

**UNIVERSITY OF SOUTH FLORIDA**

***Production of Liquid Fuels Biomass via Thermo-Chemical Conversion Processes***

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**Description:** The objective of this project is to develop technology for the economical thermo-chemical conversion of lignocellulosic biomass (non-food grade biomass such as agricultural waste, bagasse from sugar mills, citrus peels, switch grass, municipal green waste, etc.) to clean burning liquid fuels. Five of the major advantages of this process over a biochemical route to production of ethanol are: (i) it does not utilize food-grade feed stocks and therefore complements and does not compete with the agricultural food production in the state, (ii) the fuel produced is similar to those derived from petroleum unlike ethanol derived fuels which have at least a 25% lower energy content, (iii) the conversion is accomplished in using fast chemical reactions unlike the slow biological reactions for fermenting alcohol, (iv) the process does not require large amounts of water and associated energy costs of separating the water from the fuel as in bioethanol processes, (v) it can utilize a wide variety of biomass sources unlike the biochemical route which cannot work with high lignin containing biomass.

**Budget:** \$554,447

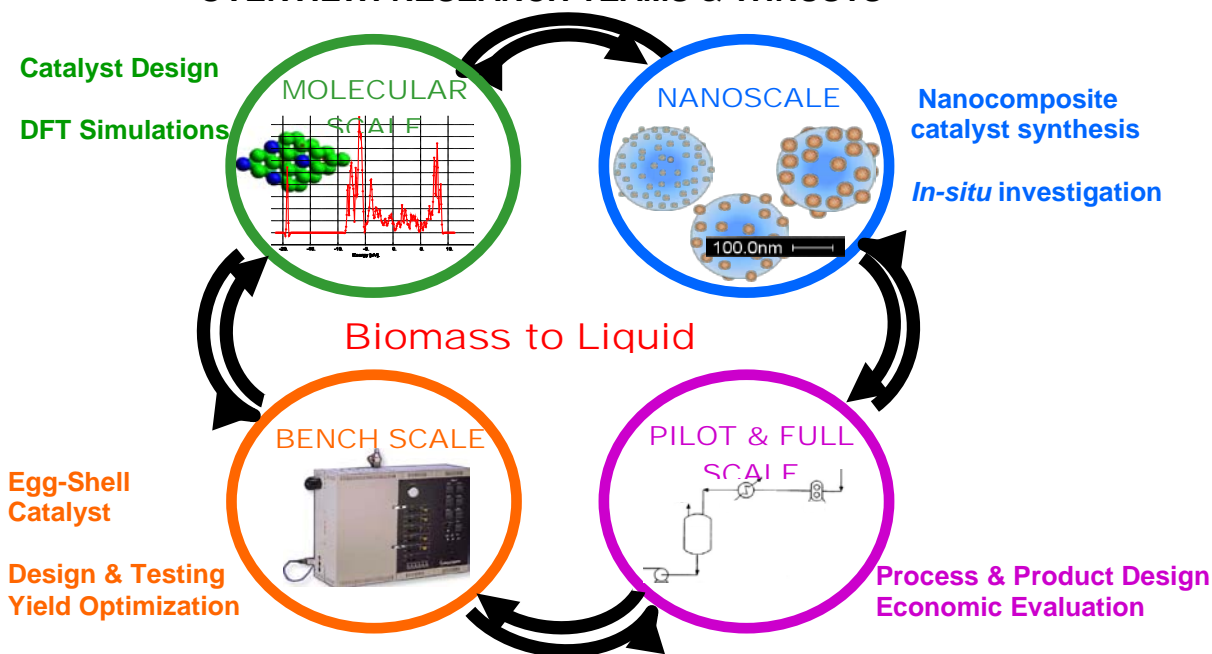
**Universities:** USF

**External Collaborators:** Prado & Associates

**Progress Summary**

During the past year, we made progress on four fronts: catalyst design using density functional theory (DFT) simulations in the molecular scale, nanocomposite catalyst synthesis in the nano-level, bench scale reactor testing for the synthesis of liquid fuels from bio gas and biomass conversion process design in the pilot and full scale.

**OVERVIEW: RESEARCH TEAMS & THRUSTS**



Our research focus is primarily based on cobalt catalysts since they represent the optimal choice for low temperature FTS processes because of higher stability, higher conversion (up to 60–70%), higher productivity, and relatively smaller negative effect of water on conversion. However, fundamental knowledge on reaction mechanisms and development of an economic technology to convert biomass to liquid fuels via FTS process is still not known. Our approach is to study FTS processes at these four different levels to achieve our objective.

In the past year, at the molecular level, we have performed DFT simulations to understand the role of promoters in the reduction of cobalt oxide which is one of the key steps required in this process for a cobalt catalyst. In the nanoscale level, we have prepared novel composite colloids such as silica supports surface decorated with cobalt nanoparticles as a model FT catalyst. This method allows control over the Co size and its aggregation on the support material. Our bench scale testing of egg-shell catalysts using our fixed bed reactor setup was successful. We were able to produce high grade liquid fuels from both mixtures of CO and H<sub>2</sub> as well as Biosyngas produced from poplar wood. In the area of process design, we have been evaluating alternative strategies to combine the energy intensive biomass gasification step with the energy producing Fisher-Tropsch synthesis of clean liquid fuels from syngas produced in the gasification step.

The product liquid produced have been analyzed and report good yield in the diesel and jet fuel range. We also continue with our catalyst characterization process.

We are exploring ways of recycling energy by using the methane off gas produced in the FTS to fuel the steam pyrolysis of biomass. Another avenue we are exploring is a novel strategy to combine solar thermal powered steam pyrolysis with the syngas production step.

We are continuing to study the mechanisms of CO dissociation on the catalyst surface using density functional theory calculations to determine the size effects and deactivation of catalysts. The effect of promoters on the CO dissociation and catalyst oxidation processes has been studied using surface alloy models and we found that Pt promoter aids in the reduction of cobalt oxide. We are focusing on establishing a volcano curve that would help us to identify promoters that enhance catalyst reduction and CO hydrogenation processes.

Catalyst synthesis efforts continue. We have successfully synthesized cobalt nanoparticles and placed them on silica Microparticles. These are currently being characterized and tested for activity.

## 2010 Annual Report

### DFT studies

Our objective was to determine the role of promoters in the reduction of cobalt oxide. Promoters have different functions such as increasing the reducibility, dispersion, activity or extending the life of a catalyst by reducing the deactivation rate. Commonly used promoters for cobalt catalysts are Ir, Rh, Re, Pt, Pd and Ru. Maintaining the metallic state of cobalt is very important in Fischer Tropsch Synthesis (FTS) as cobalt oxide is inactive for CO hydrogenation. Adding promoters to cobalt catalyst helps in the reducibility of cobalt oxide to metallic cobalt which is the active phase in cobalt based catalyst.

In this work, the effect of Pt promoter on the reduction of cobalt oxides to metallic cobalt was studied on both flat and stepped surfaces using surface alloy models where the promoter metal was dispersed on the top surface of the catalyst.

Our goal was to explore the electronic effect of promoters and the influence of Co-Pt bimetallic bonds on the reduction of CoO to metallic cobalt to gain a better understanding of the enhanced reducibility of promoted catalysts. For this purpose, the activation barrier for the reactions,  $O + 2H \rightarrow OH + H$  and  $OH + H \rightarrow H_2O$  on a promoted and

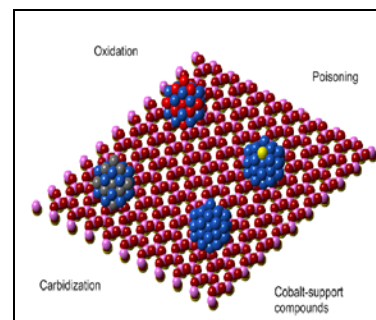


Figure: Schematic of deactivation of catalyst

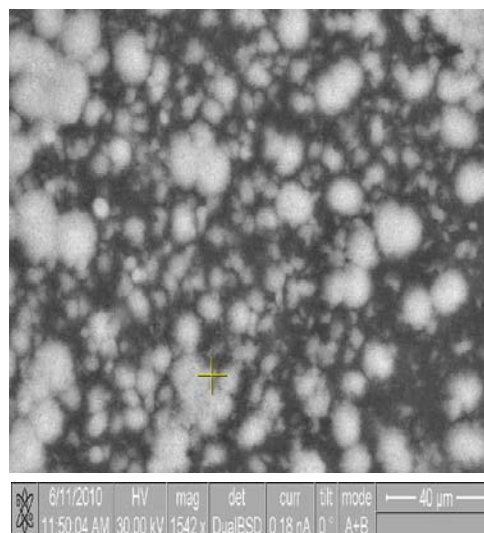
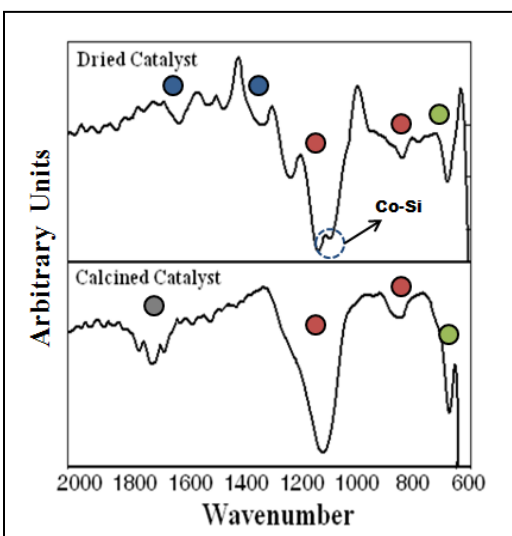
unpromoted Co (0001) surface was calculated. We found that the activation barrier on promoted catalyst was reduced compared to that on the unpromoted catalyst by about 0.3 eV. We also found that on the promoted catalyst CO dissociation was difficult.

A kinetic model will be developed and the reaction rate will be evaluated. Similarly, the activation barriers for the reduction of cobalt oxide will be evaluated on other promoters like Ir, Rh, Re, Pt, Pd and Ru. Thereafter, by establishing a relationship between the activity and binding energy of O, OH on these promoted surfaces, other potential promoters that would increase the reducibility of cobalt oxide can be identified.

### Egg-shell Catalyst Testing and Characterization

The objective of this work is to fabricate a highly selective eggshell Fischer Tropsch catalyst via interaction of hydrophobic and hydrophilic molecules on thermally treated silica gel. This catalyst is economic; scalable, robust and easily regenerated. Its surface properties; dispersion, reducibility and activity, are “state of the art”. Due to the engineered eggshell design, this catalyst is product specific and tunable depending on customer requirement. Its effectiveness has been tested by using biomass (pine chips) derived synthesis gas.

Previously, we reported the successful development of the eggshell catalyst. In order to confirm the “positive” metal-support interaction we performed FTIR analysis, the results have been provided in the previous reports. Our analysis revealed that simultaneous calcinations/reduction of a catalyst reforms its surface and improves dispersion and avoid the formation of irreducible compounds. In order to confirm these findings Scanning Electron Microscope (SEM) images

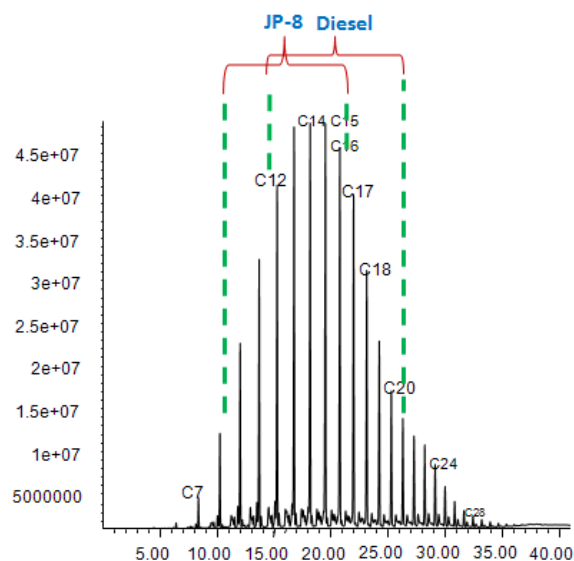


were taken. Based on the “Z Contrast” imaging, small and highly dispersed cobalt oxides particles were observed. Thus, the absence of cobalt silicates and formation of highly dispersed particles led us to the conclusion that the developed catalyst should have high activity. The selectivity of this catalyst has already been optimized by eggshell thickness.

In order to assess the activity and selectivity, the developed catalyst was tested under normal Fischer Tropsch Synthesis conditions. When compared to other test samples, this catalyst showed higher activity and a narrow paraffinic hydrocarbon distribution of ultralow sulfur diesel and aviation fuel with excellent reproducibility. The catalyst has shown strong resistance to attrition and cobalt silicate formation (due to product water) during the FTS. All these results

present a unique opportunity for the marketability of this process to diesel and “Jet Fuel” consumers. The performance of the developed sample remained consistent when biomass derived synthesis gas was used. The quality of the fuel was much superior to that derived from fossil resources with minimum contaminants and a comparable heating value. This performance reflects the raw material flexibility of this catalyst which includes coal, natural gas and even refused derived fuel (municipal waste). Further tests are in progress to ensure the viability of this catalyst on different biomass feed stocks.

The next step is to model the FTS process in order to understand the process dynamics during transient startup phase. Main emphasis is to control the initial reaction isotherm and utility of catalyst (eggshell zone) as the reaction transform from the transient to the steady state phase.

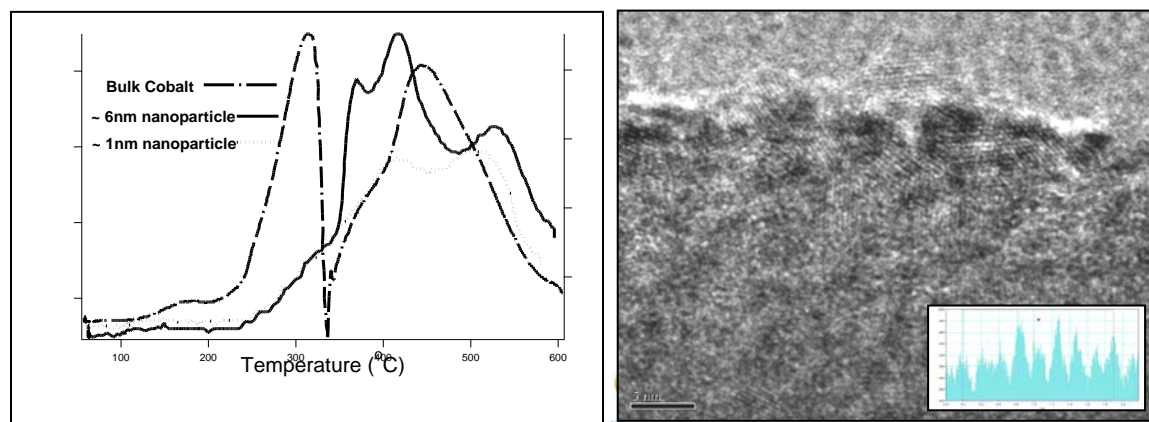


### Model Nanocomposite Co/SiO<sub>2</sub> synthesis

The objective of this part of the project was to synthesize a model catalyst of nanoparticles of cobalt on silica support to study the particle size effect on Fischer-Tropsch Synthesis of Synthetic Hydrocarbon Fuels. The influence of the size of catalysts such as cobalt (Co) metal nanoparticles has been the subject of significant debate in scientific literature on Fischer-Tropsch Synthesis (FTS). A key requirement for resolving the debate via experimental and theoretical studies is control over the Co nanoparticles and their immobilization on a support material without changes in size due to sintering, annealing, and aggregation.

In the previous annual report, we have reported successful synthesis of these novel composite colloids of silica microparticles that are surface decorated with nanoparticles of cobalt catalyst. These cobalt nanoparticles can be immobilized onto the surfaces of sub-micrometer silica particles that are surface modified with both small ligands and polymer chains. The interaction of cobalt nanoparticles with the modified silica depends upon parameters such as the functional groups of the small molecule ligands and polymer chains as well as the cobalt precursor and solvent medium that are used.

During this phase of the project, we have done additional characterization of the nanocomposite catalyst such as temperature programmed reduction (TPR) to understand more about the reducibility of the nano sized cobalt catalyst. Our studies show the reduction of nanoparticles is different compared to bulk cobalt.





Here, the bulk cobalt undergoes a bimodal reduction step where first  $\text{Co}_3\text{O}_4$  is reduced to  $\text{CoO}$  and then from  $\text{CoO}$  to  $\text{Co}$ . For the nanoparticles the reduction behavior is a broad unimodal reduction. In nanoparticles, the 2 steps may be happening simultaneously since the thickness of the oxide layer is very small. The peak shown approximately at  $535^\circ\text{C}$ , which is not present in the bulk is the amount of carbonaceous species that are evolved from the catalyst surface. The carbon deposits in the nanoparticles are from the surfactants that are used in the preparation step. Hi-resolution TEM analysis shown in the figure above also confirms qualitatively that cobalt nanoparticles with a lattice distance of  $2.12\text{\AA}$  are decorated on the surface of the silica support.

Our next goal is to gain more fundamental understanding of the nanoparticle size effect on  $\text{CO}$  hydrogenation in the FT using in situ Fourier transform infrared spectroscopy (FTIR) by examining the dynamic behavior of the carbon monoxide in a wide range of reaction conditions. Our research will help to provide a well designed experimental system for facilitating theoretical investigations in the molecular level that focus on size effects in the catalytic FTS reaction.

### Process & Plant Design

We are now developing a dynamic model of the FTS fixed bed reactor. This model would be useful for plant design and scale up. We are also developing a full process design for the combined gasification/liquefaction process starting with biomass and ending with liquid fuels. This model would be used for economic analysis of such processes.

### Ongoing and Future Work

The goal of the ongoing work is to scale up the preparation condition to obtain larger quantities of the novel composite catalyst prepared using self-assembly. This will enable use of the catalyst in in-situ reaction studies with FTIR spectroscopy to analyze the adsorption of  $\text{CO}$  or and  $\text{H}_2$  gases at high temperature. The goal will be to identify the reaction intermediates as function of the cobalt nanoparticle size, understand the impact of using self-assembled cobalt catalyst on formation of undesirable cobalt-silicates, and to provide experimental data to guide theoretical studies that focus on modeling adsorption-reaction phenomena on a cobalt nanoparticle of fixed size using density functional theory (DFT).

### Publications resulting from the work so far:

- B. D. Mankidy, C. A. Coutinho, and V. K. Gupta\*, “Probing the Interplay of Size, Shape, and Solution Environment on Macromolecular Diffusion using a Simple Refraction Experiment”, *Journal of Chemical Education* 87(5), 515-518 (2010)
- C. A. Coutinho, B. D. Mankidy, and V. K. Gupta\*, “A Simple Refraction Experiment for Probing Diffusion in Ternary Mixtures”, *Chemical Engineering Education* 44(2), 134 (2010).
- A.H. Kababji, B. Joseph, J.T. Wolan; “Silica-Supported Cobalt Catalysts for Fischer–Tropsch Synthesis: Effects of Calcination Temperature and Support Surface Area on Cobalt Silicate Formation;” *Catal. Lett* (2009) 130: 72-78
- S. A.Z. Gardezi, J. T. Wolan, B. Joseph, An Integrated Approach to the preparation of effective catalyst for Biomass-to-liquid (BTL) process, 33rd Annual AIChE Clearwater conference, June-2009
- S.A. Z. Gardezi, B. Joseph, J. T. Wolan, Metal support interaction effects in Fischer Tropsch synthesis: significance of catalyst preparation, AIChE annual meeting Nov-2009.
- C. A. Coutinho and V. K. Gupta\*, “Photocatalytic Degradation of Methyl Orange Using Polymer-Titania Microcomposites”, *J Colloid and Interface Science* 333(2), 457-464 (2009).
- Balakrishnan, N.; Bhethanabotla, V. R.; Joseph, B. In Effect of Cluster Size on  $\text{CO}$  Adsorption and Dissociation on Cobalt Catalysts: DFT Studies Using Cluster Models, Accepted for presentation in AIChE Annual Meeting, Conference Proceedings, Nashville, TN, United States, 2009.
- Balakrishnan, N.; Bhethanabotla, V. R.; Joseph, B. In Effect of Cluster Size on  $\text{CO}$  Adsorption and Dissociation on Cobalt Catalysts: DFT Studies Using Cluster Models, presented in FESC summit, USF, Tampa, United States, 2009.

- Choudhury, P.; Balakrishnan, N.; Bhethanabotla, V. R.; Stefanakos, E. In Complex Borohydride for Reversible Hydrogen Storage Accepted for presentation in AIChE Annual Meeting, Conference Proceedings, Nashville, TN, United States, 2009.
- Balakrishnan, N.; Choudhury, P.; Bhethanabotla, V. R.; Joseph, B. In Density Functional Theory Studies on a Reversible Hydrogen Storage "Li-Mg-B-N-H" System, Annual Meeting, Conference Proceedings, Philadelphia, PA, United States, 2008.
- Bijith D. Mankidy and Vinay K. Gupta, "Novel Composite Particles for Catalysis: Cobalt Nanoparticles on Silica Colloids", The Southeastern Regional Meeting of American Chemical Society, Nashville (TN), November, 2008.
- Bijith Mankidy and Vinay K. Gupta, "Cobalt Nanoparticles on Surface Modified SiO<sub>2</sub> Colloids for Fischer Tropsch Synthesis", Florida Energy Systems Consortium Summit, University of South Florida, Tampa (FL), September 29-30, 2009.
- Babu Joseph, Y. Goswami, V. Bhethanabotla, J. Wolan and V. Gupta, Production of Biomass via Thermochemical Process, FESC Summit, Tampa, Florida, Sept 2009.
- Babu Joseph, SURA Workshop on Energy: A brief update and summary, FESC Summit, Tampa, FL, Sept 2009.
- Balakrishnan, N.; Bhethanabotla, V. R.; Joseph, B. In DFT studies on the promotional effect of platinum for the reduction of CoPt bimetallic catalyst in Fischer Tropsch Synthesis, Accepted for presentation in AIChE Annual Meeting, Conference Proceedings, Salt Lake City, UT, United States, November 2010.
- Balakrishnan, N.; Bhethanabotla, V. R.; Goswami, Y.; Joseph, B. In DFT studies on the promotional effect of platinum for the reduction of CoPt bimetallic catalyst in Fischer Tropsch Synthesis, Accepted for poster presentation in FESC summit, USF, Tampa, United States, 2009