Low Cost Route to Next Generation Commercial Iron Fischer-Tropsch (FT) Catalysts for Coal-to-Liquids & Biomass-to-Liquids

Final Executive Summary

by

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Brigham Young University
in partnership with Cosmas, Inc.
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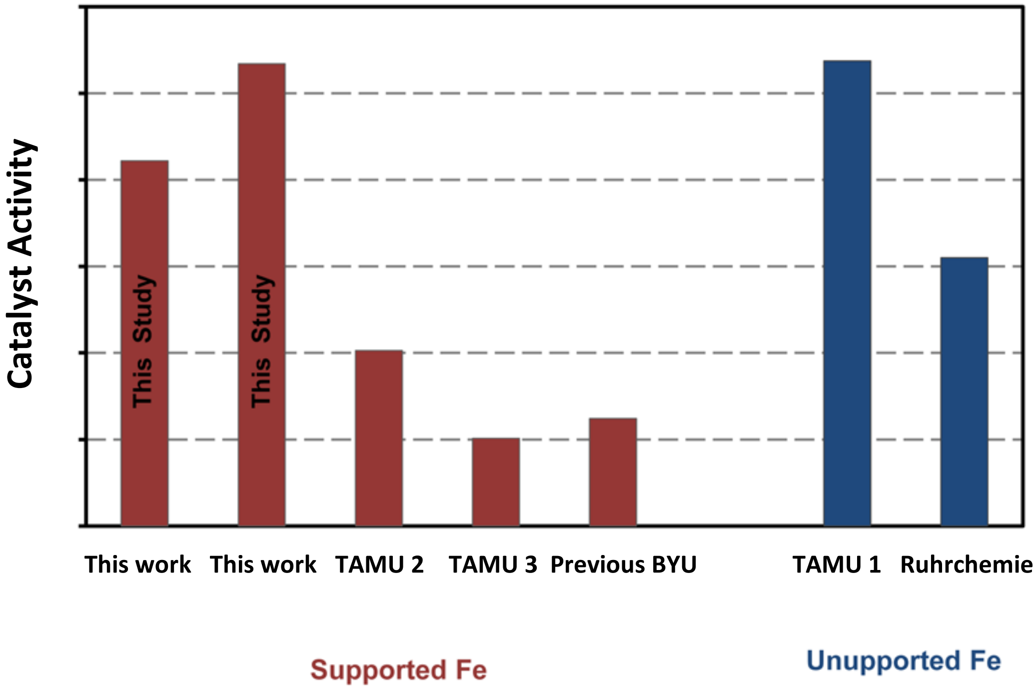

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Overview

Fischer-Tropsch (FT) synthesis is a commercially proven method for converting abundant, lower-value solids, such as coal or biomass, into more valuable liquid fuels. Efficient, low-cost iron FT catalysts are needed to supply future coal-to-liquids (CTL) and biomass-to-liquids (BTL) processes. Although iron has several advantages for BTL/CTL compared to cobalt catalysts, no commercial iron FT catalysts are available to the BTL/CTL industry. Cosmas, Inc. and Brigham Young University's Nanoscience Chemistry (NCBYU) group developed a simple and general, solvent deficient method for preparing well-defined metal oxide nanoparticles, including iron oxides. The BYU Catalysis Lab, Cosmas, and NCBYU adapted this method to prepare the FT catalysts developed during this project. This simple approach, in combination with low-cost starting materials, was explored for production of low-cost iron FT catalysts for the synfuels industry.

This research developed simple, low-cost, and environmentally-sound methods for preparation of high-performance iron FT catalysts, which are scalable for commercial manufacture. Preparation of iron/copper/potassium/silica catalysts via the Cosmas solvent deficient route produced physical, chemical, and catalytic properties comparable to those prepared by more complex conventional precipitation methods.

In addition to iron/copper/potassium/silica, the project developed other supported and unsupported iron FT catalysts, including iron/manganese/copper/potassium and iron supported on carbon nanotubes. The work focused on defining (1) the chemistry of lab scale synthesis procedures and (2) the physical, chemical, and catalytic properties of these new catalysts. The alumina-supported iron catalysts developed by this project are among the most active that have been reported. The carbon nanotube supported catalysts display desirably low methane production and good stability. Similarly, the catalysts containing manganese show promise with low methane selectivity to maximize their potential for liquids production.

Introduction

The United States, especially Wyoming, has an abundance of coal reserves. Most coal is currently burned to produce electricity. More valuable liquid fuels and chemical products could be produced by first converting the coal to a synthesis gas containing carbon monoxide and hydrogen, in a process called gasification, followed by a catalytic process to convert the carbon monoxide and hydrogen to liquid products. This process is called Fischer-Tropsch synthesis, named after the German inventors who developed the process in the early 20th Century. A catalyst is defined as a substance that causes a chemical reaction to proceed faster, but is not consumed by the reaction. Iron-based catalysts that can convert coal and biomass into more useful liquid products are not readily available on the commercial market. This project developed new catalysts for the Fischer-Tropsch process using a simple and effective production method called solvent deficient precipitation, which was developed by Cosmas Inc. and implemented in the Brigham Young University Catalysis Laboratory.

Importance of renewable fuels from coal and biomass. The U.S. faces serious energy supply, energy security, economic sustainability, and global climate issues. Greatly expanded use of domestic coal and biomass resources to produce clean, renewable liquid fuels from coal and biomass would help to address these problems. A 2009 U.S. Department of Energy National Energy Technology Laboratory (NETL) study addressed the critical need for and pathway to affordable, renewable diesel fuel from domestic coal and biomass. The key findings of this report were that:

(1) a combination of coal-to-liquids (CTL) and biomass-to-liquids (BTL), called CBTL, provides the optimal intersection of low carbon profile with economic feasibility;

(2) the optimal case involving addition of 15 wt% biomass to coal with carbon dioxide sequestration appears to be economical at a crude oil price around \$90-100/barrel, with a greenhouse gas (GHG) emissions reduction of 33% below that of petroleum; and

(3) while a 100% biomass feedstock can produce a fuel with up to a 358% lower GHG footprint, this option is unlikely to be economically viable, with a projected economic feasibility point of $170 to 240/barrel of crude oil.

These figures indicate that development of CBTL technology is likely to be economically feasible in the near future, while BTL is not. CTL, on the other hand, is considered by many to be environmentally unacceptable, since it does not adequately reduce carbon dioxide emissions.

Capital cost a barrier to development. The figures in the NETL document are based on a 50,000 barrel/day plant with a feed of 12,000 tons/day of coal and 1,412 tons/day of biomass using conventional gasification and FT technologies. Even with economies of scale, the total estimated plant cost is enormous: $5.8 billion. This huge capital cost is a barrier to investment in such a project. The need for smaller, less-expensive plants based on new low-cost technologies remains clear.

The <u>critical</u> <u>need</u> for a low-cost commercial iron Fischer-Tropsch catalyst. Iron catalysts are obviously needed for the developing CBTL industry. Most small companies engaged in CBTL research and development lack resources and knowledge to develop a viable iron catalyst, but no commercial iron catalyst is presently available.

The Brigham Young University Fischer-Tropsch Consortium was established to help CBTL start-up companies develop methods of FT catalyst preparation, characterization, and testing at the laboratory scale. If a small CBTL company be successful in developing its own catalyst (which is unlikely), it could conceivably engage a catalyst company to manufacture its catalyst. In practice, however, catalyst companies are focused on making large quantities of a given catalyst and will charge a premium for setting up to make smaller quantities of a specialty catalyst. Moreover, present preparation methods for iron FT catalysts are laborious and costly. Thus, a small CBTL company would find this venture expensive and probably uneconomical. On the other hand, CBTL companies could be enabled by a small catalyst manufacturer set up to expressly manufacture a low cost iron FT catalyst by a proven, simple route.

Cosmas, Inc. developed an exceptionally simple but general process to make high-quality, well-defined metal oxide nano-particles utilizing a method discovered at Brigham Young University. The process entails a solid state mixing of common, dry starting materials (metal salts and a base) in the absence of water to form a precursor material which is then either washed and/or heated directly to a relatively low temperature (e.g., 200-300°C) to decompose remaining byproducts, which are highly concentrated and easily collected, recycled, or sold. The process is very simple, has a low energy requirement, requires no solvent or hazardous waste disposal, and can be easily adapted to yield a very broad range of commercially viable products. The method has been named solvent deficient precipitation (SDP).

Catalyst performance and cost are defining characteristics of coal to liquid (CTL) and biomass to liquid (BTL) processes. Combined CTL/BTL (CBTL) can produce low-emissions of carbon dioxide and are more attractive in the social and political setting. Iron based Fischer Tropsch (FT) catalysts appear to provide the most economical route for conversion of Wyoming coal to much more valuable liquid fuels and chemicals, especially at a plant size that is likely to be funded and built. However, iron based FT catalysts are not available commercially. This project has developed low cost, effective FT catalysts that will be made available for commercial use through Cosmas, Inc.. Wyoming's abundant and inexpensive subbituminous coal resources are likely attractive feedstocks for iron-based FT plants because the less-expensive catalysts would be more economically favorable for these lower rank coals.

Objectives

The objective of the project was to develop a simple, low-cost, and environmentally-sound method for preparation of high-performance iron FT catalysts which can be scaled to commercial manufacture. We explored (1) a variety of relatively inexpensive starting materials; (2) a range of conditions for precipitation; and (3) a variety of post-treatment methods. The simplicity of our method enables us to prepare samples in a fraction of time required by conventional preparations and hence enabled exploration of a range of preparation and activation variables.

The near-term objectives for this project involved (1) scoping of important parameters in the preparation of promising new catalysts using the SDP method and (2) optimization of these catalysts to identify the best candidate(s) for commercial development. Now that this phase of the project is complete, future work will involve increasing production capacity of the catalysts to produce commercial quantities.

In this work, the majority of the catalysts were prepared using the SDP method, which is Cosmas's patented (US 8,211,388) process for nanoparticle preparation. Figure 1 shows a series of photographs showing the progress of a typical SDP reaction of iron nitrate with ammonium bicarbonate. As the solid starting materials, shown in Figure 1(a) are mixed without any added water, a liquid solution forms (Figures 1(b) through 1(e). The solution darkens as the reaction proceeds and as carbon dioxide is released, until the reaction is complete, which took about 20 minutes (Figure 1e). The catalysts were then dried to produce a powder, with a typical example shown in Fig. 1f.


(a) (b) (c) (d) (e) (f)

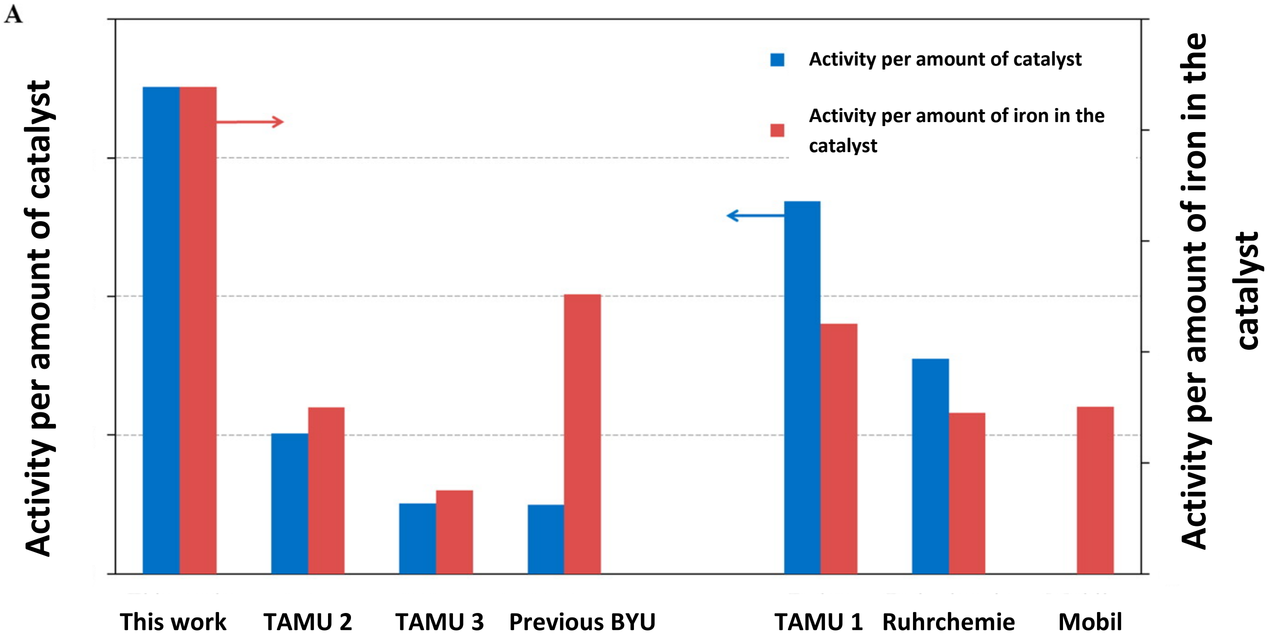
Figure 1. Progression of the SDP reaction of iron nitrate with ammonium carbonate including a) bicarbonate and metal salts before reaction, b) initial mixing, c) carbon dioxide release during early reaction, d) late reaction progress, e) cessation of carbon dioxide, and f) oven-dried iron oxide precipitate.

Results

A number of different types of iron Fischer-Tropsch synthesis (FTS) catalysts were prepared, primarily through the solvent deficient precipitation (SDP), although several conventional catalysts were prepared by established precipitation procedures for comparison purposes. In addition, several unconventional catalysts, such as those containing manganese or supported on carbon nanotubes, were also synthesized and tested as potential leading-edge technologies.

The results have been outstanding. The catalysts produced by the SDP synthesis method are among the best reported with respect to rate and productivity. The selectivities to desired products are also reasonable, although they can still be improved. Further, several of the catalysts are exceptionally stable, meaning that they should be useful for long periods of time. Although the strict definition of a catalyst is that it is not consumed during the reaction, real catalysts have finite lifetimes due to deactivation processes inherent in their use. Typical iron based Fischer-Tropsch catalysts may only have a life of six months to a year in an industrial setting, but the SDP catalysts could be useful for double or quadruple that time.

The initial goal of this work was to demonstrate that the SDP method could be used to prepare active, selective, and stable iron Fischer-Tropsch catalysts comparable to the most active FT catalysts reported, which include those developed at Texas A&M University (TAMU) as well as catalysts developed by industrial researchers, including those at Ruhrchemie and at Mobil Research and Development Corporation. Figure 2 displays a comparison of the performance of one of the best catalysts prepared in this work with results reported previously for similar iron catalysts. The length of the bars in the figure corresponds to the catalyst activity. Higher activity is generally being better because smaller amounts of catalyst placed in smaller reactors can be used to generate the same amount of product, which means that the overall plant is cheaper to build. The blue bars show how active the catalyst by itself, while the red bars show how active the catalyst is based on the amount of iron it contains, which is the active ingredient. The catalyst shown on the far left, which was developed during this study, is 3.5 times more active than the catalysts developed TAMU 2 and 7 times more active than TAMU 3, which are the most similar catalysts.



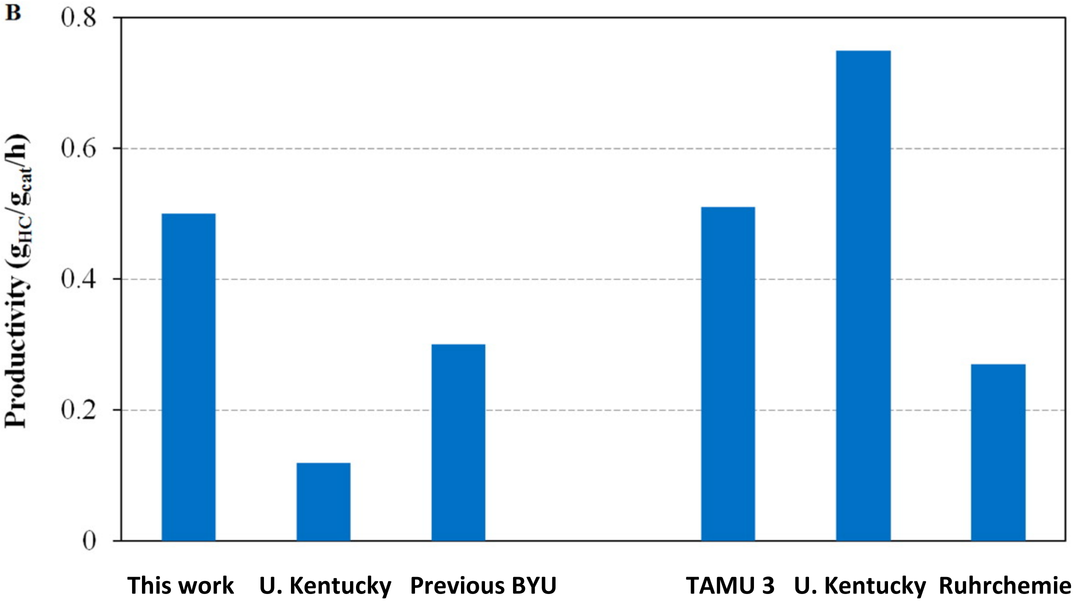


Figure 2. Comparison of (A) activities and (B) productivities ($g_{HC}/g_{cat}/h$) for various supported and unsupported iron catalysts at 260°C. The left axis in panel A represents the rate constant per gram of catalyst (blue) and the right axis is the rate constant per gram of iron (red).

The catalysts on the right of Figure 2A, TAMU 1, Ruhrchemie, and Mobil, are less similar, but previously considered superior to the formulations shown on the left. Nevertheless, the new catalyst developed in this work is more active than all of these catalysts. Further, catalyst productivity (which takes into account both activity and selectivity to the desired products) for this catalyst is equivalent to TAMU 1, as shown in Figure 2B. Recently, a group from the University of Kentucky reported preparation of an even more productive catalyst, as shown in Figure 2B, but this catalyst is much more complicated to produce than the simple methods of the SDP catalysts. Activity and productivity comparisons are also made to other unsupported and supported catalysts in Figure 2, including comparisons with industrial catalysts from Ruhrchemie and Mobil as well as other academic catalysts from the University of Kentucky.

With further refinements, several of the catalysts produced during this work compete with the best previously reported iron catalysts, as shown in Figure 3.

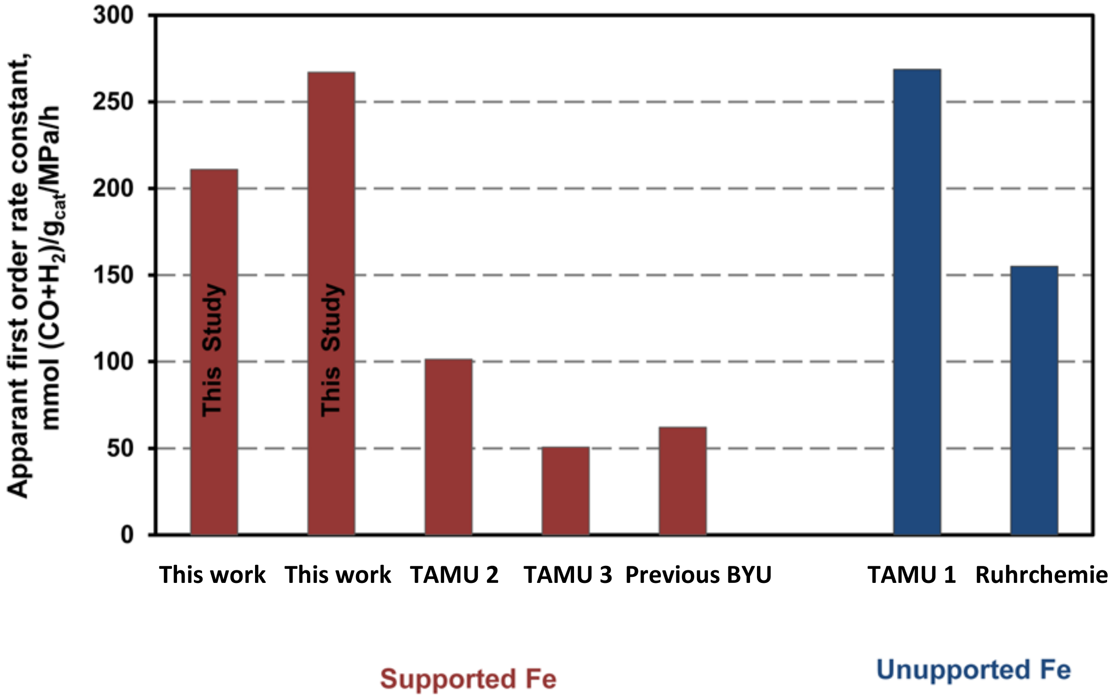


Figure 8. Comparison of activities for supported vs. unsupported iron catalysts. Two catalysts from this project (on the left) are far more active than previously reported supported catalysts and compare favorably with the best unsupported catalysts, which is unprecedented.

Work on unconventional catalysts, which include those supported on carbon nanotubes and others containing manganese, is still continuing and will be reported at the 2014 Clean Coal Symposium. In addition, a study on the hydrogen generation ability of similar iron catalysts has been conducted and is ongoing with Fischer-Tropsch synthesis experiments. One of the primary reasons for using iron based FT catalysts is they can produce necessary hydrogen during the reaction, which allows hydrogen-deficient synthesis gas sources, such as coal and biomass, to be processed without the need for a separate hydrogen generation facilities, which are typically very expensive.

In summary, this project has produced iron-based FT catalysts of exceptional activity and stability. The best catalysts are ready to be produced in larger scales that could be applied commercially. Cosmas, Inc. is now refining its business plan to take this next step.

Conclusions and Recommendations

Solvent deficient precipitation, or SDP, is a new preparation method for FT catalysts. The iron catalysts prepared in the initial part of this study, which are the first known catalysts prepared by SDP, exhibited exceptional activity, stability, and productivity properties and are competitive with those of the best iron FT catalysts reported in the literature. Because this method is so simple, iron FT catalysts produced using this method should be less expensive than those prepared by conventional methods, which was another goal of the work.

Additional work is ongoing involving some leading-edge catalyst technologies, including manganese promotion of the iron catalysts and using different starting chemicals for the SDP process. Initial indications are that some of these catalytic materials have unique properties. The results will be presented and published in the future.

Since these catalysts are intended for use with hydrogen-deficient synthesis gas from coal and biomass sources, the hydrogen generation behavior of similar iron-based catalysts prepared by the SDP method have been studied extensively during this work. The hydrogen production kinetic data will be incorporated into the BYU FT Consortium kinetic model.

Five graduate students, three at the doctoral level and two at the masters level, performed their research on aspects of this project. Two of their dissertations or theses have been completed, while the other three are anticipated to be completed this summer. Additionally, eleven undergraduates participated in the work. At least eight archival journal publications are expected based on this work. Two of these have already been published, three have been submitted and are either under review or in revision, and three more have been prepared and should be submitted next month. These publications have appeared in some of the most respected journals in the field, including *ACS Catalysis* and the *International Journal of Hydrogen Energy*, while the articles currently under consideration and expected to be published shortly are in the *Journal of Catalysis*, *Catalysis Science & Technology*, and *Topics in Catalysis*. In addition, the principal investigators and students made 24 technical presentations at regional, national, and international conferences. One patent application, "Iron and Cobalt Based Fischer-Tropsch Pre-Catalysts and Catalysts" that includes coverage for these iron-based catalysts, was filed in 2013 (US 20130274093).

The iron-based Fischer-Tropsch (FT) catalysts prepared during this study are among the most active and stable of any catalysts reported to date. Although potentially superior proprietary catalysts from companies such as Sasol may exist, they are not available for sale. The catalysts developed during this project are intended for commercialization. They are also protected by Cosmas's own existing intellectual property rights (U.S. patent 8,211,388). Therefore, the next phase of the Cosmas's business plan is to begin production of these catalysts for small-scale FT plants. These iron catalysts are ideally suited to produce liquid products from the synthesis gas produced by biomass and coal.

The recommendations for future work involve the scale-up of the catalyst production process, for which funding is actively being pursued. The work performed by the project has met the objective of identifying catalysts that appear to be suitable for commercial application. The next step is to perform these evaluations at a commercial scale.

MARKET OPPORTUNITY

The goal of Cosmas, Inc. is to adapt its very simple solvent deficient precipitation method of manufacturing metal oxide and metal nanoparticles to catalysis applications. Because of the SDP method's flexibility, nanoparticles can be easily custom made to fit customer requirements in this demanding field. Due to the method's simplicity and low energy consumption, it is likely to become the most cost effective method for manufacturing nanoparticles and their application in catalysis.

The SDP process consists of simply mixing common metal salts with ammonium bicarbonate, then heating the reaction product to a moderate temperature (~300°C). We are not aware of another method of making nanoparticles which is as environmentally friendly, as simple to implement or as energy efficient as this approach. Furthermore, it can be applied to virtually any metal or rare earth element (about 75 elements total). Any number of these metals can be combined in any exact ratio required for a specific application. Typically, no basic changes in the simple mix and bake process are needed for control of particle characteristics such as their chemical composition, oxidation state, size or crystalline phase.

Business Model

Cosmas initially established research collaborations with 13 different companies in different fields of application. However, our three most successful collaborations are in the catalyst field, and several unique opportunities exist in the catalysis field to capitalize on the simplicity of the process and its ability to produce customized nanomaterials. Hence, Cosmas has made the determination to focus on the application of its technology to this field of application. We have successfully moved production to a single vessel reactor and are designing a pilot plant-level reactor. The company is poised to start large scale production as soon as the required capital funding is obtained to set up a large production facility where it can compete effectively with its low energy/cost effective process for the production of unique products. Cosmas' first product will be an iron-based Fischer-Tropsch catalyst. The BYU Catalysis

Laboratory’s expertise in this area combined with the simple Cosmas synthetic method are merging to develop a catalyst for the rapidly emerging field for the utilization of biomass and coal to liquid fuels. We are aware of two large companies that produce iron FT catalysts, but they are maintaining them proprietary for their own internal use; therefore, these catalysts are not commercially available for smaller companies desiring to enter the biomass/coal liquefaction field. This presents a unique opportunity for market entry. (See Target Market below.)

Cosmas will pursue a split revenue model. The primary objective will be to set up manufacturing facilities and to sell nanoparticle-based catalyst supports and catalysts to the company’s various collaborative partners, then to the industrial community in general. A very substantial business is anticipated on the premise that Cosmas can effectively enter the catalyst support and catalyst markets. It can also customize its products for a large variety of niche markets where sales volumes may vary from 50-100 kg/yr up to thousands of metric tons. However, in addition to these niche markets, corporations that are involved in large-scale production will want to adopt the Cosmas’ production process. Many of these customers will likely not want to rely on a small company to meet their requirements. They will require a license to the technology for in-house production where they can be in control. In fact, in the very first conversations, Air Products, BASF, and Solvay all asked if Cosmas would consider licensing. Licenses will be non-exclusive and limited to specific products so as to not interfere with the ability of the company to expand its manufacturing business. However, with attractive terms, various degrees of exclusivity will be considered. In addition, Cosmas, Inc. is pursuing a parallel track of developing the compact Fischer-Tropsch Synthesis plant technologies that would be attractive to small scale biomass, biogas, and stranded natural gas markets. These facilities would use Cosmas catalysts, and thus provide bootstrapping to develop the commercial catalyst production facilities described above. This strategy is being pursued with strategic partners under the umbrella of Advanced X (carbon)-to-liquid Technologies, as described below.

Target Market and Target Customers

While the world catalyst market is large, and highly competitive, it is nevertheless relatively inefficient in some aspects because outdated methods still predominate. For years, catalysis was seen as a black art, but scientific developments in the past 3-4 decades have transformed the field and initiated the incorporation of science-based technologies in the chemical and petroleum industries. Today, many catalytic processes are better understood, and significant progress is being made in developing new catalyst technologies. Science-based technological development of catalyst supports has lagged, but is now receiving greater attention. Supports are critical in the management of the interface and interaction of reactants and the active catalyst material.

A few years ago, the Fisher-Tropsch Consortium at BYU was established at BYU, where industrial sponsors are supporting the development of the technology. The driving force behind the formation of the consortium is the unavailability of Fisher-Tropsch catalysts. Because they have been denied access to current catalyst sources, these companies are seeking opportunities assist in the development of commercial capabilities to supply such a product.

As the country (and world) faces a challenging future with regards to energy sources, many companies are looking toward biomass, coal, and other carbon sources, but the infrastructure including supply of necessary catalysts and other materials need to be developed. Cosmas has targeted this market niche for initial entry into the FT catalyst field. Of course, its initial customers will be the FT Consortium members. Cosmas intends to work closely with the Consortium to produce a catalyst product which would match their needs. We will then expand to others and hope to provide one of the key elements to support growth of the alternate fuel resources market.

Recently, Cosmas has developed a strategic alliance called Advanced XTL Technologies or AXT. The “X” in XTL stands for any carbon source that is to be converted into liquids, such as the coal to liquids (CTL) and biomass to liquids (BTL) that have been discussed previously. However, the “X” designation is more general, to include gas to liquids (GTL) and other carbon sources to be used in Fischer-Tropsch synthesis of liquid products.

In addition to the obvious opportunities associated with both coal and biomass, an enormous market opportunity exists for providing clean fuels produced from low-value, stranded, flared, or waste natural gases and biogases. Capturing these wasted feedstock sources would create **35 million barrels per day of fuel, at a value of $1.4 trillion U.S.** Serendipitously, converting these wastes into fuel would decrease landfills by as much as 95% and would dramatically improve air quality.

Opportunities at Small Scale: The technology to convert coal, shale, natural gas and biogas into fuel known as the Fischer-Tropsch (FT) process was invented in Germany nearly 90 years ago. During WWII, Germany produced 25% of its diesel with FT when oil supplies ran low. Current commercial facilities using FT, run by companies such as Shell, Sasol, and SynFuels China operate on a very large scale, producing thousands of barrels per day of clean diesel using coal and natural gas. Typical plant costs range between $1-$20 billion.

The market that is completely unserved by current FT firms consists of municipalities, farms, landfills, stranded oil wells, and other sources of biomass or low value carbon products that could produce 20-500 barrels per day of fuel. AXT is poised to capitalize on this niche through its unique combination of technical abilities.

Growing Interest, yet Lack of Availability of FT: Because of the obvious allure of converting waste into clean fuels, interest in the Fischer-Tropsch process is rapidly expanding all over the world. For instance, the U.S. Air Force Clean Fuels Initiative set a goal of obtaining 70% of its aviation fuel from the Fischer-Tropsch process by 2025. However, potential small and medium-scale customers looking to acquire FT technology are universally turned away due to the following constraints:

1. There are no FT operators willing to build small-scale sized FT plants.

2. The FT process relies heavily on specially formulated catalysts. Large FT firms are unwilling to sell FT catalysts to their potential competitors. This affects both medium-scale (1,000 to 10,000 barrels per day) operations and small-scale operations ($\leq$ 500 barrels per day).
3. While pieces of the overall FT process are available, there are no companies offering a full solution of services to integrate an entire FT system in a cost-effective manner to serve small and medium-scale operations.

AXT's Solution: AXT's advanced process designs will enable us to build economical, modular FT plants to service the nearly unlimited amount of small-scale biogas producers. We will produce clean-burning diesel that will help the environment and will reduce dependence on domestic or foreign oil.

In addition to building and operating FT plants, AXT will also generate significant revenues by providing the following FT solutions.

- **FT Catalyst production:** State of the art, highly effective Fischer-Tropsch catalysts that can serve any small or medium FT plant that are superior to other available catalysts.
- **FT Catalyst testing:** Catalyst testing for FT operators looking to optimize their FT plant operations.
- **Training and Consultation:** Expert advice on FT process problems and training in the fundamentals of Fischer-Tropsch catalyst and reactor optimization.

Ultimately, Cosmas, through AXT, will push forward with the commercialization of the catalysts developed during this project. These iron-based Fischer-Tropsch catalysts produced by the SDP method have demonstrated tremendous potential at the laboratory scale. The next step is to produce and test them at initial commercial scales. AXT is actively pursuing funding to accomplish this goal.