



Fischer-Tropsch Cobalt Catalyst Activation and Handling Through Wax Enclosure Methods

Jennifer L.S. Klettlinger
Glenn Research Center, Cleveland, Ohio

Chia H. Yen
University of Toledo, Toledo, Ohio

Leah M. Nakley
Sierra Lobo Inc., Fremont, Ohio

Angela D. Surgenor
Glenn Research Center, Cleveland, Ohio

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National Aeronautics and
Space Administration

Glenn Research Center
Cleveland, Ohio 44135

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Jennifer L.S. Klettlinger
National Aeronautics and Space Administration
Glenn Research Center
Cleveland, Ohio 44135

Chia H. Yen
University of Toledo
Toledo, Ohio 43606

Leah M. Nakley
Sierra Lobo Inc.
Fremont, Ohio 43420

Angela D. Surgenor
National Aeronautics and Space Administration
Glenn Research Center
Cleveland, Ohio 44135

Abstract

Fischer-Tropsch (F-T) synthesis is considered a gas to liquid process which converts syn-gas, a gaseous mixture of hydrogen and carbon monoxide, into liquids of various hydrocarbon chain length and product distributions. Cobalt based catalysts are used in F-T synthesis and are the focus of this paper. One key concern with handling cobalt based catalysts is that the active form of catalyst is in a reduced state, metallic cobalt, which oxidizes readily in air. In laboratory experiments, the precursor cobalt oxide catalyst is activated in a fixed bed at 350 °C then transferred into a continuous stirred tank reactor (CSTR) with inert gas. NASA has developed a process which involves the enclosure of active cobalt catalyst in a wax mold to prevent oxidation during storage and handling. This improved method allows for precise catalyst loading and delivery into a CSTR. Preliminary results indicate similar activity levels in the F-T reaction in comparison to the direct injection method. The work in this paper was supported by the NASA Fundamental Aeronautics Subsonics Fixed Wing Project.

Introduction

Alternative fuels research plays an important role in emissions (Refs. 1 and 4) reduction and in the effort to decrease the country's energy dependencies. The Fischer-Tropsch process provides the ability to convert the nation's natural energy resource such as coal, natural gas, and biomass into a cleaner and more economical alternative to traditional commercial jet fuel. Fischer-Tropsch jet fuel is considered a synthetic jet fuel, which is synthesized from hydrogen and carbon monoxide in the presence of a catalyst. F-T jet fuel composition differs from petroleum-based, conventional commercial jet fuel because of differences in feedstock and production methodology. Fischer-Tropsch fuel typically has a lower aromatic and sulfur content and consists primarily of iso and normal paraffins. This alternative fuel is an active area of research across the world because of its reduction in emission particulates (Refs. 1 and 4).

The Fischer-Tropsch process has three distinct steps: gasification, synthesis, and product upgrade. The gasification step produces syngas (hydrogen and carbon monoxide) from many hydrocarbon resources. The synthesis involves the conversion of syngas to syn-crude. Product upgrade processes the syn-crude and separates it into useable liquid fuels. The synthesis step can be optimized to increase yields and reduce energy inputs into the overall process.

Cobalt-based Fischer-Tropsch catalyst is typically cobalt oxides on various ceramic supports (e.g., alumina, silica, titanium oxide, etc.). This cobalt catalyst requires a reduction treatment to convert cobalt oxides to metallic cobalt which catalyzes F-T synthesis reactions. This reduction step generally requires an operating temperature around 350 °C, which is beyond the design temperature of conventional F-T slurry reactors; consequently it is carried out in a separate activation reactor. After reduction, the cobalt catalyst is preserved in an inert atmosphere in the reactor. Conventional test procedure is to pneumatically load the reduced catalyst from the activation reactor directly into the F-T synthesis reactor by using an inert gas. The activation reactor is weighed before and after the catalyst is transferred to the F-T reactor to deduce the catalyst charge. The pneumatic conveyance method has the disadvantage of insufficient catalyst quantification and the potential for losing catalyst in the inactive reactor volume. This paper proposes an alternate method to encase the reduced catalyst in a wax mold while in an inert glove box. The alternate method assures that the prescribed amount of catalyst is loaded into the reactor without re-oxidizing the active cobalt catalysts before testing.

Experimental

Activation Procedure

The activation reactor is a fixed-bed reactor designed by GRC (Ref. 2) based on requirements of a similar unit used by the Center for Applied Energy Research (CAER). Figure 1 shows this reactor with and without insulation which is used for the activation of cobalt catalysts. The reactor is fabricated from a 1 in. OD, seamless 316 stainless steel tube with a wall thickness of 0.083 in., is 12 in. long, and is designed as a simple gas heat exchanger. Two tube socket weld unions are TIG welded to the ends of the tube to produce end connections that allow the reactor to be removed from the overall system. There are no internal baffles or supports for the catalyst materials. The reactor includes instrumentation both internally and externally for monitoring temperatures and pressures.

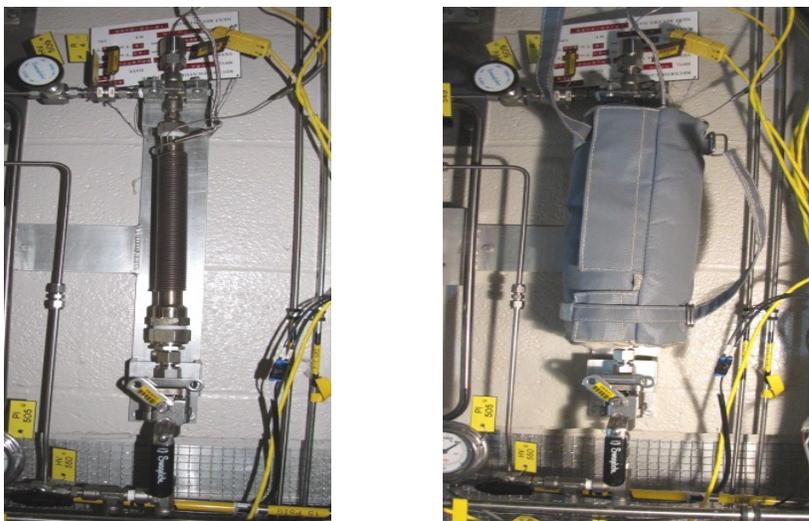


Figure 1.—Activation reactor (with and without insulation).

The reactor is designed to activate catalyst materials up to 225 psig and 430 °C with controlled flows of gaseous hydrogen, carbon monoxide, argon or nitrogen. Flow rates to the reactor can range from 0 to 120 standard liters per hour (SLPH). The reactor temperature is controlled by Labview (National Instruments) software, which provides automatic alarms and shutdowns for high temperatures and pressures. The Labview software is also used as a data acquisition system. A mighty-band coil heater surrounds the reactor with a heater power capacity of 940 W. The heater also includes an integrated type K thermocouple and can either be in a manual or automatic ramp mode with the use of the Labview control software. Two type K thermocouples are inserted from the bottom of the reactor and are at fixed lengths. One thermocouple is near the bottom of the catalyst bed while the other is centralized. Multiple thermocouple locations verify that the catalyst bed is uniformly heated to enable full catalyst activation.

Before catalyst can be loaded, the reactor must be correctly assembled with the thermocouples in their specific positions and glass wool covering the bottom of the reactor. A piece of 1/4 in. steel tubing is temporarily inserted over the thermocouples and inserted from the bottom of the reactor while securing the bottom reactor nut. This steel tube keeps the internal thermocouples centered while inserting the glass wool. Approximately 3 in. of woven glass wool is inserted from the top of the reactor with a 1/4 in. metal rod, around the steel tube and pushed down to the bottom of the reactor. Once the glass wool is evenly inserted around the steel tube, the steel tube is removed from the top of the reactor. The metal rod is then used to even out the glass wool around the thermocouples to fill in any voids. A visual inspection of thermocouple location is done from the top of the reactor to verify they are centered. Keeping the reactor in the vertical position, a weighed amount of catalyst is slowly poured into the top of the reactor and the top nut is secured. The amount of catalyst that is loaded into the reactor varies according to the test parameters. Catalyst weight loss during activation is usually 10 percent or less.

The loaded reactor is then vertically mounted by a wall support bracket (see Fig. 1). All inlet and outlet gas lines are connected and electrical wiring is attached. Once the reactor is installed onto the wall, a low pressure leak check is performed with nitrogen to verify the system is sealed. The activation process is started after a successful leak check. Inert gas flow to the activation reactor is initiated, followed by activation gas feed (typical 33 percent H₂, 67 percent inert). The activation gas flow rates are calculated based on a total flow rate of 30 SLPH/10 g-catalysts. This activation is carried out near atmospheric pressure. Figure 2 shows the reactor setup, where flow of gasses pass from top to bottom of this reactor.

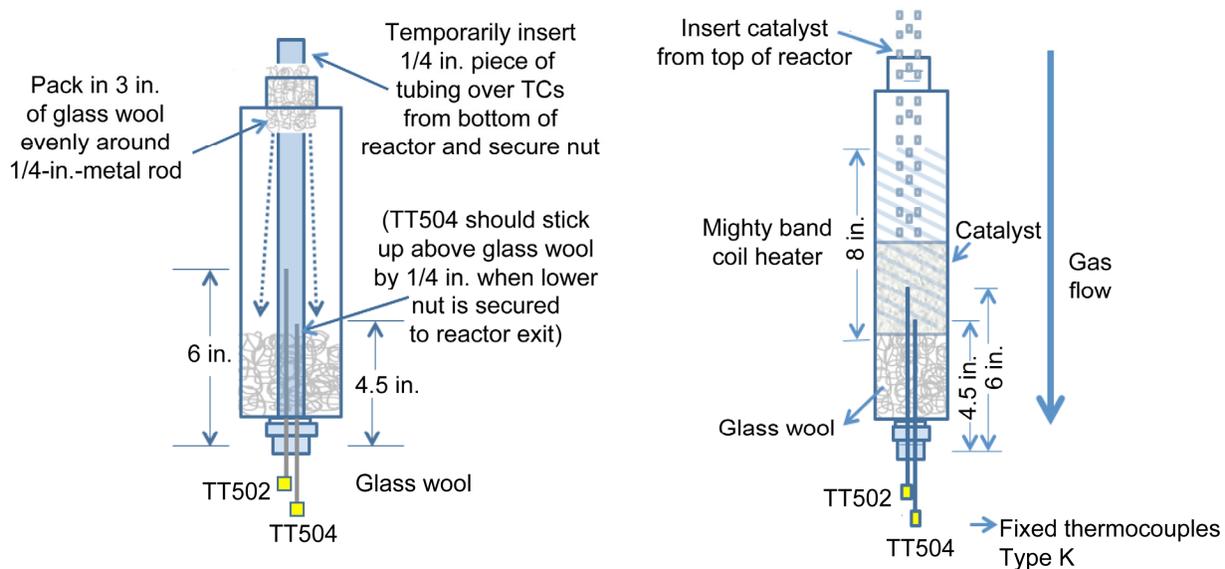


Figure 2.—Fixed bed activation reactor.

Using the ramp-soak capability of Labview software, the catalyst is heated at rate of 1 °C per minute to a pre-set target activation temperature (typically 350 °C). The catalyst is held at the designated temperature and gas flow rates for 10 hr. The reactor heater automatically turns off after 10 hr and the catalyst is cooled to room temperature with continuous gas flow. The remaining hydrogen in the reactor is purged out of the system with nitrogen and pressurized to approximately 2 psig. This slightly positive pressure is maintained by closing isolation ball valves on the reactor. Keeping the reactor under pressured nitrogen prevents the catalyst from being exposed to oxygen, thus inhibiting catalyst oxidation during handling.

Mold Making

Once activation is complete, the pressurized reactor is taken to a VAC NEXUS glove box where the catalyst is removed and weighed under inert conditions. Figure 3 shows the VAC NEXUS glove box used in this study. The reactor is loaded into a chamber where the atmospheric gases are evacuated, then transferred into the glove box's inert environment. Once inside the glove box, the activation reactor is opened and the catalyst is removed. A known amount of catalyst is weighed out and recorded.

This catalyst sample is then submerged in Polywax500 (Ref. 3) to create a solid wax enclosure. The goal is to encapsulate catalyst in a non-permeable wax mold (see Fig. 4). This is accomplished by melting Polywax500 (Ref. 3) in a beaker and proceeding with a liquid wax/catalyst layering technique (see Fig. 5). A layer of melted Polywax500 (Ref. 3) is first poured into a silicone mold (see Fig. 4).

Activated catalyst is then poured on top of the molten wax followed by additional molten wax. During the layering process, the liquid polywax (Ref. 3) infiltrates the catalyst pushing out any gas trapped between catalyst particles and creating a solid wax piece. Both catalyst weight and wax weight are recorded and accounted for in mass balance calculations. Once the catalyst enclosure cools and solidifies, it is removed from the mold and is taken out of the glove box for placement in the CSTR (see Fig. 6).

The wax mold is then transported to the CSTR, where it is loaded into the top of the reactor vessel just before closing and sealing the reactor. After the autoclave reactor is sealed, a timed inert purge is carried out to remove all oxygen in the system. Inert purge must be completed before the wax enclosure is melted to avoid potential oxidation. Normal reactor start-up procedure begins after inert purge.



Figure 3.—VAC NEXUS glovebox used for wax enclosure preparation.



Figure 4.—Empty wax mold.



Figure 5.—First layer of molten wax in mold (top left), catalyst inserted on top of molten wax in mold (top right), molten wax infiltrating cobalt catalyst (bottom left), final molten wax on top of cobalt catalyst (bottom right).



Figure 6.—Final wax enclosure solidified.

Results and Discussion

Slurry Reactor Comparison

Table 1 summarizes the comparison of three reactor runs using the same base catalyst. A baseline cobalt catalyst was prepared by CAER in 2007 for NASA testing in the newly established test facility. The purpose of NASA testing this catalyst was to verify facility operability. CAER's test results serve as the baseline for gauging the alternate catalyst handling method.

The reactor performance in NASA Run INI-001 was inferior to those achieved in the CAER's run TKD-007. The reactor conversions in the NASA GRC run (COC-001) are comparable to the reactor performance achieved by CAER considering the variation in space velocity and the state of operation.

TABLE 1.—RAW DATA COMPARISON

Run	GRC (COC-001)	GRC (INI-001)	CAER (TKD-007)
Catalyst ID	ZYQ036	Same	Same
Catalyst Composition	0.5%Pt 15%Co on Alumina support	Same	Same
Catalyst amount (g)	21.0	21.0	20.0
GHSV (SLPH/g)	5.1	5.2 (0 to 18 hr) 2.6 (18 hr to end)	5.5 (0 to 676 hr) 2.0 (676 hr to end)
H ₂ : CO molar ratio	2.0	1.8	2.0
Reactor pressure (psig)	268	275	270
Reactor temperature (°C)	220	220 to 223	220
Total run time (hr)	381	138	628 at 5.5 960 total
Mass balance (out/in)	90.6%	98.3%	

Run INI-001, the initial test performed in the Alternative Fuels Research Lab, experienced many operational problems which led to poor catalyst performance. Process variables in Run INI-001 were adjusted to compensate for poor catalyst activity: higher reactor operating temperature (223 °C vs. 220 °C in CAER run) and lower space velocity (2.6 SLPH/g-catalyst vs. 5.5 SLPH/g-catalyst in CAER run). The reasons for poor catalyst activity include the following:

- Catalyst was likely exposed to air and partially oxidized after activation. The catalyst was encased in a Polywax 3000 (Ref. 3) mold in an inert atmosphere in the glove box. The wax mold was then left in a sealed glass in ambient air for 12 days. Catalyst wax mold cracked during storage and was still loaded for this run.
- Catalyst activation may have been incomplete. Target activation temperature was 350 °C. The observed catalyst bed inlet/outlet temperatures were 352 and 247 °C, respectively. Non-uniform temperatures may have led to partial activation.
- Gas feeds (i.e., H₂ and CO) flows were interrupted due to flow meter malfunctioning.

Run COC-001 operated for 381 hr with consistent feed flows and reactor temperature/pressure control. The main objective for this run was to confirm hardware/software reliability after an extended maintenance shutdown. This run was initiated with known issues including: several instruments being out of calibration; expired GC calibration gases were used for first 320 hr of test; product gas compositions were sometimes extrapolated outside the calibration gas range; feed gas purity may vary slightly from bottle to bottle. The data scatter of run COC-001 in Figure 7 and poor mass balance in summary Table 1 are consistent with the state of operation. Never the less, the data collected during Run COC-001 confirms that the cobalt catalyst used was active and it had substantially better performance than that was achieved with an inactive catalyst during Run INI-001. Run COC-001 operated at lower operating temperature, higher space velocity while achieving similar per pass conversions as in Run INI-001. The extent of reactor conversions during Run COC-001 is also confirmed by comparing feed flow rate to the reactor effluent gas flow rate, see Figure 8. Run COC-001 result is supportive of the effectiveness of wax mold prevent active cobalt catalyst from being oxidized.

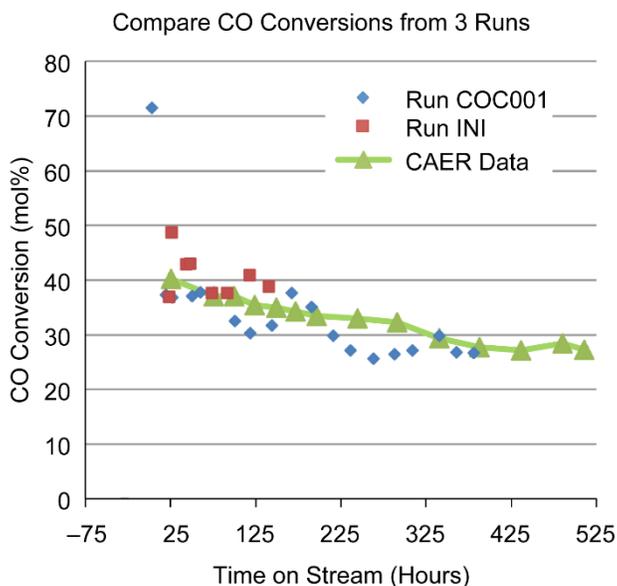


Figure 7.—CO conversion comparison of three separate runs.

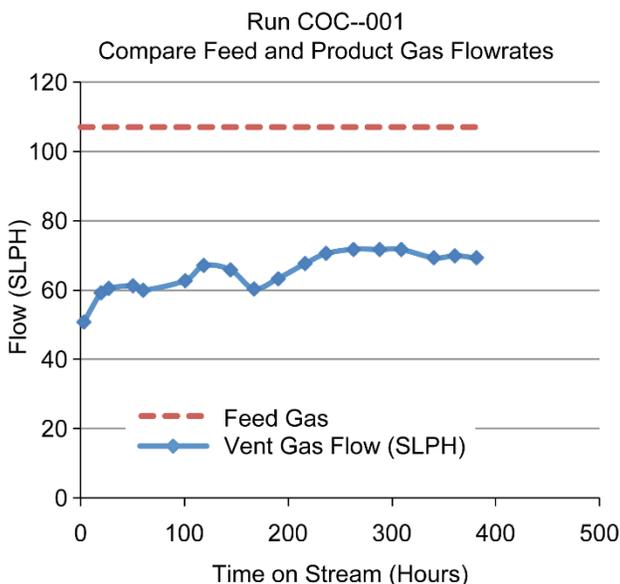


Figure 8.—Comparison of feed gases and product gas flow rates.

Scanning Electron Microscopy (SEM)

The mold making procedures previously described were followed in order to create a sample for SEM verification. These samples were made of an inactive alumina supported cobalt catalyst (25 percent cobalt, by weight). The wax enclosure mold (see Fig. 6) was too large to fit into the SEM instrument, so a portion of the sample, was cut and used for analysis. Figure 9 shows the setup of the SEM sample used and mounting of these pieces to SEM sample plate.

The sample was analyzed in multiple locations, which included the interior portion of the wax enclosure and the outside surface of the wax enclosure. Figure 10 shows each sample individually, the left image shows the external surface portion and the right image displays the internal surface portion. The white markings indicate the areas examined in the SEM. A Hitachi S-4700 Scanning Electron Microscope (SEM) was used to analyze the cobalt catalyst wax enclosure's integrity.

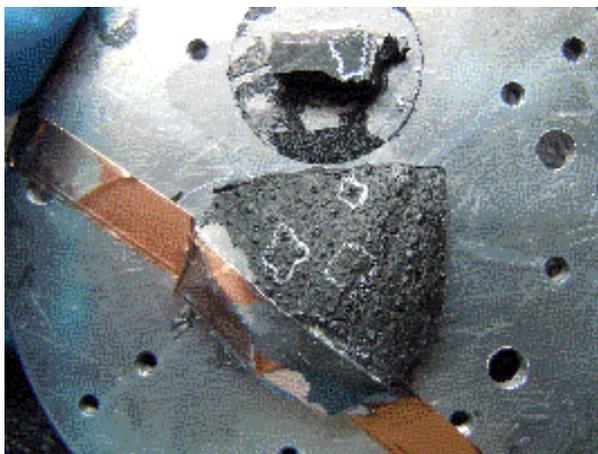


Figure 9.—Wax enclosure sample preparation for SEM.

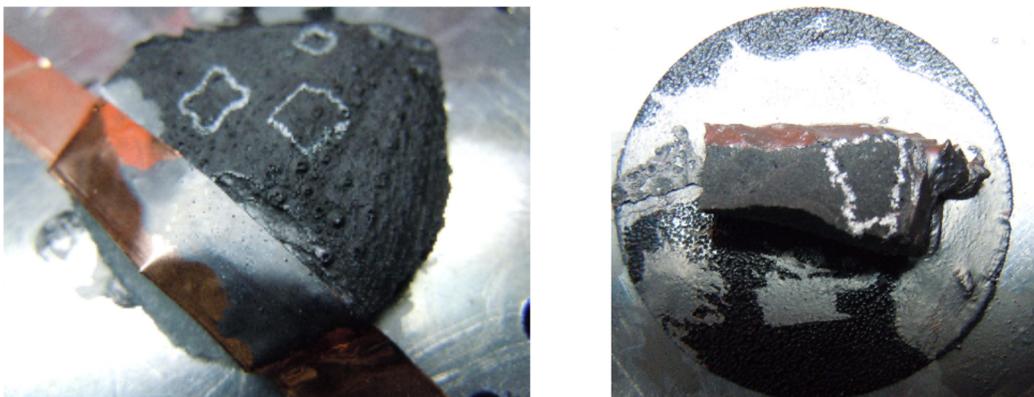


Figure 10.—Two separate SEM samples: wax enclosure outside surface (left) and internal wax enclosure surface (right).

Figure 11(a) and (b) show the SEM images of inactive plain alumina supported cobalt catalyst particles (not wax enclosed). Figure 11(c) shows the SEM image of the wax enclosed alumina supported cobalt catalyst, this image is for an interior location. Figure 11(a) and (c) have the most similar SEM settings; as indicated on the images, Figure 11(a) was taken at 12.2 mm and Figure 11(c) was taken at 10.5 mm. The distance differences between these two images was negligible, therefore it was disregarded in these interpretations. It is clear that the general morphology of the particles is different in these two images. Figure 11(a) shows more defined edges to the particles. It is reasonable to suggest that the morphology differences are due to the presence of wax coating the catalyst surface. There is also no indication of void space in Figure 11(c), this may prove that there are no gas bubbles located throughout the middle of the wax mold. The lack of gas bubbles indicates that the wax has properly infiltrated the catalyst sample and likely that each catalyst particle has been coated by wax.

Figure 12 shows the SEM image of the outside layer of wax enclosure at a higher magnification. It is interesting to note the texture of the surface and point out that there is little indication of separate particles. There is no clear indication of separate cobalt particles in comparison to the wax surface.

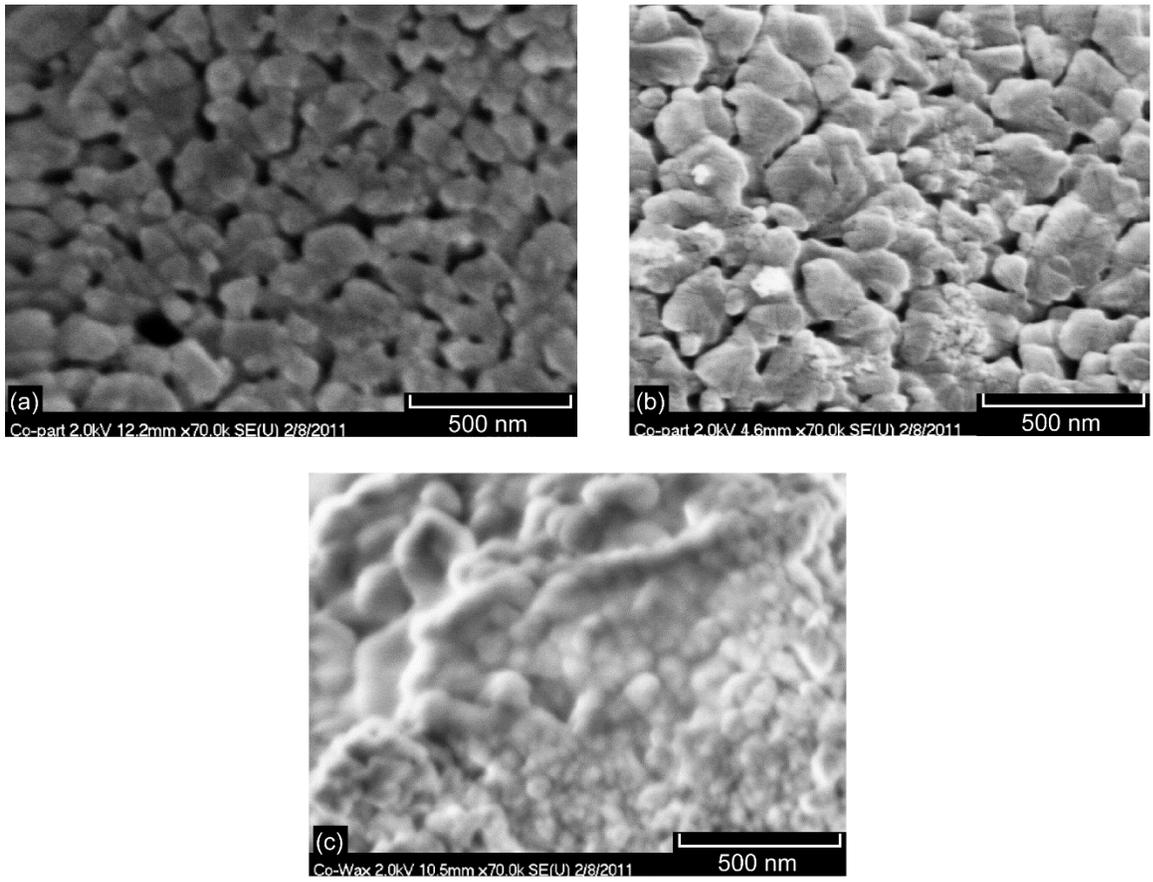


Figure 11.—SEM results. (a) SEM image of cobalt catalyst particles. (b) SEM image of cobalt catalyst particles. (c) SEM image of wax enclosed cobalt catalyst.

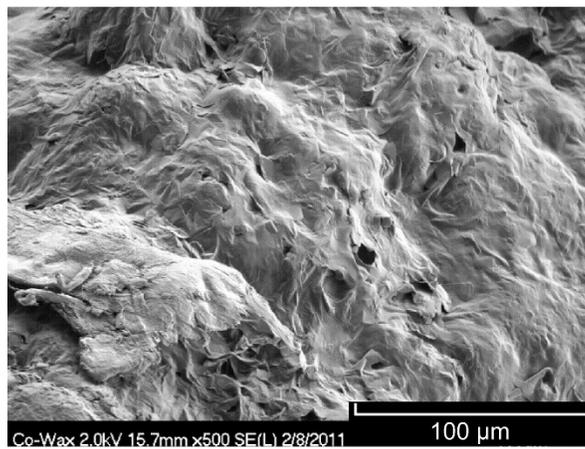


Figure 12.—SEM image of the outside layer of wax enclosure.

Conclusions

The methods described in this paper for mold making were intended to preserve activated cobalt catalyst, and facilitate precise catalyst loading in CSTR experiments. The wax mold technique prevents the reduced cobalt catalyst from being oxidized during the loading process. The F-T reactor conversions observed at the NASA Glenn Research Center are comparable to the data collected at the Center for Applied Energy Research (University of Kentucky) using the same catalyst under similar process conditions. As such, we believe that the reduced cobalt catalyst remains active in the wax mold. NASA Glenn Research Center experiments have shown some variability and lacked the stable results that CAER reported. Another CSTR experiment with the same catalyst will be conducted in the near future as operating issues at the NASA facility have been resolved. Ultra high purity gasses have been purchased and mechanical components have been calibrated and upgraded in order to reduce this oscillation in data.

The SEM images of catalyst-wax molds were collected as preliminary data. The focus of this SEM study was on the interior surface of the mold in secondary electron mode. This provided us with useful information regarding the morphology of the Co/Al₂O₃ catalyst particles coated with wax in comparison to uncoated catalyst particles. The clear differences in morphology lead us to believe that the catalyst particles are fully coated in wax. We will further investigate and verify our wax mold enclosure technique by collecting additional SEM images. We will examine the sample's cross section cut morphology to see how the catalyst particles relate to the surface and verify that there is no evidence of gas bubbles throughout the depth of the mold. We will look at the x-ray (EDS) chemistry at different locations throughout the mold. These locations will include the sample surface, as well as the internal cross section of this sample. We will compare x-ray (EDS) chemistry of a wax mold loaded with active cobalt catalyst versus inactive cobalt catalyst. This data will allow us to quantify and compare the oxygen content of the samples. As data is collected, proof of wax enclosure will be reported.

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