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Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

Long-Term Testing of Rhodium-Based Catalysts for Mixed Alcohol Synthesis – 2013 Progress Report

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MJ Gray
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Pacific Northwest National Laboratory
Richland, Washington 99352

Summary

The U.S. Department of Energy's (DOE) Pacific Northwest National Laboratory (PNNL) has been conducting research since 2005 to develop a catalyst for the conversion of synthesis gas (carbon monoxide [CO] and hydrogen [H_2]) into mixed alcohols for use in liquid transportation fuels. Initially, research involved screening possible catalysts based on a review of the literature, because at that time, there were no commercial catalysts available. The screening effort resulted in a decision to focus on catalysts containing rhodium (Rh) and manganese (Mn). Subsequent research identified iridium (Ir) as a key promoter for this catalyst system. Since then, research has continued to improve RhMnIr-based catalysts, optimizing the relative and total concentrations of the three metals, examining baseline catalysts on alternative supports, and examining effects of additional promoters.

Testing was continued in FY 2013 to evaluate the performance and long-term stability of the best catalysts tested to date. Three tests were conducted. A long-term test was conducted with the best carbon-supported catalyst. A second test of shorter duration was performed for comparison using the same catalyst formulation on an alternative carbon support. A third test of intermediate duration was performed using the best silica-supported catalyst tested to date.

The long-term test performed with the best Rh-based catalyst developed to date (catalyst H-A) operated for 2373 hr at a constant set of conditions (nominally 1200 psig, 260°C, 13,000 L/kg$_{cat}$/hr gas hourly space velocity using a feed gas containing 3.4% N_2, 3.4% CO_2, and the balance being H_2 and CO in a 1.3:1 H_2:CO ratio). During the test, the CO conversion and C_2+ oxygenate space time yield (STY) decreased, but at a decreasing rate over the course of the test, while the selectivity to C_2+ oxygenates remained essentially unchanged at about 73%. Analysis of the rates of decline of the STY during different periods in the test suggest that the catalyst would be stable at an STY of about 775 to 800 g/kg$_{cat}$/hr while operating at 260°C. Subsequent testing at 265°C and 270°C, showed that the CO conversion and C_2+ oxygenate STY could be restored to higher values with only an ~1% decline in selectivity. Furthermore, while the catalyst deactivated at higher rates at the higher temperatures, the rates of decline were significantly lower than those observed at comparable STYs at 260°C during the first phase of the test. From these results, it is concluded that, if the test had been started at a temperature between 245°C and 250°C, the C_2+ oxygenate STY could be maintained for 2 years or more at a constant selectivity, by slowly increasing the reaction temperature as needed to maintain the catalyst activity.

The catalyst supported on an alternative carbon was tested to 650 hr at the same conditions as the previously described catalyst. This catalyst initially achieved about 68% of the initial STY achieved with the best catalyst under the same operating conditions. However it was much more stable, over a comparable period of operation, experiencing only a 5% decrease in the STY and a 9% decrease in the CO conversion during the test, whereas catalyst H-A experienced decreases of 21% in the STY and a 25% decline in the CO conversion over the same operating period. The rate of decline in the STY of catalyst T-A also was comparable to that for best catalyst when the latter is evaluated during a period when its average STY was similar to that observed with catalyst with the alternative carbon support. This observation suggests that the two catalysts deactivate in a similar fashion even though their supports use different forms of carbon.

The selectivity of the catalyst also was very stable at about 70% after the first 100 hr at the design temperature, which is about 3% lower than that for the best catalyst. Like the best catalyst, this catalyst had similar selectivities during startup when the catalyst temperatures were maintained at 240°C and 250°C, again suggesting catalyst behavior similar to catalyst H-A. A more detailed breakdown in the converted carbon selectivities to various oxygenate and hydrocarbon products suggest that both catalysts are similar in this respect too. The only notable difference is that the catalyst on an alternative carbon support produced a small quantity of hydrocarbon liquid throughout the test whereas the best catalyst did not. Based on the results of both tests, it is concluded that high-surface-area carbon supports with predominantly graphitic (or graphenic) character would be suitable as supports for the Rh-based catalyst. However, additional optimization of the alternative support, both with respect to the support itself and the composition of the optimum catalytic metal, would be needed to achieve comparable performance at the same conditions.

Another intermediate-term test was performed with the best silica-supported, Rh-based catalyst developed to date mainly to document its potential performance with respect to that of the best carbon-supported catalyst. This silica-supported catalyst had a different catalytic metal composition. Previous short-term tests showed that the silica-supported catalysts were less amenable to variations in the concentrations of the three metals to improve the C_2+ oxygenate STYs or the converted CO selectivities to C_2+ oxygenates. This is presumed to be due to their greater interaction with the silica support. On the other hand, the choice of silica used as the support seems to have a greater influence on catalyst performance.

The intermediate test with the silica-supported catalyst was started using a 2:1 H_2:CO ratio so its performance could be benchmarked with that from an earlier short-term test using catalyst from the same master batch. The C_2+ oxygenates STY and converted CO selectivity were lower during the intermediate-term test. Again, this was not unusual based on the behavior of the silica-supported catalyst tested in the past. The long-term portion of the test was conducted at constant temperature for 668 hr using the same nominal testing conditions used for the previous two tests, except the catalyst temperature was maintained at 275°C, to achieve an initial C_2 oxygenate STY that was greater than 400 $g/kg_{cat}/hr$.

Over the course of the test, the silica-supported catalyst behaved somewhat differently than the carbon-supported catalysts. The CO conversion remained essentially unchanged at about 12%, while the STY declined about 2% from 430 $g/kg_{cat}/hr$ to 422 $g/kg_{cat}/hr$. The selectivity to C_2+ oxygenates decreased from ~63% to 60% over the course of the test. This decrease was accompanied by slight increases in the selectivity to methane and hydrocarbon liquids. The rate of decline in the STY was about 10%/1000 hr, which, while much lower than that observed with the carbon-supported catalysts, is more problematic because of the much lower initial STY. However, there appeared to be a decline in that rate over time, but the test was not performed over a long enough time to verify this possibility. Based on the results of this test, catalyst S-A, may be stable over a long time period, but to achieve this stability it would need to be operated at a lower initial temperature and correspondingly lower initial C_2+ oxygenate STY.

Acronyms and Abbreviations

DOE	U.S. Department of Energy
FT	Fischer-Tropsch
GC	gas chromatograph
GHSV	gas hourly space velocity
HPLC	high-pressure liquid chromatograph
PNNL	Pacific Northwest National Laboratory
STY	space-time-yield

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1.0 Introduction

The U.S. Department of Energy's (DOE) Pacific Northwest National Laboratory (PNNL) is conducting research on the conversion of synthesis gas (syngas) into mixed alcohols for use in liquid transportation fuels. Initiated in 2005, this research began with goals to identify and confirm the performance of any catalysts that were commercially available at that time, as part of DOE's effort to demonstrate mixed alcohol synthesis via indirect liquefaction. No commercially available catalysts were identified, although one company would offer a modified methanol synthesis catalyst for testing. In the absence of commercially available catalysts, the project scope was expanded to examine a variety of noncommercial catalysts and to test the most promising candidates in a bench-scale system. Potential catalysts were divided into the six general classes described below:

- Modified methanol catalysts (e.g., modified copper [Cu]/zinc [Zn]- and Cu/manganese [Mn]-based catalysts)
- Modified molybdenum (Mo) sulfide catalysts
- Modified Mo oxide catalysts
- Rhodium (Rh)-based catalysts
- Modified Fischer-Tropsch (FT) catalysts.

Representative catalysts for each class were obtained or prepared and tested under conditions that would optimize C_2+ space-time-yields (STY) at a common operating pressure (1200 psig). Ten catalysts representative of the different catalyst classes were evaluated along with a modified methanol catalyst provided by a catalyst manufacturer in 2006 and early 2007 (Gerber et al. 2007). C_2+ oxygenate STY was the primary basis of comparison with consideration given to reasonable converted carbon selectivity to C_2+ oxygenates. These criteria presupposed that nonalcoholic oxygenates could be hydrogenated further to alcohols in a subsequent step.

Only the modified FT and Rh-based catalysts achieved C_2+ oxygenate STYs that were greater than 400 $g/L_{cat}/hr$. However, FT catalysts that were modified to improve oxygenate yields had less than 10% carbon selectivity to C_2+ oxygenates; instead, they mainly produced FT liquids and hydrocarbon gases. Two Rh-based catalysts, Rh/Mn/silica (SiO_2) and Rh/Mn/Fe/SiO_2, were both very active with Rh/Mn/Fe/SiO_2 achieving a C_2+ oxygenate STY of about 400 $g/L_{cat}/hr$ (~870 $g/kg_{cat}/hr$) and converted carbon selectivity of approximately 24% to C_2+ oxygenates. Furthermore, very few C_1 oxygenates or FT liquids were produced. Based on these results, catalyst tests initiated during FY 2007 focused on the silica-supported, Rh-based catalyst to examine the effects of other promoters besides iron (Fe) on catalyst performance. The results of those tests identified several promoters that showed promise for improving C_2+ oxygenate STYs and/or improving the selectivity of the C_2+ oxygenates to alcohols (Gerber et al. 2008).

During FY 2009, the objective of the testing program shifted to optimizing the silica-supported RhMn-based catalysts that were reported by Gerber et al. (2010). Optimization involved examination of different total metals concentrations and atomic ratios of Rh and Mn as well as some of the more promising promoters identified in the earlier tests (iridium [Ir] and Lithium [Li]). In addition, limited catalyst screening continued to examine some additional promoters that had not been tested previously.

Catalyst optimization continued during FY 2010 with further examination of the concentration effects of promising catalyst promoters as well as the effects of catalyst support alternatives to the Davisil 645 silica that was used in most testing up to that time (Gerber 2012a). Limited testing to evaluate selected catalyst preparation techniques also were conducted in FY 2010.

FY2011 testing of alternative catalyst supports examined the performance of alternative silica-support materials with the Ir-promoted RhMn/SiO_2 catalyst. Research also continued to further optimize the catalyst composition for the silica- and carbon-supported catalysts (Gerber 2012b). Research also began to evaluate the effects of adding more promoters to the RhMnIr catalyst to improve converted carbon selectivity to C_2+ oxygenates, while maintaining high STYs. A long-term test was also performed at that time using the baseline carbon-supported catalyst without additional promoters to benchmark its stability at a constant set of testing conditions.

Testing in FY 2012 re-examined selected alternative silica and carbon supports to follow up on some uncertainties in the results with previous test results (Gerber et al. 2012c). Additional, tests were conducted further optimize the total and relative concentrations of Rh, Mn, and Ir on selected silica and carbon supports, and to examine selected promoters and promoter combinations based on earlier results. The effects of key operating parameters, pressure and the feed gas composition were also evaluated to establish the optimum operating conditions.

Extensive characterization measurements of selected catalysts and catalyst supports were performed in support of the catalyst optimization effort. Catalyst support characteristics such as crystallinity, surface area, and in the case of carbon supports, ash content and surface functionality were probed. Fresh and spent catalysts that had been subjected to mixed alcohols synthesis testing at various temperatures were investigated to understand the transformation of the supported metals under reaction conditions. Computational analyses (e.g., ab initio molecular dynamics and density functional theory calculations) also were performed to gain a better understanding of the roles of Rh, Mn, and Ir in the reaction network of CO with hydrogen (H_2) as well as how the metals interacted with the silica or carbon supports. The results of the characterization and computational efforts are reported separately (Albrecht et al. 2013).

During FY 2013, selected catalysts were subjected to long-term testing at constant conditions to evaluate catalyst stability with respect to selected performance parameters. One test was conducted for over 2300 hr at a single set of test conditions using a carbon nantotube supported catalyst containing Rh, Mn, Ir, and B, followed by additional testing at two higher temperatures for at least 500 hr, to examine this method for restoring catalyst activity over time. A second test was conducted using one of the same formulations but supported on a high-surface-area graphitic carbon that had shown promise in earlier testing but was not used to in catalyst optimization. The duration of this test was 650 hr, and the test conditions were the same as those used in the previous test. To provide an indication of its stability relative to the carbon-supported catalysts, a third test was also conducted for over 650 hr using the best silica-supported catalyst tested to date. The testing temperature for this catalyst was higher to obtain a reasonably high C_2+ oxygenate STY. To provide a benchmark for improvements made in the catalyst since that time, the results of the earlier test with the baseline carbon nanotube-supported catalyst are presented in the Appendix.

2.0 Catalyst Testing

2.1 Synthesis Reactor System Description

The bench-scale tubular reactor system used to test catalysts is designed to operate at pressures up to 1200 psig and temperatures up to 400°C. This system is shown in Figure 2.1. The catalyst chamber is 1.67 cm long and 0.635 cm in inner diameter. It usually is filled to a depth of 0.39 cm with porous metal frit holding the catalyst in place. A 0.159 cm outer diameter thermocouple sheath is extended through the center of the reactor, creating an annulus-shaped catalyst chamber. Two thermocouples inside the sheath are spaced so one thermocouple is located at the center of the catalyst bed and the other just upstream. The catalyst temperature during a test is based on the thermocouple temperature at the center of the catalyst bed. The reactor is heated with hot oil to obtain better temperature control because this approach more efficiently removes the heat of reaction, thus preventing a thermal excursion when the carbon conversion is too high.

All gases are metered through mass flow controllers and mixed in a common manifold. The reducing gas (10% H_2 in nitrogen [N_2]) is used during catalyst reduction. When syngas is used, it is a premixed gas. The gas mixture nominally consists of 4% each carbon dioxide (CO_2) and N_2 with the balance consisting of H_2 and carbon monoxide (CO) in a nominal 2:1 H_2:CO volume ratio. The capability to separately meter CO, H_2, and N_2 was added to the feed gas manifold so that mixtures with and without CO_2 in the syngas could be explored as well as different H_2:CO ratios.

The raw product gas leaving the reactor is passed through one of two cold traps to condense liquids at 0°C and through a back-pressure regulator that controls the system pressure. Gas flow is redirected from one trap to the other to isolate the former trap for liquid sample recovery.

The nominal feed rate to the reactor is determined by calibrating the mass flow controllers at system pressure before tests are started. A Bios DryCal flow meter located downstream of the back-pressure regulator is used for this calibration. Flow-meter readings are corrected for standard pressure and temperature. The flow meter also is used to monitor product gas flow rate downstream of the liquid sample cold traps during each test.

Dry product gas grab samples for analysis in a gas chromatograph (GC) are obtained downstream of the flow meter. Parameters monitored during tests include temperatures at the reactor inlet, catalyst bed, and cold sample traps, and the syngas feed pressure.

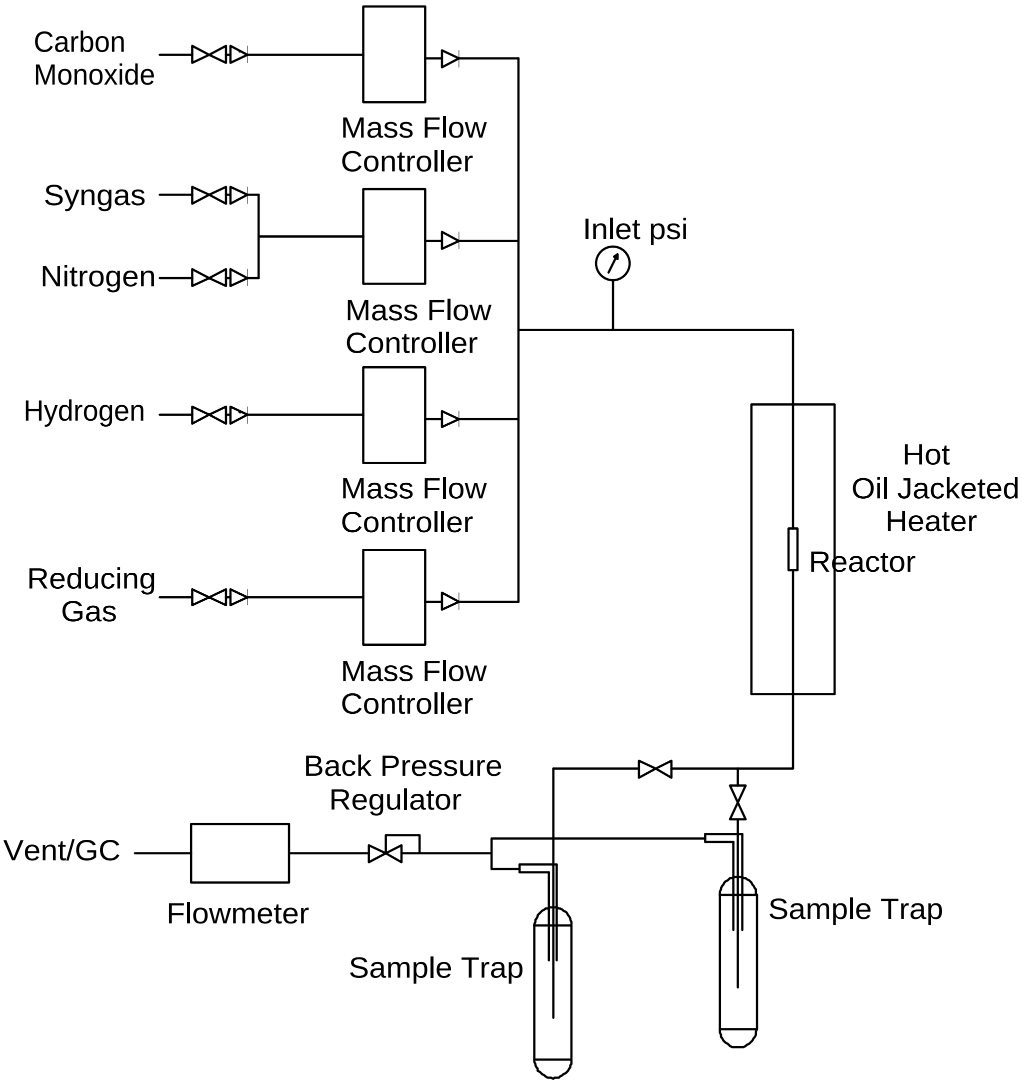

Figure 2.1. Simplified Diagram of the Reactor System Used to Test Catalysts

2.2 Catalyst Preparation

The catalysts selected for long-term testing are listed in Table 2.1. All catalyst preparations consisted of a single-step impregnation procedure using the incipient wetness technique. The appropriate quantities of a rhodium nitrate solution (10 wt% Rh concentration in solution), manganese nitrate tetrahydrate, and if used, a di-hydrogen hexachloroiridium (IV) hydrate solution (14% Ir), and boric acid were combined with enough deionized water to bring the total volume of the impregnation solution to 90% of the water adsorption pore volume of the support. The solution was impregnated onto the silica in drop-wise fashion on a vibrating table to keep the support solids in motion during impregnation. The impregnated catalysts were dried under an infrared lamp while being shaken until a steady weight was achieved, and then they were dried overnight at 110°C in a drying oven. Some of the catalysts containing Rh, Mn, and Ir in tests to optimize the metal concentrations were prepared using two impregnations with drying between impregnations to investigate the effect of the order of metal addition on catalyst performance. Each impregnation solution volume, containing the appropriate metal concentrations, was equal to the 90% of the water adsorption pore volume of the support. The dried catalysts impregnated on the silica support were calcined at 400°C in air using a muffle furnace. Catalysts supported on carbon were not calcined prior to reduction.

Table 2.1. Description of Catalysts and Testing Conditions

Catalyst Label	H-A	T-A	S-A
Catalyst Support	Hyperion CS-02C-063-XD	TIMCAL TIMREX® HSAG300	TIMCAL TIMREX® HSAG300
Catalyst Composition	8.34% Rh 3.01%Mn 5.2% Ir 0.06% B	8.34% Rh 3.01%Mn 5.2% Ir 0.06% B	8.34% Rh 2.50%Mn 1.5% Ir 0.06% B

Prior to testing, the calcined (or dried) catalysts were loaded into the reactor and reduced using a 10% H_2 balance N_2 gas mixture. All catalysts were heated in the reducing atmosphere to 220°C at a 2.5°C/min ramp-up rate and held at that temperature for 1 hr, then heated from 220°C to 260°C at a rate of 1°C/min and held at that temperature for 8 hr, and finally heated to approximately 350°C at a rate of 1.5°C/min and held at that temperature for 2 hr.

2.3 Testing Procedure

During a typical test series, a premeasured weight of catalyst was loaded into the reactor. The weight is based on the approximate quantity required to fill the reactor volume. The packing density for catalyst supported on Davisil 645, Merck Grade 7734 and Hyperion CS-02C-063 supports were typically 0.46 g/mL ±10%. The catalyst was placed in the reactor system, and reduced *in situ* at atmospheric pressure. The reactor was cooled after catalyst reduction, and the desired syngas feed rate and pressure were established.

The reactors containing the carbon-supported catalysts were heated slowly at to 240°C at 1200 psig and the nominal gas hourly space velocity (GHSV) and gas composition shown in Table 2.1 and held that temperature for at least 24 hr to allow the catalyst to age. The product stream was directed through one of the cold traps during this time. After aging the catalyst, the product stream was redirected through the other cold trap for a period sufficient for at least 10 bed volumes of gas feed (based on the operating pressure and gas feed rate) to pass through the cold trap. This period of time provides a representative gas sample and a sufficiently large liquid sample for subsequent analysis. The operating conditions were recorded before sampling with two or more grab samples of product gas obtained and analyzed in a GC along with a feed gas sample and a calibration gas sample. The liquid recovered from the cold trap was weighed and, if two phases were present, separated into an aqueous phase and an organic phase. The weighed organic phase was typically not analyzed and was assumed to have a composition comparable to hexane for purposes of a carbon balance. The weighed aqueous phase was analyzed using a high-pressure liquid chromatograph (HPLC) to quantify the C_1–C_5 oxygenates, which principally were alcohols, carboxylic acids, aldehydes, esters, and any other products associated with significant peaks identified by the HPLC. After sampling, a new set of conditions (i.e., temperature and feed rate) was established if desired, and another cold trap sample was collected at the new conditions. To calculate a representative average outlet flow rate during a sample collection period, a N_2 balance was used with the calibrated feed flow rates. The product gas flow rate downstream of the cold trap was monitored and recorded for use in estimating the product gas flow rate and to provide a rough check on the accuracy of the calculated flow using a N_2 balance. Carbon balances, measured using this method, were usually within approximately ±6%.

In the case of the carbon-supported catalysts, the temperature was increased in increments of 10°C to 260°C, which was the temperature used for the long-term tests. The silica-supported catalyst was handled in a similar manner, except that it was initially heated to 250°C using a feed gas mixture containing a 2:1 H_2:CO ratio with 4% N_2 and 4% CO_2 in the feed gas stream, and then held there for at least 24 hr to as a break-in period. The catalyst bed temperature was then increased in steps to 260°C, 265°C, and finally 275°C with sampling at each step before adjusting to feed gas to the same as that used in the tests with the carbon-supported catalysts (1.3:1 H_2:CO ratio).

3.0 Test Results

Table 3.1 summarizes the test conditions used during the long-term testing portion of each test. The reported catalyst time on-stream was based on the time that each catalyst was at the testing temperature and using the feed gas mixture with a 1.3:1.0 H_2:CO ratio. During testing with all of the catalysts, the CO conversion, C_2+ oxygenate STY and selectivity parameters were monitored for catalyst performance, with samples taken every two or three days.

Table 3.1. Summary of Test Conditions Used in Each Test

Catalyst Label	H-A	T-A	S-A
Pressure	1200 psig	1200 psig	1200 psig
Gas Composition[(a)]	1.3:1.0 H_2:CO Ratio with 3.4% N_2 and 3.4% CO_2	1.3:1.0 H_2:CO Ratio with 3.4% N_2, and 3.4% CO_2	1.3:1.0 H_2:CO Ratio with 3.4% N_2 and 3.4% CO_2
GHSV	13,000 L/kg_{cat}/hr	13,000 L/kg_{cat}/hr	13,000 L/kg_{cat}/hr
Time on line before Long-Term Test	267 hr	218hr	193hr
Total Time at Long-Term Test Conditions	2372 hr	650 hr	668 hr

(a) The nominal feed gas was achieved by mixing a measured flowrate of a gas mixture containing a 2:1 H_2:CO ratio with 4% N_2 and 4% CO_2, with a separate flowrate of 100% CO to achieve the desired 1.3:1 H_2:CO ratio. There were periods when the mixture was achieved by mixing separate flowrates of pure CO, pure H_2, and pure N_2 at rates to achieve a 1.3:1 H_2:CO ratio with 8% N_2.

Following completion of the long-term test with catalyst H-A, the temperature of the catalyst was increased to 265°C and maintained there for an additional 505 hr, and then to 270°C for an additional 574 hr to provide an indication of the catalyst performance at higher temperatures that would be required to restore catalyst activity that was lost during the long-term test.

3.1 Long-Term Tests with Carbon Nanotube-Supported Catalysts

Figure 3.1 shows the trends in the CO conversion, C_2+ oxygenate STY and converted CO selectivity to C_2+ oxygenates for all tests conducted at a constant temperature for catalyst H-A, the catalyst supported on Hyperion CS-02C-063-XD. Catalyst H-A was tested for 2372 hr at the design conditions. Table 3.2 provides a summary of the catalyst performance metrics over the test periods run at 260°C. It can be seen that significant deactivation of the catalyst occurred over the course of the run as evidenced by decreases in the CO conversions and STYs. The data show that most of the decrease in both parameters occurred during the first 900 hr of operation, reaching values that were approximately the same as the time weighted averages calculated for these two parameters over the entire run (see Table 3.2). There was an apparent increase of about 1% in the converted CO selectivity to C_2+ oxygenates, which indicates that this parameter was very stable over the course of the test. Furthermore, the catalyst had similar selectivities during startup when the catalyst temperatures were maintained at 240°C and 250°C, suggesting that the catalyst selectivity was not particularly sensitive to the catalyst temperature, at least over the range evaluated.

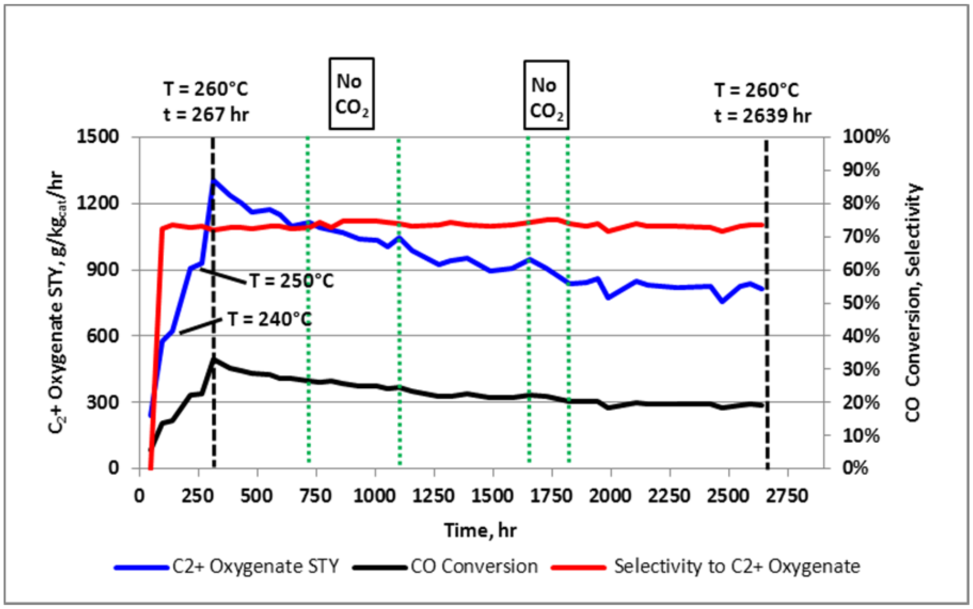

Figure 3.1. Performance of Catalyst H-A during a Long-Term Test at 260°C, 1200 psig and13,000 L/kg_{cat}/hr GHSV using a Feed Gas with a Nominal 1.3:1.0 H_2:CO ratio, with 3.4% CO_2 and 3.4% N_2

Table 3.2. Summary of Catalyst Performance during Long-Term Tests at Design Conditions for Catalyst H-A

Catalyst	Parameter	Initial Sample at Design Conditions	Final Sample at Design Conditions	Time Weighted Average
H-A	CO Conversion, %	33	19	23
	C_2+ STY, g/kg_{cat}/hr	1305	815	950
	Selectivity to C_2+ Oxygenates, %	72	73	73

During the test run, there were two instances when the feed gas mixtures were intentionally changed because of problems obtaining a supply of the mixed gas containing H_2 and CO in a 2:1 H_2:CO molar ratio and containing 4% N_2 and 4% CO_2. This occurred between 722 and 1103 total hr of operation (including time during startup at lower temperatures) and again between 1653 and 1822 total hr of operation. During these periods, a gas mixture containing 1.3:1 H_2:CO ratio to a gas mixture with 8% N_2 was obtained by mixing separate gas streams of pure CO, H_2, and N_2. Changes in CO conversion, C_2+ oxygenate STY, or converted CO selectivity to C_2+ oxygenates appear to be very small, or nonexistent, for the catalyst during these periods.

There also were three instances at 1154, 2330, and 2336 total hr of operation for catalyst H-A when the flow of the syngas mixture was lost, leaving a much smaller flow of pure CO through the reactor. There was one instance when the flow of pure CO increased about 17-fold, while the flow of the syngas mixture remained constant. This resulted in a feed gas composition with a 0.23:1 H_2:CO ratio, with approximately 1% N_2 and 1% CO_2, and a total gas GHSV that was approximately three times greater than that specified for the run. Gas and liquid samples were not collected under these conditions because they would not represent performance at the specified conditions. However, there is no evidence that the disruptions affected these performance parameters, once the specified conditions were restored.

Overall, the long-term performance of catalyst H-A is considerably better than that achieved using a baseline catalyst containing of 11.7% Rh, 3.57% Mn, and 2.17% Ir, with the same support, as described in the Appendix. That catalyst was tested under similar conditions except for the feed gas, which was only syngas with a 2:1 H_2:CO ratio with 4% CO_2 and 4% N_2. The selectivity to C_2+ oxygenates of the baseline catalyst in that test ranged from 51% at the beginning of testing at its design conditions (123 hr of total testing) to 56% after an additional 1550 hr of testing at those conditions. This selectivity level is significantly lower than the average 73% selectivity with catalyst H-A during testing at its design conditions. Only a couple percent of the improved selectivity for catalyst H-A is attributed to the lower H_2:CO ratio in the feed gas used with the latter catalyst. Catalyst H-A also maintained a much higher C_2+ oxygenate STY, decreasing from 1305 to 815 $g/kg_{cat}/hr$ over approximately 2300 hr of testing compared to the baseline catalyst, that increased from 615 to 723 $g/kg_{cat}/hr$ over a 1550 hr period. This improvement is particularly noteworthy, because the Rh, and the Rh plus Ir metal loadings were lower in catalyst H-A, and the lower 1.5:1 H_2:CO ratio used with the latter catalyst would be expected to produce significantly lower STYs (on the order of 30% lower) than what would be achieved with the higher 2:1 ratio used with the baseline test. One notable difference between the two catalysts is the significant improvement in the both the C_{2+} oxygenate STY and selectivity over 1550 hr of testing at the design conditions, compared to a constant selectivity, but a declining STY for catalyst H-A. These differences in behaviors are believed to be attributable to slow changes in the catalyst particle surfaces over time, starting from distinctly different initial compositions due to their different gross metal concentration differences.

3.2 Performance Details with Catalyst H-A

Figure 3.2 provides a gross breakdown of the converted CO selectivity for catalyst H-A to oxygenate and hydrocarbon products for selected samples spaced approximately 500 hr apart and including the first and last set of samples. No liquid hydrocarbons were produced during the test. It appears that there was very little change in the selectivity to hydrocarbons over the duration of the test at 260°C. However, there was a very distinct change in the selectivity to the C_2+ alcohols and the other C_2+ oxygenates, with a greater selectivity to the C_2+ alcohols at the expense of the other oxygenates over time.

Figure 3.3 provides a breakdown of the oxygenate product STY by species, for catalyst H-A, for selected samples spaced approximately 500 hours apart and including the first and last set of samples. The other oxygenates consist almost exclusively of C_3 and C_4 aldehydes. It can be seen that after the first 500 hours of testing at 260°C, the ethanol STY remains nearly constant, with progressively less production of the other oxygenates.

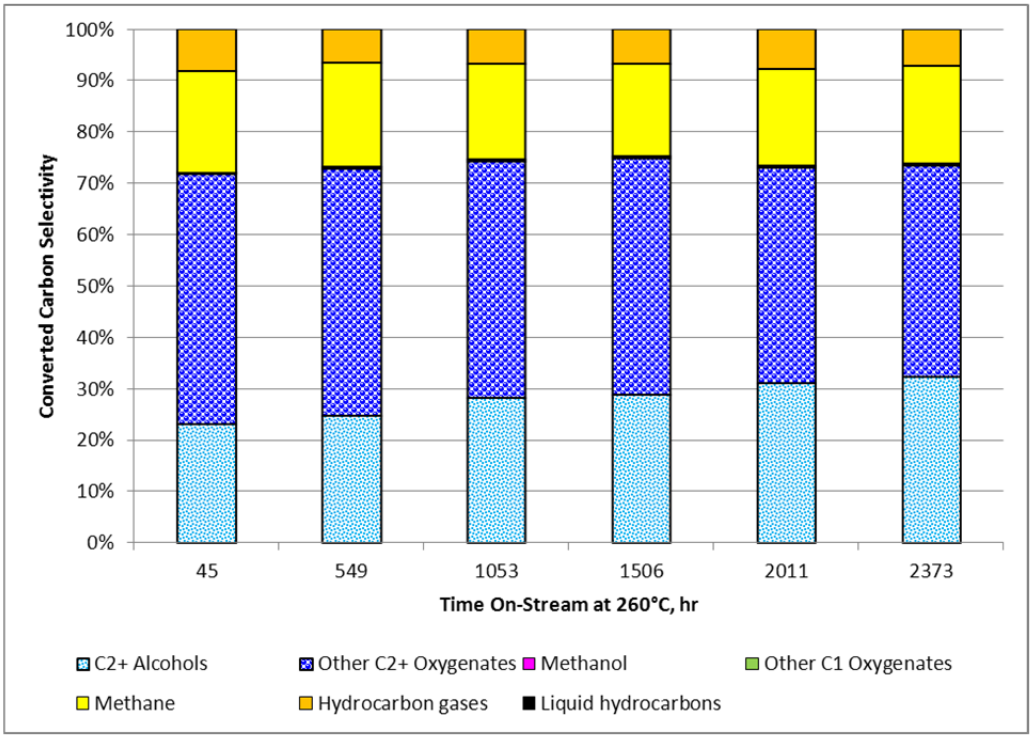

Figure 3.2. Converted CO Selectivity for Catalyst H-A to Different Classes of Products for Selected Times On-Stream at 260°C

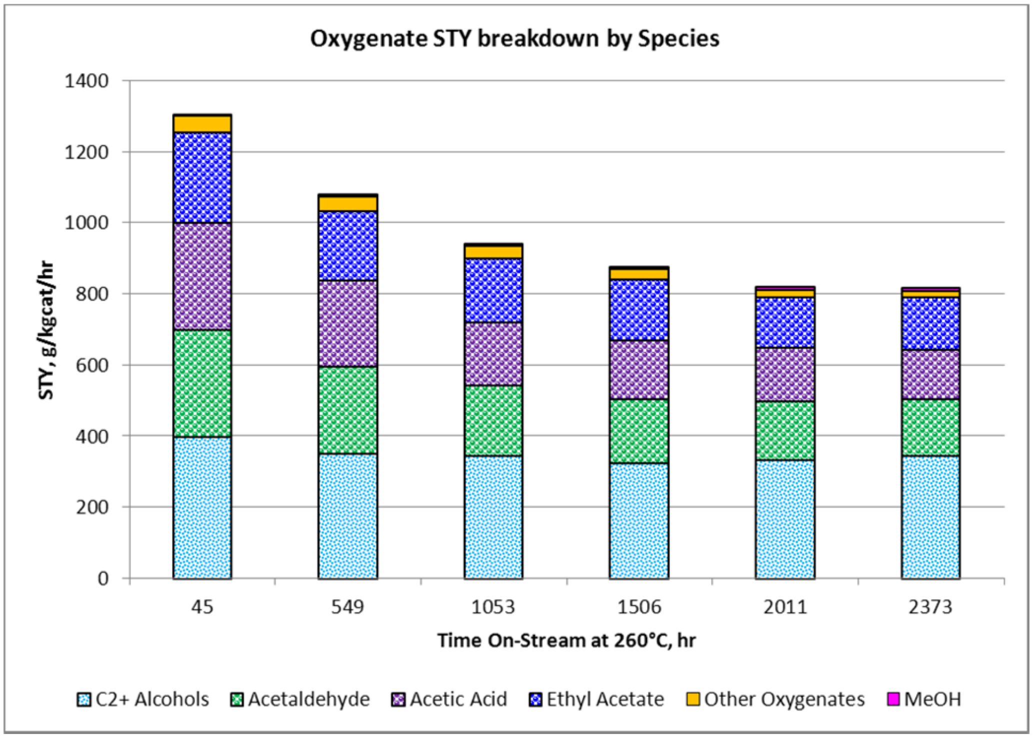

Figure 3.3. Breakdown of the Oxygenate STY by Species at Selected Points of Times On-Stream of Testing at 260°C for Catalyst H-A

Figure 3.4 shows the corresponding carbon distribution among the oxygenate classes (normalized to 100%) for catalyst H-A. The selectivity to C_2+ alcohols increased from about 32% of the total oxygenate carbon at the beginning of the test at 260°C to about 44% at the end of the testing period at that temperature. This was achieved with decreases in the carbon distribution to all of the other classes of C_2+ oxygenates, although it appears that there was very little change in selectivity to the different species during the last 362 hr of testing. Higher alcohols accounted for about 17% of the C_2+ alcohols at the beginning of the test and about 8% at the end of the test. Methanol accounted for less than 1% over the entire period.

Figure 3.5 shows the carbon distribution among the hydrocarbon products for catalyst H-A. From 1053 hr of testing at the design conditions and beyond, there appeared to be very little change in any of the hydrocarbon species, which would be consistent with the catalyst becoming more stable after that point in testing.

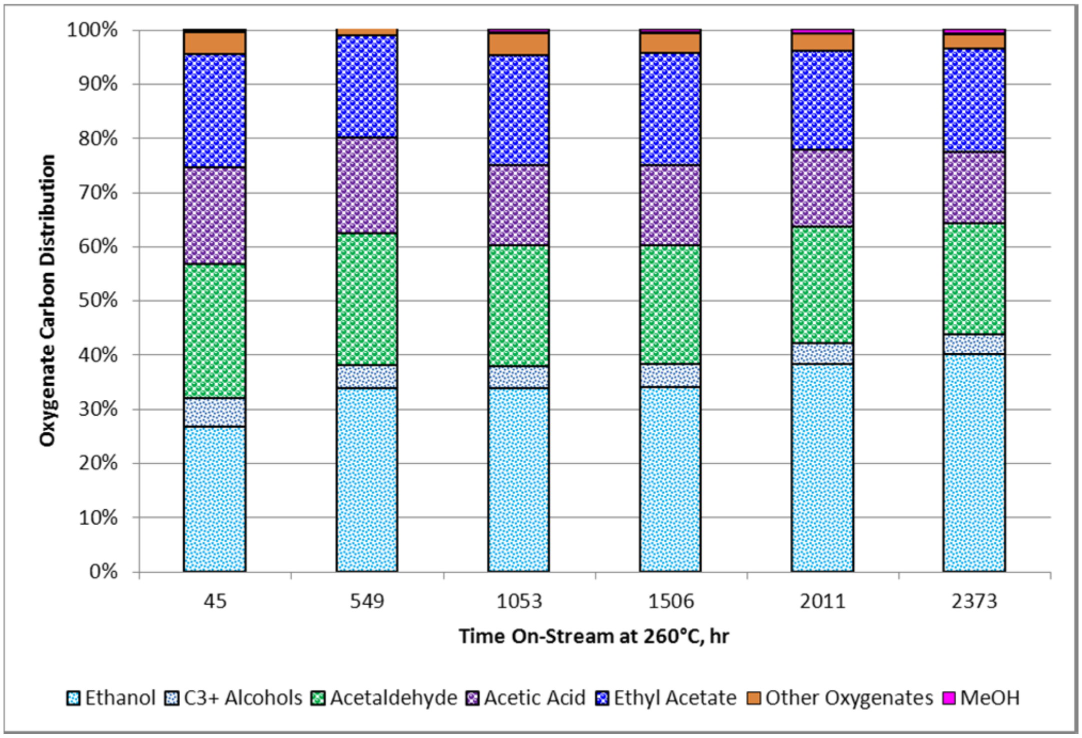

Figure 3.4. Carbon Distribution among Various Oxygenate Species at Selected Times On-Stream at 260°C for Catalyst H-A

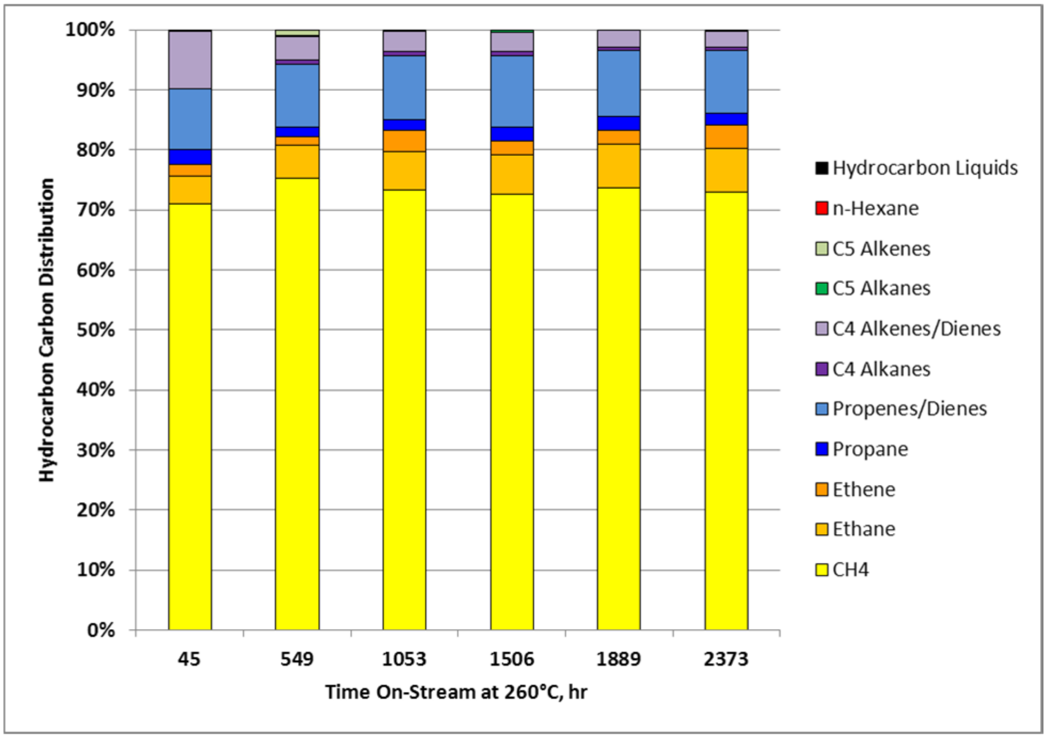

Figure 3.5. Carbon Selectivity among Various Hydrocarbon Product Species at Selected Times On-Stream at 260°C for Catalyst H-A

Following the completion of the long-term test for catalyst H-A at the design temperature of 260°C, the temperature was increased to 265°C and maintained there for 505 hr and then increased to 270°C for an additional 574 hr to determine the effect of increasing the temperature to restore the catalyst CO conversion and STY. Table 3.3 summarizes the values for CO conversion, C_2+ oxygenate STY and converted CO selectivity to C_2+ oxygenates from samples taken at the start and end of each period at these temperatures. Figure 3.6 shows the effect of the temperature over time on the trends in these parameters for the catalyst. The decreases in CO conversion and selectivity to C_2+ oxygenates over the 505 hr of operation were very small and possibly not significant over that period. The change in the C_2+ oxygenate STY was more measureable decreasing by about 2% over the period.

Table 3.3. Summary of Catalyst Performance during Short Duration Tests at 265°C and 270°C Conditions for Catalyst H-A

Temperature/Time at Temperature	Parameter	Initial Sample at Design Conditions	Final Sample at Design Conditions	Average	Standard Deviation
265°C/505 hr	CO Conversion, %	23	23	23	0.4
	C_2+ STY, $g/kg_{cat}/hr$	950	924	960	22$^{(a)}$
	Selectivity to C_2+ Oxygenates, %	72	71	72	0.6
270°C	CO Conversion, %	29	26	27	0.9
	C_2+ STY, $g/kg_{cat}/hr$	1165	1077	1114	35
	Selectivity to C_2+ Oxygenates, %	72	72	71	0.5

(a)Approximately 2% of average STY

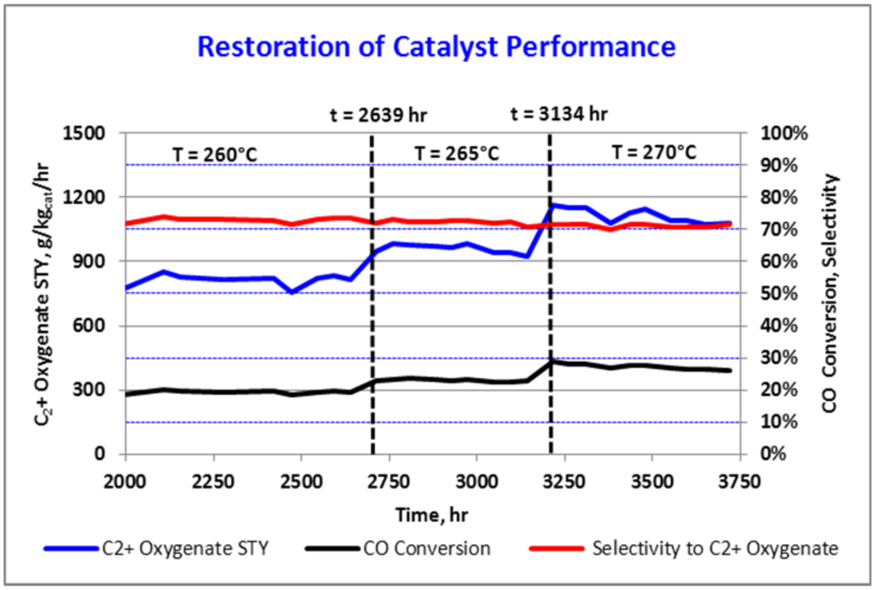

Figure 3.6. Effect of Increasing Temperature on Catalyst Performance

Figure 3.7, Figure 3.8, Figure 3.9, and Figure 3.10 provide additional detail on the STY and selectivity to various products at the beginning and end of each period at the two elevated temperatures. Figure 3.7 shows that there was a small but measurable decrease in the selectivity to the C_2+ oxygenates (alcohols and other oxygenates) with an increase in the operating temperature. This appears to be accompanied by a corresponding decrease in the selectivities to C_2+ oxygenates, with the selectivity to methane remaining relatively constant. Figure 3.8 shows a more detailed breakdown in the C_2+ oxygenated STY by product class, while Figure 3.9 shows the effect of the temperature increases on the carbon distribution among the different oxygenate classes. It can be seen that much of the STY increase can be attributed to an increase in the C_2+ alcohol STY. The sum of the carbon distributions to C_2+ alcohols and acetaldehyde remains relatively constant, suggesting additional production of ethanol at the expense of acetaldehyde. On the other hand, there is a similar increase in the carbon distribution to ethyl acetate at the expense of acetic acid. This would imply that some of the ethanol product is reacting with more of the acetic acid to produce ethyl acetate, and could indicate an equilibrium effect between the three species at the higher temperatures.

Figure 3.10 shows the effect of the operating temperature on the carbon distribution among the different hydrocarbon gas species. Because of the scatter in the carbon distribution data for methane, it is difficult to form any firm conclusions. In general, there appears to be very small increase in the carbon distribution to propenes, butanes, and butenes.

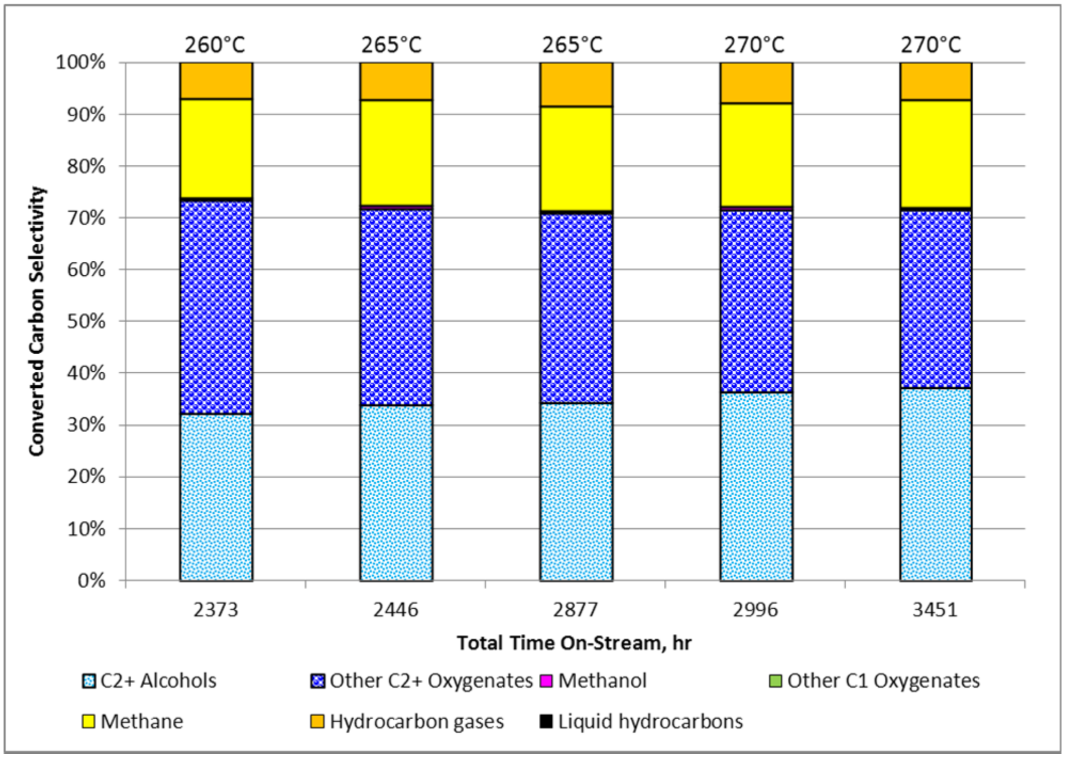

Figure 3.7. Effect of Increasing Temperature on Converted CO Selectivity to Different Product Classes

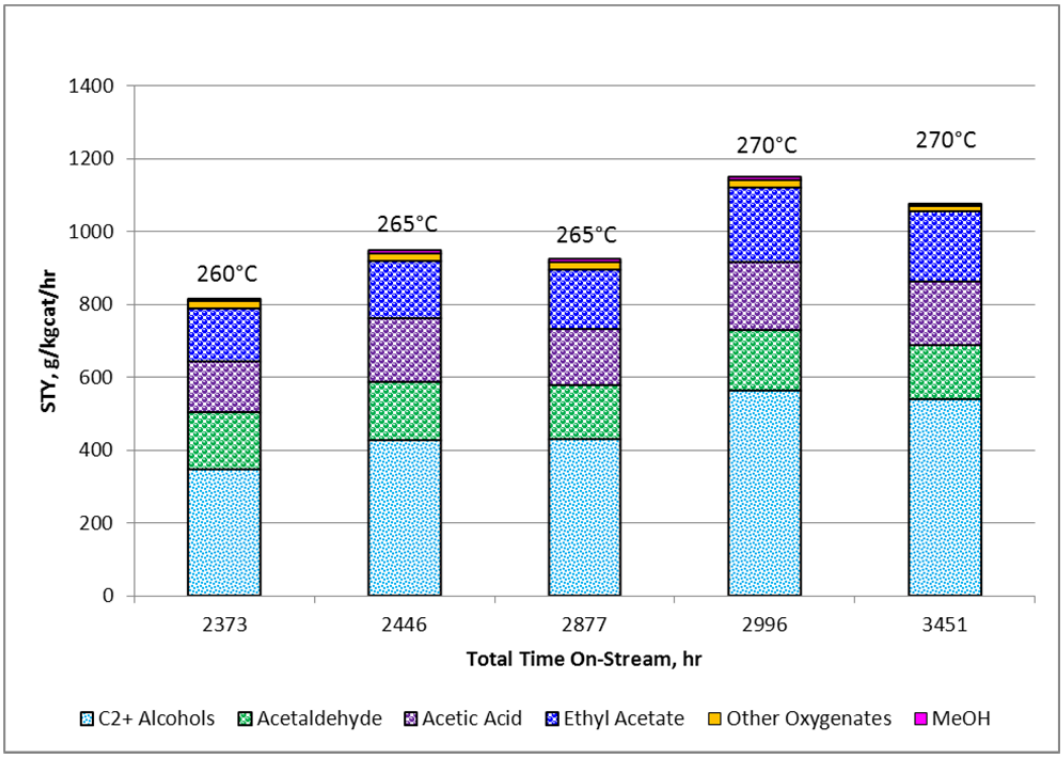

Figure 3.8. Effect of Increasing Temperature on the Breakdown of the Oxygenate STY by Species

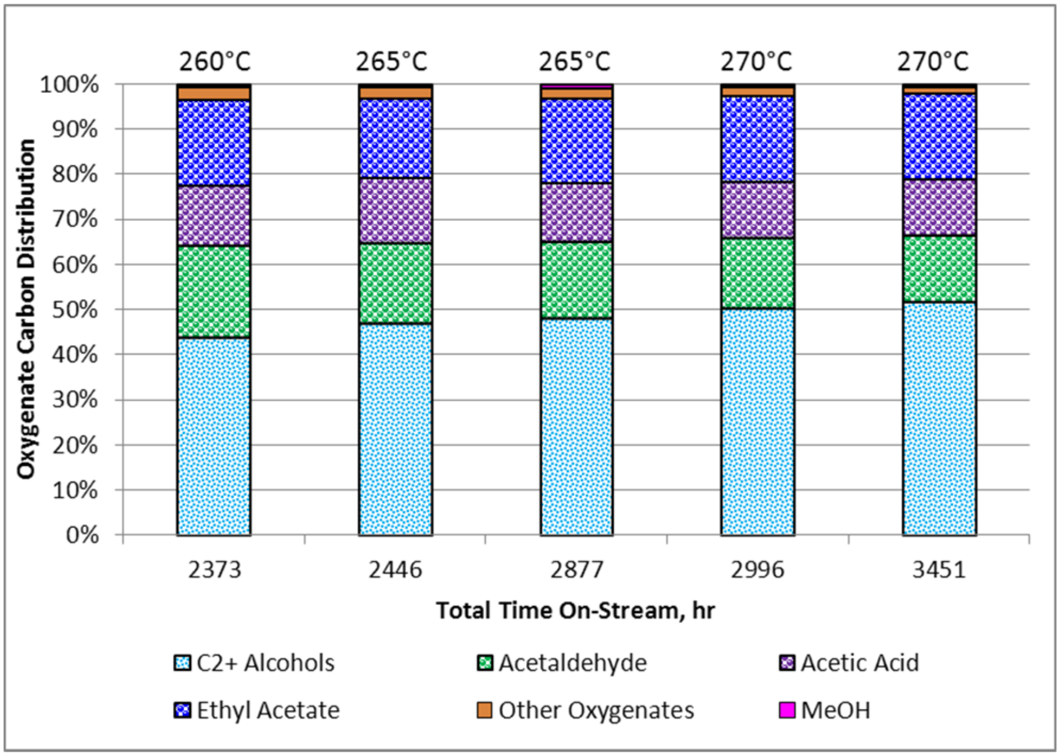

Figure 3.9. Effect of Increasing Temperature on Carbon Distribution among the Various Oxygenate Species

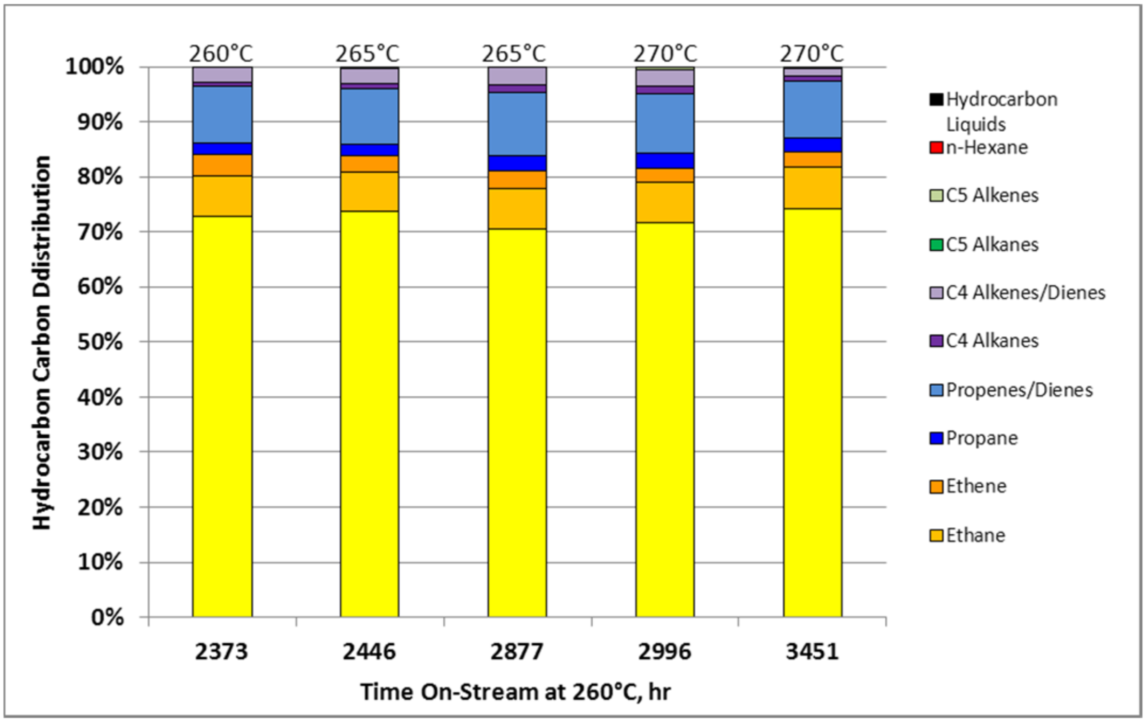

Figure 3.10. Effect of Temperature on the Carbon Distribution among the Various Hydrocarbon Product Species at Selected Times On-Stream at 260°C for Catalyst H-A

A best-fit analysis of the three parameters in Figure 3.6 was performed using Microsoft Excel trend-line analysis of the graphical data to estimate their rates of change during the tests at the higher temperatures. For comparison, a similar analysis was performed on the data during the test at 260°C, selecting portions of the testing period where the STYs were similar to those initially observed at the higher testing temperatures. Table 3.4 tabulates the results of this analysis. Figure 3.11 shows how the STY deactivation rates correlate with the average STYs for the different time and temperature intervals evaluated.

It appears that the deactivation rate of the catalyst with respect to either the CO conversion or the C_2+ oxygenate STY is at least roughly correlated to the value of either parameter. In the case of the rate of STY decline as shown in Figure 3.11, decreased almost linearly with the STY at 260°C, approaching a projected rate of zero at a STY of about 775 $g/kg_{cat}/hr$. Examination of the rates of decline of the STYs at 265°C and 270°C, relative to the earlier rates of decline at comparable STYs when tested at 260°C, suggest that the catalyst may also be approaching an equilibrium value over time. This would indicate that the apparent linear behavior between the STY and its rate of change is likely due to both the time at the reactor temperature as it approaches equilibrium and a likely decline in the temperature of individual catalyst metal clusters within the catalyst as the reaction rates decline with over time at a constant temperature.

Using the results in Figure 3.11, if the catalyst had started at a lower design temperature that produced a STY of about 800 g/kg/cat/hr, it is reasonable to suggest that the initial rate of decline in the STY would have been close to zero, requiring considerably less frequent adjustments in the catalyst bed temperature to maintain the STY rate. Examination of Figure 3.11 shows that the STYs measured at catalyst bed temperatures during the start of the testing were about 600 $g/kg_{cat}/hr$ at 240°C and 900 $g/kg_{cat}/hr$ at 250°C. This indicates that a starting temperature between 245°C and 250°C would achieve a starting STY of approximately 800 $g/kg_{cat}/hr$. The corresponding selectivities to C_2+ oxygenates at these temperatures, would be nearly 73% according to this figure.

There does not appear to be a similar correlation with the selectivity to C_2+ oxygenates because the catalyst is irreversibly changing over time with respect to the product slate, with the overall selectivity to C_2+ oxygenates appearing to increase during the first 1450 hr of operation at 260°C and then very slowly decreasing thereafter. Increasing the operating temperature does not restore the selectivity, but may, in fact be decreasing it slightly. However, the rate of that decrease appears to increase by a factor of about 15. If this is the case then there is some concern that continued operation by increasing the temperature to maintain a higher STY of approximately 950 $g/kg_{cat}/hr$ could ultimately result in an unacceptably low selectivity to the C_2+ oxygenates after a year or more of continuous operation. Alternatively, however, it may more practical to initially operate the catalyst at about 245°C to obtain an initial STY of about 800 $g/kg_{cat}/hr$ (see first and second plateau in the STY in Figure 3.12 during catalyst break-in at 240°C and 250°C [STYs of ~ 600 $g/kg_{cat}/hr$, and ~900 $g/kg_{cat}/hr$, respectively] prior to initiating testing at 260°C). By operating at a 15°C lower initial operating condition, the rate of change of the all three parameters will be significantly reduced consistent with their rate of change at the end of testing at 260°C in the test with catalyst H-A. With lower rates of change in the STY and the lower initial operating temperature, it should be possible to maintain the STY at 800 $g/kg_{cat}/hr$ for a year or more without increasing the temperature more than 5 to 10°C over time.

Table 3.4. Comparison of Parameter Changes over Time for Catalyst H-A at Selected Times and Test Conditions Based on Determining the Best-Fit Linear Curves (Microsoft Excel trend-line analysis)

		Average for Period			Change/1000 hr		
Temperature °C	Time period in Test at Temperature hr	CO Conversion %	STY g/kg$_{cat}$/hr	Selectivity to C_2+ Oxygenates %	CO Conversion %	C_2+ Oxygenate STY g/kg$_{cat}$/hr	Selectivity to C_2+ Oxygenates %
260	0 – 500	26.8	1110	73.4	-8	-292	4
260	837 – 1459	22.1	930	73.8	-2	-88	3
260	1840 – 2373	19.3	815	73	-0.8	-13	-0.2
265	0 – 505	23.0	960	72.2	-2	-89	-3
270	0 – 573	27.3	1115	71.2	-5	-172	-0.7

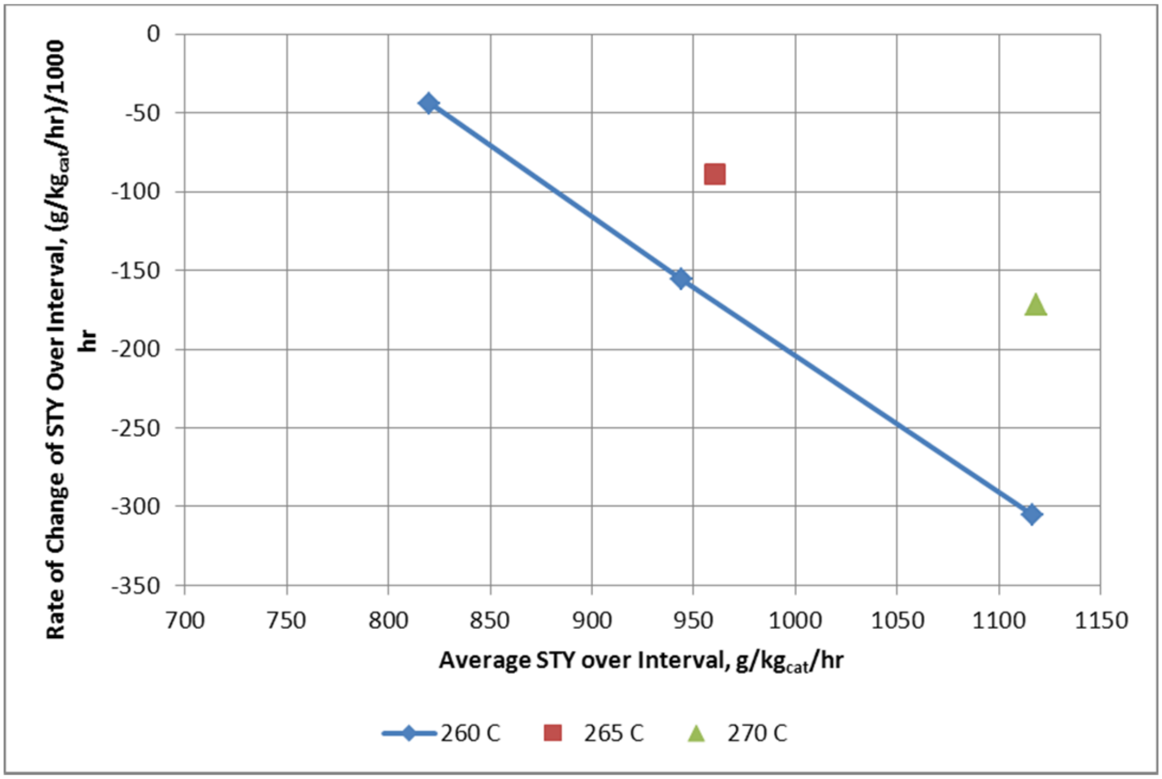

Figure 3.11. Correlation between the Average STYs and the Rate of Change for Catalyst for Different Time Intervals and Temperatures

3.3 Long-Term Test with Catalyst Supported on a High-Surface-Area Graphitic Carbon

Catalyst T-A was similar to catalyst H-A except that it was supported on high surface-area-graphitic carbon instead of the Hyperion carbon nanotube support. Catalyst T-A was only tested for 650 hr at the design conditions to provide an indication of the potential for utilizing an alternative carbon support on catalyst performance. This catalyst used the same metal composition as catalyst H-A, but utilized a high-surface-area graphite (Timcal Timrex HSAG300) instead of a carbon nanotube (Hyperion CS-02C-063-XD) as the support. The graphite-supported catalyst was never specifically optimized to this composition. However, earlier tests with catalysts with the same metal compositions (11.7% Rh, 3.6% Mn, and 2.2% Ir) on these two supports showed the graphite-supported catalyst to have comparable selectivity to C_2+ oxygenates, and a higher C_2+ oxygenate STY(Gerber 2012b).

Table 3.5 and Figure 3.12 provide summaries of catalyst performance over the time period at the design conditions. It can be seen that catalyst T-A was less active than the H-A catalyst but was much more stable, over a comparable period of operation. It experienced only a 5% decrease in the STY and a 9% decrease in the CO conversion over 650 hr of operation at 260°C, whereas catalyst H-A experienced 20% and 25% declines, respectively, over the same operating period. The selectivity of catalyst T-A also was very stable at approximately 70% after the first 100 hr at the design temperature. As with catalyst H-A, this catalyst had similar selectivities during startup when the catalyst temperatures were maintained at 240°C and 250°C, again suggesting that the catalyst selectivity for catalyst T-A was not particularly sensitive to the catalyst temperature, at least over the range evaluated.

Table 3.5. Summary of Catalyst Performance during Long-Term Tests at Design Conditions for Catalyst T-A

Catalyst	Parameter	Initial Sample at Design Conditions	Final Sample at Design Conditions	Time Weighted Average	Rate of Parameter Change/1000 hr
T-A	CO Conversion, %	24	22	23	-3.7
	C_2+ STY, g/kg$_{cat}$/hr	890	845	865	-64
	Selectivity to C_2+ Oxygenates, %	67	71	69	5.1

The rate of decline of catalyst T-A over the testing period was approximately -64 (g/kg$_{cat}$/hr)/(1000 hr) at an average 865 g/kg$_{cat}$/hr STY. This compares favorably with the rate of decline of catalyst H-A (Table 3.5) over the time period from 837 to 1439 hr (rate decline of about [88 g/kg$_{cat}$/hr]/[1000 hr]) where its average STY was 930 g/kg$_{cat}$/hr. This suggests, again, that the rate of STY decline for both carbon-supported catalysts is related at least in part to the STY when operating at a nominal 260°C.

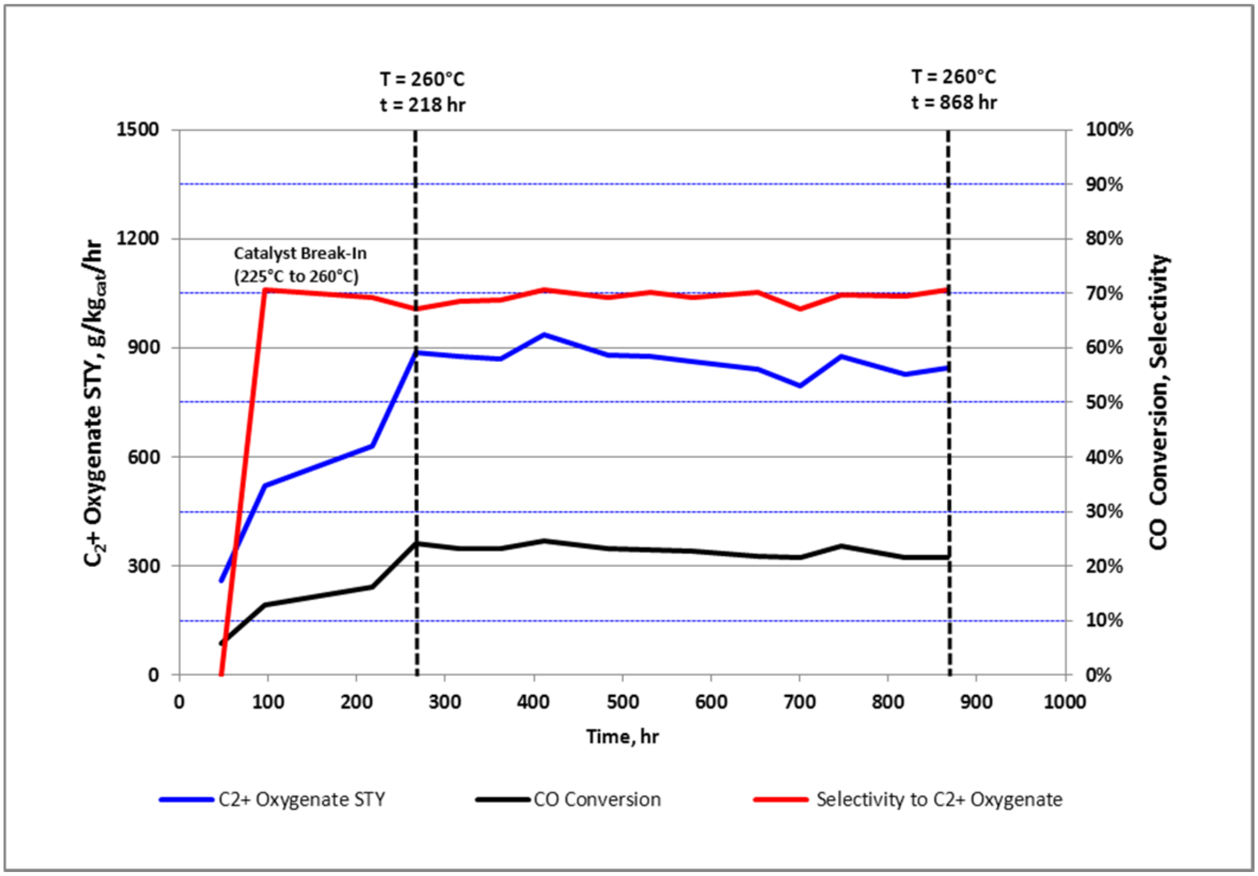

Figure 3.12. Performance of Catalyst T-A during a Long-Term Test at 260°C, 1200 psig and a 13,000 L/kg_{cat}/hr GHSV using a Feed Gas with a Nominal 1.3:1.0 H_2:CO Ratio, with 3.4% CO_2 and 3.4% N_2

3.4 Performance Details with Catalyst T-A

Figure 3.13, Figure 3.14, Figure 3.15, and Figure 3.16 provide additional detail on the STYs and selectivities to various products at the beginning and end of each period at the two elevated temperatures. Figure 3.13 shows that there was a small but measurable increase in the selectivity to the C_2+ oxygenates (alcohols and other oxygenates) over the testing period. This appears to be accompanied by a corresponding decrease in the selectivities to hydrocarbon liquids and the C_2+ hydrocarbon gases. The selectivity to methane, however, remained essentially unchanged. It is noteworthy that this catalyst produced significant quantities of hydrocarbon liquids while at 250°C (0.8% of converted CO) during the startup phase and during the first 49 hr of testing (2.1% of converted CO) at 260°C. This decreased immediately after 483 hr of testing when significant quantities of waxes (2.7% of converted CO) were recovered in the cold trap. Recovery of waxes in the cold trap continued over the remaining samples during the test but at declining amounts (0.6% of converted CO at 650 hr). The fact that hydrocarbon liquids were collected at the very beginning of the test and waxes were recovered at the end could suggest that the waxes also were produced early in the test but did not slough off of the walls of the cold trap to be recovered until late in the test. Thus, it is possible that hydrocarbon liquids and waxes were not produced in significant quantities after the first 49 hr of testing.

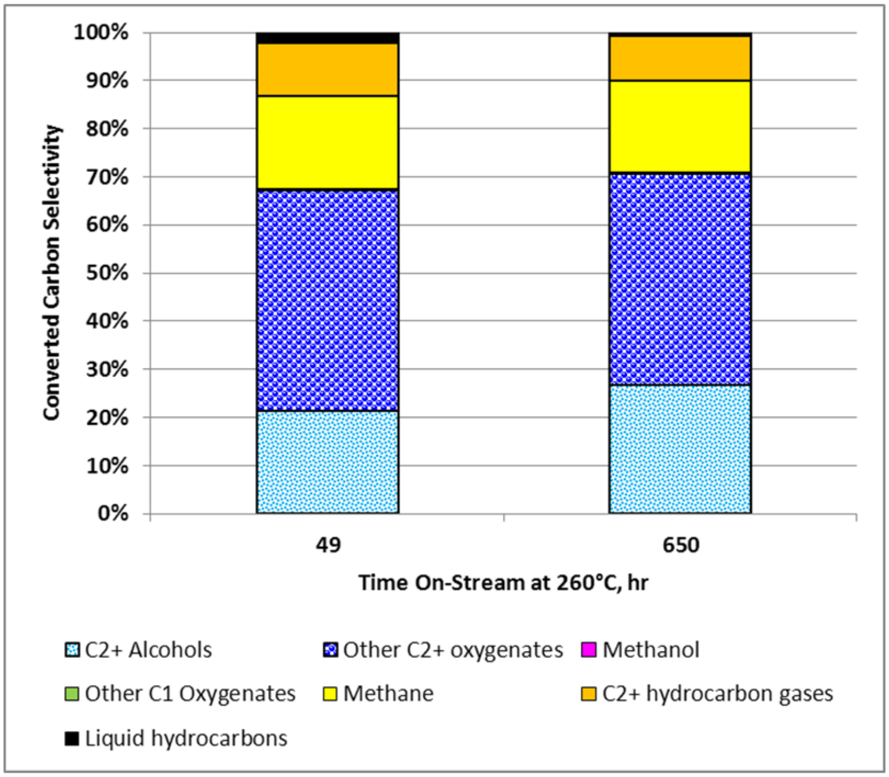

Figure 3.13. Converted CO Selectivity for Catalyst T-A to Different Product Classes at the Beginning and End of Testing at 260°C

Figure 3.14 shows a more detailed breakdown in the C_2+ oxygenated STY by product class. While the overall STY to C_2+ oxygenates decreased from about 890 g/kg_{cat}/hr to 865 g/kg_{cat}/hr over the testing period, the C_2+ alcohol STY increased from about 270 g/kg_{cat}/hr to 310 g/kg_{cat}/hr over that same period.

Figure 3.15 shows the corresponding carbon distributions among oxygenates (normalized to 100%) for catalyst T-A at the beginning and end of the test. The carbon distribution to ethanol increased from about 32% of the total oxygenate carbon at the beginning of the test at 260°C to about 38% at the end of the testing period at that temperature. This was achieved with decreases in the carbon distribution to acetic acid, acetaldehyde, and the other higher oxygenates that mainly consisted of propionaldehyde and butyraldehyde. Interestingly, there was a significant increase in the carbon distribution to ethyl acetate at the expense of acetic acid over the testing period. This could suggest that acetic acid and additional ethanol were reacting to produce additional ethyl acetate. Methanol accounted 0.5% or less over the testing period.

Figure 3.16 shows the carbon distribution among the different hydrocarbon gas species at the beginning and end of the test. The carbon distribution to methane appears to come mainly at the expense of the hydrocarbon liquids and to a lesser extent C_3+ hydrocarbon gases. There also appears to be a slight increase in selectivity to ethane. When considered with Figure 3.13, this behavior could suggest a general deactivation of the catalyst with respect to higher hydrocarbon production, leading to a greater production of C_2+ alcohols. There is no evidence of a reduced production of methane leading to methanol.

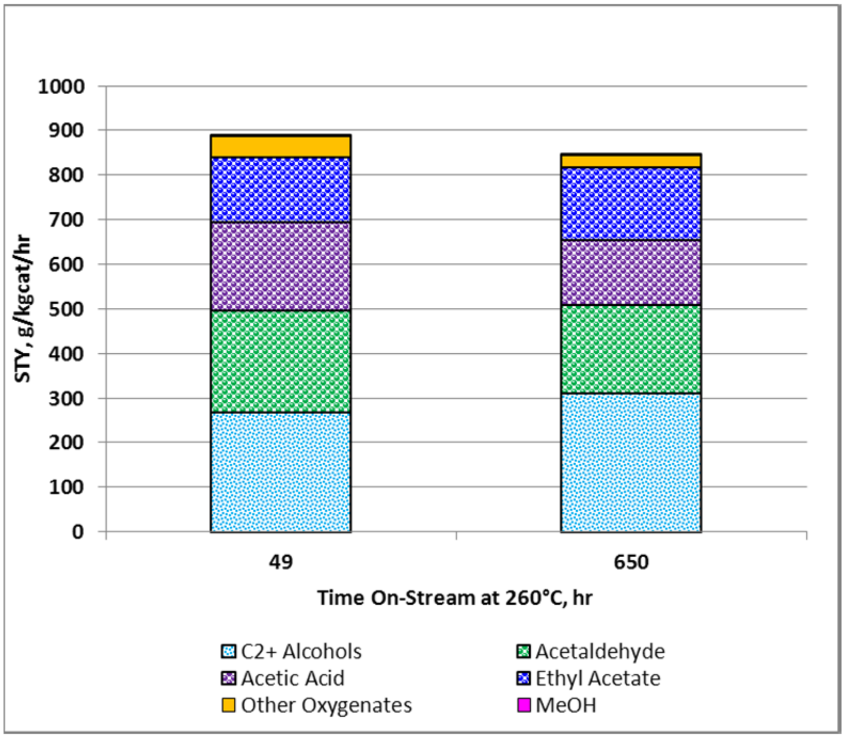

Figure 3.14. Breakdown of the Oxygenate STY by Species at the Beginning and End of Testing at 260°C for Catalyst T-A

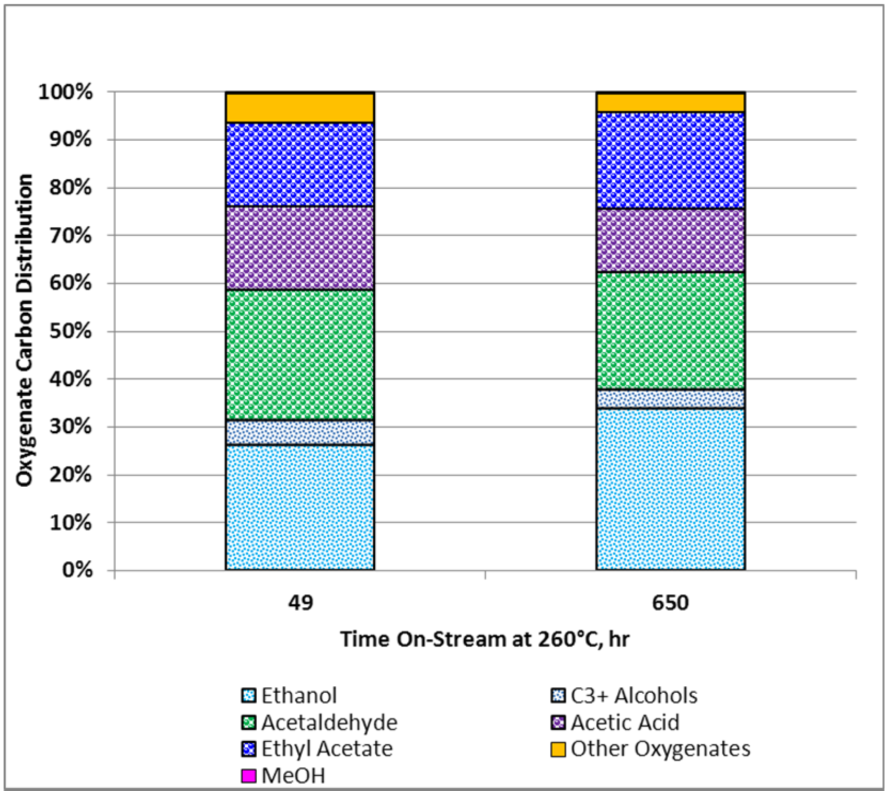

Figure 3.15. Carbon Distribution among the Various Oxygenate Species at the Beginning and End of Testing at 260°C for Catalyst T-A

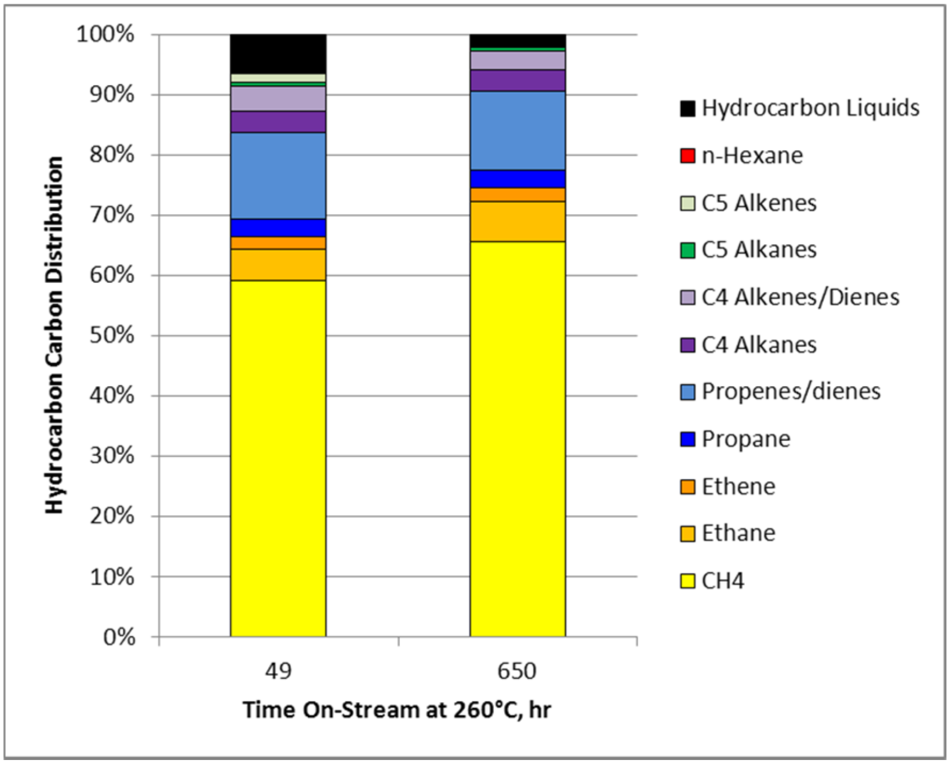

Figure 3.16. Effect of Temperature on Carbon Distribution among the Various Hydrocarbon Product Species at the Beginning and End of Testing at 260°C for Catalyst T-A

3.5 Long-Term Test with Catalyst Supported on Silica

While considerable testing was performed previously to optimize Rh, Mn, and Ir on silica supports, they were not amenable to significant increases in either Mn or Ir to improve the selectivity to C_2+ oxygenates. The selectivity was more responsive to the source of silica (Gerber 2012a, b).

The best performing silica-supported catalyst (catalyst S-A) contained 8.34% Rh, 2.53% Mn, and 1.54% Ir on Merck Grade 7734 silica gel. This catalyst was previously evaluated in a short-term test at 1200 psig, and a feed gas GHSV of 13,000 L/kg_{cat}/hr over a range of temperatures using a feed gas mixture containing a 2:1 H_2:CO ratio with 4% N_2 and 4% CO_2. The performance of this catalyst at three different temperatures (i.e., 250, 260, and 275°C) is shown in Table 3.6. During testing the catalyst was able to achieve a C_2+ oxygenate selectivity on the order of 70% and 68%, and corresponding STYs of 400 g/kg_{cat}/hr and 710 g/kg_{cat}/hr when tested at 260°C and 275°C, respectively.

Catalyst S-A used in the long-term test was from the same master batch of catalyst used in the previously discussed short-term test. This catalyst was initially started on the same feed gas composition used in the earlier test to ascertain how its performance compared to the earlier test. The performance of catalyst S-A at the different temperatures during the catalyst break-in period is shown in Figure 3.17 and summarized in Table 3.6. It can be seen that the catalyst used in the long-term test had a much lower activity and selectivity than that achieved in the short-term test. While disappointing, the behavior is not without precedence in earlier tests with silica-supported catalysts.

Table 3.6. Comparison of Catalyst S-A Performance in this Test during Startup and in an Earlier Test under Similar Testing Conditions

Catalyst	Parameter	250°C	260°C	275°C
This Test	CO Conversion, %	7.1	8.5	15.7
	C_2+ STY, g/kg$_{cat}$/hr	310	330	550
	Selectivity to C_2+ Oxygenates, %	58	65	61
Earlier Test	CO Conversion, %	9.7	13.5	24.7
	C_2+ STY, g/kg$_{cat}$/hr	300	400	710
	Selectivity to C_2+ Oxygenates, %	70	68	68

Test Conditions: 1,200 psig, 13,000 L/kg$_{cat}$/hr GHSV, feed gas with a nominal 2.0:1.0 H_2:CO ratio, with 3.4% CO_2 and 3.4% N_2.

Following catalyst break-in to 275°C, the gas mixture was switched to that used with catalysts H-A and T-A, and operated at the new conditions for 506 hrs. Catalyst performance during the long-term phase of testing is also shown in Figure 3.17 and summarized in Table 3.7.

Table 3.7. Summary of Catalyst Performance during Long-Term Tests at Design Conditions for Catalyst S-A

Catalyst	Parameter	Initial Sample at Design Conditions	Final Sample at Design Conditions	Time Weighted Average	Rate of Parameter Change/1000 hr
S-A	CO Conversion, %	11.7	12.2	12.2	0.30
	C_2+ STY, g/kg$_{cat}$/hr	430	422	424	-47
	Selectivity to C_2+ Oxygenates, %	63	60	60.8	-6

Test Conditions: 1,200 psig, 275°C, 13,000 L/kg$_{cat}$/hr GHSV, feed gas with a nominal 1.3:1.0 H_2:CO ratio, with 3.4% CO_2 and 3.4% N_2.

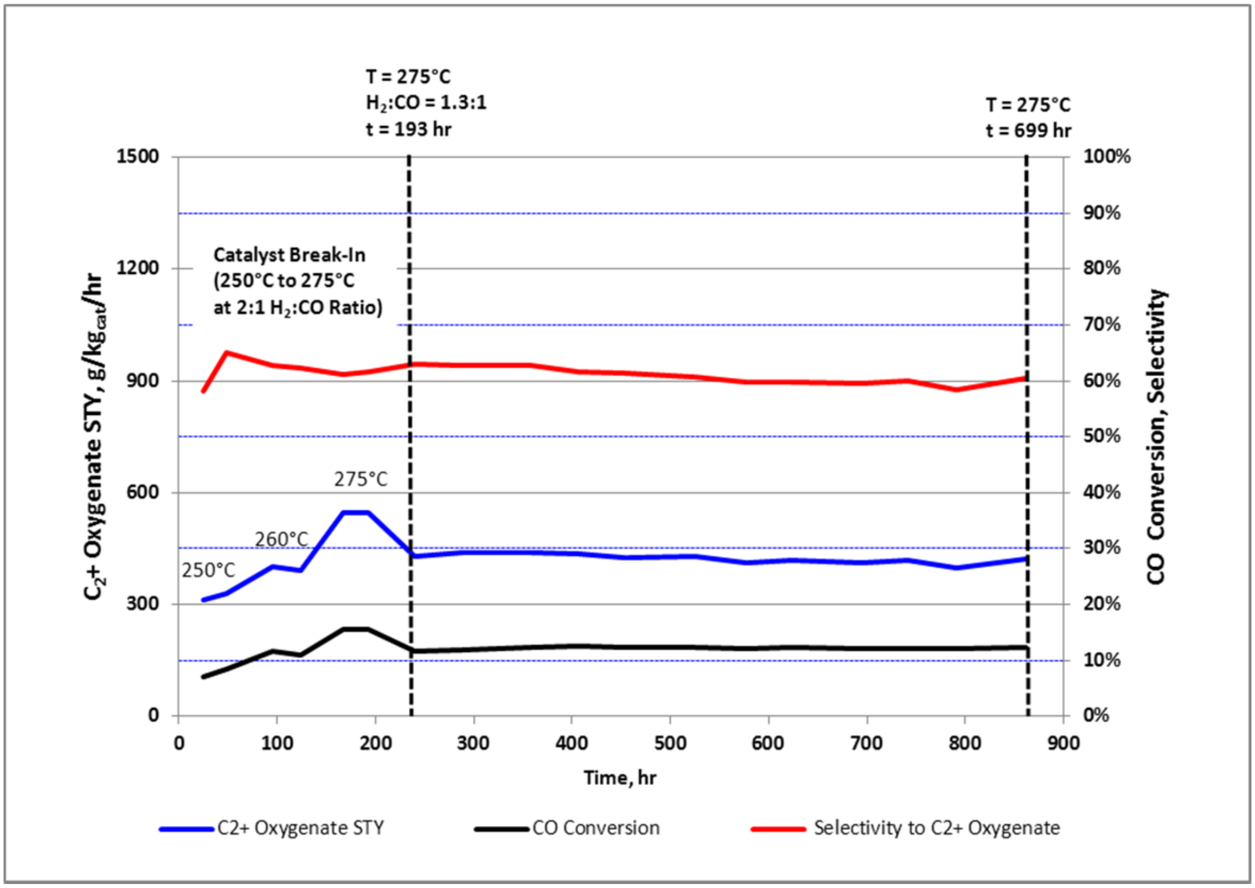

Figure 3.17. Performance of Catalyst S-A during a Long-Term Test at 260°C, 1200 psig, and a 13,000 L/kg_{cat}/hr GHSV using a Feed Gas with a Nominal 1.3:1.0 H_2:CO Ratio, with 3.4% CO_2 and 3.4% N_2

Reducing the H_2:CO ratio from 2.0 to 1.3, resulted in an immediate 28% decrease in the C_2+ oxygenate STY from 550 g/kg_{cat}/hr to 430 g/kg_{cat}/hr and a 25% decrease in CO conversion from 15.7% to 11.7%. These declines are attributed to the corresponding decrease in the H_2 partial pressure in the feed gas and are consistent with results from other tests that examined the effect of the H_2:CO ratio on the C_2+ STY and CO conversion. The selectivity to C_2+ oxygenates increased from 61% to 63% when the H_2:CO ratio was reduced, which is also consistent with earlier tests.

The rate of change of the C_2+ oxygenate STY over the period of testing were -47 (g/kg_{cat}/hr)/(1000 hr) and 6%/(1000 hr), which correspond to approximately 10%/1000 hr for both parameters. The CO conversion, on the other hand, remained essentially constant, which suggests that the decline in the STY is due to the decreased selectivity to C_2+ oxygenates rather than an overall decline in the catalyst activity as measured by CO conversion. Inspection of Figure 3.17 suggests that both the C_2+ oxygenate STY and selectivity may have begun to stabilize about halfway through the testing period at 275°C. However, the scatter in the data requires a longer period of testing to confirm this hypothesis.

3.6 Performance Details with Catalyst S-A

Figure 3.18, Figure 3.19, Figure 3.20, and Figure 3.21 provide additional details on the STYs and selectivities to various products at the beginning and end of the testing period at 275°C. Figure 3.18 shows that there was a small decrease selectivity to the C_2+ oxygenates (alcohols and other oxygenates) over the testing period (~3% according to Table 3.7). About two-thirds of this decrease is accounted for in the increase in selectivity to C_2+ hydrocarbons, while the remaining one-third is attributed to an increase in the selectivity to methane. The production of organic liquids first occurred when the H_2:CO ratio was decreased from 2.0:1 to 1.3:1 at 275°C. Selectivity to the organic liquids increased very slightly over the next 160 hr of testing and then remained relatively constant over the remainder of the test.

Figure 3.19 shows a more detailed breakdown in the C_2+ oxygenated STY by product class. While the overall STY to C_2+ oxygenates decreased slightly from about 430 g/kg_{cat}/hr to 422g/kg_{cat}/hr over the testing period, the C_2+ alcohol STY increased from about 50 g/kg_{cat}/hr to 100 g/kg_{cat}/hr over that same period. This was offset by decreases in acetaldehyde, acetic acid and the other C_2+ oxygenates which were mainly propionaldehyde, butyraldehyde, and methyl acetate.

Figure 3.20 shows the corresponding carbon distribution among the oxygenate classes (normalized to 100%) for catalyst S-A at the beginning and end of the test. The carbon distribution to ethanol increased from about 16% of the total oxygenate carbon at the beginning of the test at 260°C to about 20% at the end of the testing period at that temperature. The C_2+ alcohols also increased slightly over this period. This was mainly accompanied by decreases in the carbon distribution to acetaldehyde, propionaldehyde, and butyraldehyde. It is noteworthy that selectivity to ethanol on the silica-supported catalyst was much lower than that achieved on any of the carbon-supported catalysts. Methanol accounted 0.3% or less over the testing period.

Figure 3.21 shows the carbon distribution among the different hydrocarbon gas species at the beginning and end of the test. The slight decrease in the carbon distribution to methane appears to be offset by increases in the selectivity to hydrocarbon liquids and C_2, C_3, and C_4 olefins. There also appears to be a slight increase in selectivity to ethane. When considered along with the results in Figure 3.19 and Figure 3.20, it appears that the aldehydes are converting to alcohols and the alcohols are further converting to olefins. There is no evidence of a reduced production of methane leading to methanol.

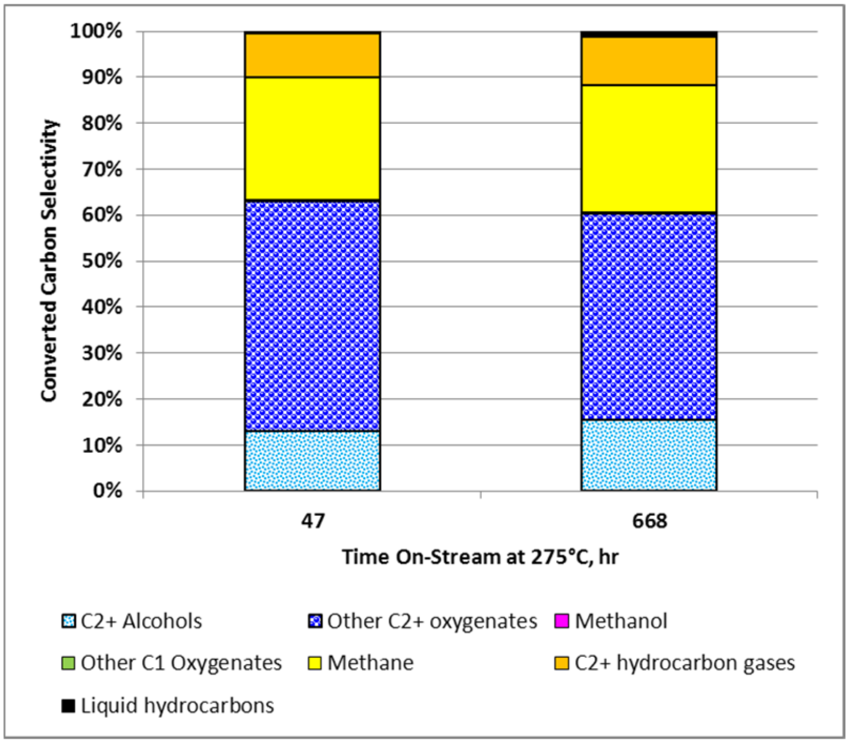

Figure 3.18. Converted CO Selectivity for Catalyst S-A to Different Product Classes at the Beginning and End of Testing at 260°C

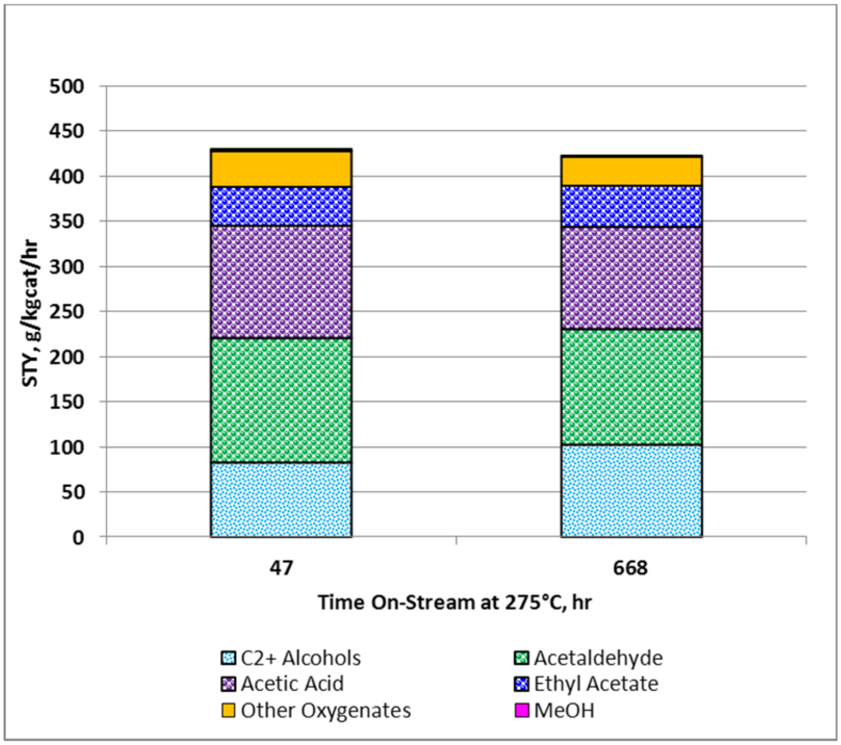

Figure 3.19. Breakdown of Oxygenate STYs by Species at the Beginning and End of Testing at 260°C for Catalyst S-A

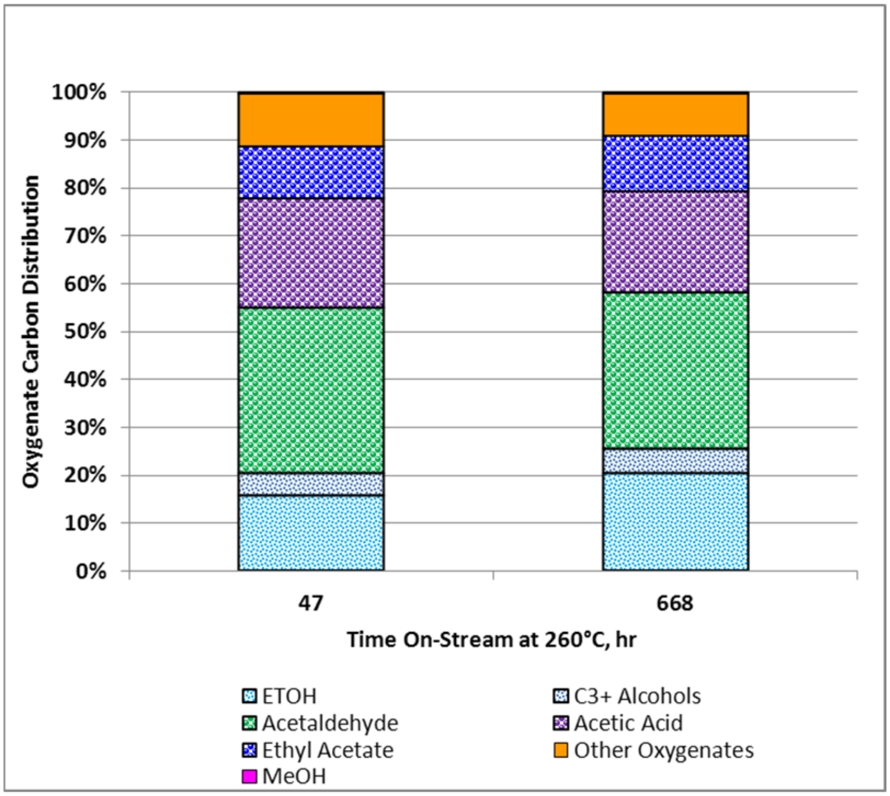

Figure 3.20. Carbon Selectivity among the Various Oxygenate Species at the Beginning and End of Testing at 260°C for Catalyst S-A

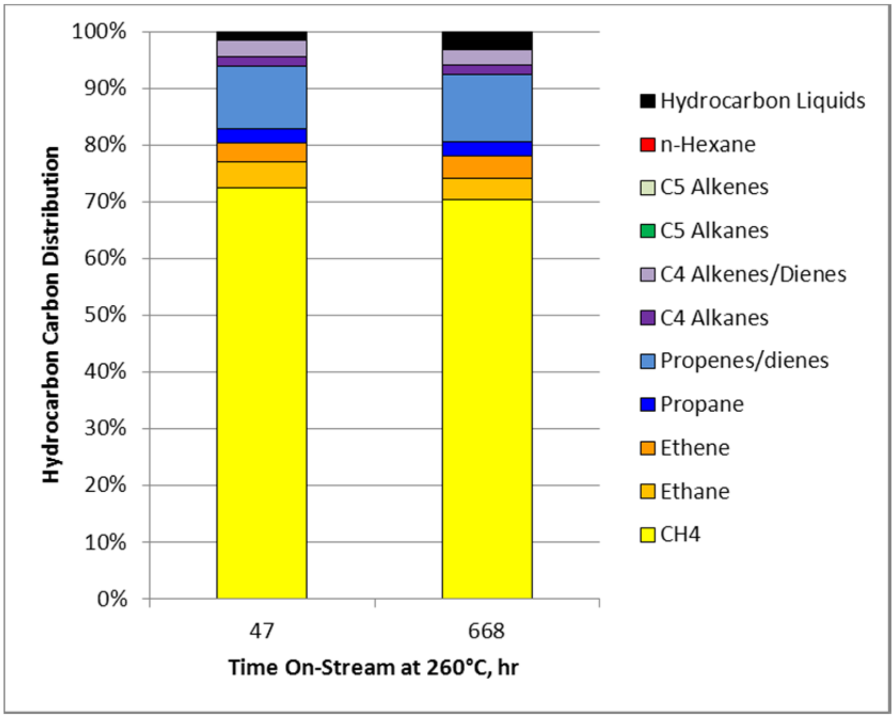

Figure 3.21. Effect of Temperature on Carbon Distribution among the Various Hydrocarbon Product Species at the Beginning and End of Testing at 260°C for Catalyst S-A

4.0 Conclusions

The long-term test performed with the best Rh-based catalyst developed to date (catalyst H-A) operated for 2373 hr at a constant set of conditions (nominally 1200 psig, 260°C, 13,000 L/kg_{cat}/hr GHSV using a feed gas containing 3.4% N_2 and 3.4% CO_2 with the balance being H_2 and CO in a 1.3:1 H_2:CO ratio). During the test, the CO conversion and C_2+ oxygenate STY decreased, but at a decreasing rate over the course of the test, while the selectivity to C_2+ oxygenates remained essentially unchanged at about 73%. It was noted that this selectivity also was achieved earlier at 240°C and 250°C during at the beginning of the test before the final 260°C temperature was set in the reactor for long-term evaluation of catalyst performance. An evaluation of the rate of decline in the STY at different points in the test suggested that the rate would approach zero once the STY reached a value of about 775 g/kg_{cat}/hr while operating at 260°C.

Subsequent testing at 265°C and 270°C, showed that the CO conversion and C_2+ oxygenate STY could be restored to higher values with only an approximate 1% decline in the selectivity. Furthermore, while the catalyst deactivated at higher rates at the higher temperatures, the rates of decline were significantly lower than those observed at comparable STYs at 260°C during the first phase of the test. This suggests that, if the test had been run in a manner in which the STY was held constant with periodic increase in the reaction temperature, the time period between temperature changes would be extended over time as the catalyst approached a steady-state condition.

Examination of the STYs at 240°C and 250°C obtained during the startup phase of the test indicate that an initial temperature between 245°C and 250°C would be sufficient to obtain a 775 to 800 g/kg_{cat}/hr STY, while still obtaining the same selectivity observed at 260°C. By starting a long-term test at the lower temperature and corresponding STY, the initial rate of STY decline the initial rate of STY decline would be much lower than that observed at 260°C, and could approach zero over the course of operation, without the need to increase the temperature as much as was observed in the current test at 260°C. Under these conditions, it may be possible to operate the reactor at a nearly stable STY for a period of time that could exceed 2 years.

An intermediate-term test was also conducted with catalyst T-A, which had the same formulation as catalyst H-A, except that it used a high-surface-area graphitic carbon as the support instead of a carbon nanotube support. This test was conducted in the same manner as the previous test with catalyst H-A, but it was only tested at 260°C for 650 hr, to provide a comparison to the initial performance of catalyst H-A. In earlier short-term tests, the high-surface-area graphitic carbon with a different catalyst metal formulation was shown to behave similarly to ones prepared using the carbon nanotube support. However, catalyst optimization was not performed using this support.

Catalyst T-A initially achieved about 68% of the initial STY achieved with the H-A catalyst achieved under the same operating conditions. It was much more stable over a comparable period of operation, experiencing only a 5% decrease in the STY and a 9% decrease in the CO conversion during the test, whereas catalyst HA experienced decreases of 21% in the STY and a 25% decline in the CO conversion over the same operating period. The rate of decline in the STY of catalyst T-A also was comparable to that for catalyst H-A when the latter is evaluated during a period when its average STY was similar to that observed with catalyst T-A. This observation suggests that the two catalysts deactivate in a similar fashion even though their supports use different forms of carbon.

The selectivity of the catalyst was also very stable at about 70% after the first 100 hr at the design temperature, which is about 3% lower than that for catalyst H-A. Like catalyst H-A, this catalyst had similar selectivities during startup when the catalyst temperatures were maintained at 240°C and 250°C, again suggesting that similar catalyst behavior to catalyst H-A. A more detailed breakdown in the converted carbon selectivities to various oxygenate and hydrocarbon products suggests that both catalysts also are similar in this respect. The only notable difference is that catalyst T-A produced a small quantity of hydrocarbon liquid throughout the test whereas catalyst H-A did not. Based on the results of both tests, it is concluded that high-surface-area carbon supports with graphitic (graphenic) character are suitable as supports for the Rh-based catalyst. However, additional optimization of the high-surface-area graphitic support both with respect to the support itself and as the optimum catalytic metal composition would be needed to achieve comparable performance at the same conditions.

Another intermediate-term test was performed with the best silica-supported, Rh-based catalyst developed to date mainly to document its potential performance with respect to that of catalyst H-A. This catalyst (S-A) had a different catalytic metal composition. Previous short-term tests showed that the silica-supported catalysts were less amenable to variations in the concentrations of the three metals to improve the C_2+ oxygenate STYs or the converted CO selectivities to C_2+ oxygenates. This is presumed to be due to their greater interaction with the silica support. On the other hand, the choice of silica used as the support seems to have a greater influence on the catalyst performance.

The intermediate-term test with catalyst S-A was started using a 2:1 H_2:CO ratio so that its performance could be benchmarked with that from an earlier short-term test using catalyst from the same master batch. C_2+ oxygenate STY and converted CO selectivity were lower during the intermediate-term test. Again, this was not unusual based on the behavior of the silica-supported catalyst tested in the past. The long-term portion of the test was conducted at constant temperature for 668 hr using the same nominal testing conditions used for the two tests previously described, except that the catalyst temperature was maintained at 275°C, to achieve an initial C_2+ oxygenate STY that was greater than 400 $g/kg_{cat}/hr$.

Over the course of the test, the catalyst experienced somewhat different behavior than the carbon-supported catalysts. The CO conversion remained essentially unchanged at about 12%, while the STY declined about 2% from 430 $g/kg_{cat}/hr$ to 422 $g/kg_{cat}/hr$. The selectivity to C_2+ oxygenates declined by about 5% from 63% to 60% over the course of the test. This was accompanied by slight increases in the selectivity to methane and hydrocarbon liquids. The rate of decline in the STY was about 10%/1000 hr, which was much lower than that observed with the carbon-supported catalysts, is more problematic due to the much lower initial STY. However, there appeared to be a decline in that rate over time, but the test was not long enough to verify this possibility. Based on the results of this test, catalyst S-A may be stable over a long period of time, but it would need to be operated at a lower initial temperature and correspondingly lower initial C_2+ oxygenate STY.

5.0 References

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Appendix

Long-Term Tests with a Baseline Carbon Nanotube-Supported Catalyst

Appendix

Long-Term Tests with a Baseline Carbon Nanotube-Supported Catalyst

Another long-term test was conducted prior to testing of the preferred catalyst (catalyst H-A) to provide a preliminary assessment of catalyst stability and performance at a constant set of conditions. The previously tested catalyst consisted of 11.7% Rh, 3.57% Mn, and 2.17% Rh on the Hyperion CS-02C-063-XD carbon nanotube. The support was prepared in the same manner as supports for the preferred catalysts. This catalyst formulation had the same baseline Rh:Mn:Ir atomic ratio of 1.0:0.57:0.10 used in most of the previous tests with other supports, albeit at a higher total metals loading. It was used as the baseline catalyst formulation to evaluate the addition of a fourth promoter or fourth and fifth promoters to the catalyst (Gerber et al. 2012b).

The baseline catalyst was loaded and reduced *in situ* using the same procedure used for the preferred catalyst. Testing was conducted in a similar manner at 1200 psig but using just the syngas mixture containing a 2:1 H_2:CO ratio, 4% CO_2 and 4% N_2 with a corresponding feed gas GHSV of 17,000 L/kgcat/hr for a similar CO GHSV of about 5200 L/kgcat/hr. Startup conditions consisted of 50 hr at 225°C, 24 hr at 240°C, and 49 hr at 256°C before setting the final temperature at 260°C. Operating data and gas and liquid samples were collected and analyzed in the same manner as for the preferred catalyst test.

Figure A.1 shows the trends in the CO conversion, C_2+ oxygenate STY, and converted CO selectivity to C_2+ oxygenates over the entire test for the baseline catalyst. Table A.1 provides a summary of the catalyst performance metrics at selected points during the test. The baseline catalyst was tested for 2220 hr at the design conditions. It can be seen from the figure that there was considerable scatter in the data for the first six sets of data collected at 260°C. It was concluded that a portion of the liquid product from one of the sample traps was being held up in the upstream tubing and later diverted to the other trap when it was used to collect samples. To alleviate this problem during the test, subsequent sampling only used the latter trap.

During the testing period between 123 hr and 1673 hr of total testing (1550 hr testing at the design conditions) the catalyst experienced a gradual 18% increase in the C_2+ oxygenate STY from 615 to 723 g/kgcat/hr, accompanied by an approximate 10% increase in CO conversion from 22% to 24%, and a 10% increase in the selectivity to C_2+ oxygenates, from 51% to 56%.

After 1550 hr of testing at the design temperature (1673 hr total time), the system experienced an unscheduled periodic loss and resumption of flow over a period of 2 days due to problems with the setting of the supply gas pressure to the syngas mass flow controller. Upon resumption of steady flow conditions, the catalyst achieved an abrupt 33% increase in the CO conversion rate from 24% to 32%, and a 15% increase in the C_2+ oxygenate STY from 723 to 832 g/kgcat/hr. This was accompanied by an abrupt 13% decrease in the selectivity to C_2+ oxygenates from 56% to 49%, with the latter level of selectivity still being above its initial value at the start of the testing at 260°C. Over the remaining 700 hour of operation, the catalyst appeared to be slowly returning to its pre loss-of-flow performance, with a gradual 12% decrease in CO conversion, a 12% decrease in the STY, and a 4.5% increase in selectivity. The test was continued until a total of 2130 hours of operation was achieved, and then the test was discontinued.

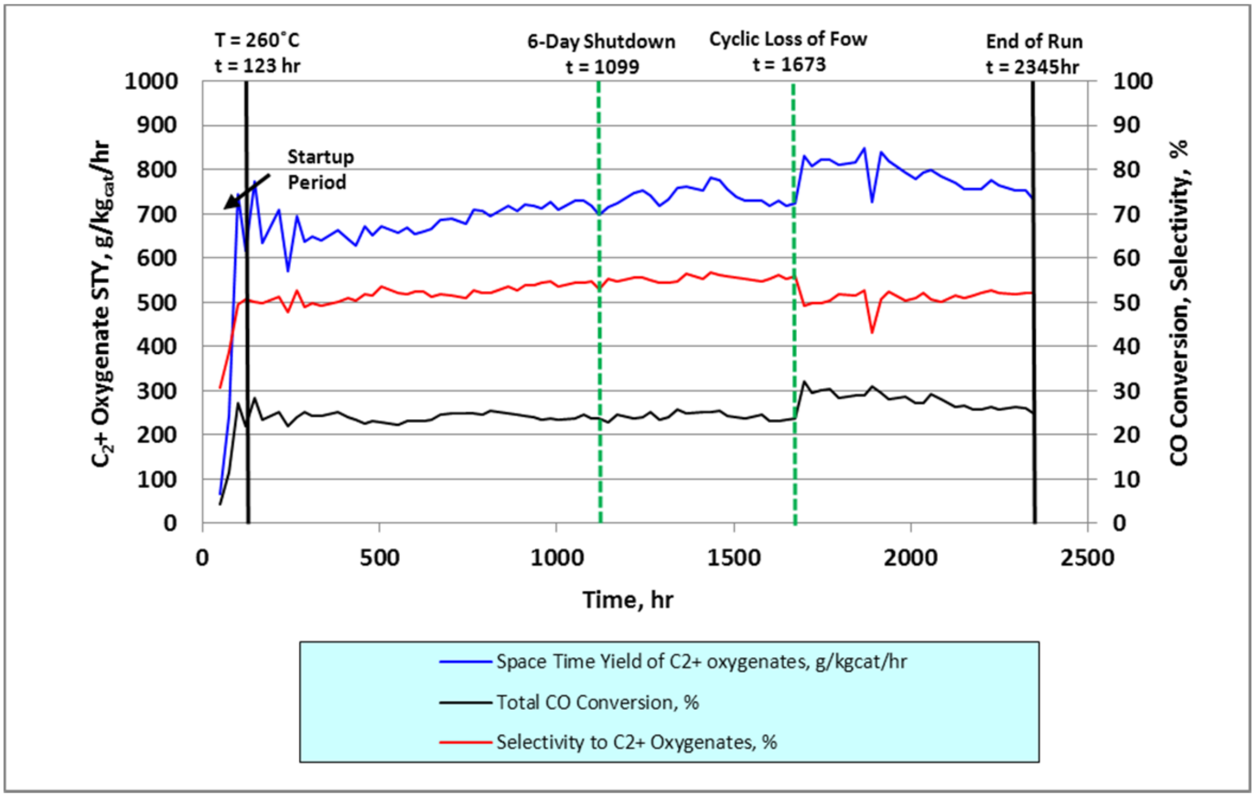

Figure A.1. Performance of Baseline Catalyst during a Long-Term Test at 260°C, 1200 psig, and a 17,000 L/kgcat/hr GHSV using a Feed Gas with a Nominal 2.0:1.0 H_2:CO ratio and 4% CO_2 and 4% N_2

Table A.1. Summary of Catalyst Performance during Long-Term Tests at Design Conditions with the Baseline Catalyst

Parameter	Initial Sample at Design Conditions	Sample at 1550 hr of Testing at Design Conditions(a)	Sample at 1576 hr of Testing at Design Conditions(a)	Final Sample at Design Conditions
CO Conversion, %	22	24	32	25
C2+ STY, g/kgcat/hr	615	723	832	732
Selectivity to C2+ Oxygenates, %	51	56	49	52

(a) Design conditions established after 123 hr of total operating time.

Also during the testing at the design conditions, there was a scheduled system shutdown for one week (not counted in the total hours) that took place after 976 hr of testing at the design conditions (1099 hr of total testing). During the shutdown period, the reactor was cooled to ambient temperature and maintained at pressure under a reduced flow rate of syngas. Following the shutdown, the design gas feed rate was restored and the reactor slowly heated back up to the design temperature. This event did not appear to produce any changes in the catalyst performance.

Figure A.2 provides a gross breakdown of the converted CO selectivity for the baseline catalyst to oxygenate and hydrocarbon products for selected samples spaced approximately 500 hr apart and including the first and last set of samples. It appears that there was very little change in the selectivity to methane or the hydrocarbon gases over the duration of the test at 260°C. However, there was a continuous decline in the selectivity to hydrocarbon liquids at 260°C, up until 1550 hr time on-stream at that temperature, when there were no liquid hydrocarbons observed in the product stream. Following the cyclic interruption-of-flow event, production of liquid hydrocarbons resumed at a comparatively modest level, and then was no longer present after 500 hr of additional testing. There also was a very distinct increase in the selectivity to C_2+ alcohols at the expense of the decrease in hydrocarbon liquids and a more modest decrease in selectivity to the other C_2+ oxygenates. Following the interruption-of-flow event, the selectivity to C_2+ alcohols decreased significantly and then gradually increased to the value observed prior to the event. Again, this mainly took place at the expense of the liquid hydrocarbons.

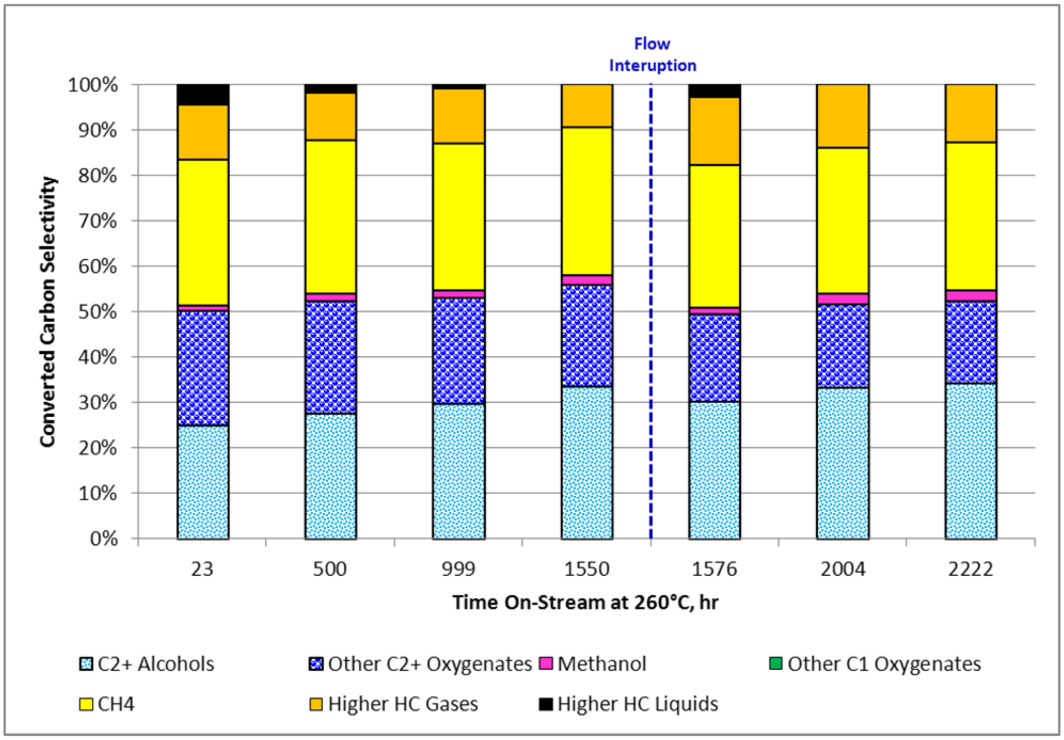

Figure A.2. Converted CO Selectivity for Baseline Catalyst to Different Product Classes for Selected Times On-Stream at 260°C

Figure A.3 provides a breakdown of the oxygenate product STY by species, for the baseline catalyst, for selected samples spaced approximately 500 hr apart and including the first and last set of samples. The other oxygenates consist almost exclusively of methyl acetate. The decrease in the C_2+ alcohol STY between the start of testing at 250°C and the sample at 500 hr is attributed to the problems with liquid product collection when two traps were used at the beginning of the test. As described above, this problem was solved. At 500 hr of testing at 260°C and beyond, the C_2+ alcohol STY increased over time, including a much larger increase after the cyclic interruption-of-flow event. After the event, the C_2+

alcohol STY declined modestly to a value close to where it was at prior to the interruption-of-flow event. The increase in the C_2+ alcohol STY was accompanied by a decline in the acetaldehyde STY. The acetaldehyde STY also increased significantly after the interruption-of-flow event, but quickly declined to values that were lower than those observed before the interruption-of-flow event. The acetic acid STY was relatively unaffected throughout the test although it too increased substantially following the interruption-of-flow event before returning to previous levels. There were very modest changes in the other component categories.

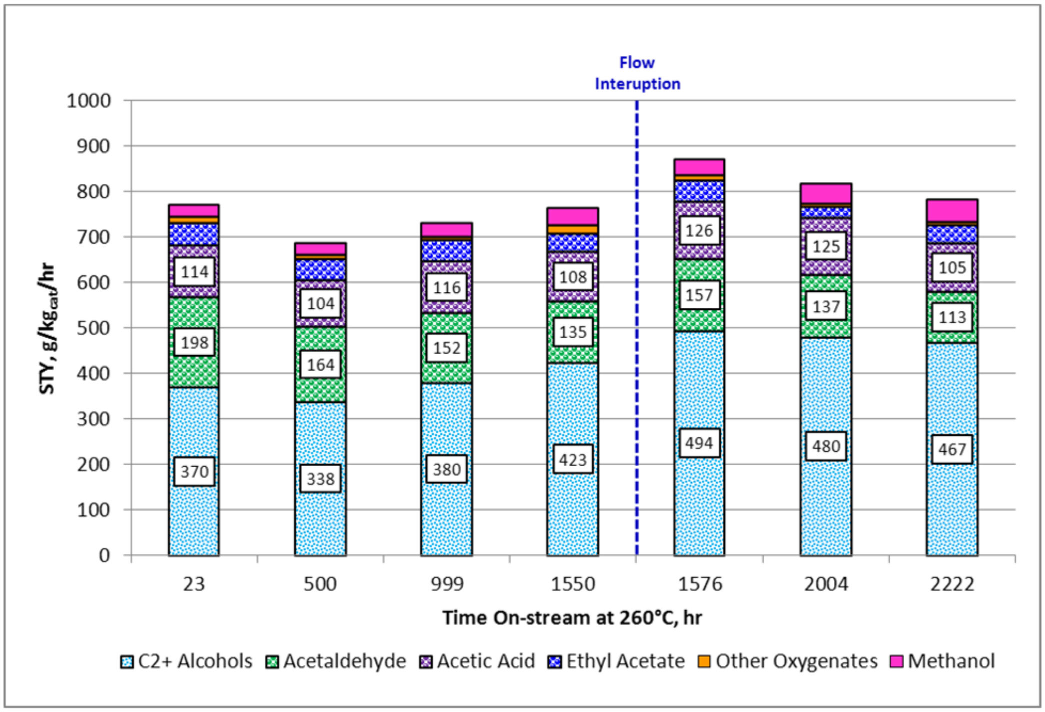

Figure A.3. Breakdown of the Oxygenate STYs by Species at Selected Points of Times On-Stream of Testing at 260°C for the Baseline Catalyst

Figure A.4 shows the corresponding carbon distribution among the oxygenate classes (normalized to 100%) for the baseline catalyst. There appears to be a consistent correlation between increases in the carbon distribution to ethanol at the expense of acetaldehyde. Prior to the cyclic interruption-of-flow event, the higher alcohols remained constant at about 4% (except for the set of data collected at the beginning of the testing at 260°C). After the event, the higher alcohols increased to about 7%, and then declined slightly to about 6% thereafter. There also appeared to be a slight increase in the distribution of carbon to methanol over time that was retarded for a short period following the event. The other oxygenate classes remained relatively constant throughout the testing.

Overall, it appears that the increase in CO conversion, prior to the cyclic interruption-of-flow event, is at least partially accounted for by an increase in the production rate of C_2+ oxygenates. This is primarily accounted for by an even greater increase in the production rate of ethanol that is partially offset by a decline in the production rate of acetaldehyde. There also appears to be a reduction in the higher hydrocarbon liquids over time, suggesting that carbon chain growth beyond C_4 (i.e., higher hydrocarbon liquids) is diminished over time. The effect of time on the production rate of the hydrocarbon gases is less clear, however, as a modest decline in their selectivities can be accounted for by the increased production rate of the oxygenates.

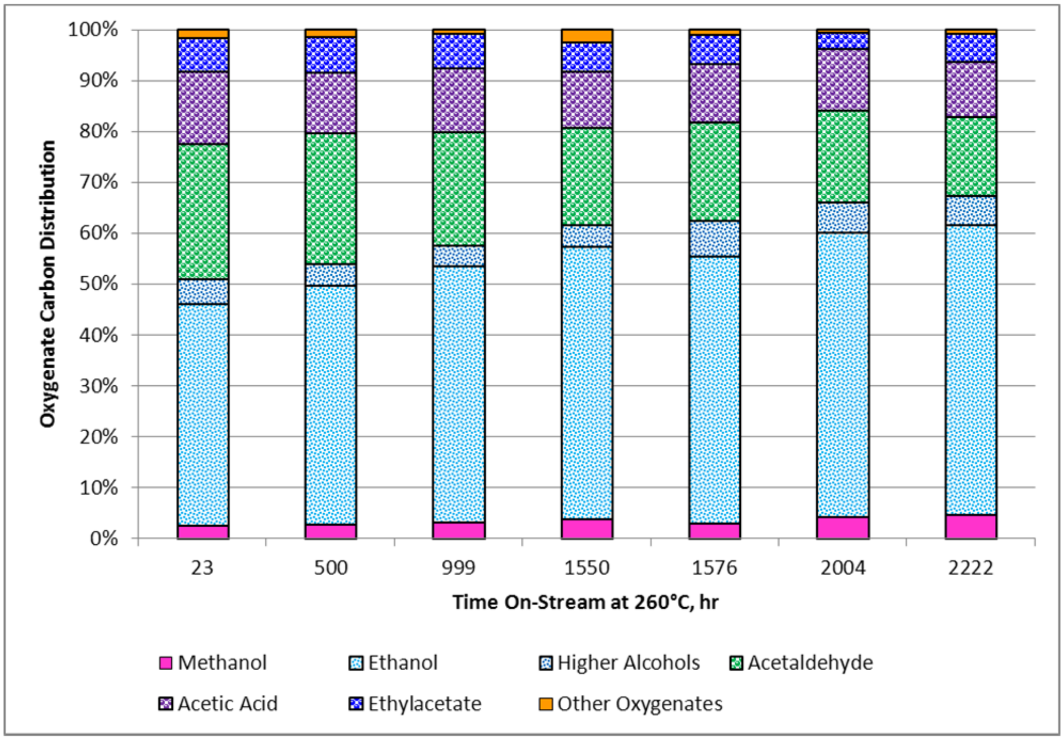

Figure A.4. Carbon Distribution among the Various Oxygenate Species at Selected Times On-Stream at 260°C for Catalyst H-A

The cyclic flow interruption event produced an immediate increase CO conversion that is mainly accounted for by increases in the C_2+ hydrocarbon gases and liquids (increase in the selectivity to these species as well as an increase in the production rate of ethanol and acetaldehyde as evidenced by their increased STYs). The subsequent trends in these components suggest that the catalyst may have been approaching a steady condition of performance before the event and that it was returning to these conditions afterwards. This behavior suggests that catalyst aging is not so much a typical deactivation mechanism such as sintering, as it is a gradual alteration of the catalyst surface to an equilibrium arrangement that for this particular catalyst produces a better performance after aging than it did as a freshly reduced catalyst. The cyclic flow interruption event altered this arrangement to produce an even more active but less selective C_2+ oxygenate catalyst, that again over time was rearranging its surface back to its equilibrium arrangement.

In summary, a long-term test that lasted a total of 2222 hr at design test conditions showed very good performance stability for a baseline carbon-supported catalyst even though it experienced a significant upset in the feed gas flowrate about three-quarters of the way through the test. These results are important because they show the potential for the catalyst to obtain the long lifetimes needed in an industrial setting.

While continued improvement in the catalyst is needed to obtain higher selectivities to C_2+ oxygenates, these results are encouraging because they show that the current catalyst is robust in terms of its potential for long-term operation.

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