. This process was carried out for each peak temperature established from the hydrogen TPR tests. For example, when analyzing Fe-Zn-Ru/γ-alumina, the first test was conducted at 230 °C until no further weight change was observed. Then the temperature was increased in an inert atmosphere to 415 °C following which reduction test was conducted isothermally at this temperature.
The second set of reduction tests that were performed in the TGA were isothermal reduction tests. For these experiments, the catalyst was loaded into the TGA and then the temperature was increased to the second TPR peak temperature under nitrogen flow. The flow was then switched to hydrogen after the weight and temperature had stabilized. The test ended with nitrogen passing through the system after the weight change had ended. For example, for the Fe-Zn-Ru/γ-alumina catalyst this test was conducted at 415 °C. This test was performed again for catalysts that exhibited three peaks under hydrogen TPR. The test was repeated with a fresh catalyst at the third peak temperature.

The observed weight change at each temperature was then compared to the theoretical weight change for each iron reduction step (provided in the TPR section).

Task 5. Bench Scale Studies of the Fischer Tropsch Synthesis

Fisher-Tropsch synthesis tests were conducted in a fixed bed reactor manufactured by Parr Instruments (Moline, IL). A schematic of this reactor can be seen in the Appendix, page A-1. Mass flow controllers were used to electronically control the flow rate of the syngas, nitrogen, and hydrogen. The internal reactor temperature was controlled by two separate temperature controllers, an upper zone heater and a lower zone heater. The pressure in the reactor was controlled using a back pressure regulator. As the gases flowed through the reactor, they were preheated in the upper heater zone. After leaving the reactor, the gases then traveled through a water cooled heat exchanger in order to condense the liquid products. These liquids were collected in a liquid trap so they could be collected at the end of each FT experiment. Next, the gases pass through a back pressure regulator in order to control the pressure of the reactor. The outlet gases were then connected to a Hiden Quadrupole analyzer to identify the gaseous products. This measured the mass of each gas that was released from the reactor. The liquid samples that were collected from the run were analyzed using an Agilent GC/MS.

Prior to each FT experiment, the catalyst was reduced in situ at 400 °C with hydrogen flowing at 30 ml/min for 12 hours. After catalyst reduction, nitrogen flow was started at 30 ml/min in order to flush out the hydrogen before the FT experiment was conducted. Once the hydrogen was removed from the reactor, syngas with a H₂:CO ratio of 2:1 was introduced into the reactor at 30 ml/min. Using this syngas, the reactor was then pressurized to 350 psi. Each experiment ran for 48 hours, and the Quadrupole was used to collect data every 12 hours. At the conclusion of the 48 hour run, liquids were collected, the temperature was adjusted to the desired value of the next experiment, and nitrogen was used to flush out the reactor for 12 hours before the next experiment commenced. The temperatures for these experiments were 300 °C, 350 °C, and 400 °C, respectively.

Task 6. Molecular-level Modeling
Density functional theory (DFT) calculations in the pseudo-potential framework within the periodic slabs were carried out using the Vienna ab-initio simulation package (VASP). The projector augmented wave method was employed to describe the ion-electron interactions and the generalized gradient approximation (GGA) within the Purdew-Burke-Ernzehof scheme was chosen for the exchange and correlation potential. A plane wave basis set with a cutoff energy of 400eV and automatically generated Monkhorst-Pack grids with a 2x2x2 k-points mesh was used. The structures were relaxed using the conjugated gradient algorithm and the quasi-Newton scheme until the forces on the atoms were less than 0.03 eV/Å. The spin polarizations were included in all calculations.

The hydroxylated (110) surface model of nonspinel $\gamma$-Al$_2$O$_3$ was obtained from our previous work. The same size of supercell slab in a dimension of 8.404Å x 8.018Å x 19.182Å was used, including 12Å vacuum to separate the slabs. Twelve Al$_2$O$_3$ molecules were distributed across six layers. The binding of Co$_3$Cu and Cu$_3$Co clusters on above hydroxylated surface were first explored in both planar and tetrahedral configuration. CO$_2$ was further added around the adsorbed cluster. In all calculations, the bottom two layers were fixed in their bulk position, while the top four layers, the adsorbed clusters and CO$_2$ were allowed to relax. Bader-charge analysis was used to further characterize the nature of the stable structural configuration. The adsorption energy for CO$_2$ was defined as:

$$\Delta E_{\text{ad}} = E_{\text{CO}_2-\text{cluster}/\gamma-\text{Al}_2\text{O}_3} - E_{\text{cluster}/\gamma-\text{Al}_2\text{O}_3} - E_{\text{CO}_2}$$

where $E_{\text{CO}_2-\text{cluster}/\gamma-\text{Al}_2\text{O}_3}$, $E_{\text{cluster}/\gamma-\text{Al}_2\text{O}_3}$, $E_{\text{CO}_2}$, are the total energies of slab with the cluster and CO$_2$ molecule adsorbed, the surface with only cluster adsorbed, and an isolated CO$_2$ molecule, respectively. The more negative adsorption energy represents the stronger interaction of CO$_2$ with the adsorbed cluster and surface.

Ab initio molecular dynamics simulation within the same framework of DFT and pseudopotential was performed for CO$_2$ adsorption. The cutoff energy was set to 300ev due to the computational cost and the trajectory simulation was run at constant temperatures, 300K and 500K. The timestep used was 0.5fs and the length of the simulation was 2.5ps. The most favored adsorption configures of CO$_2$ on both supported clusters were selected as the starting structures for the trajectory study and the initial velocities are set randomly according to a Maxwell-Boltzmann distribution by the simulation temperature.

RESULTS AND DISCUSSION

Task 1. Catalysts Preparation
Four distinct Fisher-Tropsch catalysts were prepared through the incipient wetness technique. These catalysts were Fe-Zn-Ru/γ-alumina, Fe-Zn-Ru/K/γ-alumina, Fe-Zn-Ru/silica, and Fe-Zn-Ru/K/silica.

**Task 2. Physical Characterization of the Catalysts**

SEM- Micrographs were created for each catalyst to show the morphology of the particles. These micrographs can be found on pages A-2 and A-3 in the Appendix. The differences in morphology between the silica and the γ-alumina are very apparent in these images. The silica images show it is composed of smaller, finer particles that are more powder like in composition than the γ-alumina support.

EDS- The results of the EDS analysis are summarized in Table 1, which displays each catalyst and the elemental weight percentages. These results confirm the presence of the supports and promoter elements in each catalyst.

<table>
<thead>
<tr>
<th>Element (%)</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe-Zn-Ru/γ-alumina</td>
</tr>
<tr>
<td>Al</td>
<td>84.76</td>
</tr>
<tr>
<td>Si</td>
<td>0</td>
</tr>
<tr>
<td>K</td>
<td>0</td>
</tr>
<tr>
<td>Fe</td>
<td>12.79</td>
</tr>
<tr>
<td>Zn</td>
<td>2.44</td>
</tr>
<tr>
<td>TOTAL</td>
<td>100</td>
</tr>
</tbody>
</table>

**Table 2. BET results**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface Area (m²/g)</th>
<th>Catalyst</th>
<th>Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Zn-Ru/γ-Al₂O₃</td>
<td>125.53</td>
<td>Fe-Zn-Ru/SiO₂</td>
<td>87.18</td>
</tr>
<tr>
<td>Fe-Zn-Ru/K/γ-Al₂O₃</td>
<td>116.14</td>
<td>Fe-Zn-Ru/K/SiO₂</td>
<td>90.76</td>
</tr>
</tbody>
</table>

BET- BET analysis was performed on each of the four catalysts. Table 2 summarizes the results found through BET analysis. It can be noted that the catalysts that are supported on γ-alumina display a higher surface area than the catalysts that are supported on silica.

**XRD-** The XRD confirmed the presence of the support of each catalyst, as well as the Fe₂O₃ that was a major catalyst component. The Zn, Ru, and K are present in the catalyst in smaller amounts, so XRD did not detect these elements. This is due to the fact that the machine has roughly 5% threshold; therefore smaller concentrations of phases were not detected. XRD spectra comparisons of bare supports and after catalyst impregnation are attached in the Appendix (A-4 and A-5).
Particle Size Analysis- The results from the particle size analyses are summarized in the following table. It is noted that the catalysts that were supported on silica show a much larger average particle size than the catalysts that were supported on alumina. This could be due to the fact that the average particle size was taken as a wet measurement. The silica formed large chunks when it was moist during catalyst preparation. This could have occurred again during the particle size analyses, causing the larger average particle sizes to be reported. The results of these analyses are reported in Table 3 below.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Average Particle Size (microns)</th>
<th>Median Particle Size (microns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Zn-Ru/γ-alumina</td>
<td>31.73</td>
<td>31.84</td>
</tr>
<tr>
<td>Fe-Zn-Ru/K/γ-alumina</td>
<td>31.56</td>
<td>29.94</td>
</tr>
<tr>
<td>Fe-Zn-Ru/silica</td>
<td>103.5</td>
<td>92.84</td>
</tr>
<tr>
<td>Fe-Zn-Ru/K/silica</td>
<td>113.6</td>
<td>108.39</td>
</tr>
</tbody>
</table>

Task 3. TPR Studies

For the TPR studies, three reducing agents were utilized (H₂, CO, and H₂:CO=1). All four catalysts underwent TPR experiments with each of the reducing agents. The results, with catalysts categorized by support, are shown in figures attached in the Appendix (pages A-6, A-7, and A-8). The peak temperatures exhibited by each catalyst under H₂ and CO are provided in Tables 4 and 5, respectively.

Only two peaks are observed for the catalysts supported on γ-alumina under hydrogen flow. The shift of the first peak from 230 °C to 290 °C can be attributed to the addition of potassium. Peak two shifts by 270 °C, and this is also due to the addition of the potassium promoter. Unlike the catalysts supported on γ-alumina, the catalyst supported on silica show three peaks during the H₂ TPR. Although not as large as the shift observed for the γ-alumina supported catalysts during H₂ TPR, the addition of potassium to the silica supported catalyst does increase the peak temperatures a very small amount. For example, it increases the first peak temperature only 10 °C. Only two peaks were present for each silica supported catalyst under CO. The second peak that occurred during the CO TPR was much broader indicating other reactions were occurring simultaneously.

Table 4. Peak temperatures under H₂

<table>
<thead>
<tr>
<th>Peak 1 [°C]</th>
<th>Peak 2 [°C]</th>
<th>Peak 3 [°C]</th>
</tr>
</thead>
</table>

18
<table>
<thead>
<tr>
<th></th>
<th>Peak 1 [°C]</th>
<th>Peak 2 [°C]</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Zn-Ru/γ-alumina</td>
<td>230</td>
<td>415</td>
<td>Not present</td>
</tr>
<tr>
<td>Fe-Zn-Ru/K/γ-alumina</td>
<td>290</td>
<td>685</td>
<td>Not present</td>
</tr>
<tr>
<td>Fe-Zn-Ru/silica</td>
<td>290</td>
<td>405</td>
<td>750</td>
</tr>
<tr>
<td>Fe-Zn-Ru/K/silica</td>
<td>300</td>
<td>430</td>
<td>800</td>
</tr>
</tbody>
</table>

Table 5. Peak temperatures under CO

For the TPR experiments which used syngas as the reducing agent, it should be noted that the alumina supported catalysts exhibited a significantly different result. This could be due to a variety of different reasons. The areas in the graph that show a negative signal could be caused by the fact that products, such as CH₄, that would simulate excess H₂ and CO are being released. The thermal conductivities of the various gases that may be formed during this reaction vary greatly and may result in the observed plots. It should also be noted that the signal only goes slightly negative on the graph displaying the silica catalyst results from syngas TPR. The observed data for the alumina catalysts under syngas could be explained by the reducibility of the alumina catalyst less than the silica catalyst. Also, the Fe could be dispersed more evenly on the silica than the alumina. It would be necessary to analyze the outlet gases from the TPR in order to make a definite conclusion.

**Task 4. TGA Studies**

The TPR results show the two temperatures of interest for Fe-Zn-Ru/K/γ-alumina are 290 °C and 685 °C. At 290 °C during H₂ reduction, the weight change observed was from 46.5194 grams to 45.6067 grams. This corresponds to 10.30% decrease in weight. The temperature was then increased to 685 °C under nitrogen and then isothermal reduction under H₂ was conducted at this temperature. The weight change observed during the part of the experiment was from 45.6067 grams to 45.0834 grams, which corresponds to a 13.18% weight loss. The weight change observed during the second TGA test, the isothermal test at the second peak temperature (685°C), was from 95.6225 grams to 93.5719 grams, which is a 26.53% weight loss. Graphs of Fe-Zn-Ru/K/γ-alumina TGA tests at 290 °C, 685 °C, and the isothermal TGA test at 685 °C are provided in the Appendix (page A-9). These graphs are characteristic of the results displayed from every catalyst.

Similar analysis was conducted on all catalysts. The resultant conversions percent reductions in weight are listed in Tables 6-9. Equations listed in the TPR experimental section show that the reduction of Fe₂O₃ to Fe₃O₄ would result in a weight change of 3.3
The reduction from Fe₂O₃ to FeO would cause a 10% reduction in weight, while the reduction from Fe₂O₃ to metallic iron results in a weight change of 30%. The results of these experiments show that during the first set of tests, the total of these tests together equals approximately 30%, and during the second set of isothermal tests, each test exhibits a weight change of around 30%. The slight variation from 30% could be due to inaccuracies in the calculation of the catalyst loading or in the measured weight. These results show that the iron was completely reduced at these specific temperatures. These results are summarized in the following tables.

Table 6. Fe-Zn-Ru/γ-alumina Fe conversion results

<table>
<thead>
<tr>
<th>Test</th>
<th>% Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Zn-Ru/γ-alumina Test at 230 °C</td>
<td>16.0</td>
</tr>
<tr>
<td>Fe-Zn-Ru/γ-alumina Test at 415 °C</td>
<td>16.0</td>
</tr>
<tr>
<td>TOTAL</td>
<td>32.3</td>
</tr>
<tr>
<td>Fe-Zn-Ru/γ-alumina Isothermal Test at 415 °C</td>
<td>23.4</td>
</tr>
</tbody>
</table>

Table 7. Fe-Zn-Ru/K/γ-alumina Fe conversion results

<table>
<thead>
<tr>
<th>Test</th>
<th>% Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Zn-Ru/K/γ-alumina Test at 290 °C</td>
<td>10.3</td>
</tr>
<tr>
<td>Fe-Zn-Ru/K/γ-alumina Test at 685 °C</td>
<td>13.2</td>
</tr>
<tr>
<td>TOTAL</td>
<td>23.5</td>
</tr>
<tr>
<td>Fe-Zn-Ru/K/γ-alumina Isothermal Test at 685 °C</td>
<td>26.55</td>
</tr>
</tbody>
</table>

In the case of Fe-Zn-Ru/γ-alumina a 16.3% weight reduction was observed before the weight change stabilized. This shows that the product as a result of reduction at 290 °C would be a combination of FeO and metallic iron. FeO cannot be completely converted to Fe at this temperature. This could be due to equilibrium between the two phases at this temperature. For Fe-Zn-Ru/K/γ-alumina catalyst, at 290 °C, the Fe₂O₃ reduces to FeO and no reduction to Fe occurs.

For the Fe-Zn-Ru/silica catalyst, a 15.9% weight reduction occurs before the weight change stabilizes. This indicates the Fe₂O₃ is reducing to a mixture of FeO and Fe. Because no further weight change was observed at this temperature and further weight change did occur with a temperature increase at 290 °C, there was some form of equilibrium between the two phases. Increasing the temperature to 405 °C led to a further weight change of 10.2%. Further reduction took place, and the product was still a combination of FeO and Fe. Complete reduction to Fe occurred when the temperature was increased to 750 °C. The same changes were reflected in the isothermal tests which were conducted at 405 °C and 750 °C, with more weight change taking place at the higher temperature. The addition of potassium to the silica supported catalyst showed that at 300 °C, the Fe₂O₃ was primarily converted to FeO. Conversion to Fe occurred only at higher temperatures, with the complete conversion at 800 °C. From the data obtained from the TGA studies, it can be concluded that the addition of K resulted only in the
reduction of Fe$_2$O$_3$ to FeO at the lowest temperature. In the absence of potassium, the reduction at the lowest temperature was a mixture of FeO and Fe.

Table 8. Fe-Zn-Ru/silica Fe conversion results

<table>
<thead>
<tr>
<th>Test</th>
<th>% Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Zn-Ru/silica Test at 290 °C</td>
<td>15.9</td>
</tr>
<tr>
<td>Fe-Zn-Ru/silica Test at 405 °C</td>
<td>10.2</td>
</tr>
<tr>
<td>Fe-Zn-Ru/silica Test at 750 °C</td>
<td>6.7</td>
</tr>
<tr>
<td>TOTAL</td>
<td>32.8</td>
</tr>
<tr>
<td>Fe-Zn-Ru/silica Isothermal Test at 405 °C</td>
<td>28.6</td>
</tr>
<tr>
<td>Fe-Zn-Ru/silica Isothermal Test at 750 °C</td>
<td>33.7</td>
</tr>
</tbody>
</table>

Table 9. Fe-Zn-Ru/K/silica Fe conversion results

<table>
<thead>
<tr>
<th>Test</th>
<th>% Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Zn-Ru/K/silica Test at 300 °C</td>
<td>12.8</td>
</tr>
<tr>
<td>Fe-Zn-Ru/K/silica Test at 430 °C</td>
<td>9.8</td>
</tr>
<tr>
<td>Fe-Zn-Ru/K/silica Test at 800 °C</td>
<td>6.8</td>
</tr>
<tr>
<td>TOTAL</td>
<td>29.2</td>
</tr>
<tr>
<td>Fe-Zn-Ru/K/silica Isothermal Test at 430 °C</td>
<td>26.5</td>
</tr>
<tr>
<td>Fe-Zn-Ru/K/silica Isothermal Test at 800 °C</td>
<td>36.3</td>
</tr>
</tbody>
</table>

Task 5. Bench Scale Studies of the Fischer Tropsch Synthesis

The data that was collected from the FT experiments was used to make comparisons on the performance of each catalyst at different reaction conditions. The H$_2$ and CO conversion for each catalyst was compared at the three different reaction temperatures and the results are displayed graphically in Figures 1-6. Each of the figures indicate that the system requires approximately 24 hours to reach steady state. At 350 psi and 300 °C, the Fe-Zn-Ru/γ-alumina catalyst displays the highest H$_2$ conversion at the temperature, which is just over 50%. The results for CO conversion at the same conditions show that the Fe-Zn-Ru/K/γ-alumina had the greatest CO conversion of all the catalysts of nearly 70%. Comparatively, at 350 psi and 350 °C, the Fe-Zn-Ru/K/silica catalyst exhibits the highest H$_2$ conversion of 60% at that specific temperature. Finally, at 350 psi and 400 °C, the Fe-Zn-Ru/silica catalyst demonstrates the highest H$_2$ conversion that was observed in any of the experiments of over 80%. At the two temperatures of 350 °C and 400 °C, the Fe-Zn-Ru/K/silica catalyst displayed the highest CO conversion. The conversion was around 80% at both temperatures for this catalyst, with the results at 400 °C being slightly higher. The Fe-Zn-Ru/K/silica catalyst demonstrates the most consistent H$_2$ conversions throughout the experiments. The overall highest H$_2$ conversions were observed at 350 psi and 400 °C, at around 80%. The Fe-Zn-Ru/K/γ-alumina catalyst demonstrates a high CO conversion at each temperature in comparison to the other catalysts. The Fe-Zn-Ru/silica catalyst performs very poorly at both 300 °C and 350°C, as it shows a very low conversion. This particular catalyst produces a much higher conversion at 400 °C. The overall highest CO conversions for all catalysts were demonstrated at 350 psi and 400 °C, around 80%.
Figure 1. Hydrogen conversions at 350 psi and 300 °C

Figure 2. CO conversions at 350 psi and 300 °C
Figure 3. Hydrogen conversions at 350 psi and 350 °C

Figure 4. CO conversions at 350 psi and 350 °C
Figures 5-6 display the product distribution in the liquid phase for the FT experiments. Figure 5 shows the product distribution that was obtained at 350 psi and 400 °C. This
product distribution shows the Fe-Zn-Ru/γ-alumina catalyst produced the widest range of hydrocarbons, varying from C₈ to C₁₆. The Fe-Zn-Ru/K/γ-alumina catalyst produced hydrocarbons ranging from C₈ to C₁₅. This catalyst produced larger percentages of liquids in the range of C₈-C₉, which is in the gasoline fraction. Both of the silica-supported catalysts produced a large number of oxygenates and very few hydrocarbons at 300°C. Figure 8 shows the product distribution that was produced at 350 psi and 350°C. At these conditions, the Fe-Zn-Ru/γ-alumina catalyst produced a very wide range of hydrocarbons, from C₇-C₂₈. The Fe-Zn-Ru/K/γ-alumina catalyst had a narrower range, from C₈-C₁₃, once again yielding products in the gasoline fraction. The silica-supported catalysts performed better at 350 °C, generating more hydrocarbons than oxygenates. The Fe-Zn-Ru/silica catalyst produces a greater amount of hydrocarbons in the diesel range, with products varying from C₉-C₁₆. The Fe-Zn-Ru/K/silica catalyst also exhibits products from C₉-C₁₃, but in much smaller amounts than the other silica-supported catalyst. It also produced oxygenates of 2-methyl-1-butanol and 1-pentanol at these conditions. Figure 9 shows the results of the FT experiments that were conducted at 350 psi and 400 °C. Once again, the Fe-Zn-Ru/γ-alumina catalyst shows a very wide distribution, from C₇-C₂₃, but in very small amounts. The Fe-Zn-Ru/K/γ-alumina catalysts produced a much smaller range of hydrocarbons, only from C₁₄-C₁₇. The silica-supported catalysts produced their widest range of hydrocarbons at this temperature. The Fe-Zn-Ru/silica catalyst exhibited products from C₈-C₁₇, while the Fe-Zn-Ru/K/silica catalysts yielded a range from C₉-C₁₅, along with a small amount of oxygenates.

Comparatively, the γ-alumina catalysts produced a wider range of hydrocarbons in larger amounts than the silica-supported catalysts at 350 psi and 300 °C. On the other hand, the silica-supported catalyst yielded higher percentages of hydrocarbons at 350 psi and 400 °C. Both supports produced wide ranges of hydrocarbons at 350 psi and 350 °C. This set of conditions proved to produce the best results for these particular catalysts during the FT experiments. The oxygenate/hydrocarbon ratio for each catalyst at each test condition is presented in Table 10. This table displays the total percentage of oxygenates divided by the total percentage of hydrocarbons. This shows that silica-supported catalysts result in more alcohols and the addition of potassium to the silica-supported catalyst results in more branches alcohol.

<table>
<thead>
<tr>
<th>Test Conditions</th>
<th>Oxygenate/Hydrocarbon Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe-Zn-Ru/γ-alumina</td>
</tr>
<tr>
<td>350 psi 300 °C</td>
<td>0</td>
</tr>
<tr>
<td>350 psi 350 °C</td>
<td>0</td>
</tr>
<tr>
<td>350 psi 400 °C</td>
<td>0</td>
</tr>
</tbody>
</table>
Figure 7. Product distribution at 350 psi and 300 °C

Figure 8. Product distribution at 350 psi and 350 °C
Task 6. Molecular-level Modeling

Under task 6, DFT calculations were used to determine the CO$_2$ interaction with γ-Al$_2$O$_3$ supported transition dimers. The results showed that CO$_2$ adsorbs on M$_2$/γ-Al$_2$O$_3$ negatively charged and in bent configuration, indicating a partial activation of CO$_2$. Both the supported metal dimer and the support, either dry or partially hydroxylated γ-Al$_2$O$_3$, contribute to the activation of CO$_2$ by donating their electronic charges to the adsorbed CO$_2$. The most favorable adsorption site for CO$_2$ on M$_2$/γ-Al$_2$O$_3$, either dry or partially hydroxylated support, is the interface between the metal dimer and the support. The electronic charges on the adsorbed CO$_2$ make CO$_2$ distort from its linear configuration in the gas phase. The presence of the metal dimer enhances the binding of CO$_2$ with the substrate. As such, the adsorption energy of CO$_2$ on M$_2$/γ-Al$_2$O$_3$ is much higher than that on the γ-Al$_2$O$_3$ surfaces without supported metal dimer. The binding strength of CO$_2$ with M$_2$/γ-Al$_2$O$_3$ was also demonstrated to correlate with the electron-donating ability of the substrate. Both distortion energy and CO$_2$ binding energy show a linear dependence on the amount of charge on the adsorbed CO$_2$. The 3d metal on the left of the periodic table has a greater electron-donating ability which resulted in a stronger CO$_2$ binding. Hydroxylation of the support surface reduces the amount of charge transferred to CO$_2$ for the same metal dimer and weakens the CO$_2$ chemisorption bonds. Highly dispersed metal particles maintained at a small size are expected to exhibit good activity toward CO$_2$ adsorption and activation. Figure 10 shows schematically two binding modes of CO$_2$ on the metal dimer supported on the hydroxylated γ-Al$_2$O$_3$. CO$_2$ interactions with a supported Fe$_4$ cluster and a Fe-Zn bimetallic cluster were also studied. Stables structures for each were calculated and are shown in Figures 11 and 12.
An examination of CO₂ interactions with other supported binary metal clusters, in particular, the γ-Al₂O₃ supported Co-Cu and Fe-Zn clusters, is in progress. The study is based on the hypothesis that the catalytic property of a supported metal catalyst can be tuned by introducing a second metal. Catalysts based on Cu and Zn are traditionally used for methanol synthesis whereas Fe and Co are for hydrocarbon formation in Fischer-
Tropsch process. Relaxed structures of Co$_3$Cu and CoCu$_3$ clusters on a $\gamma$-Al$_2$O$_3$ have been generated and are shown in Figure 13.

![Figure 13. Relaxed structures of Co$_3$Cu and CoCu$_3$ clusters on $\gamma$-Al$_2$O$_3$](image)

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions and recommendations were drawn upon the completion of this endeavor:

- Energy dispersive X-ray (EDS) and X-ray diffraction (XRD) both confirmed the presence of the catalyst components.

- BET analysis showed that the $\gamma$-alumina-supported catalysts possess a higher surface area than the silica-supported catalysts.

- Particle size analysis determined that the $\gamma$-alumina catalysts had a smaller particle size than the silica-supported catalysts.

- During the FT experiments at 350 psi and 300 °C, the Fe-Zn-Ru/$\gamma$-alumina displayed the highest H$_2$ conversion of just over 50%.

- At 350 psi and 350 °C, the Fe-Zn-Ru/K/silica exhibited the highest H$_2$ conversion during the FT tests of 60%.

- For the FT tests conducted at 350 psi and 400 °C, the Fe-Zn-Ru/K/silica catalysts possessed the highest H$_2$ conversion of 80%.

- The overall highest H$_2$ conversions for each catalyst were observed at 350 psi and 400 °C.

- The CO conversion for 350 psi and 300 °C was the greatest for the Fe-Zn-Ru/K/$\gamma$-alumina catalyst.
- The highest CO conversion during the FT tests at 350 psi and 350 °C and 350 psi and 400 °C was exhibited by the Fe-Zn-Ru/K/silica catalyst. For both conditions, the conversion was 80%.

- The overall highest CO conversions for each catalyst were observed at 350 psi and 400 °C, which was 80%.

- The Fe-Zn-Ru/silica catalyst had very low CO conversions at both 350 psi and 300 °C and 350 psi and 350 °C, but comparable CO conversions were observed at 350 psi and 400 °C.

- During the FT experiments at 350 psi and 300 °C, γ-alumina-supported catalysts produced the widest range of hydrocarbons and no oxygenates.

- At 350 psi and 300 °C, the silica-supported catalysts produced large amounts of oxygenates.

- For the FT tests conducted at 350 psi and 350 °C, the Fe-Zn-Ru/γ-alumina produced the widest range of hydrocarbons and no oxygenates.

- The use of silica as support resulted in the formation of alcohols.

- At 350 psi and 350 °C, the silica-supported catalysts produced more hydrocarbons than oxygenates.

- During the FT tests at 350 psi and 400 °C, the Fe-Zn-Ru/γ-alumina catalyst produced a wide range of hydrocarbons in small amounts.

- At 350 psi and 400 °C, the silica-supported catalysts demonstrated the widest range of hydrocarbons. This shows that the use of silica as a support facilitates chain growth more than the γ-alumina-supported catalysts.

- At 350 psi and 400 °C, the Fe-Zn-Ru/K/silica catalyst still produced a small amount of oxygenates.

- The γ-alumina-supported catalysts produced a wider range of hydrocarbons with fewer oxygenates at 350 psi and 300 °C.

- The silica supported catalysts produced a wider range of hydrocarbons and a small amount of oxygenates at 350 psi and 400 °C.

- The best FT experimental conditions in this research were identified as 350 psi and 350 °C for all catalysts.

- Further FT tests should be conducted at varying pressures to identify the catalyst activity at other conditions.
According to DFT calculations, CO₂ adsorbs on M₂/γ-Al₂O₃ negatively charged and in bent configuration, indicating a partial activation of CO₂.

Both the supported metal dimer and the support, either dry or partially hydroxylated γ-Al₂O₃, contribute to the activation of CO₂ by donating their electronic charges to the adsorbed CO₂.

The most favorable adsorption site for CO₂ on M₂/γ-Al₂O₃, either dry or partially hydroxylated support, is the interface between the metal dimer and the support.

The use of SiO₂ as a support for the metal clusters should be explored further.

REFERENCES


DISCLAIMER STATEMENT

This report was prepared by Tomasz Wiltowski, Southern Illinois University, with support, in part, by grants made possible by the Illinois Department of Commerce and Economic Opportunity through the Office of Coal Development and the Illinois Clean Coal Institute. Neither Tomasz Wiltowski & Southern Illinois University, nor any of its subcontractors, nor the Illinois Department of Commerce and Economic Opportunity, Office of Coal Development, the Illinois Clean Coal Institute, nor any person acting on behalf of either:

(A) Makes any warranty of representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately-owned rights; or

(B) Assumes any liabilities with respect to the use of, or for damages resulting from the use of, any information, apparatus, method or process disclosed in this report.

Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring; nor do the views and opinions of authors expressed herein necessarily state or reflect those of the Illinois Department of Commerce and Economic Opportunity, Office of Coal Development, or the Illinois Clean Coal Institute.

Notice to Journalists and Publishers: If you borrow information from any part of this report, you must include a statement about the state of Illinois' support of the project.
APPENDIX A

SUPPORTING INFORMATION
Fixed Bed Reactor Schematic (Parr Instruments, Moline, IL)
SEM micrographs of Fe-Zn-Ru/γ-alumina (a) 700x, (b) 3500x

SEM micrographs of Fe-Zn-Ru/K/γ-alumina (a) 700x (b) 3500x
SEM micrographs of Fe-Zn-Ru/silica (a) 700x (b) 3500x

SEM micrographs of Fe-Zn-Ru/K/silica (a) 700x (b) 3500x
XRD comparison of Fe-Zn-Ru/γ-alumina and Fe-Zn-Ru/K/γ-alumina
XRD comparison of Fe-Zn-Ru/silica and Fe-Zn-Ru/K/silica
\begin{align*}
\text{\gamma-alumina supported catalysts TPR results under hydrogen} \\
\text{Silica supported catalysts TPR results under hydrogen}
\end{align*}
\(\gamma\)-alumina supported catalysts TPR results under carbon monoxide

Silica supported catalysts TPR results under carbon monoxide
γ-alumina supported catalysts TPR results under syngas

Silica supported catalysts TPR results under syngas
Fe-Zn-Ru/K/γ-alumina TGA test at 290 °C

Fe-Zn-Ru/K/γ-alumina TGA test at 685 °C

Fe-Zn-Ru/K/γ-alumina Isothermal TGA test at 685 °C