

FMRI RET 2016-Synthesizing Catalysts for Conversion of Landfill Gases into Fuel

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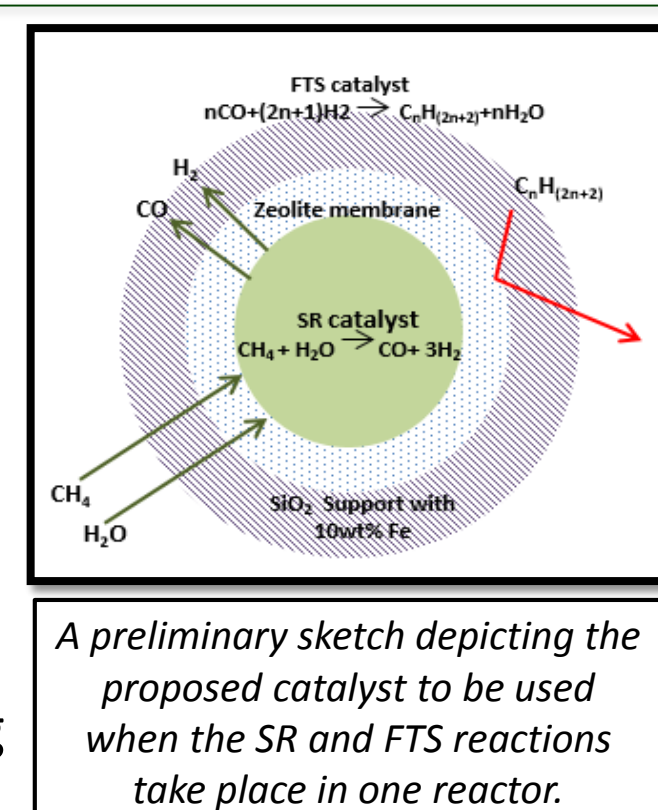
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Abstract

The overall goal of this project is to recycle gas coming from landfills by efficiently converting them into usable liquid fuels. There are two separate reactions needed to create fuel from landfill gases--steam reforming (SR) and the Fischer-Tropsch (FT) reactions. Our current research is attempting to make both of these reactions more efficient by having them react simultaneously in one reactor. Work this summer focused specifically on determining structure-function relationships and optimizing pre-treatment conditions of the iron-based Fischer-Tropsch catalyst to successfully run at higher temperatures.

Objectives

The objective of this work was to determine the structure-function relationships and find the optimal conditions and catalyst preparation to run the Fischer Tropsch reaction at 450°C while not building up pressure in the microreactor.



Approach

Synthesis of Catalyst

The creation of the catalyst was done through a wet impregnation technique. In a beaker pellets of silica support (SiO₂) were combined with a solution of metal nitrate salts and distilled water. The solution consisted of iron nitrate, potassium nitrate, and copper nitrate. The solution was dripped into the silica support slowly and stirred as to not immediately saturate the solution. This allows the metal salts to penetrate the pores. Once completely mixed the solution was placed in a furnace and calcined at 300°C and another sample at 550°C.

Preparation of Physical Mixture of Catalyst with SiC

The Fischer Tropsch Reaction was performed in a fixed bed quartz U-tube microreactor with an internal diameter of 4mm. The catalyst was mechanically mixed with silicon carbide and then loaded between two layers of high temperature quartz wool. The U-tube reactor was inserted into a Thermoscientific Thermolyne tube furnace with temperature controlled by using a Eurotherm 3110 PID controller. The gas was fed into the U-tube via a manifold that was connected to Alicat Scientific mass flow controllers. Helium gas is the carrier gas in the system. Total flow rate was 50 sccm at any given point of experimentation. The reactor outlet was connected to a Perkin Elmer Gas Chromatography (GC) to analyze the effluent gas from reactor using Haysep-D packed column and thermal conductivity detector (TCD). All of the feed and outlet lines were wrapped with heating tape to prevent condensation.

Activation of Catalyst with H₂ Gas

While at room temperature the catalyst was activated by sending 5 sccm of pure H₂ gas and 45 sccm Helium gas for 24 hours. After the 24 hours, 50 sccm of He for 15 minute was sent through to clear the U-tube reactor of any residual H₂ gas.

Fischer-Tropsch Reaction

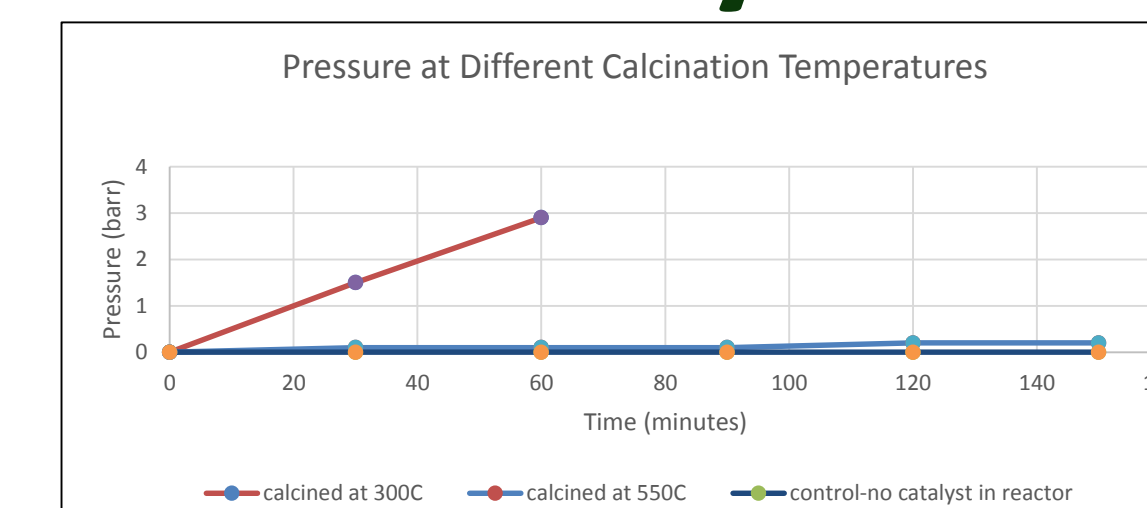
The furnace was set to a temperature of 550°C (increasing at a rate of 10°C per minute). Once up to temperature and the peak adjustment of the gas chromatography was complete allowed CO (2 sccm), H₂ (20 sccm) and He (28 sccm) to pass through the U-tube reactor. Measurements were made with the GC 3 times per hour. At the time of each reading pressure was also monitored.

CO Conversion

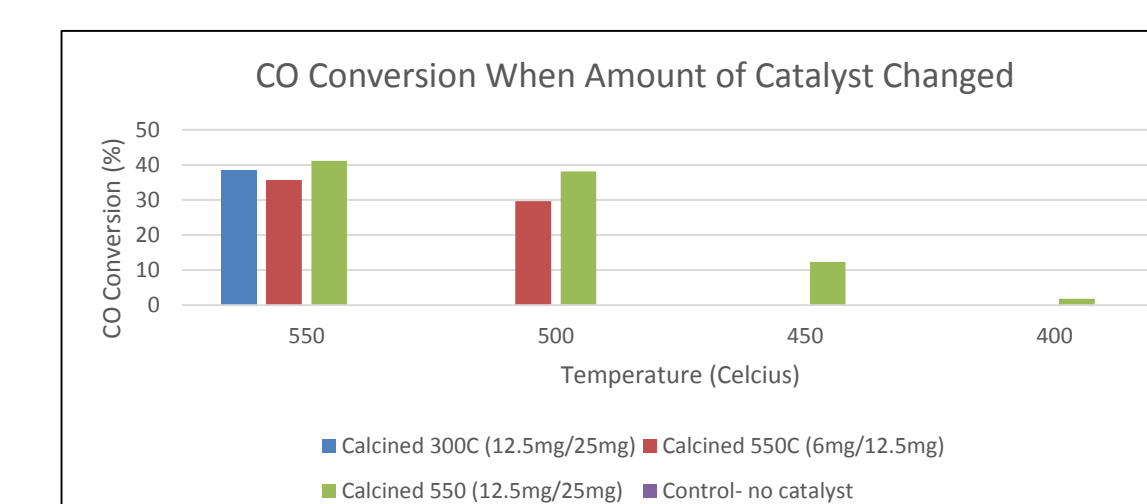
CO conversion was calculated using the following equation:

$$\text{CO conversion} = X_{\text{CO}} = \frac{\text{CO mole in} - \text{CO mole out}}{\text{CO mole in}} \times 100$$

Preliminary Results



The catalyst calcined at 550°C did not experience a significant rise in pressure. The missing data in the sample calcined at 300°C is due to safety constraints. The microreactor is not rated to contain more than 3 bars of pressure.



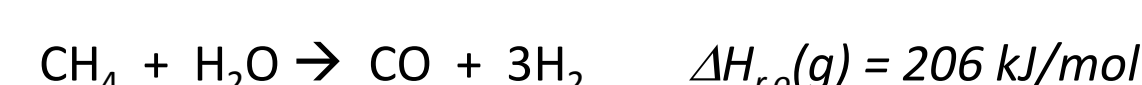
Calcing at the higher temperature did not effect the production of the FT synthesis, as evidenced by CO conversion. However, using more catalyst did increase the CO conversion regardless of calcination temperature.

Background

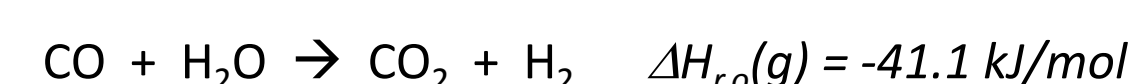
The SR reaction is first used to convert methane into CO and H₂. This reaction is typically done at very high temperatures (900 °C) and is highly endothermic.¹ The CO and H₂ are then used as the reactants in the FT synthesis to produce hydrocarbon chains of various lengths. The FT reaction usually runs at lower temperatures (around 250-300 °C) and is exothermic.²

Our current research is attempting to make both of these reactions more efficient by having them react simultaneously in one reactor. If these reactions occurred within the same reactor, they would potentially run more efficiently as the released energy of the FT would provide some input of energy needed for SR to occur. Additionally, there would not be a loss of material and additional supplies needed in the transfer of materials from one reactor to the next.

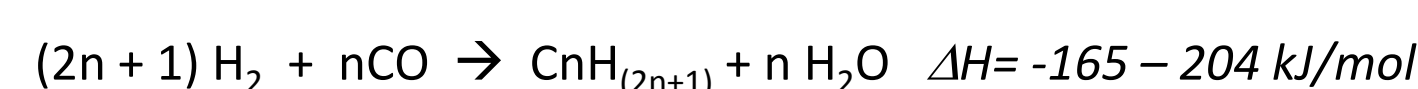
Steam Reforming:



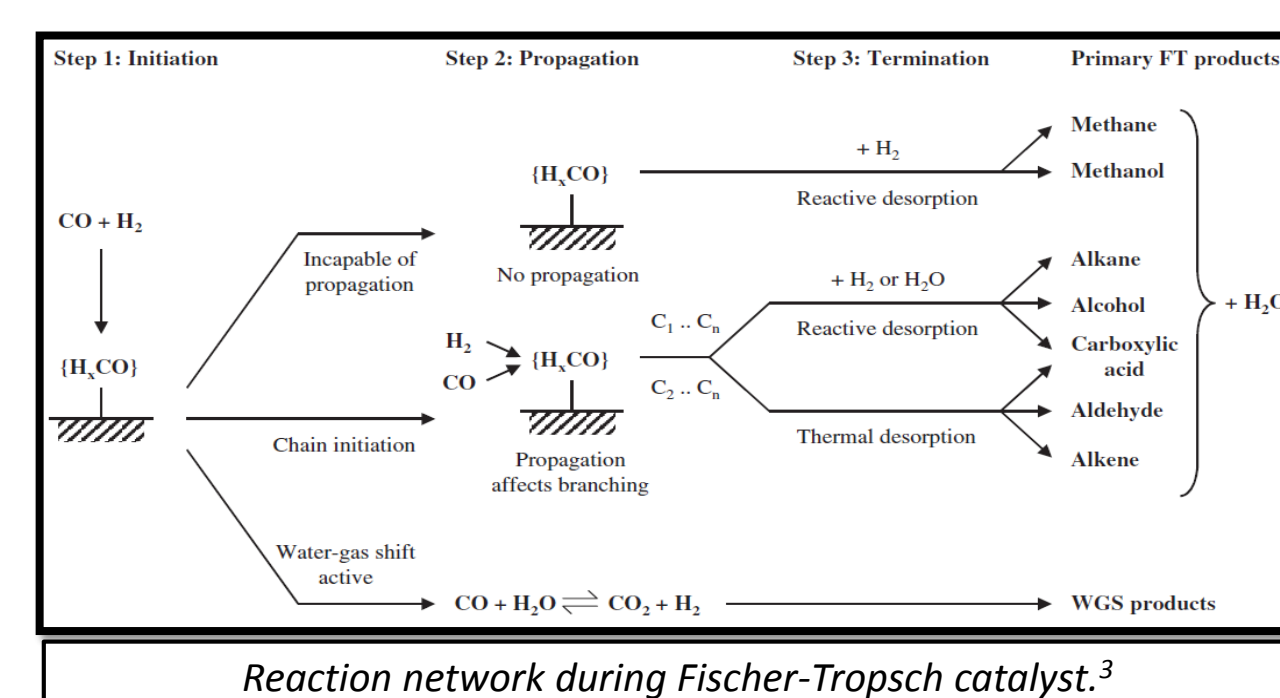
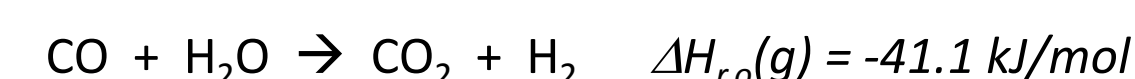
Water-Gas Shift:



Fischer-Tropsch:



Water-Gas Shift:



Currently these two reactions are done in separate reactors as they run at vastly different temperatures and various products and by-products of each reaction will deactivate the catalysts of the other reaction. Our current research is focused on engineering catalysts to allow each respective reaction to run at unideal temperatures while not deactivating the respective catalysts.

Prior work with a zeolite coated catalyst has shown successful SR at lower temperatures (450 °C) and the zeolite worked as an effective filter for allowing reactants and products to pass while blocking larger particles that deactivate the catalyst.⁴ Work this summer focused on getting the FT reaction to successfully run at lower temperatures.

Conclusions

Further testing still must be done, but preliminarily under ideal conditions (10:1 H₂ to CO gas, controlled temperature, no competing reactions) it appears the FT catalyst must be calcined at 550° C, activated in pure H₂ for 24 hours and more of it used to get higher CO conversion.

Referenced Resources

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