

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 lingocellulosic 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.

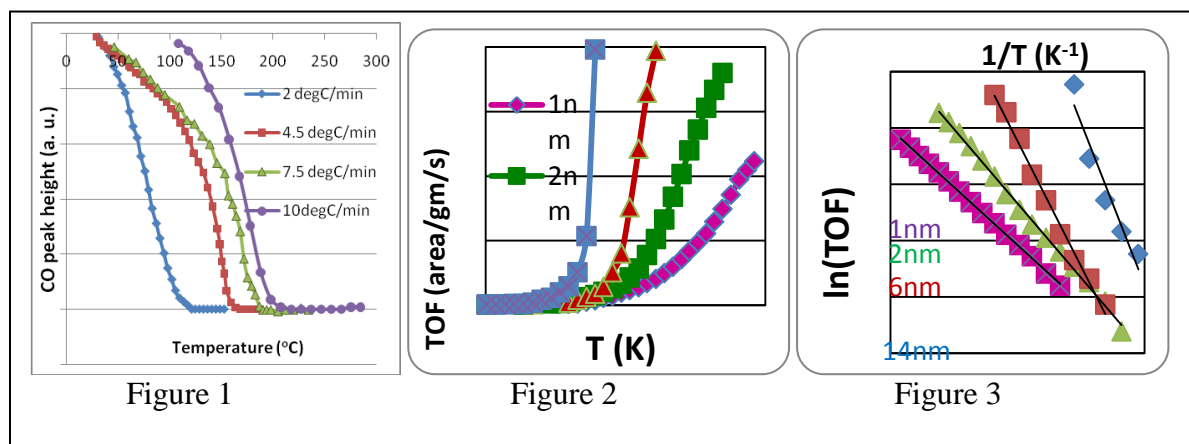
Budget: \$554,447

Universities: USF

External Collaborators: Prado & Associates

Progress Summary

To advance Fischer Tropsch conversion of synthesis gas from biomass, we have shown that we can synthesize cobalt (Co) nanoparticles with precise size control (1-14nm) to establish the effect of nanosized catalyst. By immobilizing these Co nanoparticles on sub-micron sized SiO₂ supports, we have recently focused on utilizing an in situ AABSPEC reactor to study the dependency of size on catalytic activity. Since chemical interaction of CO gas on the catalyst surface is a primary step in FTS, we investigated an elementary reaction such as CO oxidation on Co-oxide nanoparticle surface. CO dissociation energy has been calculated from its dissociation profiles measured during temperature programmed reaction studies at different heating rates. Figure 1 shows that by increasing the heating rate, CO dissociation temperature shifts towards higher temperatures. These temperature values can be used to calculate activation energy for CO dissociation. Figure 2 shows the turnover frequency of CO₂ formation as a function of temperature for different nanoparticle sizes. Activation energies for CO₂ formation on cobalt nanoparticles were also calculated based on plotting Arrhenius plots (figure 3) from turnover frequency data.



In summary, we have established a strong Co nanoparticle size effect and the trend in the activation energy for CO dissociation and CO₂ formation is $E_{14nm} > E_{6nm} > E_{2nm} > E_{1nm}$. We propose to use these techniques next to establish a size dependency relationship in FTS reaction of CO with H₂.

DFT studies: Here the objective was to determine the role of promoters in FTS. The economics of the Fischer-Tropsch process strongly depends on the performance of the catalyst used. Few desired properties of a catalyst are improved selectivity, higher activity and longer catalyst life and promoters are often added to improve these properties. Promoters can increase reducibility, dispersion of catalyst thereby improving the activity and/or selectivity. It can also prevent the deactivation of catalysts caused by oxidation or carburization.

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. We found that the activation barrier for the removal of O 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 was developed for the removal of O and TOF was higher for the promoted surface compared to the unpromoted Co surface. We also evaluated the activation barrier for CO hydrogenation on the stepped surfaces using the same model surface and found that the promoted surface had lower activation energy for the hydrogenation of CO. This reduction in activation barrier is due to the change in the electronic structure of the cobalt surface due to the presence of Pt promoter. The change in the electronic structure changes the most favorable sites on the promoted surface and leads to a reduced barrier.

Reaction Studies:

Fischer Tropsch synthesis run using pine chips derived biomass gas has been planned. One of the pending issues was removing the contaminants from the syngas. For this purpose, pine chips derived syngas was analyzed using mass spectrometer. Its results show the presence of contaminants like benzene, toluene, ammonia and high moisture content. For this purpose, scrubbing filters have been installed in series and performance tested. Complete removal of contaminants has been ensured.

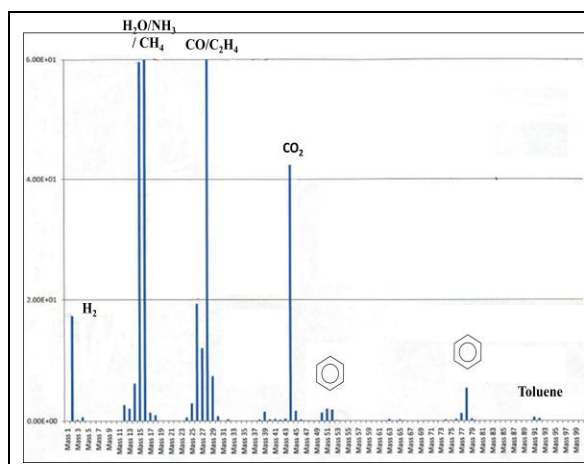


Figure 4. Mass spectrometer analysis of Syngas

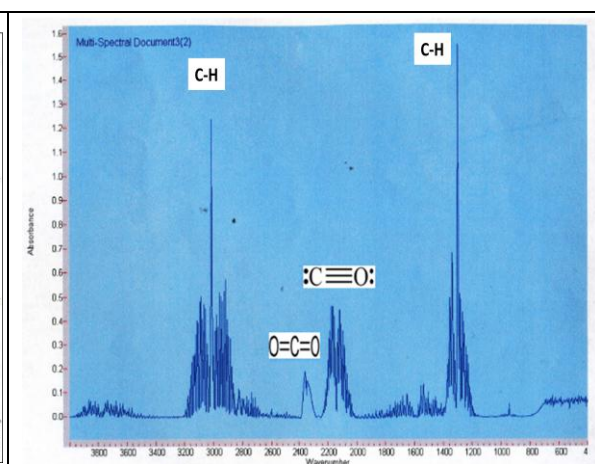


Figure 5. FTIR analysis of cleansed gas

In conjunction with analytic studies, FTS modeling is being performed on MATLAB. The focus is on the startup non-steady state process. Efficient heat removal has been a constant problem during our analytical work. In this regard we have developed the reactant conversion model, product pore filling duration and axial/radial temperature profile. By using this model we have successfully controlled the heat transfer in

our fixed bed reactor. In addition to the ongoing analytical work, this model will also help in the scale up of Fischer Tropsch process.

| New collaborations: | | |
|----------------------------|---|----------------------------------|
| Partner name | Title or short description of the collaboration | Funding, if applicable |
| Pearson Ass. | We have started discussion on the submission of a new DOE proposal for building a pilot plant for FTS | Proposal preparation in progress |

| Proposals | | | | | |
|----------------------|---------------|---|------------------------------|-----------------|---------------------------|
| Title | Agency | Investigators/ Collaborators | Funding requested | Duration | Date submitted |
| FTS catalyst studies | NSF | B. Joseph | \$480,000 | 3 years | Mar, 2011 |