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Optimization of Rhodium-Based Catalysts for Mixed Alcohol Synthesis – 2009 Progress Report

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NATIONAL LABORATORY

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Executive Summary

The U.S. Department of Energy's (DOE) Pacific Northwest National Laboratory (PNNL) and National Renewable Energy Laboratory (NREL) are conducting research to investigate the feasibility of producing mixed alcohols from biomass-derived synthesis gas (syngas). PNNL is tasked with screening promising mixed alcohol catalysts in a laboratory-scale reactor system. The most promising catalysts are provided to NREL for testing using a slipstream from a pilot-scale biomass gasifier.

After a review of the literature in 2006 and conversations at that time with companies that produce catalysts, we concluded that commercial catalysts for synthesizing mixed alcohols were not publically available. One catalyst manufacturer did supply a modified methanol catalyst (MeOH-X) that was tested in the PNNL laboratory-scale system and then provided to NREL for further testing. PNNL also prepared and tested the behavior of 10 other catalysts that represented the distinct catalyst classes that are used to synthesize mixed alcohols. The catalyst with the best combination of C_2+ oxygenates space time yield (STY) and selectivity was a silica-supported catalyst containing rhodium (Rh) and manganese (Mn). These results of these tests were reported by Gerber and co-workers (Gerber et al. 2007).

Based on the catalyst screening test results, subsequent testing during 2007 and 2008 focused on the performance of the Rh-based catalyst to determine the effects of adding metals to Rh catalysts in addition to the Mn promoter already being used. A total of 28 tests were conducted to evaluate 22 different metals as well as the modified catalyst. These tests were described by Gerber and co-workers (Gerber et al. 2008).

The catalyst modified with iridium (Ir) significantly improved the STY of oxygenates with an observed maximum STY of approximately 810 g/L_{cat}/hr. Platinum (Pt) followed with an observed maximum STY of 660 g/L_{cat}/hr. The catalysts modified with gold (Au), lithium (Li), nickel (Ni), molybdenum (Mo), and ruthenium (Ru) also had observed maximum STYs that were higher than that achieved for the unmodified RhMn/SiO_2 catalyst (~ 440 g/L_{cat}/hr C_2+ oxygenates STY), although the Ru- and Mo-modified catalysts rapidly deactivated during testing, and are considered unsuitable.

Of all of the catalysts evaluated, Li-modified catalysts had the highest carbon selectivity to C_2+ oxygenates (47%) under the conditions at which the maximum C_2+ oxygenates STYs were obtained. The catalysts modified with Ir, Pt, and Au had carbon selectivity to C_2+ oxygenates at maximum C_2+ oxygenates STYs, of 39, 39, and 37%, respectively, which were better than the unpromoted catalyst (with a carbon selectivity of 32%). All of the modified catalysts with C_2+ oxygenates STYs greater than the baseline catalyst mostly produced oxygenates other than C_2+ alcohols. Only the gallium (Ga)- and indium (In)-modified catalysts had reasonably high C_2+ oxygenates STYs (albeit lower than the unmodified catalyst) had very high ratios of C_2+ alcohols to total C_2+ oxygenates ratios, with ratios of 0.67 and 0.71, respectively. These same catalysts had total alcohol:oxygenates ratios of 0.87 and 0.89, respectively.

In During 2009, the main goal of the testing program shifted to optimizing selected RhMn- based catalysts. Optimization involved examining different total concentrations and atomic ratios of Rh and Mn as well as that of the more promising promoters (Ir and Li) identified in the earlier screening studies. Optimization primarily involved catalyst performance improvements with respect to the STY and

converted carbon selectivity to C_2+ oxygenates, with additional consideration given to the fraction of the oxygenates that were C_2+ alcohols.

Based on the results obtained to date, it appears that the optimum Rh concentration is about 5.56 wt% (1X the baseline concentration used in promoter screening tests) when used in combination with Mn in which the Mn:Rh atomic ratio was 0.57 (1.69% Mn). It may be possible to get further improvements at slightly higher Rh concentrations, but in a test at 1.5X the baseline concentration, the combination of high hydrocarbon concentrations in the product gas and heat management problems at temperatures as low as 271°C made evaluation very difficult.

It also appears that the optimum manganese concentration is about 1.13 wt% (2/3X the baseline concentration used in promoter screening tests) when Rh is at the baseline concentration of 5.56 wt%. This concentration provides the highest C_2+ oxygenates STY, while not significantly compromising the converted carbon selectivity to C_2+ oxygenates. The selectivity of the C_2+ oxygenates to alcohols does not appear to be affected significantly by Mn concentrations above 0.55%.

The optimum Ir concentration is between 0.34% and 1.03% (1/3X and 1X the baseline concentration), at which the RhMn concentrations are at their baseline concentration (5.56wt% Rh and 1.69 wt% Mn). This concentration range provides high C_2+ oxygenates STYs accompanied by a favorable converted carbon selectivity of about 45% to 52% to C_2+ oxygenates. The selectivity of the C_2+ oxygenates to alcohols is relatively low over this concentration range, but none of the conditions achieved a very good selectivity. The selectivity ranged from about 15% to 35% over the range of temperatures and Ir concentrations evaluated.

The addition of Li to the RhMn catalyst improves the converted carbon selectivity to both the C_2+ oxygenates and ethanol; however, the STYs of both decrease significantly. Consequently, it is not possible to specify an optimum Li concentration. Instead, it becomes an issue as to which parameter is more important—STY or selectivity—within the constraint that a catalyst temperature that is too high will cause the catalyst to deactivate.

The combination of Ir and Li modifiers on the same RhMn catalyst did not improve C_2+ oxygenates STYs over that when only Li was present in the catalyst. However, it does appear to modestly improve the converted carbon selectivity to both C_2+ oxygenates and ethanol. There also was evidence that heating catalysts containing both metals to higher temperatures (up to 345°C) resulted in increased catalytic activity, but the carbon selectivity to C_2+ oxygenates decreased. This behavior has not been fully studied.

In addition, limited catalyst screening continued to examine some additional promoters (magnesium [Mg], vanadium [V], lanthanum [La], cerium [Ce], boron [B], tungsten [W], and sodium [Na]) that were not previously tested. These tests also were conducted using the baseline RhMn/SiO$_2$ catalyst composition of 5.56 wt% Rh and 1.69 wt% Mn on Davisil 645 silica. The promoters were added at concentrations corresponding to a Rh:M atomic ratio of 1.0:0.1, where M was Mg, V, La, Ce, B, or W, and a Rh:M atomic ratio of 1.0:0.30 for Na. The latter atomic ratio was selected so it could be compared to that used to evaluate Li in previous tests (Gerber et al. 2008). All catalysts were prepared using a single impregnation to add the Rh, Mn, and additional promoter M to the catalyst support. This approach differs from the procedure previously reported for catalyst promoter screening in the earlier tests. None of these catalysts was more active than the RhMn/SiO$_2$ catalyst. However, the B-, Mg-, and La-promoted

catalysts did achieve comparable or better converted carbon selectivity to C_2+ oxygenates at both the conditions where they achieved their maximum C_2+ oxygenates STYs and at the common testing temperature of 300°C, with the Mg- and La-promoted catalysts achieving significantly greater selectivity to alcohols. In that case, there is merit in retesting these three catalysts using two impregnations (as was done in the earlier tests) to determine if this method of adding the promoters further improved their performance.

   Further testing is continuing, primarily to examine the effects of catalyst preparation and activation methods as well as the effects of alternative catalyst support on catalyst performance. Examination of the effects of selected additional operating parameters such as pressure and the H_2:CO ratio also will be conducted on the more promising catalyst formulations.

Acronyms and Abbreviations

Au	gold
B	boron
Ce	cerium
CO	carbon monoxide
Co	cobalt
CO_2	carbon dioxide
DOE	U.S. Department of Energy
FT	Fischer-Tropsch
Ga	gallium
GC	gas chromatograph
GHSV	gas hourly space velocity
H_2	hydrogen
HPLC	high-pressure liquid chromatograph
In	indium
Ir	iridium
La	lanthanum
Li	lithium
Mg	magnesium
Mn	manganese
Mo	molybdenum
N_2	nitrogen
Na	sodium
Ni	nickel
NREL	National Renewable Energy Laboratory
Pt	platinum
PNNL	Pacific Northwest National Laboratory
Rh	rhodium
Ru	ruthenium
SiO_2	silica
STY	space-time yield
syngas	synthesis gas
V	vanadium
W	tungsten
Zn	zinc

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1.0   Introduction

As part of its thermochemical platform to efficiently produce biobased fuels and co-products via thermochemical conversion, the U.S. Department of Energy (DOE) is conducting a program to produce mixed alcohols from lignocellulosic biomass using synthesis gas (syngas) produced from a biomass gasifier. The platform aligns its research and development with the program's goals, which include using stand-alone thermochemical conversion and integrating efficient, complementary thermochemical-conversion technology into a model biorefinery.

During 2007, DOE's National Renewable Energy Laboratory (NREL) conducted a technical and economic assessment of the feasibility of producing mixed C_2+ alcohols as a primary product from biomass-derived syngas to complement alcohol fuel biosynthesis in an integrated biorefinery (Phillips et al. 2007). The model for the mixed alcohol synthesis section was based on the expected performance of a cobalt (Co)/molybdenum (Mo) sulfide catalyst using methanol recycle in the synthesis reactor. Operating conditions and catalyst performance assumptions were based in part on 1) the catalysts developed and tested by Quarderer (1986) and Quarderer and Cochran (1986) and patented by Dow Chemical Company and 2) on typical values reported in the literature for similar catalysts in this class. The mixed alcohol synthesis catalyst chosen as the reference for this evaluation was based on a class of catalysts consisting of alkali-doped Mo sulfide with other metals such as Co added to promote the selective production of mixed alcohols. DOE then began a research program involving NREL and Pacific Northwest National Laboratory (PNNL) to select a catalyst and experimentally validate the performance assumptions used in the model.

After a review of the literature and discussions with selected catalyst manufacturers, PNNL determined that no Mo-based catalysts were available commercially at that time. In fact, the only mixed alcohol synthesis catalyst offered by a catalyst manufacturer at the time of our initial investigation was a modified methanol catalyst (MeOH-X). The only other company found to have previously offered a commercial catalyst was the Institut Francais du Petrole in France, which developed catalysts based on copper (Cu)/Co and Cu/nickel (Ni) systems. Their work has been discontinued, and there is no longer any catalyst available for testing.

In the absence of commercial catalysts that can promote the higher alcohol production rates needed to achieve economic viability, this project was undertaken to identify the most promising catalysts from the information published in the literature and to test the most promising ones in a bench-scale system. Potential catalysts were divided into six general classes:

- Modified methanol catalysts (based on Cu/zinc [Zn] and Cu/manganese [Mn] combinations)
- Modified Mo sulfide catalysts
- Modified Mo oxide catalysts
- Rhodium (Rh)-based catalysts
- Modified Fischer-Tropsch (FT) catalysts.

Our initial approach was to obtain or prepare catalysts that were either representative of each class of catalysts or that had the potential to achieve high space-time yields (STYs) for C_2+ oxygenates, and to test the prepared catalysts under conditions that would optimize C_2+ STYs at a common operating pressure (80 atm). Ten catalysts representative of the different catalyst classes were prepared and tested in 2006

and early 2007 along with a modified methanol catalyst product provided by a catalyst manufacturer (Gerber et al. 2007). Of these catalysts, only the modified FT and rhodium (Rh)-based catalysts showed promise for achieving the necessary STYs. The two FT catalysts, which were modified to improve oxygenate yields, achieved C_2+-oxygenates STYs that were within a recommended range for screening purposes (nominally 800 to 1300 $g/L_{cat}/hr$). However, because of their much higher selectivity to FT liquids, the STYs for total organic liquids exceeded the recommended range under optimum operating conditions. Under test conditions that produced a total organic liquid within the recommended range (i.e., 1200$g/L_{cat}/hr$ total organic liquids STY), one of these catalysts achieved a much lower C_2+ oxygenates STY (230 $g/L_{cat}/hr$) that, while higher than that achieved by the modified methanol and modified molybdenum catalysts, was still well below the recommended STY range. Carbon selectivity to C_2+ oxygenates was only about 10% under these conditions.

The two Rh-based catalysts, Rh/Mn/silica (SiO_2) and Rh/Mn/iron (Fe)/SiO_2, were very selective to C_2+ oxygenates. The Rh/Mn/Fe/SiO_2 achieved higher C_2+ oxygenates STYs under optimum conditions than any of the modified methanol and Mo-based catalysts tested at their optimum conditions and the FT catalysts at conditions that limited the total organic STYs to within the recommended range. The maximum achieved C_2+ oxygenates STY (approximately 400 $g/L_{cat}/hr$), however, was still below the recommended minimum. The carbon selectivity to C_2+ oxygenates under this condition was approximately 24%, which was significantly better than the FT catalysts. This Rh catalyst also was unique because it produced very few C_1+ oxygenates or FT liquids.

During 2007, a second set of catalyst testing was performed at PNNL to evaluate 22 promoters for the RhMn/SiO_2 catalysts including the Fe-promoted catalyst that was tested in previous catalyst screening. All of these catalysts used the same Rh:Mn:M atomic ratio (M representing the promoter) except one that used lithium (Li) as the promoter. The results of these tests identified several promoters that showed promise for improving the C_2+ oxygenates STY and/or improving the selectivity of the C_2+ oxygenates to alcohols (Gerber et al. 2008).

During 2009, the testing program shifted to optimization of the SiO_2 supported RhMn based catalysts. Optimization involved examination of different total concentrations and atomic ratios of Rh and Mn as well as that of some of the more promising promoters identified in the earlier screening studies (iridium [Ir] and Li). In addition, limited catalyst screening continued to examine some additional promoters not previously tested. This report summarizes the progress made to date on catalyst optimization and screening.

1.1 Catalyst Performance Requirements

The performance of the catalyst affects the capital costs of the mixed alcohols synthesis process in terms of reactor vessel size for a given throughput and gas recycle requirements, as well as vessel wall materials and thickness to meet design requirements for the expected operating pressure and temperature. Catalyst performance also affects the operating costs of the process, in terms of energy required to pressurize and heat the incoming gas feed and the yield and distribution of key products (higher alcohols) and potential byproducts with significant economic value. For a catalyst to be considered suitable for mixed C_2+ alcohol synthesis, it must be able to achieve a sufficiently high production rate of mixed higher alcohols in the synthesis reactor so that the capital costs of the reactor are not prohibitively high. At the same time, the catalyst needs to minimize the production of undesirable byproducts (carbon

dioxide [CO_2] and hydrocarbons) that either reduce the yield of the desired product or require converting them back into syngas for recycle to the reactor to maintain an acceptable product yield. Both of the latter approaches result in additional process costs for a given productivity and overall product yield. This project uses three criteria for evaluating the performance of the catalysts:

1. Acceptable catalyst activity for C_2+ oxygenates

2. Acceptable catalyst selectivity to C_2+ oxygenates

3. Acceptable catalyst selectivity of the C_2+ oxygenates to C_2+ alcohols.

The three performance criteria are interrelated, because as improvements are made in any one criterion, more latitude in the improvements required for the other two criteria is gained.

The primary screening and selection criterion for catalyst performance is the STY of C_2+-oxygenated hydrocarbons, with consideration given to the co-production of methanol and liquid hydrocarbons. STY is a measure of catalyst activity with respect to the desired products. The criterion is based on the production of all C_2+ oxygenates under the premise that the nonalcoholic oxygenates can be further converted into alcohols (albeit at a greater expense), thereby providing an upper limit for the expected C_2+ alcohol STY resulting from the catalyst. While the NREL techno-economic study (Phillips et al. 2007) cited an STY of 250 to 350 g mixed alcohol/L_{cat}/hr as a productivity rate typical of the Mo catalysts, this value is considered marginal based on the assessment made by Stiles et al. (1991), who found that the STYs of catalysts used in commercial methanol synthesis plants ranged from approximately 670 to 1,340 g_{MeOH}/L_{cat}/hr. According to Stiles and his co-workers, higher methanol production rates create heat dissipation requirements that are difficult to manage. Production rates involving higher alcohol production create higher exothermic heat loads than a comparable production rate of methanol. Furthermore, when significant methane or methane and higher hydrocarbons are produced along with the alcohols, heat dissipation can become unmanageable at the higher production rates. Consequently, it may not be practical to obtain higher alcohol production rates at the upper end of the range for methanol production in conventional fixed-bed reactor systems. On the other hand, rates significantly lower than the lower production range for methanol will likely result in unacceptable process economics. For catalyst evaluation, a minimum C_2+ oxygenates STY of at least 800 g/L_{cat}/hr is needed for a mixed alcohol synthesis catalyst with higher STYs required as catalyst selectivity decreases.

The second most important performance criterion is the selectivity of the catalyst to C_2+ oxygenates. In the case of the RhMn-based catalysts, the main byproducts other than the nonalcoholic C_2+ oxygenates are hydrocarbons; previous tests have shown that CO_2 is not a significant product of alcohol synthesis using RhMn-based catalysts. Hydrocarbons are undesirable because they act as diluents if they are recycled to the alcohol synthesis reactor along with unconverted hydrogen [H_2] and carbon monoxide (CO), thereby requiring a higher total pressure to preserve adequate partial pressures for the H_2 and CO in the syngas. The only ways to eliminate hydrocarbons from the recycle gas stream is to either purge a portion of the recycle gas stream as a relatively low value fuel gas, thereby reducing overall product yield, or divert the recycle gas stream to a reformer to reconvert the hydrocarbons to syngas. The latter option adds considerable cost to hydrocarbon reforming in an integrated system. Most of the catalysts tested to date have had converted carbon selectivity to hydrocarbons greater than 50% when the catalyst achieves high C_2+ oxygenates activity. Under these conditions, the concentration of the hydrocarbons in the product gas following liquid product removal is about 3%. This concentration level is considered to be low enough to allow some product gas recycle to the alcohol synthesis reactor before unacceptable

dilution effects occur, but would be unacceptably high in terms of overall product yield. For purposes of catalyst evaluation, carbon selectivity to hydrocarbons of less than 30% has been selected as a target.

The third performance criterion is the selectivity of the C_2+ oxygenates to alcohols. Consequences of producing nonalcoholic C_2+ oxygenates are the needs to either 1) further convert them into alcohols in a separate process prior to recovery from the product gas stream or 2) undergo a more complex separation process to purify the alcohols recovered in the liquid product stream. The latter option produces byproduct oxygenates that would need to be recovered and sold as byproducts or further converted into alcohols in a separated step. Both options increase the overall production cost for the product alcohols. At this time, there is only a qualitative goal of maximizing the selectivity to alcohols while meeting the other two criteria. However, achieving carbon selectivity to C_2+ alcohols exceeding 80% are considered to be noteworthy if the C_2+ oxygenates STY is high.

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 450°C. This system is shown in Figure 2.1. The catalyst chamber is 1.67 cm long and 0.635 cm in diameter. 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 at the center of the catalyst bed and the other just upstream. 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.

The syngas fed to the reactor is metered through a mass flow controller. The system also meters reducing gas (10% H_2 in nitrogen [N_2]) and N_2 to the reactor during catalyst reduction. 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 the tests. A Bios DryCal flow meter located downstream of the back-pressure flow 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 back-pressure regulator in a line separate from that containing the bubble flow meter, as shown in Figure 2.1. The reactor inlet, catalyst bed, cold sample trap, ambient temperature, and the upstream gas and ambient pressures are monitored during tests.

Gas cylinders containing a specified syngas mixture are used in the tests. The gas mixture consists of H_2, CO, CO_2, and N_2. Most of the tests conducted with the Rh-based catalysts used a gas that had a nominal H_2:CO ratio of 1.8, with the ratio ranging from 1.7 to 1.9. The nominal concentrations of CO_2 and N_2 were each 4% in the gas mixture. Variations in the H_2:CO ratios in the feed gas are attributed to variations in the composition of the individual gas cylinder mixtures supplied for the tests.

2.2   Catalyst Preparation

Catalysts tested during this portion of the testing program were based on a baseline catalyst composition of 5.56% Rh and 1.69% Mn on SiO_2, and a promoter other than Li and Na added at a concentration so that the Rh:Mn:M (M = promoter) atomic ratios were 1.00:0.57:0.10, respectively. When Li or Na were used as the promoter, the baseline Rh:Mn:M atomic ratio was 1.00:0.57:0.30. Catalyst optimization tests involved variations in the overall metals concentrations while maintaining the baseline atomic ratios, and/or varying one of the three components of a three-component catalyst from the baseline atomic ratio.
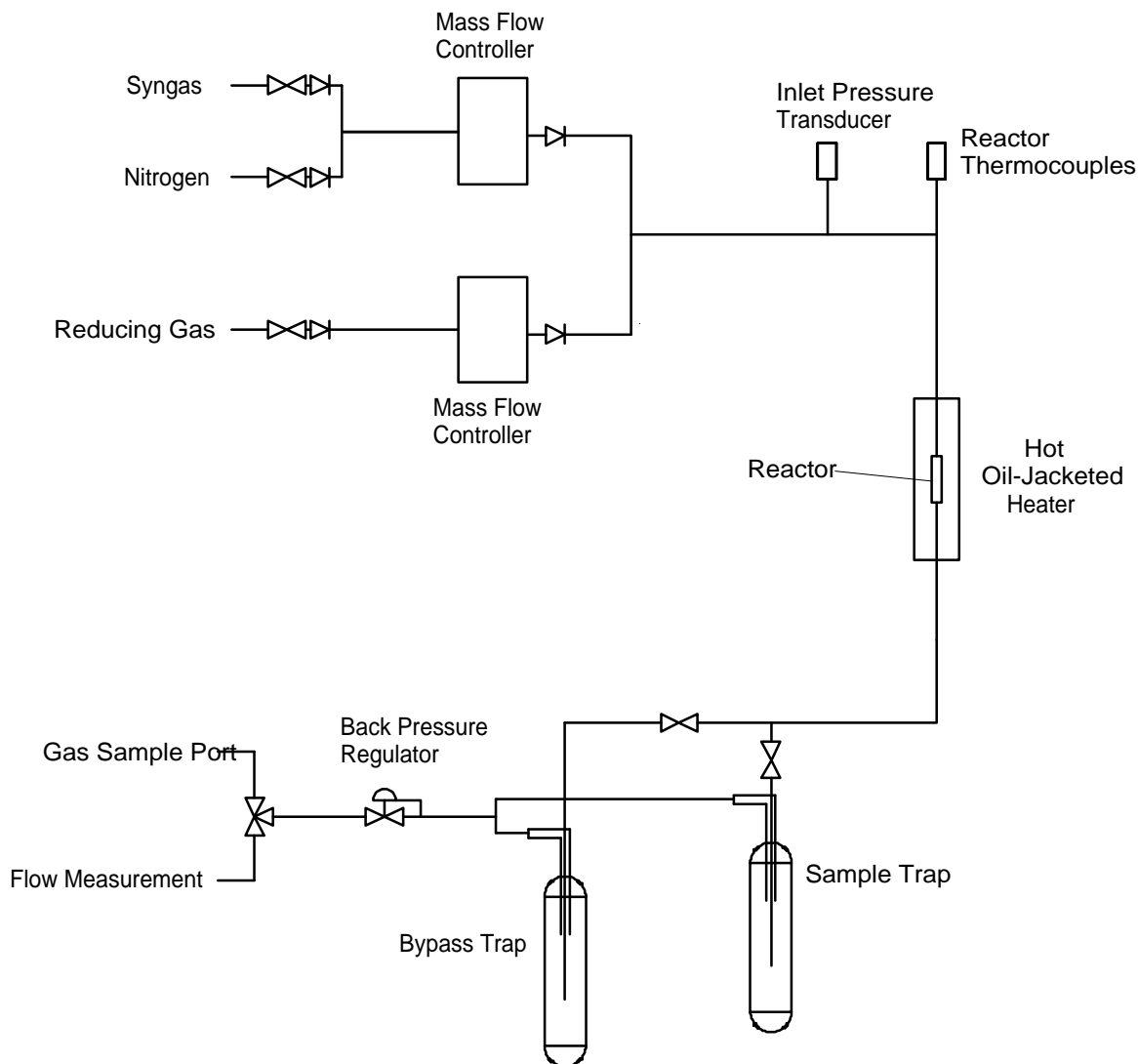
Figure 2.1. Simplified Diagram of the Reactor System Used to Test Catalysts

The catalysts that were tested were supported on Davisil 645 high-surface-area SiO_2. In addition, three tests that used Rh and Mn at different concentrations were performed using Davisil LC 150 SiO_2. Catalyst preparation consisted of a single-step impregnation procedure using the incipient wetness technique. This procedure is different than that reported in previous reports (Gerber et. al. 2007, Gerber et. al. 2008). The SiO_2 was pretreated by calcining at 500°C for 2 hours (ramping up at a 5°C/min rate during heating and ramping down at 10°C/min during cooling). The appropriate quantities of a rhodium nitrate solution (10 wt% Rh concentration in solution) and manganese nitrate tetrahydrate and a soluble compound (usually a nitrate salt) of the selected promoter were combined with enough deionized water to bring the total volume of the impregnation solution to the water adsorption pore volume of the support. The solution was impregnated onto the SiO_2 in drop-wise fashion, dried under an infrared lamp while being shaken until a steady weight was achieved, and then dried overnight at 110°C in a drying oven. The dried catalyst was calcined at 400°C in air using a muffle furnace. Catalysts with other supports were prepared in a similar manner but using methods that were compatible with the type of catalyst support used.

Before conducting the tests, the calcined catalysts were loaded into the reactor and reduced using a 10% H_2-in-N_2 gas mixture. All catalysts were heated in the reducing atmosphere to 220°C at 2.5°C/min ramp-up rate and held that temperature for 1 hour, then heated from 220°C to 260°C at a rate of 1°C/min and held at that temperature for 8 hours, and finally heated to approximately 350°C at a rate of 1.5°C/min and held at that temperature for 2 hours.

2.3   Testing Procedure

During a typical test series, a measured volume of catalyst was loaded into the reactor, and its net weight was determined. The reactor 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 reactor was heated slowly to a temperature at which the reaction rate was significant and maintained at that temperature for at least 24 hours 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 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, 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, and another cold trap sample was collected at the new conditions. This procedure was repeated until a representative set of conditions was obtained to evaluate catalyst performance in terms of STY, carbon selectivity, and single-pass carbon conversion. In most cases, tests progressively advanced to higher temperatures with one or more space velocities examined during each test. In most tests, an earlier test condition was re-examined to determine whether further catalyst ageing during testing affected the performance of the catalyst.

To calculate a representative average outlet flow rate during a sample collection period, an 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 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 $\pm 6\%$.

3.0 Reactor System Performance

As was reported in previous progress reports (Gerber et. al. 2007, Gerber et. al. 2008), heat management was still a problem with the more active catalysts during this phase of testing even when using circulating hot oil to maintain reactor temperature instead of a furnace. When the more reactive catalysts were operated at reaction rates approaching the limits of the ability of the hot oil to remove excess heat, small changes in reactor temperature could cause large fluctuations in the catalyst bed temperature. These excursions lasted anywhere from a few hours to a half a day and, in some cases, produced a periodic temperature cycle that ranged as much as 20°C over time. When this happened, a new set of conditions was sought that produced a stable temperature and data, and a liquid sample was collected. As a result, not all test conditions were evaluated by all of the catalysts. When stable conditions existed, the temperature of the reactor generally stayed within a ± 3°C during the liquid sample collection period.

4.0 Test Results

The majority of testing to optimize the RhMn-based catalysts has centered on evaluating the effects that alter the concentrations of the various catalyst materials on a SiO_2 support, including Rh, Mn, Ir, and Li as the active components. In addition, a few tests were conducted to examine promoters that were not evaluated in the previous screening tests. For the purpose of comparison, the compositions tested were based on baseline compositions in which the baseline Rh concentration was 5.56 g/g catalyst, and the Rh:Mn atomic ratio was 1.0:0.57. The baseline Rh:M_1 ratios for the screened promoters metals were 1.0:0.1 except for Na in which the Rh:M_1 ratio was 1.0:0.3. Where four catalytic components were tested, the baseline Rh concentration and the Rh:Mn:M_1:M_2 atomic ratios followed the same rules as the three-component catalysts. The test results are presented for the optimization tests and catalyst screening tests of the SiO_2-supported catalysts. Table A.1 in Appendix A summarizes the optimization test results while Table A.2 summarizes the screening test results. The screening test results according to the type of promoter added to the RhMn/SiO_2 catalyst are discussed in more detail in Appendix B.

4.1 Silica Supported Catalyst Optimization Tests

Several test series were conducted to examine the effects of varying the total concentration of active components and/or the atomic ratios of components for catalysts containing Rh and Mn with and without Ir and Li as additional promoters. Iridium was selected for evaluation because it achieved the highest C_2+ oxygenates STY during the promoter screening tests (Gerber et al. 2008) in which a baseline composition (e.g., 5.56% Rh with a Rh:Mn:Ir atomic ratio of 1:0.57:0.10) was used. Lithium was selected because it also achieved one of the better STYs in the promoter screening tests at its baseline condition (5.56% Rh with a Rh:Mn:Ir atomic ratio of 1:0.57:0.30) while also showing some improvement in the carbon selectivity to C_2+ oxygenates compared to the other active catalysts.

The specific test series investigated the following:

- Effect of overall metal concentration with RhMn catalyst on different SiO_2 supports
- Effect of Mn concentration on a RhMn/SiO_2 catalyst
- Effect of Ir concentration on a RhMnIr/SiO_2 catalyst (fixed Rh and fixed Rh+Mn)
- Effect of Li concentration on a RhMnLi/SiO_2 catalyst (fixed Rh and fixed Rh+Mn)
- Effect of Li on a RhMnIrLi/SiO_2 catalyst (fixed Rh and fixed Rh+Mn+Ir).

All of these tests used Davisil 645 SiO_2 from the same lot obtained from Fischer Scientific. It should be noted that this lot of Davisil SiO_2 may produce slightly different results than the Davisil SiO_2 obtained from Altech that was used for most of the catalyst promoter screening tests (Gerber et al. 2008). Specifically, the new lot of SiO_2 may achieve slightly lower catalyst activities for similar compositions under similar operating conditions, as well as slightly higher selectivity to methanol (MeOH). These differences are believed to be attributable to slightly different impurity levels in the SiO_2, which will be evaluated in future tests. It also should be noted that the three- and four-component catalysts used in these tests were prepared using a single impregnation, while the three-component catalysts used during the previous catalyst promoter screening tests (Gerber et al. 2008) were prepared from a single impregnation of Rh and Mn followed by drying and a second impregnation of the third component.

It also should be noted that the parametric studies were not exhaustive in scope. In most cases, a limited number of tests conditions were examined to optimize selected parameters. In several cases, further examination to confirm trends were not conducted because the levels of activity and/or selectivity were so far away from desired targets as to render any further conclusions moot. However, in some cases additional tests may be warranted but have not been conducted to date.

4.1.1   Effect of Overall Metal Concentration on Catalyst Performance

Four tests were conducted using different fractions of the baseline composition for RhMn/SiO$_2$ catalysts using the Davisil 645 SiO$_2$ support to examine the effect of the overall metal concentration on the catalyst performance. The compositions tested included:

- Baseline composition (5.56 wt% Rh, 1.69 wt% Mn)
- 2/3X baseline composition
- 1/2X baseline composition
- 1/3X baseline composition.

A fourth test was also performed using 4/3X the baseline composition. This composition was very reactive, producing much higher concentrations of hydrocarbons at temperatures as low as 246°C. However, because of heat management problems, it could not be tested above 271°C.

In addition, three tests were conducted using Davisil LC 150 SiO$_2$ as the support. The concentrations of the metals evaluated were at 1/2X, 2/3X, and 3/3X of the baseline Rh and Mn concentrations.

Figures 4.1 through 4.4 provide comparative data for two test conditions: 1) 275°C and 7,500/hr gas hourly space velocity (GHSV) and 2) 300°C and 11,000/hr GHSV. These conditions were chosen because the maximum C$_2$+ oxygenates STYs were achieved at 300°C and the data at 275°C provides additional information on the trends at lower temperatures. Although data were obtained at higher temperatures, it is apparent that some deactivation was occurring at these temperatures at the higher concentrations, thus making side-by-side comparisons of different tests difficult. Carbon conversions obtained at lower temperatures were less than 5%; therefore, hydrocarbon gases with compositions close to their detection limits produced results that may not be comparable.

Figure 4.1 compares the carbon conversions for the different metal concentrations and supports at 275°C and 300°C. It is clear that there is a significant effect in carbon conversion as the metals concentrations change. For example, increasing the metal concentrations by a factor of 1.5X from 2/3 to 3/3 of the baseline composition, results in a 7X increase in the carbon conversion at 275°C and a 2.5X increase at 300°C for the Davisil 645 support, and a 5X increase at 275°C and a 3.9X increase at 300°C for the Davisil LC150 SiO$_2$ support. The effect of concentration on carbon conversion is less pronounced for lower metal concentrations. We hypothesize that the heat generation rate, for carbon conversions greater than about 5%, becomes sufficiently significant, so that the actual catalyst temperatures within the catalyst particles, and with respect to their spatial position in the catalyst bed, become higher than that represented by the temperature measured by the thermocouple located in the middle of the catalyst bed.

275°C, 1,200 psig, 7,500/hr GHSV

300°C, 1,200 psig, 11,000/hr GHSV
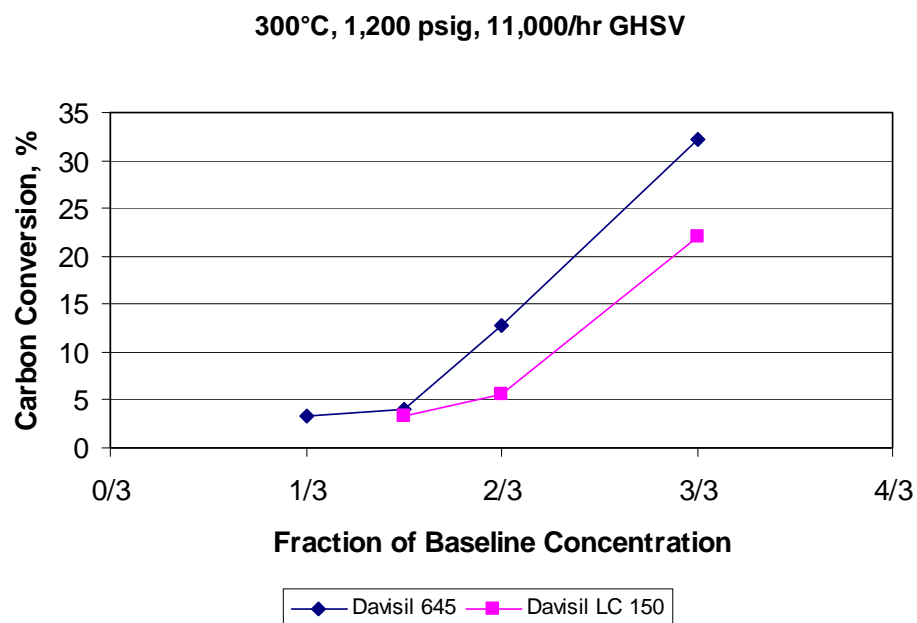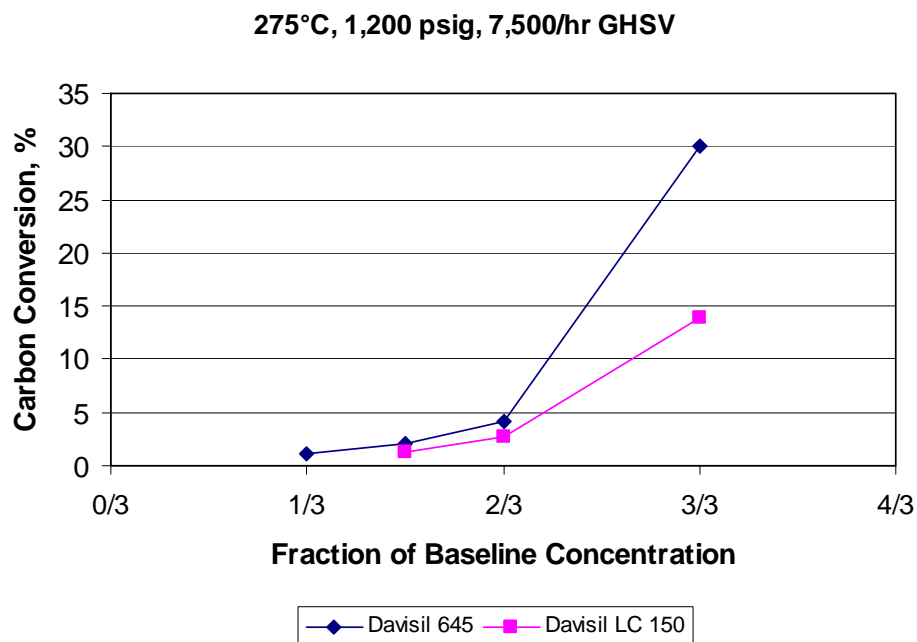
Figure 4.1. Effect of Total Metal Concentration on Carbon Selectivity to C_2+ Oxygenates for the Davisil 645 SiO_2-Supported RhMn Catalysts

275°C, 1,200 psig, 7,500/hr GHSV

Davisil 645 — Davisil LC 150

300°C, 1,200 psig, 11,000/hr GHSV

Davisil 645 — Davisil LC 150
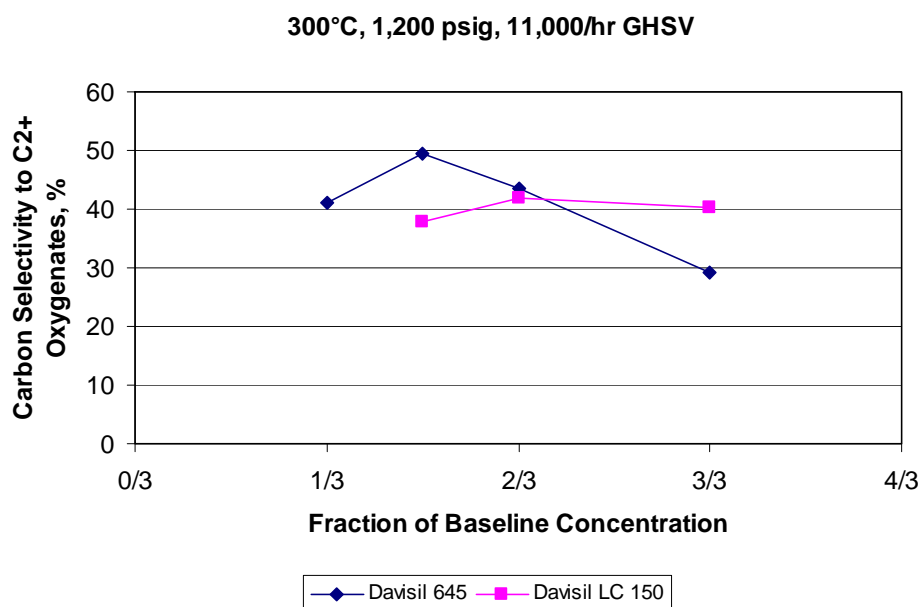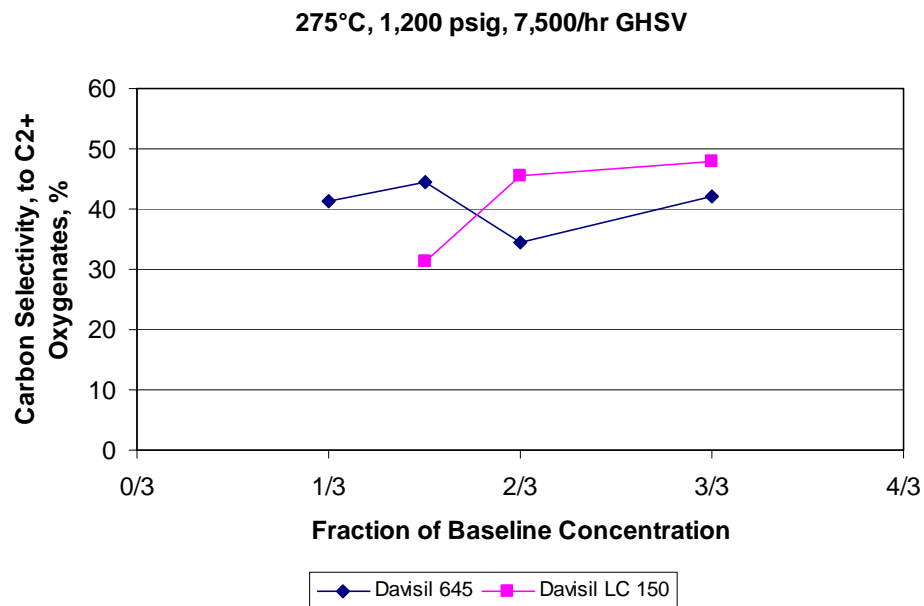
Figure 4.2. Effect of Total Metal Concentration on Carbon Selectivity to C_2+ Oxygenates for the Davisil 645 SiO_2-Supported RhMn Catalysts

275°C, 1,200 psig, 7,500/hr GHSV

275°C, 1,200 psig, 7,500/hr GHSV
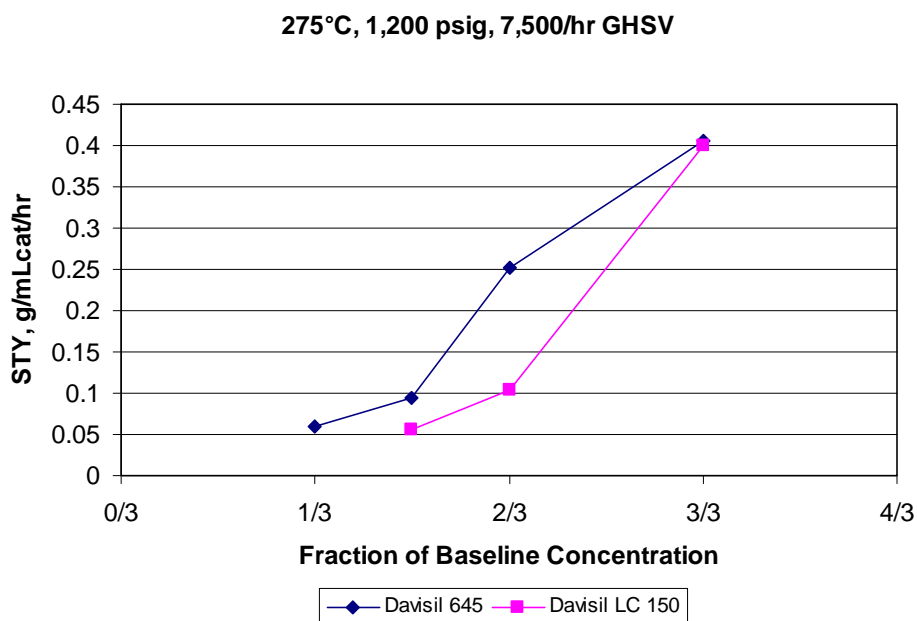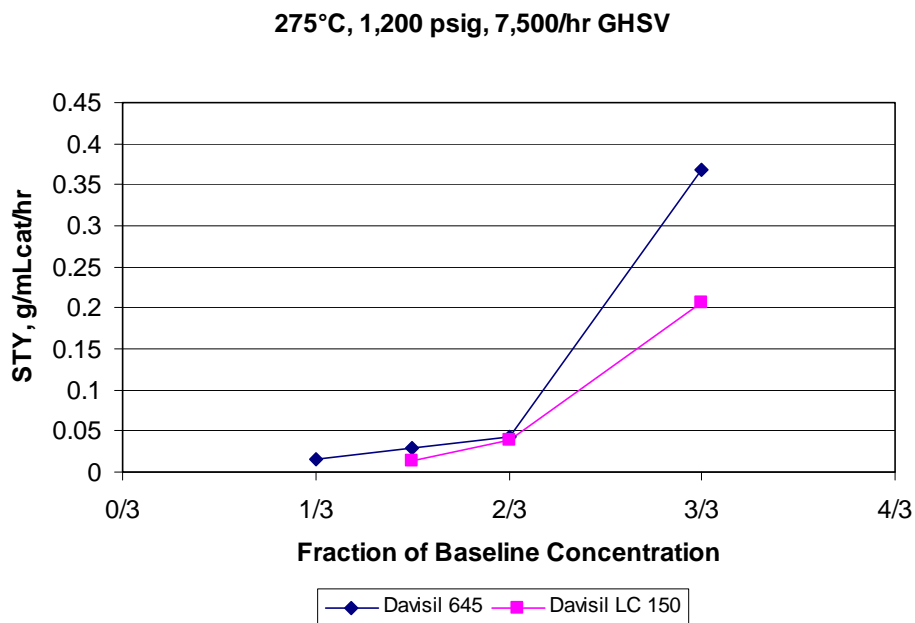
Figure 4.3. Effect of Total Metal Concentration on C_2+ Oxygenates STYs for the Davisil 645 SiO_2 Supported RhMn Catalysts

275°C, 1,200 psig, 7,500/hr GHSV

300°C, 1,200 psig, 11,000/hr GHSV

Figure 4.4. Effect of Total Metal Concentration on Carbon Selectivity of C_2+ Oxygenates to Alcohols for the Davisil 645 SiO_2-Supported RhMn Catalysts

Figure 4.2 compares the converted carbon selectivity to C_2+ oxygenates for the different metal concentrations at 275°C and 300°C. There is no clear trend in the effect of the metal concentrations on carbon selectivity to C_2+ oxygenates for the Davisil 645 SiO_2-supported catalysts with the data falling within a 10% range centered on approximately 40% conversion. At 300°C, a similar trend, within a 10% range centered on approximately 45% carbon selectivity, occurred for metal concentrations below the baseline concentration. However, at the baseline concentration, the carbon selectivity decreases to 29%, which is well below the range of the other data. The Davisil LC150 SiO_2-supported catalysts showed similar behavior, but with more scatter in the data obtained at 275°C. There is no obvious explanation for the scatter in the data at this time. It could be speculated that that some combination of a high exotherm, partial deactivation, and a higher GHSV could account for the scatter. Overall, there does not appear to be any optimal concentration with regard to carbon selectivity to C_2+ oxygenates for either support.
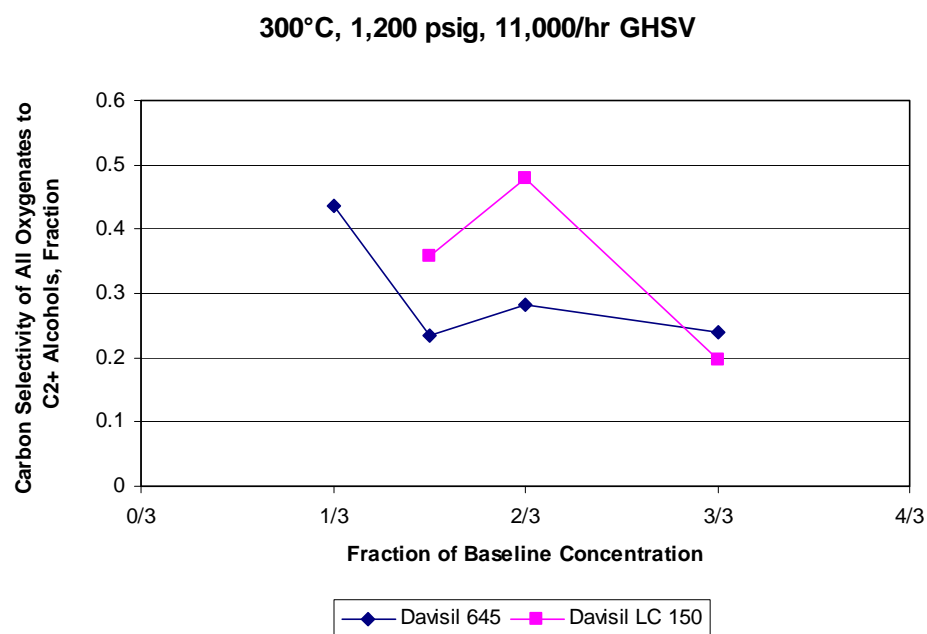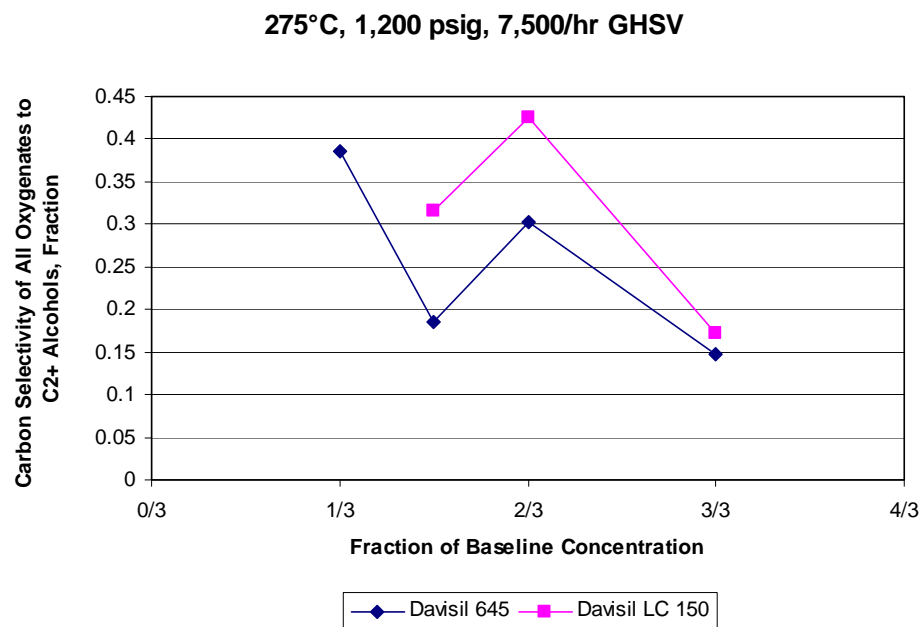
Figure 4.3 compares the C_2+ oxygenates STY for the different metal concentrations at 275°C and 300°C. In general, the STY at both temperatures follows the same trend as the carbon conversion for both SiO_2 supports, with the highest STYs occurring at the highest metal concentrations.

Figure 4.4 compares the carbon selectivity of the oxygenates to C_2+ alcohols for the different metal concentrations at 275°C and 300°C for both SiO_2 supports. While there is some scatter in the data, selectivity appears to trend away from C_2+ alcohols as the metal concentration increases, particularly at the highest concentration. However, there may be an anomaly at 2/3X the baseline composition on both SiO_2 supports, suggesting that there is a localized maximum in the selectivity towards C_2+ alcohols. However, considering the scatter in the selectivity data to C_2+ oxygenates in Figure 4.2, any conclusions would be speculative at this time.

Overall, it appears that the optimum RhMn concentration is near 5.56% (1X the baseline concentration), where the maximum C_2+ oxygenates STY occurs. At this concentration, the converted-carbon selectivity to C_2+ oxygenates is fairly insensitive to the Rh concentration, while the carbon conversion is very significantly affected. The selectivity of the oxygenates to C_2+ alcohols is low at this concentration, but the range of selectivity over the range of temperatures and Rh concentrations also were relatively low, ranging from about 15% to 50%. It may be possible to get further improvements at high Rh concentrations, but the heat management problem at high conversion rates makes evaluation of this possibility very difficult at this time.

4.1.2 Effect of Mn Concentration on Catalyst Performance for RhMn/SiO$_2$ Catalysts

Six tests were conducted using different concentrations of Mn co-impregnated with the baseline concentration of Rh (5.56% Rh) using the Davisil 645 SiO_2 support to examine the effect of the Mn concentration on the catalyst performance The Mn concentrations investigated included:

- wt% (no Mn)
- 0.28 wt% (1/6X baseline concentration)
- 0.56 wt% (1/3X baseline concentration)
- 1.13 wt% (2/3X baseline concentration)
- 1.69 wt% (3/3X baseline concentration)
- 2.25 wt% (4/3X baseline concentration).

Figures 4.5 through 4.8 provide comparative data for the following two test conditions: 1) 300°C and 11,000/hr GHSV and 2) 315°C and 11,000/hr GHSV. These conditions were chosen because the maximum C_2+ oxygenates STYs were achieved in this temperature range. Although data were obtained at higher temperatures, it is apparent that some deactivation was occurring at these temperatures at the higher concentrations. The general behavior of the catalysts at lower temperatures and space velocities (255°C and 275°C at 7500/hr GHSV) with respect to the effects of the Mn concentrations, were similar to the behavior observed at 300°C and 315°C.

Figure 4.5 compares the carbon conversions for different Mn concentrations at 300°C and 315°C. It appears that the carbon conversion increases significantly as the Mn concentration increases to about 2/3X of the baseline concentration (1.13 wt% Mn), and then levels off at higher concentrations. The leveling of carbon conversion at the higher Mn concentrations is concurrent with relatively high conversion rates (38% to 43%). Under these conditions, some deactivation at 300°C and 315°C may occur at these high conversion rates because of locally elevated temperatures within individual catalyst particles and with respect to spatial positions within the bed.

Figure 4.6 compares the converted carbon selectivity to C_2+ oxygenates for the different Mn concentrations at 275°C and 300°C. The addition of 0.28% Mn (1/6X baseline Mn) to the Rh catalyst appears to significantly improve the carbon selectivity to C_2+ oxygenates for the Davisil 645 SiO_2 support. However, further increases in the Mn concentration appear to result in a gradual decline in the selectivity.

Figure 4.7 compares the C_2+ oxygenates STY for the different Mn concentrations at 300°C and 315°C. In general, the STY at both temperatures follows the same general trend as the carbon conversion with a significant improvement in the STY with the addition of up to 2/3X of the baseline Mn concentration (1.13% Mn). At higher Mn concentrations, the STYs decrease modestly because of a leveling off of carbon conversion and a continual decrease in selectivity to the C2+ oxygenates.

Figure 4.8 compares the carbon selectivity of oxygenates to C_2+ alcohols for the different Mn concentrations at 300°C and 315°C. There appears to be a gradual decrease in the selectivity to C_2+ alcohols with increasing Mn concentration up to 1/3X the baseline concentration (0.56% Mn) followed by little if any increase in the selectivity at higher concentrations.

Overall, it appears that the optimum manganese concentration is near to 2/3X of the baseline composition of 1.69%. This concentration (1.13% Mn) provides the highest C_2+ oxygenates STY without significantly sacrificing, converted carbon selectivity to C_2+ oxygenates, which are slightly higher at Mn concentrations as low as 0.56%. At even lower Mn concentrations, the loss of catalyst activity because of carbon conversion overrides any further improvement in selectivity, while concentrations above 1.13% Mn produce modest decreases in both C_2+ oxygenates STYs and selectivity. The selectivity of the C_2+ oxygenates to alcohols does not appear to be affected significantly by Mn concentrations above 0.55%.
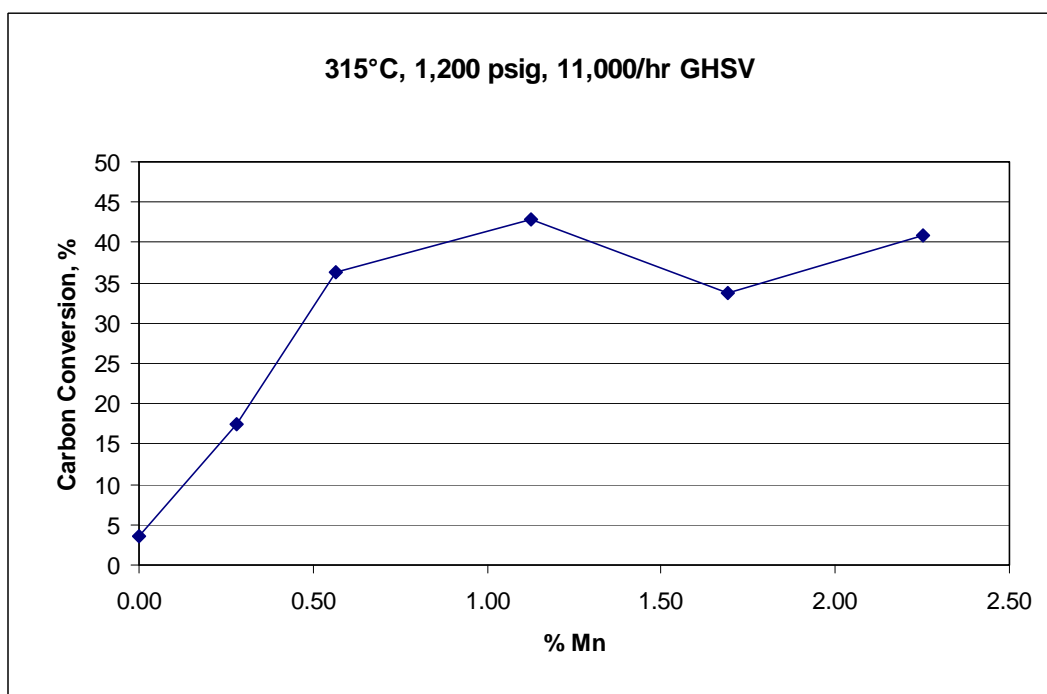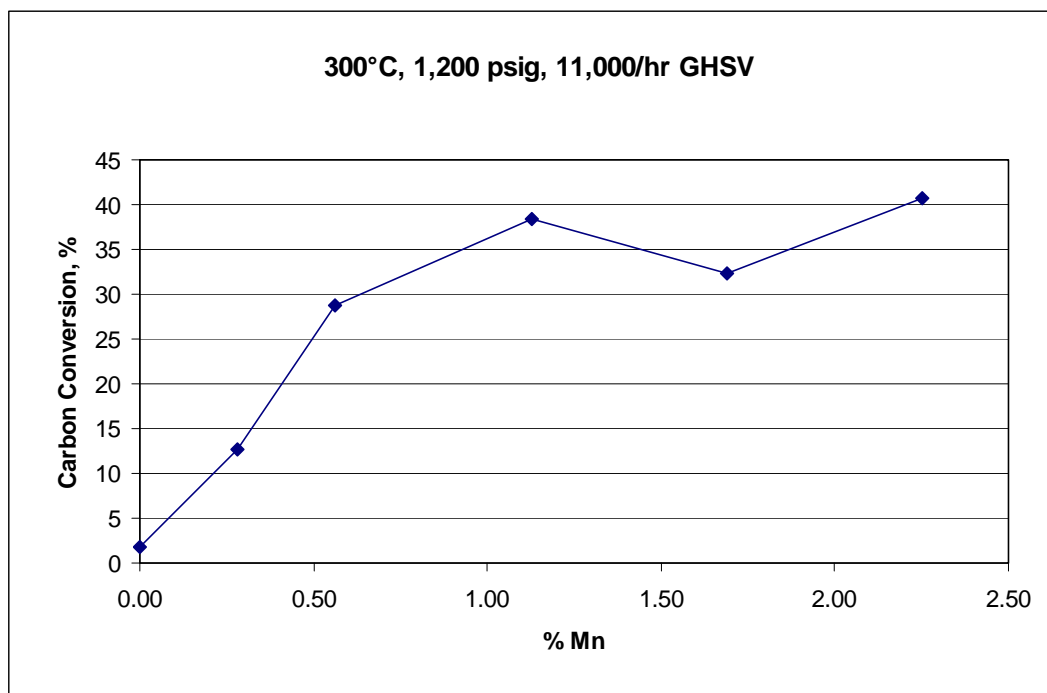
Figure 4.5. Effect of Mn Concentration on Carbon Conversion for the Davisil 645 SiO_2-Supported RhMn Catalysts at 300°C and 315°C

300°C, 1,200 psig, 11,000/hr GHSV

315°C, 1,200 psig, 11,000/hr GHSV
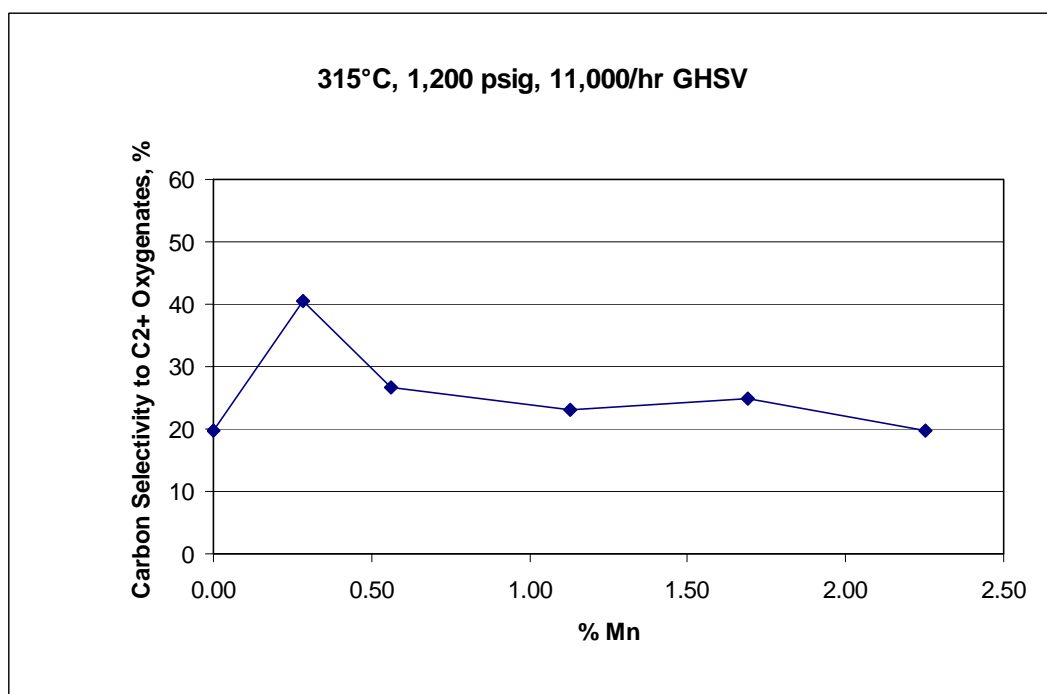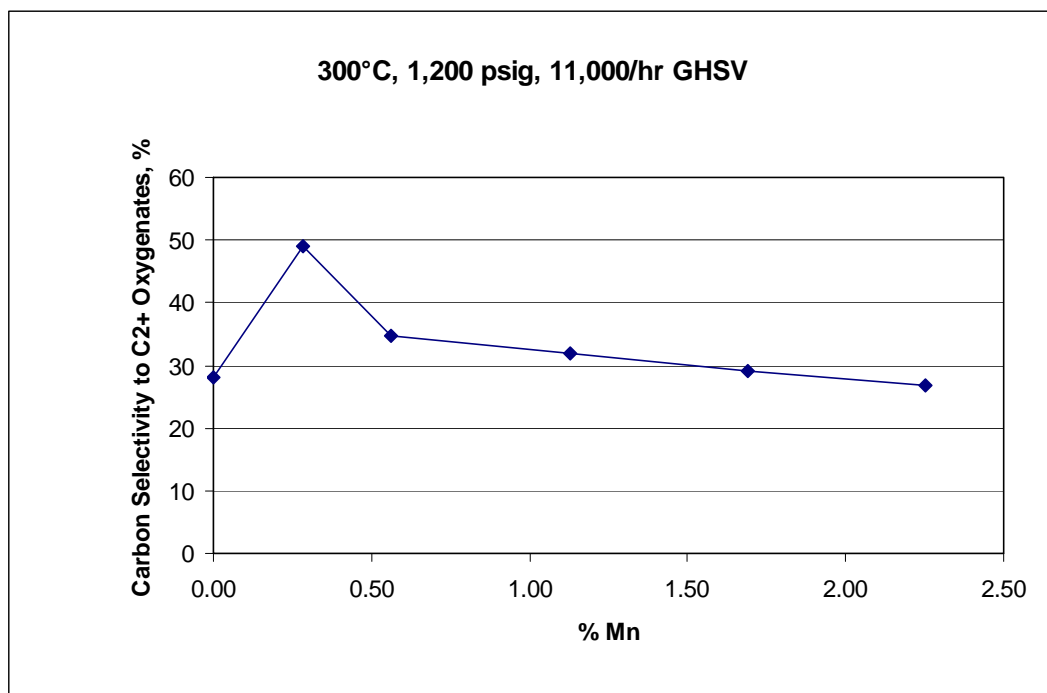
Figure 4.6. Effect of Mn Concentration on Carbon Selectivity to C_2+ Oxygenates for the Davisil 645 SiO$_2$-Supported RhMn Catalysts at 300°C and 315°C

4.10
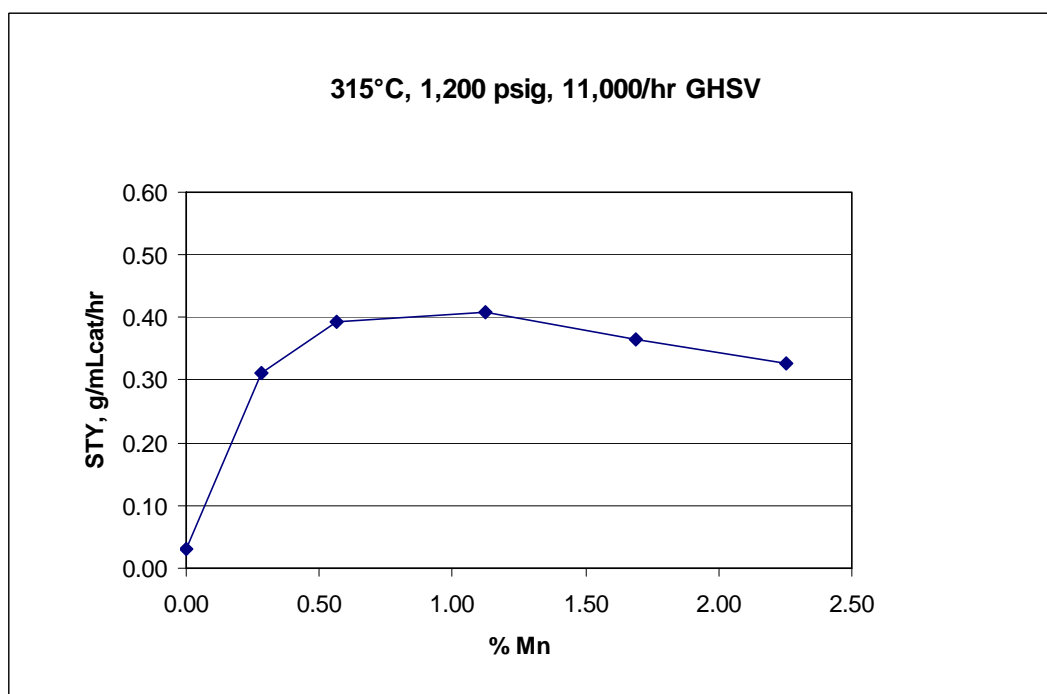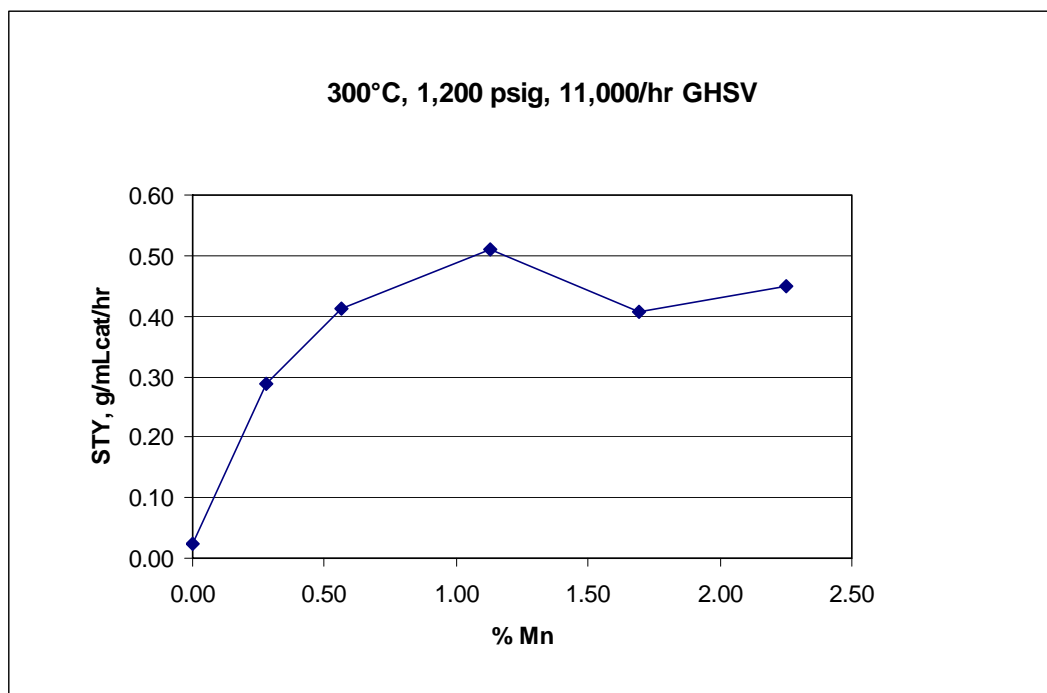
Figure 4.7. Effect of Mn Concentration on C_2+ Oxygenates STY for the Davisil 645 SiO_2-Supported RhMn Catalysts at 300°C and 315°C

300°C, 1,200 psig, 11,000/hr GHSV

Carbon Selectivity of All Oxygenates to C2+ Alcohols, Fraction vs % Mn

315°C, 1,200 psig, 11,000/hr GHSV

Carbon Selectivity of All Oxygenates to C2+ Alcohols, Fraction vs % Mn

Figure 4.8. Effect of Mn Concentration on Carbon Selectivity of C_2+ Oxygenates to Alcohols for the Davisil 645 SiO_2-Supported RhMn Catalysts at 300°C and 315°C

4.1.3   Effect of Iridium Concentration on Catalyst Performance for Rh-Mn/SiO$_2$ Catalysts

Six tests were conducted using different concentrations of Ir co-impregnated with the baseline concentrations of Rh (5.56% Rh) and Mn (1.69% Mn) using the Davisil 645 SiO$_2$ support to examine the effect of the Ir concentration on the catalyst performance. The Ir concentrations investigated included:

- wt% (no Ir)
- 0.017 wt% (1/60X baseline concentration)
- 0.34 wt% (1/3X baseline concentration)
- 1.03 wt% (3/3X baseline concentration)
- 1.37 wt% (4/3X baseline concentration)
- 2.72 wt% (5/3X baseline concentration).

Figures 4.9 through 4.12 provide comparative data for the following two test conditions: 1) 275°C and 7500/hr GHSV and 2) 300°C and 11,000/hr GHSV. These conditions were chosen because the maximum C$_2$+ oxygenates STYs were achieved at 300°C, and the data at 275°C provides additional information on the trends at lower temperatures. Although data were obtained from higher temperatures, it is apparent that some deactivation was occurring at these temperatures at the higher concentrations, thus making side-by-side comparisons of different tests difficult.

Figure 4.9 compares the carbon conversions for different Ir concentrations. The addition of very little Ir (0.017% or 1/60 of the baseline concentration) resulted in an immediate decrease in the carbon conversion. Further increases in Ir concentration, however, resulted in an increase in carbon conversion. It should be noted, however, that there was very little increase in carbon conversion at either temperature as the Ir increased from 1/3X to 1X of the baseline concentration (0.34% to 1.03% Ir). This behavior occurred at all tested temperatures and, in particular, at 256°C where the carbon conversion increased from about 10% to 17%, which is well below the carbon conversions where the effect of the exothermic reactions might significantly influence actual catalyst temperatures as discussed previously. It is possible that very different behaviors occur in this concentration range than occur at higher concentrations. Alternatively, there may have been a problem with the experiment using 1X of the baseline concentration of Ir. Further evaluation in this concentration range would be needed to further refine the effect of Ir.

Figure 4.10 compares the converted carbon selectivity to C$_2$+ oxygenates for the different Ir concentrations. Again, adding very little Ir had a pronounced effect on the selectivity. However, the behavior was different at 256°C (not shown) where the Ir addition resulted in a decrease in the selectivity compared to 300°C and higher temperatures where the Ir addition resulted in a pronounced increase in the selectivity (there was very little effect at 275°C). Differences in behavior depending on the reaction temperature also occurred with further increasing the Ir concentration up to 1X baseline concentration (1.03% Ir). At 256°C and 275°C, the highest selectivity to C$_2$+ oxygenates occurred at 1/3X of the baseline concentration followed by a gradual decrease in selectivity at 1X of the baseline concentration. At 300°C and 315°C, the maximum converted carbon selectivity to C$_2$+ oxygenates occurred at 1X the baseline Ir concentration. Increasing the Ir concentration above 1X the baseline concentration resulted in a significant decrease in the carbon selectivity at all catalyst temperatures although there was significant scatter in the data. The decrease in converted carbon selectivity to C$_2$+ oxygenates coincides with a significant increase in carbon conversion over the same concentration range suggesting that the exotherms are producing higher than measured temperatures in

the catalyst bed, as previously discussed, and some deactivation that may be changing the selectivity of the catalysts.
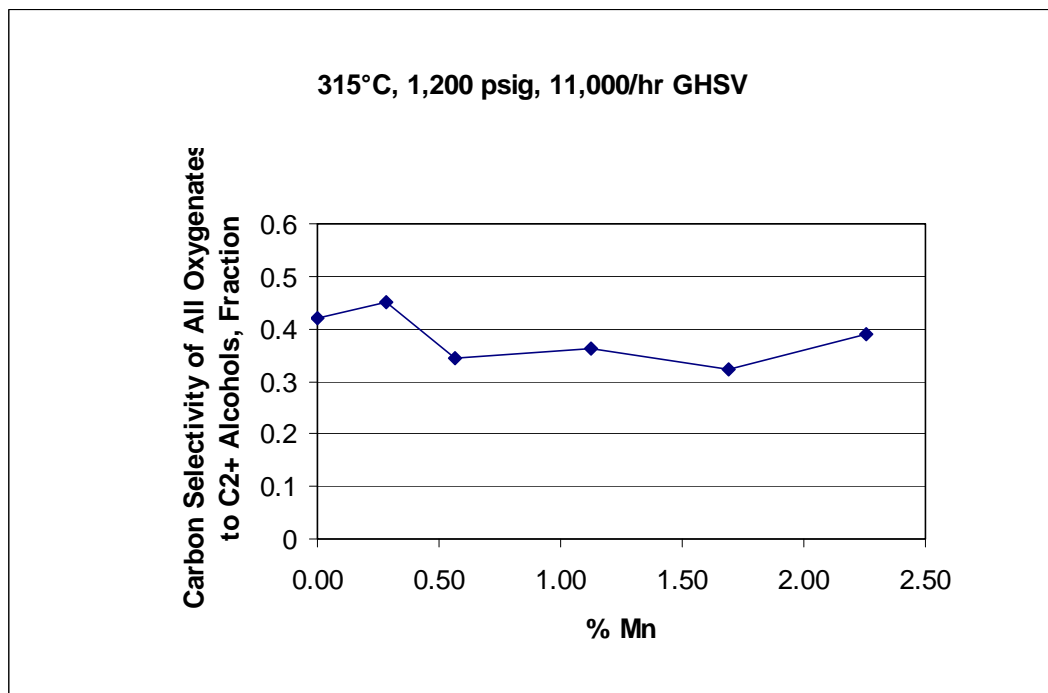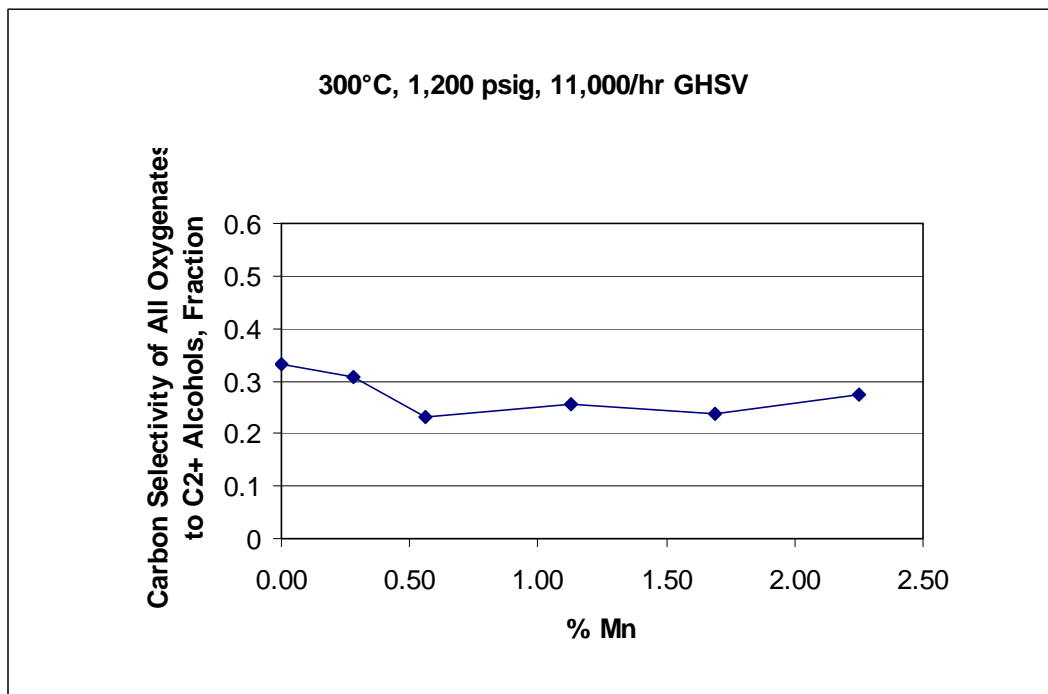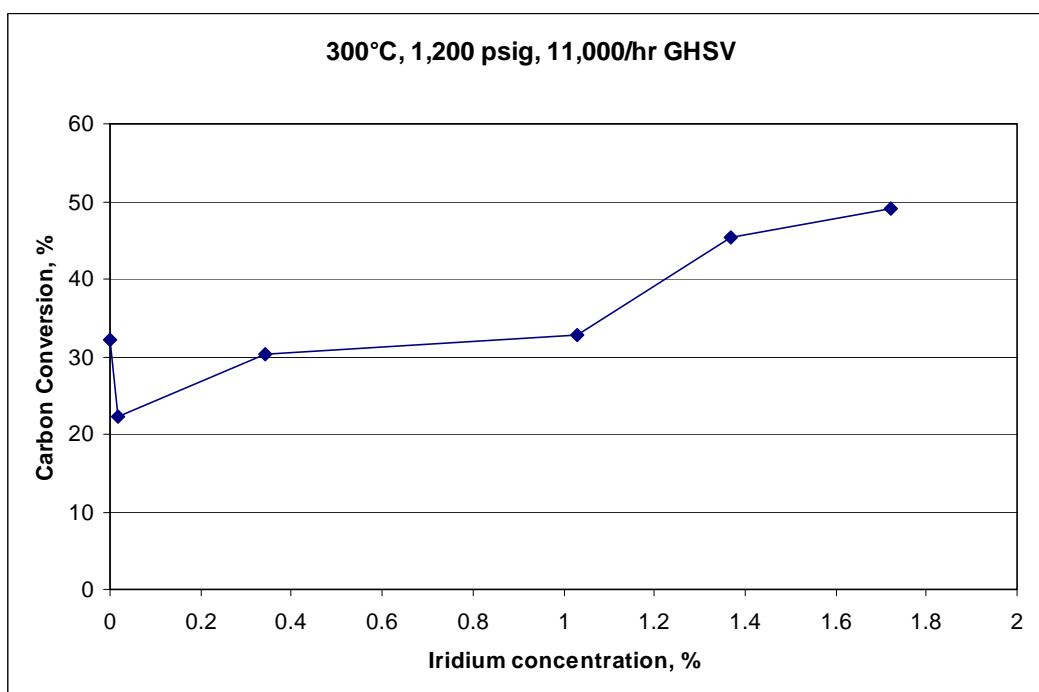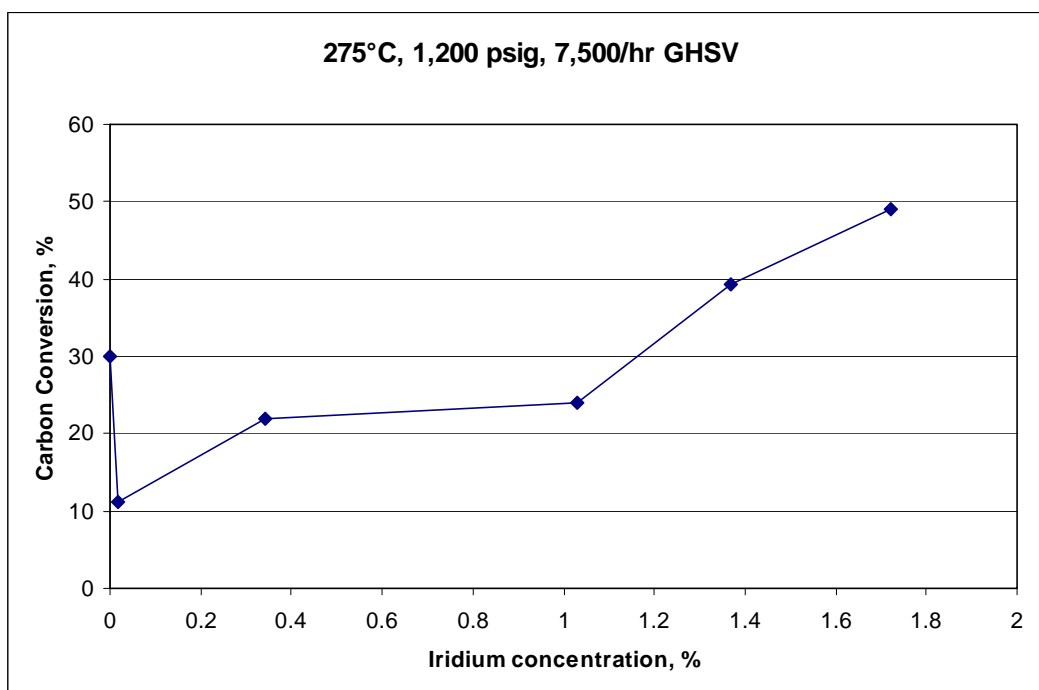

Figure 4.9. Effect of Ir Concentration on Carbon Conversion for the Davisil 645 SiO_2-Supported RhMn Catalysts at 275°C and 300°C
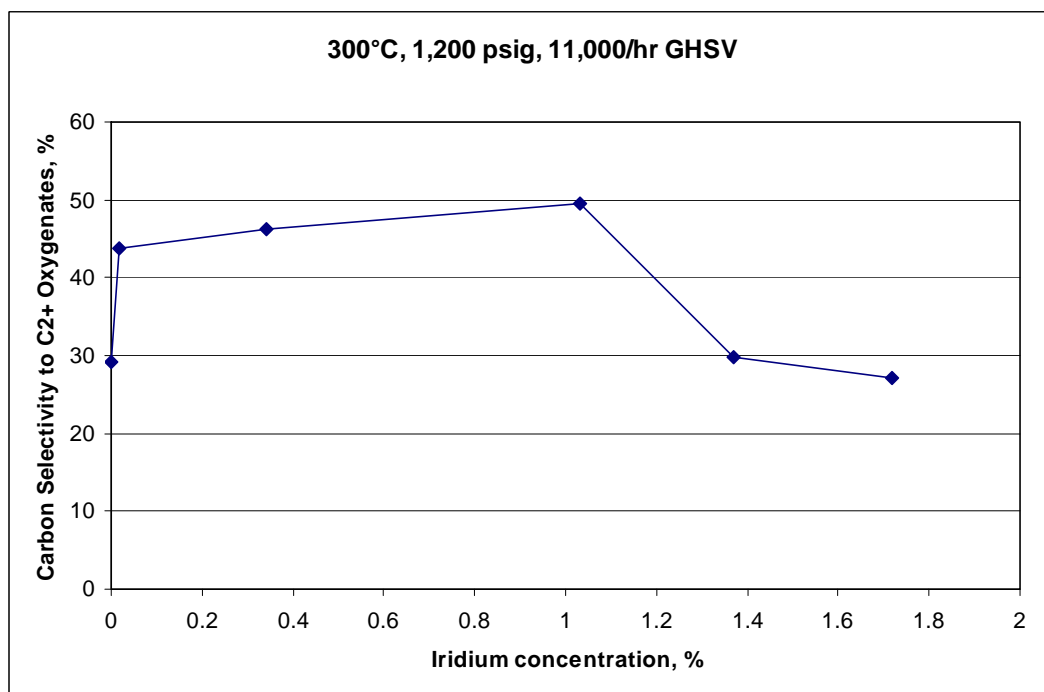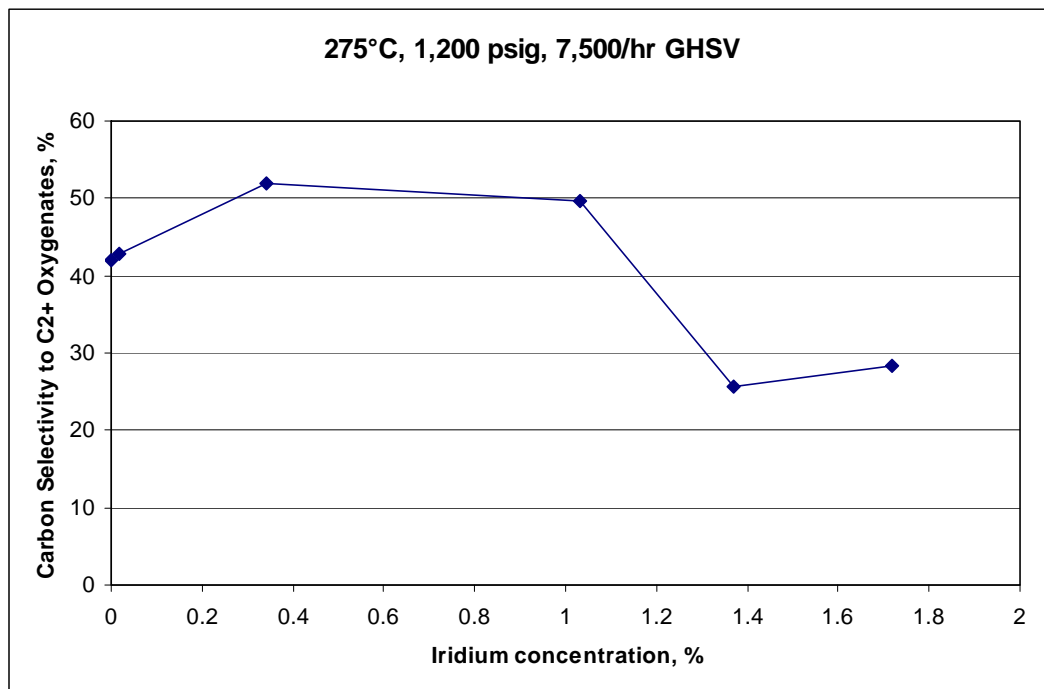
Figure 4.10. Effect of Ir Concentration on Carbon Selectivity to C_2+ Oxygenates for the Davisil 645 SiO_2-Supported RhMn Catalysts at 275°C and 300°C

275°C, 1,200 psig, 7,500/hr GHSV

300°C, 1,200 psig, 11,000/hr GHSV
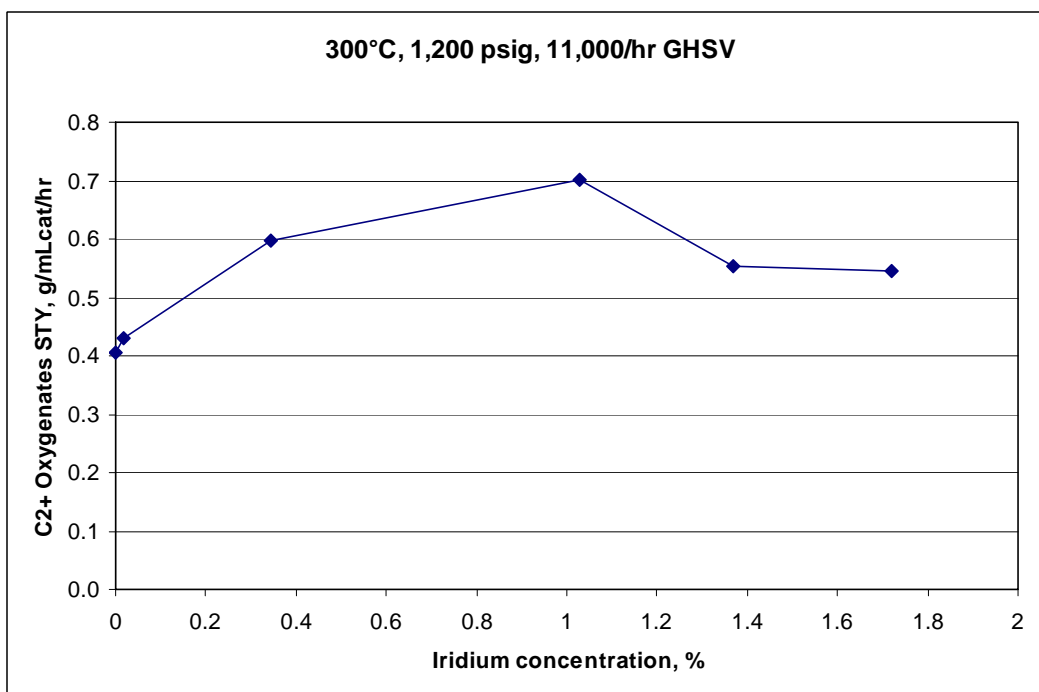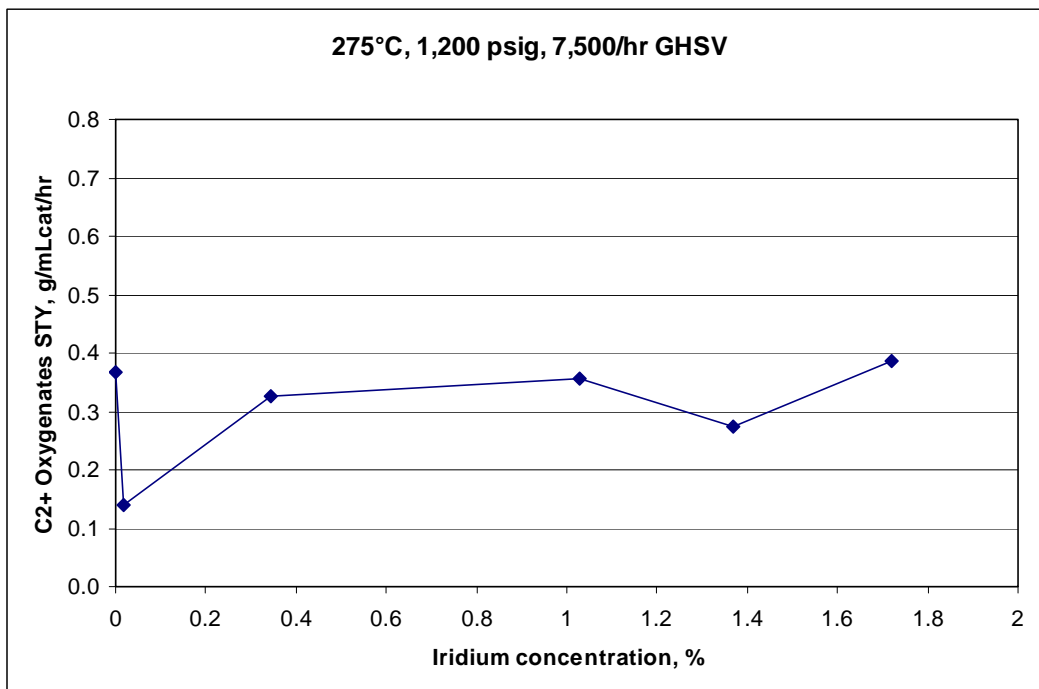
Figure 4.11. Effect of Ir Concentration on C_2+ Oxygenates STY for the Davisil 645 SiO_2-Supported RhMn Catalysts at 275°C and 300°C
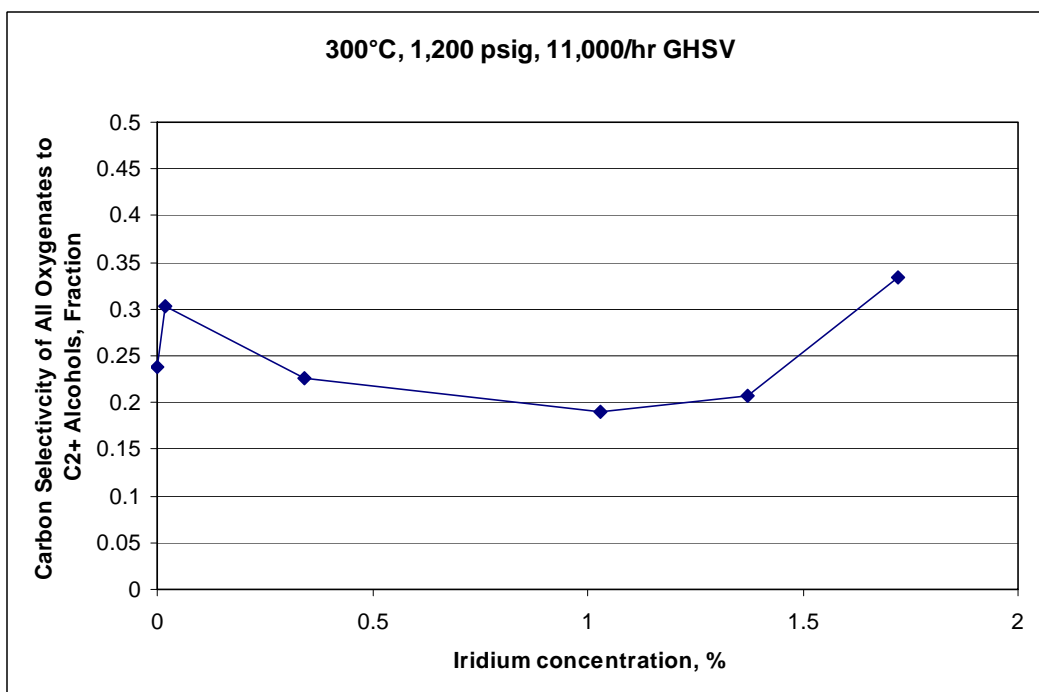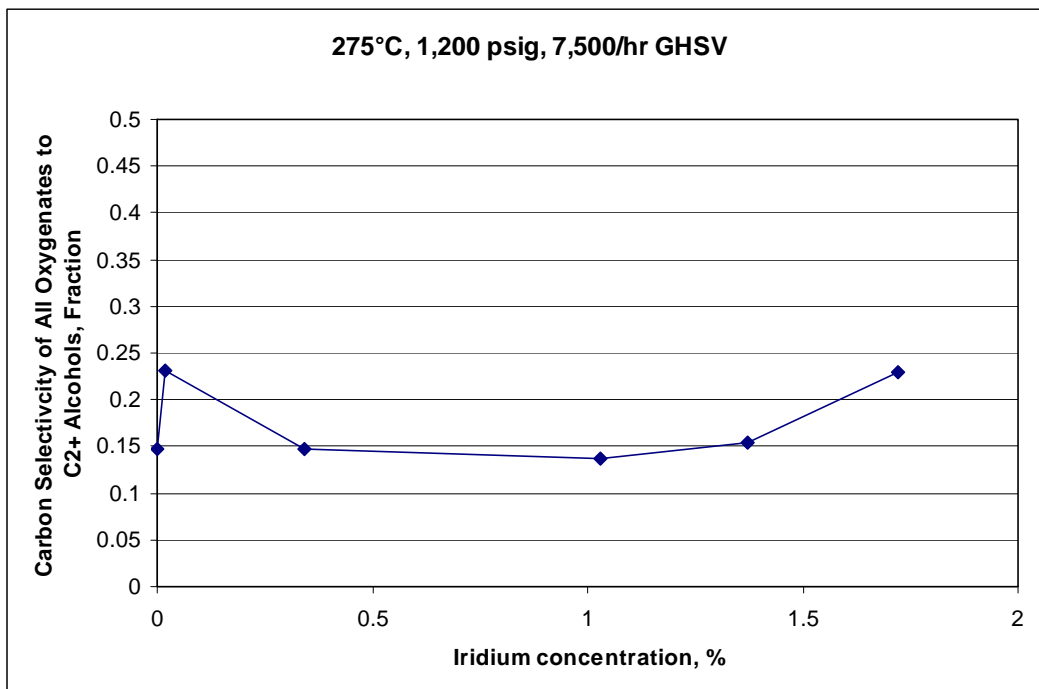
Figure 4.12. Effect of Ir Concentration on Carbon Selectivity of C_2+ Oxygenates to Alcohols for the Davisil 645 SiO_2-Supported RhMn Catalysts at 275°C and 300°C

Figure 4.11 compares the C_2+ oxygenates STY for different Ir concentrations. In general, the STY at 256°C (not shown) and 275°C showed significant decreases in STY with the addition of 1/60X the baseline Ir concentration, followed by a significant increase in the STY at a Ir concentration of 1/3X the baseline concentration. Higher Ir concentrations produced a gradual further increase in the STY with considerable scatter in the data. At 300°C and 315°C (not shown), the opposite behavior in the STY occurred with the addition of 1/60X of the baseline concentration. The peak STY at 300°C occurred at 1X the baseline Ir concentration, while at 315°C, the peak STY occurred at 1/3X the baseline concentration, (although very little decrease occurred at concentrations up to the baseline concentration at this temperature). Further increases in the Ir concentration above the baseline at the higher temperatures resulted in a decrease in the C_2+ oxygenates STYs. This latter behavior is attributed to some level of catalyst deactivation at the higher temperatures.

Figure 4.12 compares the carbon selectivity of oxygenates to C_2+ alcohols for different Ir concentrations. Again, the addition of very 1/60 of the baseline Ir concentration had a pronounced effect on the selectivity of oxygenates to C_2+ alcohols, with a significant increase in the selectivity at all temperatures. Further increases in Ir concentrations to about 1/3X of the baseline concentration resulted in a significant decrease in the selectivity at all reaction temperatures. With further increases in the Ir concentration to 1X the baseline composition, the selectivity increases very slightly at 256°C and decreases at the higher reaction temperatures. At higher Ir concentrations, the selectivity of the C_2+ oxygenates to alcohols increased at all reaction temperatures.

Overall, it appears that the optimum Ir concentration is no higher than 1.03% (1X baseline concentration), and probably is between 1.03% and 0.34%. This concentration range provides a high C_2+ oxygenates STY accompanied by favorable carbon selectivity to C_2+ oxygenates. Selectivity of the oxygenates to C_2+ alcohols is relatively low over this concentration range but none of the conditions achieved a very good selectivity, with the selectivity ranging from about 20% to 50% over the range of temperatures and Ir concentrations evaluated.

4.1.4 Effect of Lithium and Lithium Plus Iridium Concentration on Catalyst Performance for Rh-Mn/SiO₂ Catalysts

Four tests were conducted using different concentrations of Li co-impregnated with the baseline concentrations of Rh (5.56 wt% Rh) and Mn (1.69 wt% Mn) using the Davisil 645 SiO_2 support to examine the effect of the Li concentration on the catalyst performance The Li concentrations investigated included:

- 0.00 wt% (no Li)
- 0.0113 wt% (1X baseline concentration)
- 0.170 wt% (3/2X baseline concentration)
- 0.226 wt% (2X baseline concentration).

A second set of tests was conducted using three different concentrations of Li co-impregnated with the baseline concentrations of Rh, Mn, and Ir (1.03% Ir) to investigate the effect of Li addition to the Ir-promoted baseline RhMn catalyst. The Li concentrations investigated included:

- 0.00% (no Li)
- 0.170% (3/2X baseline concentration)
- 0.226% (2X baseline concentration).

Figures 4.13 through 4.16 provide comparative data for both sets of catalysts at the following test conditions: 1) 300°C and 11,000 GHSV and 2) 315°C and 11,000/hr GHSV. These conditions were chosen because the maximum C_2+ oxygenates STYs were achieved at 300°C, and carbon conversion at lower testing temperatures was very low to nonexistent, which made comparisons impractical. However, while the tests can be compared at 315°C, the data suggests some evidence of deactivation. Data also was obtained from higher temperatures that showed significant deactivation making comparisons impractical.
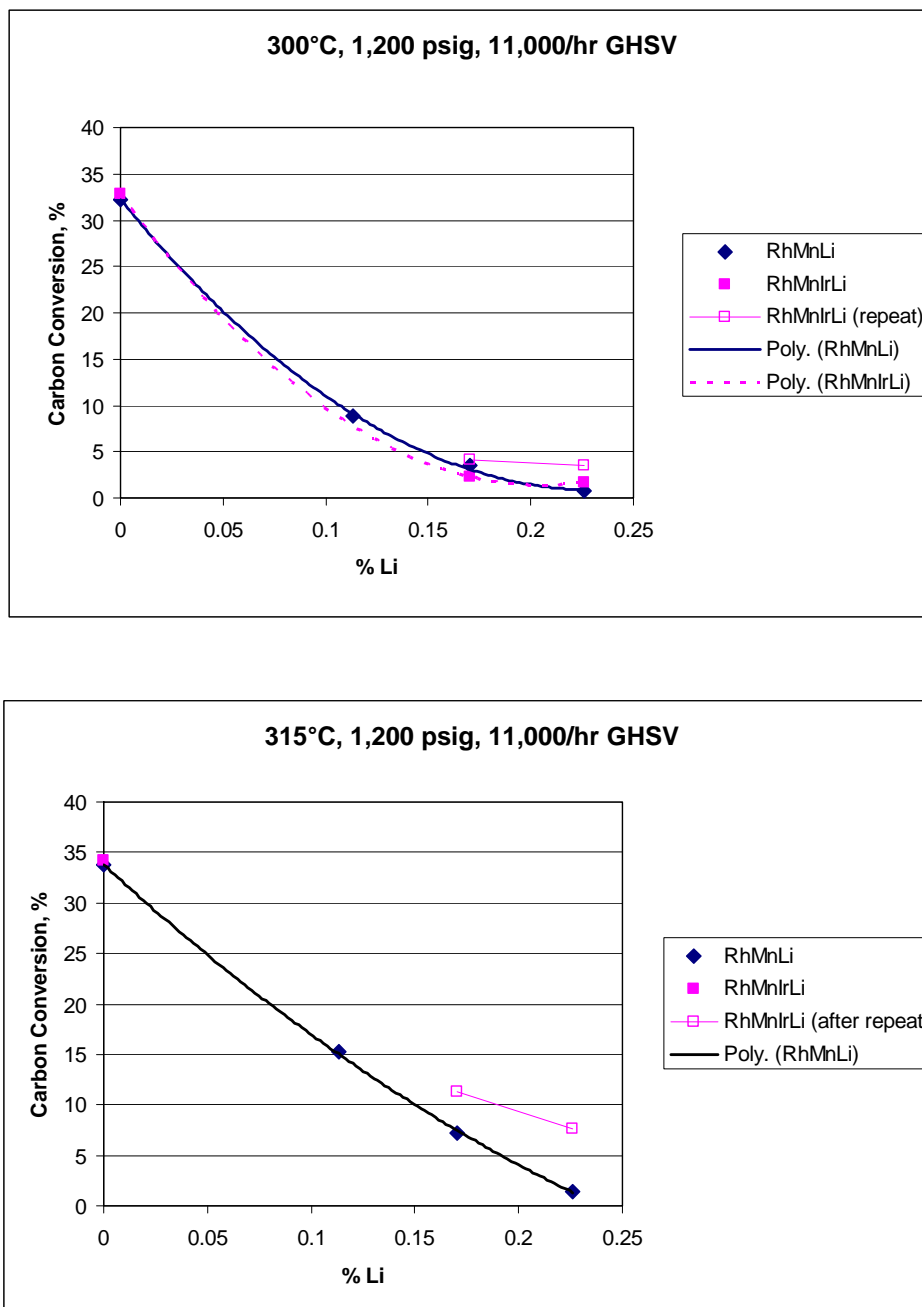
Figure 4.13. Effect of Li Concentration on Carbon Conversion for the Davisil 645 SiO_2-Supported RhMn and RhMnIr Catalysts at 300°C and 315°C

4.19
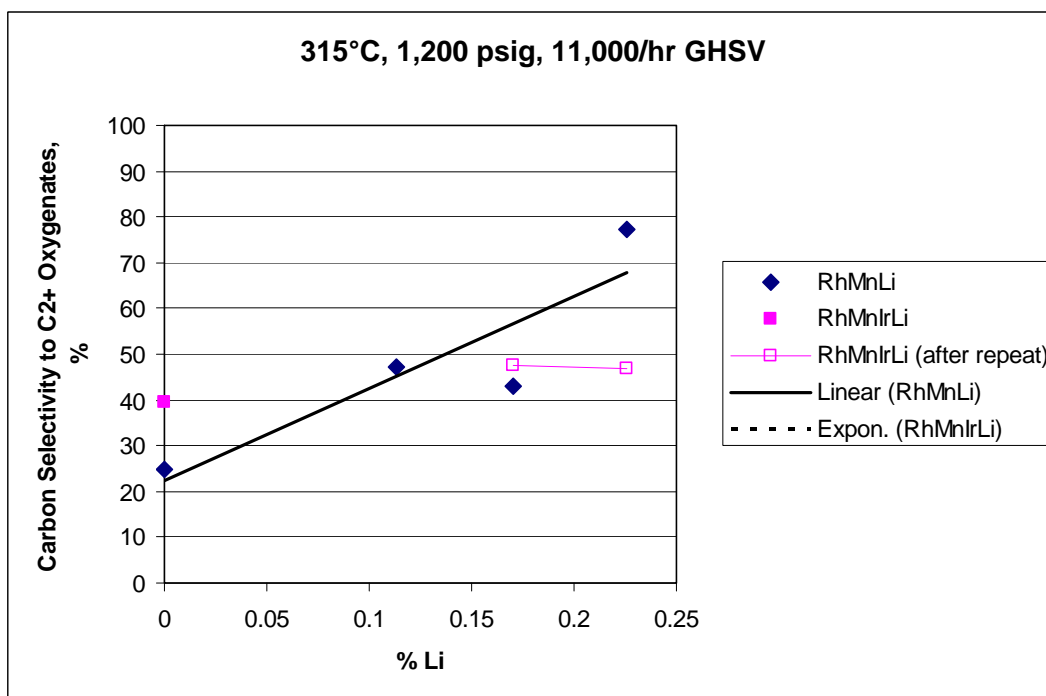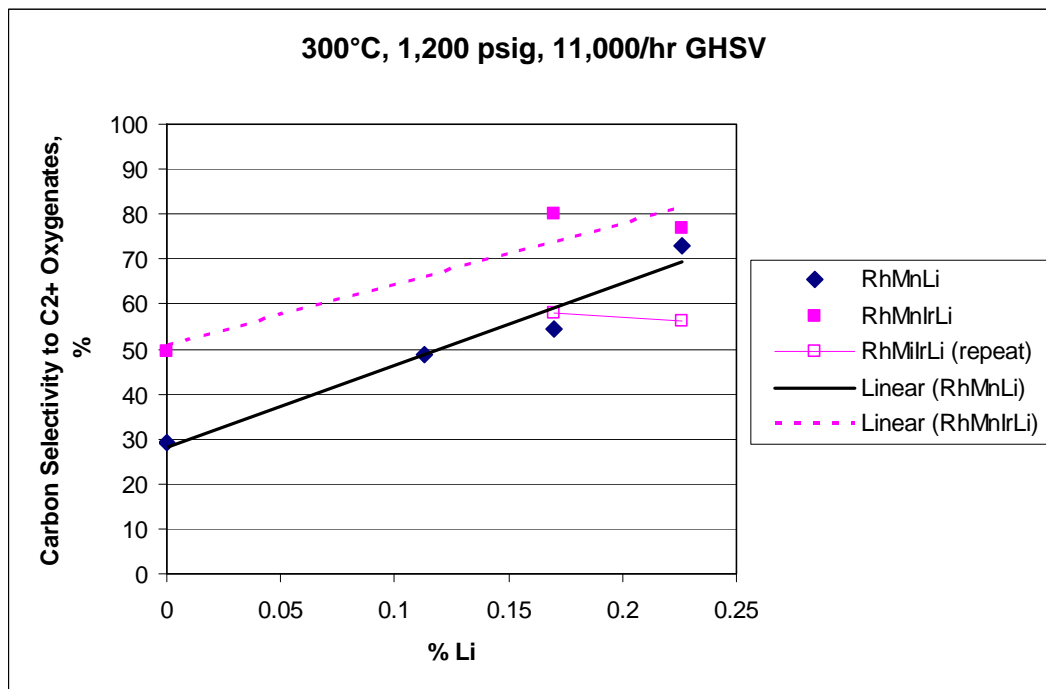
Figure 4.14. Effect of Li Concentration on Carbon Selectivity to C_2+ Oxygenates for the Davisil 645 SiO$_2$-Supported RhMn and RhMnIr Catalysts at 300°C and 315°C
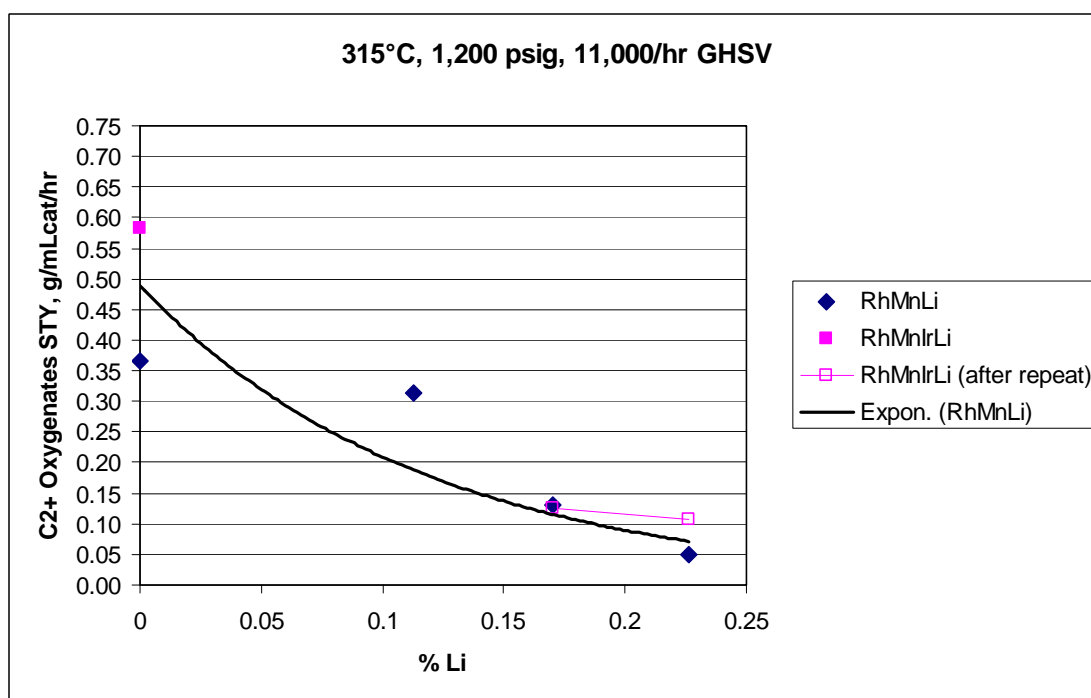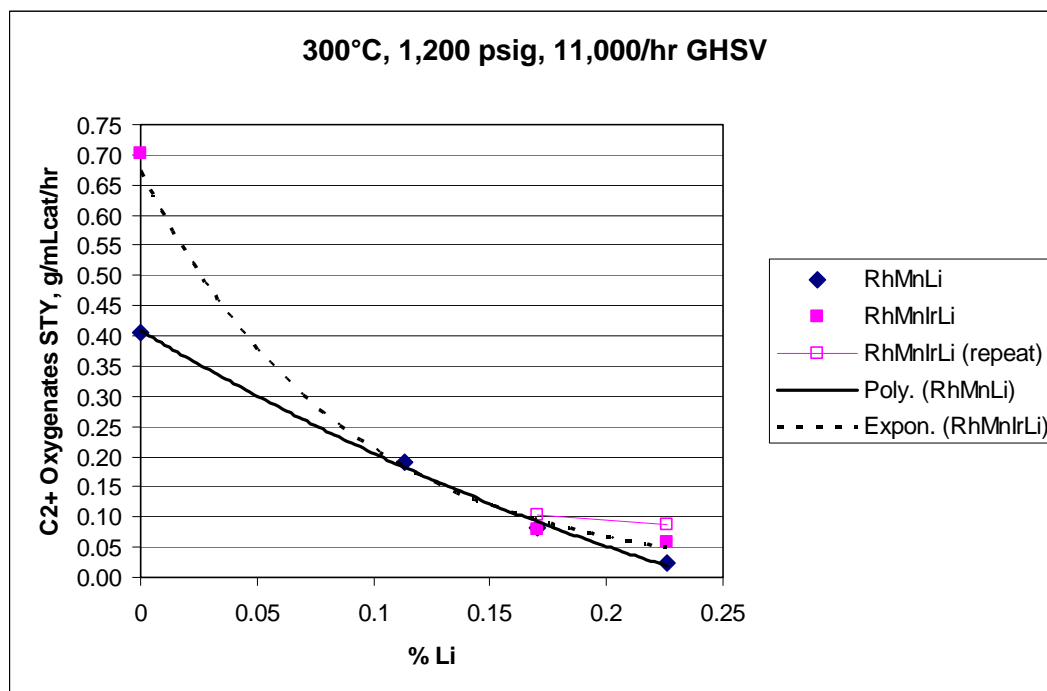
Figure 4.15. Effect of Li Concentration on C_2+ Oxygenates STY for the Davisil 645 SiO_2-Supported RhMn and RhMnIr Catalysts at 300°C and 315°C
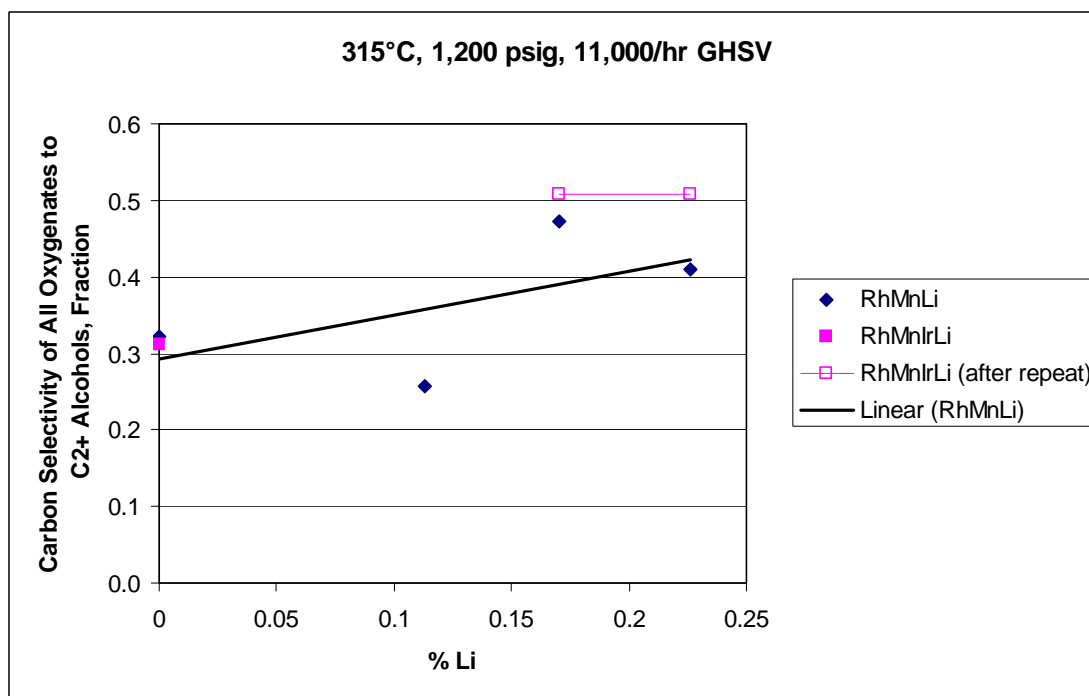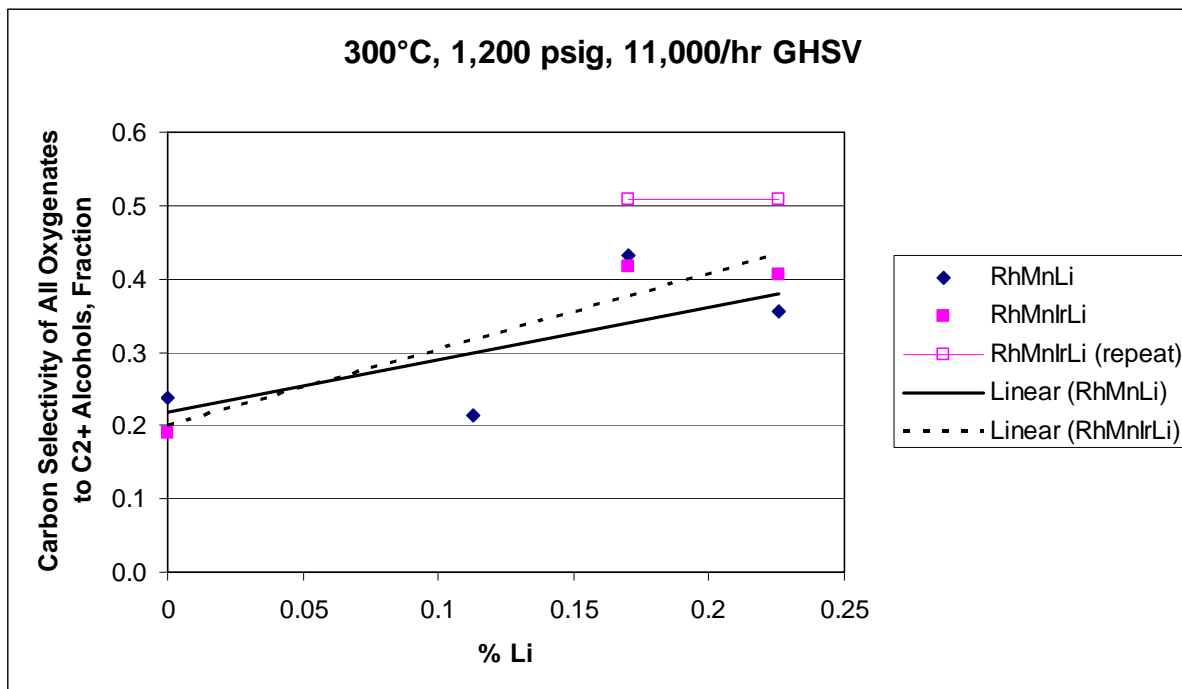
Figure 4.16. Effect of Li Concentration on Carbon Selectivity of C_2+ Oxygenates to Alcohols for the Davisil 645 SiO_2-Supported RhMn and RhMnIr Catalysts at 300°C and 315°C

Figure 4.13 compares the carbon conversions for different Li concentrations. Before examining the results, it should be noted that the conversion data for the 1.5 X and 2X Li with 1X Ir were obtained after the catalyst had been heated to testing temperatures as high as 345°C. A repeat of the test conditions at 300°C before testing at 315°C indicated that the catalyst had not deactivated and, in fact, had become slightly more active, at least with respect to carbon conversion. It also should be noted that no methane was detected by the GC for both of these catalysts when they were first evaluated at 300°C (a trace quantity of higher hydrocarbon gases were detected for the catalyst containing 1.5X Li and Ir), but methane was detected and reported when the conditions were repeated(see Appendix A). The catalyst with 2X Li also did not have any hydrocarbons detected by the GC when it was tested at 300°C. Neither the catalyst with 2X Li nor 1.5X Li were tested at 345°C, and the conditions were not repeated after being tested at 325°C.

Taking into account the caveats described above, it appears that the addition of increasing concentrations of Li resulted in a corresponding substantial decrease in carbon conversion. Furthermore, the incorporation of Ir provided no significant improvement in carbon conversion over the range of Li concentrations investigated. However, there did appear to be an improvement in carbon conversion when the two catalysts containing Ir were first tested at temperatures up to 345°C and then cooled to retest 300°C and 315°C. None of the other catalysts were tested at repeated conditions for comparison.

Figure 4.14 compares the converted carbon selectivity to C_2+ oxygenates for different Li concentrations. The addition of increasing concentrations of Li appears to result in a corresponding substantial increase in the carbon selectivity. It also appears that the presence of Ir significantly improves the selectivity at 300°C provided the catalyst has not seen higher temperatures. However, as previously discussed, the two catalysts containing 2X Li (with and without Ir) and the catalyst containing 1.5X Li with Ir did not produce measurable quantities of hydrocarbons, and the selectivity values result only from methanol production (see data in Appendix A). After the two catalysts containing Ir had been tested at 345°C, methane and other hydrocarbon gases were detected resulting in a significant decrease in carbon selectivity to the C_2+ oxygenates. The results from the tests run at 315°C are similar to those run at 300°C, but there are no comparable test conditions for the catalysts containing Li with and without Ir to make further comparisons of a possible beneficial effect of Ir on selectivity.

Figure 4.15 compares the C_2+ oxygenates STYs for different Li concentrations. The STYs for both the RhMn and RhMnIr catalysts generally followed the trend of carbon conversion with little, if any, benefit from the presence of Ir in the catalyst.

Figure 4.16 compares the carbon selectivity of oxygenates to C_2+ alcohols. Even though there is considerable scatter in the data, it appears that the addition of Li to the catalyst improves the selectivity to ethanol, and the presence of Ir provides additional, although modest, improvement.

Overall, the addition of Li to the RhMn catalyst improves the converted carbon selectivity to both the C_2+ oxygenates and ethanol, but at the expense of a significant decrease in the STYs of both. Consequently, it is not possible to specify an optimum Li concentration. Instead, it becomes an issue as to which parameter is more important, STY or selectivity, within the constraint that too high a catalyst temperature will cause the catalyst to significantly deactivate.

The presence of Ir in the catalyst does not improve the C_2+ oxygenates STYs when Li is present in the catalyst. However, it does appear to modestly improve the converted carbon selectivity to both C_2+ oxygenates and oxygenates to C_2+ alcohols.

4.2 Catalyst Screening Tests

A total of seven tests were conducted to screen additional promoters using the baseline RhMn/SiO$_2$ catalyst composition of 5.56% Rh and 1.69% Mn (Rh:Mn atomic ratio of 1:0.57) on Davisil 645 SiO$_2$. The promoters were added at concentrations corresponding to a Rh:M atomic ratio of 1.0:0.1, where M represents Mg, vanadium (V), lanthanum (La), Ce, B, or tungsten (W), which was the atomic ratio used to screen other promoters, except for Li, in earlier tests. A Rh:M atomic ratio of 1.0:0.30 was used for Na, so it could be compared to the ratio used to evaluate Li. RhMn/SiO$_2$ and Rh/SiO$_2$ catalysts also were prepared for comparison to catalysts with promoters added. All catalysts were prepared using a single impregnation to add the Rh, Mn, and additional promoter M to the catalyst support. This differs from the procedure previously reported for catalyst promoter screening (Gerber et al. 2008).

Two bases were used to compare the performance of the catalysts: 1) at the conditions under which the maximum STYs were achieved and 2) at a common set of operating conditions (300°C and 11,000 L/L$_{cat}$/hr). The results for conditions under which the maximum STYs were achieved acknowledges the possibility that the different test conditions may be needed to maximize STYs because of differences in the interplay among temperature, space velocity, carbon conversion, and selectivity to C$_2$+ oxygenates. Comparison of catalyst performance under a common set of conditions provides a common basis for those comparing carbon conversion and selectivity to products. The chosen set of conditions was selected because better catalysts also performed very well under these conditions, and in most cases, the catalysts had not undergone significant deactivation because of operating at higher temperatures. It also is the same set of conditions for comparison used in the previous report (Gerber et al. 2008).

Table 4.1 lists the test conditions at which the maximum C$_2$+ oxygenates STYs were achieved for the various promoters along with the corresponding carbon and CO conversions and liquid-product STYs. The STYs under these conditions are compared in Figure 4.17. In all cases, the maximum STY was obtained at a space velocity of 11,000 L/L$_{cat}$/hr. The carbon selectivity to various products are listed and compared in Tables 4.2 and Figure 4.18, respectively. Tables 4.3 and 4.4 and Figures 4.19 and 4.20 list and compare similar performance parameters for catalysts tested at the same operating conditions (300°C and 11,000 L/L$_{cat}$/hr).

It can be seen from Figure 4.17 that the Mg and B promoted catalysts performed nearly as well as the similarly prepared RhMn/SiO$_2$ catalyst in terms of the C$_2$+ oxygenates STYs. The W- and La-promoted catalysts achieved STYs that were more than 50% of that achieved by the RhMn/SiO$_2$ catalyst, while the V-promoted catalyst had a STY that was just below 50% of that achieved by the RhMn/SiO2 catalyst. The Ce- and Na-promoted catalysts were not very active. As expected, the Rh/SiO$_2$ catalyst also was not very active even at 345°C. When compared at a common temperature of 300°C (Figure 4.18), the ranking of the catalysts are nearly the same, with the exceptions that only the B-promoted catalyst had C$_2$+ oxygenates STY that was comparable to the unpromoted catalysts with a STY of about 90% of that achieved by the unpromoted MgMn/SiO2 catalyst. The Mg- and W-promoted catalysts had similar STYs that were about 75% of that achieved by the unpromoted catalyst. The La-promoted catalysts was only marginally active with a STY that was less than 40% of that achieved by the unpromoted catalysts and the V-promoted catalyst was nearly inactive with an STY that was less than 20% of that achieved by the unpromoted catalyst. While the Rh/SiO$_2$ catalyst is slightly more active than the Na-Promoted RhMn/SiO$_2$ catalyst, both were considered to be essentially inactive. Repeating the test conditions at

300°C for the B-, Mg-, La-, and W-promoted catalysts (not shown in the figure) showed that the catalysts did deactivate during tests at temperatures above 300°C as did the RhMn catalyst tested earlier.

Table 4.2 summarizes the carbon selectivity to the various oxygenated organics and hydrocarbon products for the catalysts under the conditions for achieving maximum C_2+ oxygenates STYs, and Table 4.4 summarizes the carbon selectivity at the common operating conditions (300°C and 11,000 $L/L_{cat}/hr$ GHSV), respectively. Figures 4.19 and 4.20 compare the selectivity of the catalysts for these respective test conditions. It can be seen that of the more active promoted catalysts (i.e., the Mg, B, W, and La promoters) only the La-promoted catalysts had significantly greater converted carbon selectivity to C_2+ oxygenates, while operating at their conditions for maximum C_2+ oxygenates STYs. When operating at the common testing temperature of 300°C, the Mg- and B-promoted catalysts also had higher selectivity. Both the Mg- and the La-promoted catalysts had significantly greater selectivity to C_2+ alcohols at both the common temperature of 300°C and at their conditions for achieving maximum C_2+ oxygenates STYs.

Overall, none of the promoted catalysts was more active than the unpromoted $RhMn/SiO_2$ catalyst. However, the B-, Mg-, and La-promoted catalysts did achieve comparable or better converted carbon selectivity to C_2+ oxygenates at both the conditions where they achieved their maximum C_2+ oxygenates STYs and at the common testing temperature of 300°C, with the Mg- and La-promoted catalysts achieving significantly greater selectivity to alcohols. Considering these results, the remaking of catalysts with these three promoters added in a second impregnation would be warranted to see if this method of adding the promoters could improve performance of the catalysts.

Table 4.1. Comparison of Carbon Conversions and STYs of Promoted RhMn/SiO$_2$ Catalysts at Conditions Maximizing C$_2$+ Oxygenates STYs

Catalyst	Space Velocity, L/L$_{cat}$/hr	Temp., °C	Carbon Conv., %	CO Conv., %	CO Conv. to CO$_2$, %	STY (g/mL$_{cat}$/hr) MEOH	C$_2$+ Alcohols	Other C$_2$+ Oxygenates	HC Liquids	Total Liquids	Carbon Balance (C$_{out}$/C$_{in}$), %
RhMn	11000	301	32.24	36.36	-0.17	0.01	0.10	0.31	0.03	0.44	98
RhMnMg	11000	323	24.64	27.35	-0.60	0.03	0.17	0.23	0.00	0.43	98
RhMnB	11000	325	31.44	34.96	-0.35	0.02	0.13	0.27	0.01	0.43	99
RhMnW	11000	314	30.06	37.05	3.30	0.02	0.10	0.22	0.02	0.36	98
RhMnLa	11000	325	14.21	15.16	-0.87	0.04	0.16	0.09	0.00	0.28	98
RhMnV	11000	343	11.22	12.03	-0.70	0.02	0.13	0.07	0.00	0.22	99
RhMnCe	11000	327	5.31	4.99	-1.00	0.03	0.06	0.02	0.00	0.12	98
RhMnNa	11000	345	4.32	5.61	0.78	0.04	0.04	0.04	0.00	0.11	98
Rh	11000	345	8.25	9.14	-0.12	0.02	0.04	0.02	0.00	0.08	99
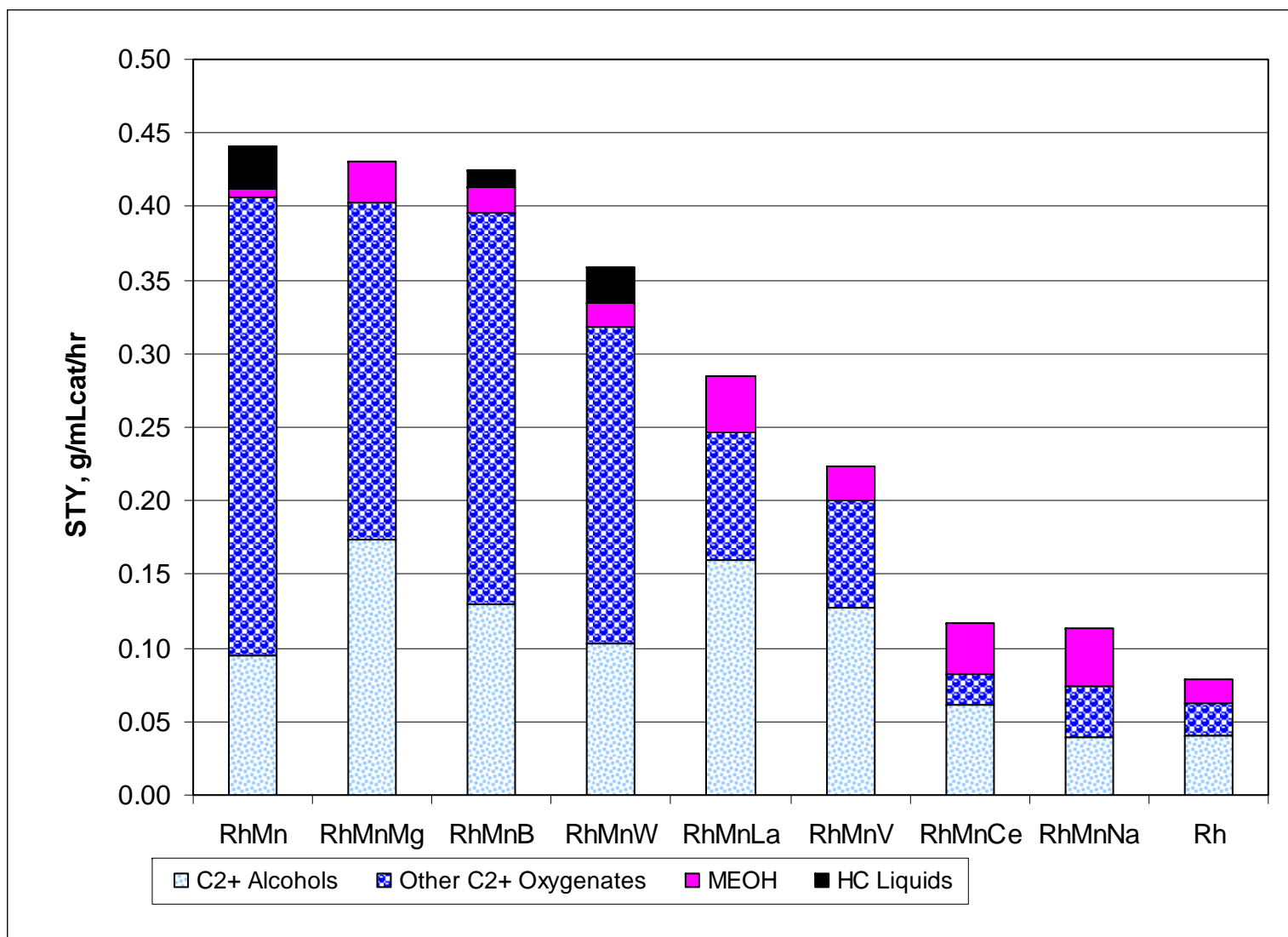
Figure 4.17. STYs of Promoted Catalysts at Conditions for Maximum STYs

Table 4.2. Comparison of Carbon Selectivity to Products of Promoted RhMn/SiO$_2$ Catalysts at Conditions Maximizing C$_2$+ Oxygenates STYs

| Catalyst | Space Velocity, L/L/hr | Temp., °C | Carbon Conv., % | Carbon Selectivity (C-Mol%) | | | | | | |
				MEOH	Other C$_1$ Oxygenates	C$_2$+ Alcohols	Other C$_2$+ Oxygenates	Methane	Higher HC Gases	Higher HC Liquids (est)
RhMn	11,000	301	32.24	0.29	0.00	7.04	22.20	50.41	16.71	3.36
RhMnMg	11,000	323	24.64	1.98	0.00	17.17	13.38	55.20	12.26	0.00
RhMnB	11,000	325	31.44	0.93	0.00	10.01	18.96	53.54	15.07	1.49
RhMnW	11,000	314	30.06	0.88	0.00	8.44	16.59	45.67	25.30	3.12
RhMnLa	11,000	325	14.21	4.55	0.00	26.56	9.12	48.96	10.81	0.00
RhMnV	11,000	343	11.22	3.49	0.00	27.36	9.91	49.32	9.92	0.00
RhMnCe	11,000	327	5.31	11.02	0.00	27.28	8.69	49.97	3.03	0.00
RhMnNa	11,000	345	4.32	15.25	0.00	21.84	17.70	41.06	4.15	0.00
Rh	11,000	345	8.25	3.17	0.00	11.53	5.97	65.14	14.19	0.00
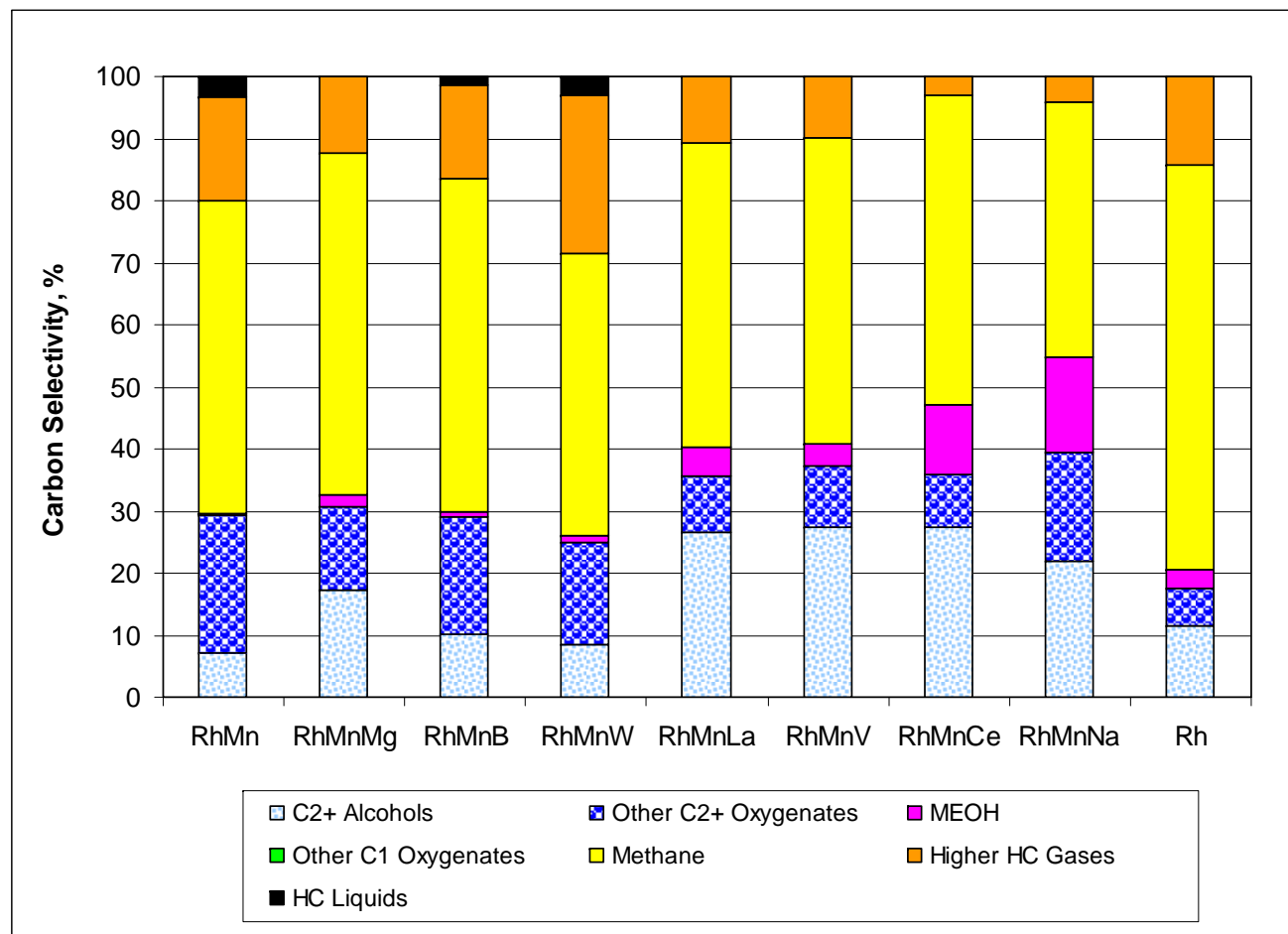
Figure 4.18. Carbon Selectivity of Promoted Catalysts at Conditions for Maximum STYs

Table 4.3. Comparison of Carbon Conversions and STYs of Promoted RhMn/SiO$_2$ Catalysts at 300°C, 11,000 L/L$_{cat}$/hr

Catalyst	Space Velocity, L/L/hr	Temp., °C	Carbon Conv., %	CO Conv., %	CO Conv. to CO$_2$, %	STY (g/mLcat/hr)					Carbon Balance (C$_{out}$/C$_{in}$), %
						MEOH	C$_2$+ Alcohols	Other C$_2$+ Oxygenates	HC Liquids	Total Liquids	
RhMn	11,000	301	32.24	36.36	-0.17	0.01	0.10	0.31	0.03	0.44	99
RhMnB	11,000	301	21.45	23.73	-0.27	0.01	0.08	0.29	0.01	0.39	98
RhMnMg	11,000	300	13.91	14.81	-0.86	0.02	0.10	0.20	0.00	0.31	97
RhMnW	11,000	299	25.26	31.32	2.98	0.01	0.09	0.20	0.02	0.33	98
RhMnLa	11,000	301	7.96	8.38	-0.55	0.02	0.07	0.09	0.00	0.18	98
RhMnV	11,000	300	2.89	2.47	-0.78	0.01	0.03	0.04	0.00	0.08	98
RhMnCe	11,000	301	2.17	1.92	-0.52	0.02	0.02	0.02	0.00	0.05	99
Rh	11,000	301	1.76	1.34	-0.63	0.00	0.01	0.01	0.00	0.03	98
RhMnNa	11,000	301	0.33	0.07	-0.30	0.01	0.00	0.01	0.00	0.02	98
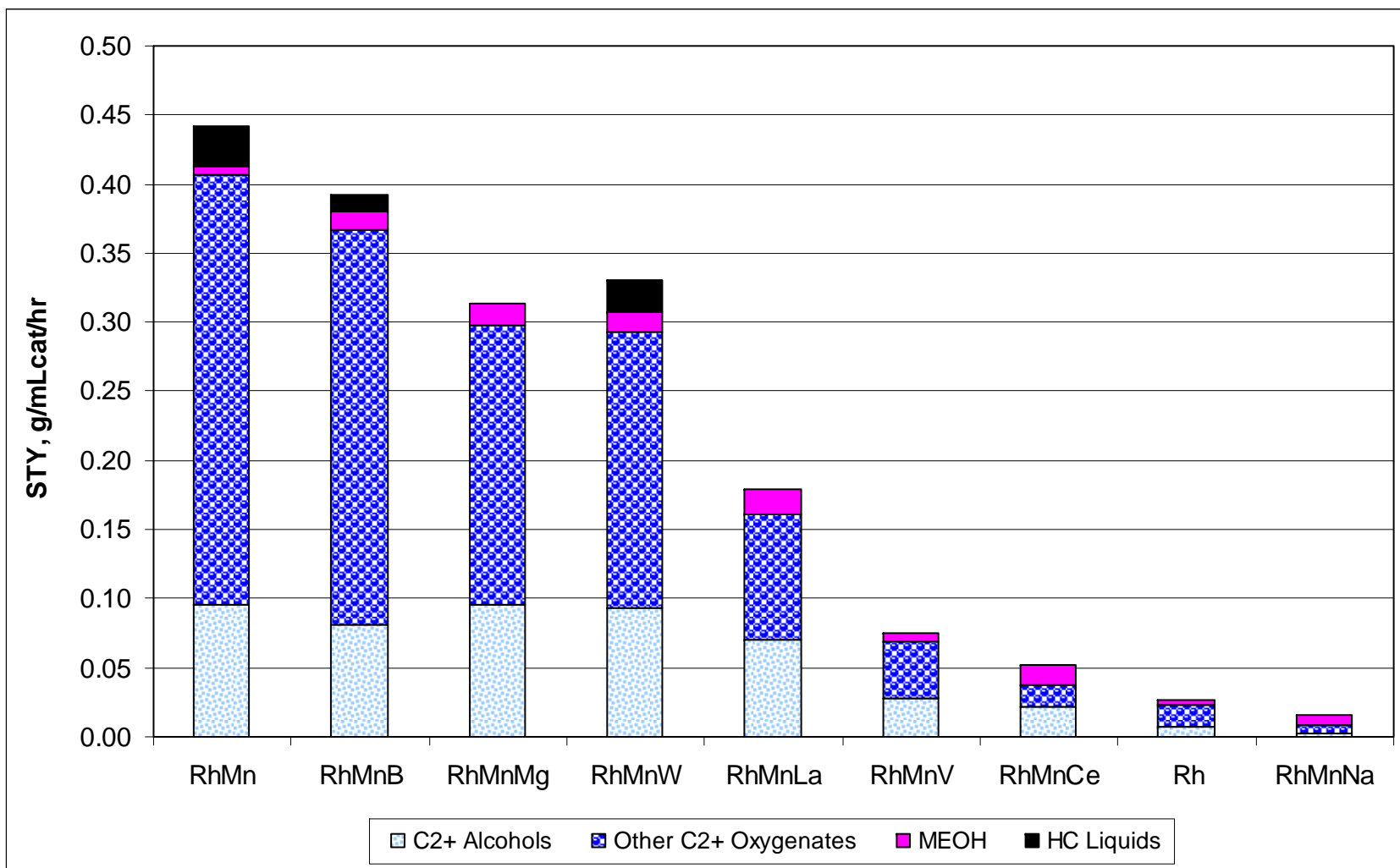
Figure 4.19. STYs of Promoted Catalysts at 300°C and 11,000 L/Lcat/hr

Table 4.4. Comparison of Carbon Selectivity to Products of Promoted RhMn/SiO$_2$ Catalysts at 300°C and 11000 L/L$_{cat}$/hr

| Catalyst | Space Velocity, L/L$_{cat}$/hr | Temp., °C | Carbon Conv., % | Carbon Selectivity (C-Mol%) | | | | | | |
				MEOH	Other C$_1$ Oxygenates	C$_2$+ Alcohols	Other C$_2$+ Oxygenates	Methane	Higher HC Gases	Higher HC Liquids (est)
RhMn	11,000	301	32.24	0.29	0.00	7.04	22.20	50.41	16.71	3.36
RhMnB	11,000	301	21.45	1.03	0.00	9.14	29.21	41.52	16.93	2.17
RhMnMg	11,000	300	13.91	1.98	0.00	16.68	21.50	46.22	13.61	0.00
RhMnW	11,000	299	25.26	0.95	0.00	8.94	17.61	41.46	27.73	3.32
RhMnLa	11,000	301	7.96	3.93	0.00	21.53	17.46	42.16	14.93	0.00
RhMnV	11,000	300	2.89	3.96	0.00	23.02	22.29	46.98	3.75	0.00
RhMnCe	11,000	301	2.17	11.95	0.00	24.34	14.82	45.21	3.68	0.00
Rh	11,000	301	1.76	3.68	0.00	10.53	17.61	64.23	3.95	0.00
RhMnNa	11,000	301	0.33	34.71	0.00	21.13	35.40	0.00	8.76	0.00
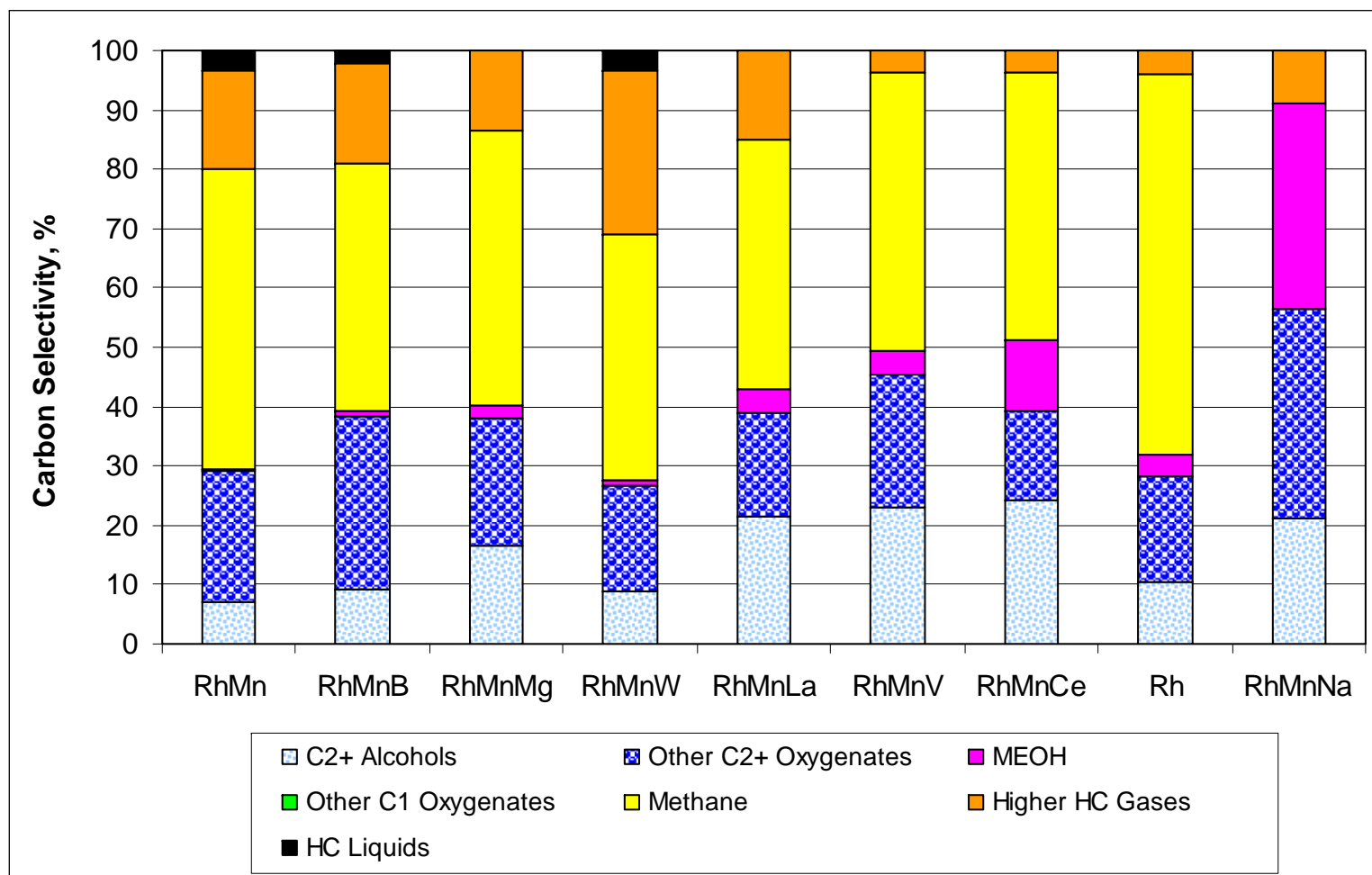
Figure 4.20. Carbon Selectivity of Promoted Catalysts at 300°C and 11,000 L/L$_{cat}$/hr

5.0   Conclusions and Recommendations

Parametric tests were conducted to optimize the amounts of Rh, Mn, Li, and Ir on a SiO_2 support with respect to the C_2+ oxygenates carbon conversion, STY, converted carbon selectivity to C_2+ oxygenates, and selectivity of the C_2+ oxygenates to alcohols. Based on the results of the parametric tests, several conclusions were reached.

It appears that the optimum Rh concentration is about 5.56 wt% (1X the baseline concentration) when used in combination with Mn in which the Mn:Rh atomic ratio was 0.57 (1.69% Mn). It may be possible to get further improvements at slightly higher Rh concentrations, but in a test at 1.5X the baseline concentration, the high hydrocarbon concentrations in the product gas accompanied by heat management problems at temperatures as low as 271°C made evaluation very difficult.

It also appears that the optimum manganese concentration is about 1.13 wt% (2/3X the baseline concentration) when Rh is at the baseline concentration of 5.56 wt%. This concentration provides the highest C_2+ oxygenates STY, while not significantly compromising the converted carbon selectivity to C_2+ oxygenates. The selectivity of the C_2+ oxygenates to alcohols does not appear to be affected significantly by Mn concentrations above 0.55%.

The optimum Ir concentration is between 0.34% and 1.03% (1/3X and 1X the baseline concentration), when the RhMn concentrations are at their baseline concentrations (5.56 wt% Rh and 1.69 wt% Mn). This concentration range provides high C_2+ oxygenates STYs accompanied by favorable converted carbon selectivity on the order of 45% to 52% to C_2+ oxygenates. The selectivity of the C_2+ oxygenates to alcohols is relatively low (about 15% to 25%) over this concentration range, but none of the conditions achieved a very good selectivity, with the selectivity ranging from about 15% to 35% over the range of temperatures and Ir concentrations evaluated.

The addition of Li to the RhMn catalyst improves the converted carbon selectivity to both the C_2+ oxygenates and ethanol but at the expense of a significant decrease in the STYs of both. Consequently, it is not possible to specify an optimum Li concentration. Instead, it becomes an issue as to which parameter, STY or selectivity, is more important within the constraint that too high of a catalyst temperature will cause the catalyst to deactivate.

The presence of Ir in a catalyst also containing Li does not improve the C_2+ oxygenates or ethanol STYs. However, it does appear to modestly improve the converted carbon selectivity to both C_2+ oxygenates and ethanol. There also is an indication that alteration of the catalyst containing Ir at higher temperatures (up to 345°C) may improve the catalyst activity and the converted carbon selectivity of the oxygenates to C_2+ alcohols, although at the expense of converted carbon selectivity to C_2+ oxygenates.

Seven tests were conducted to screen Mg, V, La, Ce, B, W, and Na as possible additives using the baseline $RhMn/SiO_2$ catalyst composition of 5.56 wt% Rh and 1.69 wt% Mn on Davisil 645 SiO_2. Overall, none of the modified catalysts was more active than the $RhMn/SiO_2$ catalyst. However, the B-, Mg-, and La-promoted catalysts did achieve comparable or better converted carbon selectivity to C_2+ oxygenates at both the conditions where they achieved their maximum C_2+ oxygenates STYs and at the common testing temperature of 300°C, with the Mg- and La-promoted catalysts achieving significantly greater selectivity to alcohols. Based on these results, remaking these three catalysts using two

impregnations (as was done in the earlier tests) would be warranted to see if this method of adding the promoters could further improve the performance of these catalysts.

6.0 References

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Appendix A

Catalyst Testing Data

Appendix A

Catalyst Testing Data

Table A.1. Summary Catalyst Optimization Test Results

Parameter	Catalyst Concentrations, wt% Rh/Mn/Ir/Li	Space Velocity L/L/hr	Temp. °C	Carbon Conv. %	CO Conv. %	CO Conv. to CO2, %	Carbon Selectivity (C-Mol%)						STY (g/mL$_{cat}$/hr)						Carbon Balance (C$_{out}$/C$_{in}$), %
							MEOH	Other C$_1$ Oxygenates	C$_2$+ Alc.	Other C$_2$+ Oxygenates	Methane	Total Higher HCs (est)	C$_2$+ Alcohols	Other C$_2$+ Oxygenates	Total C$_2$+ Oxygenates	HC Liquids	MEOH	Total Liq.	
Total RhMn metals concentration	1.85/0.56/0/0	7500	275	1.17	1.06	-0.26	3.92	0.02	17.41	23.79	53.96	0.90	0.006	0.009	0.015	0.000	0.002	0.016	97.54
	2.78/0.84/0/0	7500	275	2.08	2.10	-0.24	1.55	0.00	8.54	35.91	43.93	10.07	0.005	0.024	0.029	0.000	0.001	0.030	96.61
	3.71/1.13/0/0	7500	276	4.20	4.51	-0.21	0.86	0.00	10.65	23.74	56.54	8.21	0.013	0.031	0.043	0.001	0.001	0.046	95.77
	5.56/1.69/0/0	7500	275	29.99	33.47	-0.51	0.65	0.00	6.27	35.75	30.34	27.00	0.052	0.316	0.368	0.064	0.008	0.440	99.64
	1.85/0.56/0/0	11000	300	3.30	4.52	0.80	3.41	0.00	19.39	21.69	50.82	4.69	0.026	0.033	0.059	0.000	0.007	0.066	103.67
	2.78/0.84/0/0	11000	301	4.08	4.30	-0.33	1.26	0.00	11.87	37.63	47.95	1.29	0.020	0.073	0.094	0.000	0.003	0.097	97.77
	3.71/1.13/0/0	11000	302	12.69	13.87	-0.38	0.91	0.00	12.55	30.99	41.41	14.14	0.067	0.184	0.252	0.000	0.007	0.259	93.62
	5.56/1.69/0/0	11000	301	32.24	36.36	-0.17	0.29	0.00	7.04	22.20	50.41	20.07	0.095	0.311	0.407	0.029	0.006	0.441	97.69
Manganese Concentration	5.56/0/0/0	11000	301	1.76	1.34	-0.63	3.68	0.00	10.53	17.61	64.23	3.95	0.008	0.015	0.023	0.000	0.004	0.027	98.09
	5.56/0.28/0/0	11000	300	12.66	13.93	-0.23	1.45	0.00	15.52	33.54	36.94	12.55	0.085	0.202	0.287	0.000	0.011	0.298	99.31
	5.56/0.56/0/0	11000	298	28.71	32.56	0.10	0.71	0.01	8.22	26.62	47.62	16.83	0.093	0.319	0.413	0.000	0.011	0.424	98.03
	5.56/1.13/0/0	11000	297	38.32	43.35	-0.02	0.68	0.00	8.31	23.63	48.90	18.48	0.129	0.381	0.511	0.022	0.015	0.547	98.49
	5.56/1.69/0/0	11000	301	32.24	36.36	-0.17	0.29	0.00	7.04	22.20	50.41	20.07	0.095	0.311	0.407	0.029	0.006	0.441	97.69
	5.56/2.25/0/0	11000	298	40.72	46.58	0.44	0.49	0.00	7.47	19.31	55.02	17.71	0.122	0.328	0.451	0.007	0.011	0.469	99.80
	5.56/0/0/0	11000	316	3.53	3.66	-0.30	2.85	0.00	9.46	10.20	54.54	22.94	0.014	0.017	0.032	0.000	0.006	0.038	98.67
	5.56/0.28/0/0	11000	315	17.56	19.29	-0.34	1.42	0.00	18.92	21.58	45.50	12.58	0.141	0.171	0.312	0.001	0.015	0.328	97.83
	5.56/0.56/0/0	11000	314	36.28	42.21	1.07	0.50	0.00	9.34	17.32	57.83	15.00	0.135	0.258	0.393	0.000	0.010	0.403	97.39
	5.56/1.13/0/0	11000	315	42.91	50.07	1.61	0.57	0.00	8.64	14.55	61.74	14.48	0.148	0.259	0.408	0.000	0.014	0.421	100.68
	5.56/1.69/0/0	11000	315	33.73	38.84	0.70	0.44	0.00	8.16	16.71	56.34	18.34	0.117	0.249	0.366	0.000	0.009	0.375	95.71
	5.56/2.25/0/0	11000	316	40.94	47.35	1.07	0.51	0.00	7.89	11.89	66.39	13.32	0.128	0.199	0.327	0.000	0.012	0.339	99.66
Iridium Concentration	5.56/1.69/0/0	7500	275	29.99	33.47	-0.51	0.65	0.00	6.27	35.75	30.34	27.00	0.052	0.316	0.368	0.064	0.008	0.440	99.64
	5.56/1.69/0.0172/0	7500	276	11.19	12.28	-0.26	1.01	0.00	10.15	32.75	33.92	22.17	0.031	0.109	0.140	0.000	0.004	0.145	95.57
	5.56/1.69/0.343/0	7500	276	21.99	24.67	-0.01	1.31	0.00	7.80	44.15	29.10	17.64	0.046	0.279	0.325	0.000	0.011	0.336	96.19
	5.56/1.69/1.03/0	7500	275	24.03	27.18	0.38	0.90	0.00	6.90	42.78	27.24	22.18	0.046	0.309	0.355	0.000	0.009	0.364	98.71
	5.56/1.69/1.37/0	7500	275	39.35	43.45	-0.59	0.13	0.01	3.96	21.63	29.83	44.45	0.039	0.235	0.274	0.069	0.002	0.345	95.55
	5.56/1.69/1.72/0	7500	276	49.02	54.20	-0.67	0.43	0.01	6.61	21.81	31.00	40.15	0.085	0.301	0.386	0.146	0.008	0.541	96.45
	5.56/1.69/0/0	11000	301	32.24	36.36	-0.17	0.29	0.00	7.04	22.20	50.41	20.07	0.10	0.31	0.41	0.03	0.01	0.44	97.69
	5.56/1.69/0.0172/0	11000	300	22.28	24.75	-0.26	1.25	0.00	13.66	30.19	34.16	20.75	0.13	0.30	0.43	0.00	0.02	0.45	100.81
	5.56/1.69/0.343/0	11000	299	30.24	34.10	0.13	0.94	0.00	10.64	35.60	36.86	15.96	0.13	0.47	0.60	0.00	0.02	0.61	98.29
	5.56/1.69/1.03/0	11000	299	32.75	36.89	0.22	0.81	0.00	9.55	39.91	31.59	18.14	0.13	0.57	0.70	0.00	0.02	0.72	100.56

Table A.1. (cont'd)

Parameter	Catalyst Concentrations, wt% Rh/Mn/Ir/Li	Space Velocity L/L/hr	Temp. °C	Carbon Conv. %	CO Conv. %	CO Conv. to CO_2, %	Carbon Selectivity (C-Mol%)						STY (g/mL$_{cat}$/hr)						Carbon Balance (C_{out}/C_{in}), %
							MEOH	Other C_1 Oxygenates	C_2+ Alc.	Other C_2+ Oxygenates	Methane	Total Higher HCs (est)	C_2+ Alcohols	Other C_2+ Oxygenates	Total C_2+ Oxygenates	HC Liquids	MEOH	Total Liq.	
	5.56/1.69/1.37/0	11000	300	45.39	50.53	-0.06	0.08	0.01	6.19	23.57	33.12	37.03	0.109	0.443	0.552	0.062	0.002	0.616	98.87
	5.56/1.69/1.72	11000	301	49.14	54.61	-0.51	0.31	0.00	9.14	17.96	48.48	24.12	0.18	0.37	0.55	0.02	0.01	0.57	97.62
Lithium Concentration (RhMn on Catalyst)	5.56/1.69/0/0	11000	301	32.24	36.36	-0.17	0.29	0.00	7.04	22.20	50.41	20.07	0.095	0.311	0.407	0.029	0.006	0.441	97.69
	5.56/1.69/0/0.113	11000	301	8.83	9.65	-0.27	2.14	0.00	10.83	37.81	28.75	20.47	0.039	0.152	0.191	0.000	0.011	0.202	98.56
	5.56/1.69/0/00.170	11000	300	3.47	3.24	-0.69	8.29	0.00	27.01	27.37	30.28	7.05	0.037	0.044	0.081	0.000	0.016	0.097	97.57
	5.56/1.69/0/00.227	11000	300	0.72	0.13	-0.69	26.93	0.00	35.54	37.53	0.00	0.00	0.010	0.013	0.024	0.000	0.011	0.035	98.23
	5.56/1.69/0/0	11000	315	33.73	38.84	0.70	0.44	0.00	8.16	16.71	56.34	18.34	0.117	0.249	0.366	0.000	0.009	0.375	95.71
	5.56/1.69/0/0.113	11000	316	15.33	16.88	-0.30	1.60	0.00	12.55	34.80	33.90	17.15	0.079	0.235	0.314	0.000	0.015	0.329	98.60
	5.56/1.69/0/00.170	11000	316	7.17	8.05	-0.03	6.09	0.00	23.28	19.80	33.13	17.71	0.068	0.062	0.130	0.000	0.025	0.155	97.12
	5.56/1.69/0/00.227	11000	315	1.47	1.44	-0.22	22.79	0.00	40.88	36.33	0.00	0.00	0.025	0.026	0.051	0.000	0.019	0.070	97.55
Lithium Concentration (RhMnIr on Catalyst)	5.56/1.69/1.03/0	11000	299	32.75	36.89	0.22	0.81	0.00	9.55	39.91	31.59	18.14	0.128	0.574	0.702	0.000	0.016	0.718	100.56
	5.56/1.69/1.03/0.170	11000	300	2.33	2.14	-0.49	14.72	0.00	39.43	40.56	0.00	5.29	0.037	0.043	0.080	0.000	0.019	0.099	97.31
	5.56/1.69/1.03/0.170	11000	300 (repeat)	4.17	4.27	-0.43	9.37	0.00	30.52	27.36	29.81	2.93	0.051	0.053	0.104	0.000	0.022	0.126	99.11
	5.56/1.69/1.03/0.227	11000	301	1.71	1.41	-0.51	23.23	0.00	40.48	36.29	0.00	0.00	0.028	0.029	0.057	0.000	0.023	0.080	97.68
	5.56/1.69/1.03/0.227	11000	301 (Repeat)	3.57	3.56	-0.46	11.95	0.00	29.79	26.50	29.08	2.67	0.043	0.045	0.087	0.000	0.024	0.112	99.15
	5.56/1.69/1.03/0	11000	314	34.16	38.52	0.28	0.66	0.00	12.47	26.89	42.28	17.71	0.179	0.404	0.582	0.000	0.013	0.596	98.86
	5.56/1.69/1.03/0.170	11000	315 (after repeat)	6.36	6.63	-0.57	8.59	0.00	28.47	18.93	40.09	3.91	0.073	0.052	0.125	0.000	0.031	0.156	97.14
	5.56/1.69/1.03/0.227	11000	315 (after Repeat)	5.51	5.76	-0.47	9.41	0.00	28.70	18.32	39.83	3.74	0.064	0.045	0.108	0.000	0.029	0.138	97.50

Table A.2. Summary of Catalyst Screening Test Results

Catalyst	Space Velocity, L/L/hr	Temp. °C	Carbon Conv. %	CO Conv. %	CO Conv. To CO_2	Carbon Selectivity (C-Mole%)						STY (g/mL$_{cat}$/hr)						Carbon Balance (C_{out}/C_{in}) %
						MeOH	Other C_1 Oxygenates	C_2+ Alc.	Other C_2+ Oxygenates	Methane	Total Higher HCs (est)	C_2+ Alcohols	Other C_2+ Oxygenates	Total C_2+ Oxygenates	HC Liquids	MeOH	Total Liq.	
RhMnV/SiO$_2$	7500	256	0.82	0.64	-0.29	10.11	0.01	36.79	53.08	0.00	0.00	0.01	0.02	0.02	0.00	0.00	0.03	98.87
	7500	276	0.40	-0.39	-0.84	8.80	0.00	36.73	54.48	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.01	96.62
	11000	300	2.89	2.47	-0.78	3.96	0.00	23.02	22.29	46.98	3.75	0.03	0.04	0.07	0.00	0.01	0.08	97.64
	11000	325	6.93	6.99	-0.83	3.20	0.00	23.95	10.38	49.39	13.08	0.07	0.05	0.12	0.00	0.01	0.13	97.55
	11000	343	11.22	12.03	-0.70	3.49	0.00	27.36	9.91	49.32	9.92	0.13	0.07	0.20	0.00	0.02	0.22	99.20
RhMnMg/SiO$_2$	7500	257	3.72	3.86	-0.34	4.22	0.01	20.39	39.15	32.00	4.23	0.02	0.06	0.08	0.00	0.01	0.09	98.44
	7500	276	6.87	6.92	-0.85	2.08	0.00	13.17	17.23	49.07	18.45	0.02	0.05	0.08	0.00	0.01	0.08	95.54
	11000	300	13.91	14.81	-0.86	1.98	0.00	16.68	21.50	46.22	13.61	0.10	0.20	0.30	0.00	0.02	0.31	96.84
	11000	315	19.36	21.05	-0.80	2.01	0.00	18.14	16.06	56.59	7.20	0.14	0.22	0.36	0.00	0.02	0.38	95.15
	11000	323	24.64	27.35	-0.60	1.98	0.00	17.17	13.38	55.20	12.26	0.17	0.23	0.40	0.00	0.03	0.43	98.12
	11000	302	11.82	11.94	-1.43	2.42	0.00	15.10	17.80	49.78	14.90	0.07	0.15	0.22	0.00	0.02	0.24	96.66
RhMnLa/SiO$_2$	7500	256	0.69	0.93	0.16	11.29	0.00	36.88	44.79	0.00	7.04	0.01	0.01	0.02	0.00	0.00	0.02	97.70
	7500	276	3.76	4.09	-0.12	3.43	0.00	15.27	15.95	42.11	23.23	0.02	0.03	0.04	0.00	0.00	0.05	97.46
	11000	301	7.96	8.38	-0.55	3.93	0.00	21.53	17.46	42.16	14.93	0.07	0.09	0.16	0.00	0.02	0.18	98.36
	11000	315	10.95	11.74	-0.53	3.94	0.00	24.40	10.43	47.65	13.58	0.11	0.08	0.19	0.00	0.03	0.21	97.76
	11000	325	14.21	15.16	-0.87	4.55	0.00	26.56	9.12	48.96	10.81	0.16	0.09	0.25	0.00	0.04	0.28	98.30
	11000	301	6.48	7.13	-0.15	5.34	0.00	25.51	14.49	40.99	13.67	0.07	0.06	0.13	0.00	0.02	0.15	98.92
	7500	325	17.21	19.52	0.16	4.24	0.00	24.58	6.71	53.91	10.55	0.12	0.05	0.17	0.00	0.03	0.20	96.84
	7500	344	26.63	31.12	1.07	3.80	0.00	22.18	4.68	61.33	8.01	0.17	0.06	0.22	0.00	0.04	0.26	98.14
	11000	345	19.44	23.48	1.51	4.10	0.00	21.65	3.47	62.53	8.25	0.17	0.05	0.22	0.00	0.05	0.27	100.54
	11000	301	4.49	4.14	-0.90	6.55	0.00	30.66	10.97	48.58	3.24	0.06	0.03	0.09	0.00	0.02	0.11	98.61
RhMnCe/SiO$_2$	7500	257	0.31	0.47	0.13	16.85	0.00	36.66	46.49	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.01	99.05
	7500	276	0.28	0.19	-0.12	26.69	0.00	42.60	30.70	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.01	97.79
	11000	301	2.17	1.92	-0.52	11.95	0.00	24.34	14.82	45.21	3.68	0.02	0.02	0.04	0.00	0.02	0.05	98.71
	11000	315	3.39	3.19	-0.61	11.39	0.00	26.02	11.51	49.39	1.69	0.04	0.02	0.05	0.00	0.02	0.08	97.83
	11000	327	5.31	4.99	-1.00	11.02	0.00	27.28	8.69	49.97	3.03	0.06	0.02	0.08	0.00	0.03	0.12	97.87
RhMn/SiO2	7500	257	14.57	15.29	-1.20	0.88	0.00	5.90	45.77	29.14	18.31	0.02	0.20	0.23	0.00	0.01	0.23	91.44
	7500	275	29.99	33.47	-0.51	0.65	0.00	6.27	35.75	30.34	27.00	0.05	0.32	0.37	0.06	0.01	0.44	99.64
	11000	301	31.22	35.73	0.30	0.26	0.00	6.23	20.77	53.88	18.86	0.08	0.29	0.37	0.00	0.00	0.38	96.13
	11000	301	32.24	36.36	-0.17	0.29	0.00	7.04	22.20	50.41	20.07	0.10	0.31	0.41	0.03	0.01	0.44	97.69
	11000	315	33.73	38.84	0.70	0.44	0.00	8.16	16.71	56.34	18.34	0.12	0.25	0.37	0.00	0.01	0.38	95.71
	15000	315	26.98	31.69	1.05	0.54	0.00	7.76	13.98	64.41	13.31	0.12	0.22	0.34	0.00	0.01	0.35	103.25
	11000	326	41.96	53.16	5.35	0.10	0.00	2.92	5.18	84.71	7.08	0.05	0.09	0.15	0.00	0.00	0.15	105.23
	11000	303	18.65	20.26	-0.86	0.58	0.00	7.82	21.74	54.37	15.48	0.06	0.17	0.23	0.00	0.01	0.24	91.86
Rh/SiO$_2$	7500	257	0.12	0.15	0.02	7.54	0.00	22.98	69.48	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	99.15
	7500	275	0.29	0.19	-0.13	9.80	0.00	26.56	63.64	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.01	97.78
	11000	301	1.76	1.34	-0.63	3.68	0.00	10.53	17.61	64.23	3.95	0.01	0.01	0.02	0.00	0.00	0.03	98.09
	11000	316	3.53	3.66	-0.30	2.85	0.00	9.46	10.20	54.54	22.94	0.01	0.02	0.03	0.00	0.01	0.04	98.67
	11000	326	5.07	5.18	-0.50	3.77	0.00	13.14	11.43	53.76	17.91	0.03	0.03	0.06	0.00	0.01	0.07	98.90
	11000	345	8.25	9.14	-0.12	3.17	0.00	11.53	5.97	65.14	14.19	0.04	0.02	0.06	0.00	0.02	0.08	99.34

| Catalyst | Space Velocity, L/L/hr | Temp. °C | Carbon Conv. % | CO Conv. % | CO Conv. To CO_2 | Carbon Selectivity (C-Mole%) | | | | | | STY (g/mL$_{cat}$/hr) | | | | | | Carbon Balance (C_{out}/C_{in}) % |
						MeOH	Other C_1 Oxygenates	C_2+ Alc.	Other C_2+ Oxygenates	Methane	Total Higher HCs (est)	C_2+ Alcohols	Other C_2+ Oxygenates	Total C_2+ Oxygenates	HC Liquids	MeOH	Total Liq.	
RhMnNa/SiO$_2$	7500	256	0.00	0.03	0.03	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	0.00	0.00	0.00	0.00	0.00	0.00	99.59
	7500	276	0.00	-0.43	-0.43	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	0.00	0.00	0.00	0.00	0.00	0.00	98.45
	11000	301	0.33	0.07	-0.30	34.71	0.00	21.13	35.40	0.00	8.76	0.00	0.01	0.01	0.00	0.01	0.02	98.22
	11000	316	0.87	0.65	-0.32	34.85	0.00	27.01	38.13	0.00	0.00	0.01	0.02	0.03	0.00	0.02	0.04	98.04
	11000	326	1.38	1.08	-0.48	32.36	0.00	29.98	37.66	0.00	0.00	0.02	0.03	0.04	0.00	0.03	0.07	97.40
	11000	345	4.32	5.61	0.78	15.25	0.00	21.84	17.70	41.06	4.15	0.04	0.04	0.07	0.00	0.04	0.11	97.68
RhMnB/SiO$_2$	7500	257	3.98	4.53	0.08	1.12	0.00	7.63	41.01	34.75	15.48	0.01	0.05	0.06	0.00	0.00	0.06	98.25
	7500	276	11.62	12.69	-0.34	0.86	0.00	5.82	22.60	37.59	33.13	0.02	0.08	0.10	0.02	0.00	0.12	96.37
	11000	301	21.45	23.73	-0.27	1.03	0.00	9.14	29.21	41.52	19.10	0.08	0.29	0.37	0.01	0.01	0.39	98.48
	11000	316	30.60	34.24	-0.07	0.97	0.00	9.82	20.68	50.90	17.63	0.12	0.28	0.40	0.01	0.02	0.43	98.35
	11000	325	31.44	34.96	-0.35	0.93	0.00	10.01	18.96	53.54	16.57	0.13	0.27	0.40	0.01	0.02	0.43	99.23
	11000	302	13.79	15.31	-0.11	1.12	0.00	8.39	22.34	46.46	21.69	0.05	0.13	0.18	0.01	0.01	0.20	98.05
RhMnW/SiO$_2$	7500	256	5.92	6.08	-0.53	2.94	0.00	23.09	40.44	20.74	12.79	0.04	0.07	0.11	0.00	0.01	0.12	101.44
	7500	275	17.88	23.57	3.58	0.00	0.00	9.69	9.96	45.79	34.57	0.05	0.05	0.10	0.01	0.00	0.11	93.13
	11000	299	25.26	31.32	2.98	0.95	0.00	8.94	17.61	41.46	31.04	0.09	0.20	0.29	0.02	0.01	0.33	97.70
	11000	311	28.46	34.99	2.99	0.88	0.00	8.77	16.94	44.30	29.11	0.10	0.21	0.31	0.02	0.01	0.35	97.56
	11000	314	30.06	37.05	3.30	0.88	0.00	8.44	16.59	45.67	28.42	0.10	0.22	0.32	0.02	0.02	0.36	97.65
	11000	301	26.25	34.34	5.00	0.74	0.00	5.94	15.31	47.50	30.50	0.07	0.18	0.24	0.02	0.01	0.28	94.72

Appendix B

Summary of Individual Test Results

Appendix B

Summary of Individual Test Results

A total of seven tests were performed to examine V, La, Ce, Mg, B, W, and Na as promoters on the RhMn/SiO$_2$ catalyst. We also tested the unpromoted RhMn/SiO$_2$ and the Rh/SiO$_2$ catalyst.

All of the catalysts were prepared used Davisil 645 high-surface-area SiO$_2$ as the support. Catalyst preparation consisted of a single-step impregnation procedure using the incipient wetness technique. This procedure is different than that reported in previous reports (Gerber et. al. 2007, Gerber el. al. 2008). The SiO$_2$ was pretreated by calcining at 500°C for 2 hours (ramping up at a rate of 5°C/min during heating and ramping down at a rate of 10°C/min during cooling). The appropriate quantities of a rhodium nitrate solution (10 wt% Rh concentration in solution) and manganese nitrate tetrahydrate and a soluble compound (usually a nitrate salt) of the selected promoter were combined with enough deionized water to bring the total volume of the impregnation solution to the water adsorption pore volume of the support. The solution was impregnated onto the SiO$_2$ in drop-wise fashion, dried under an infrared lamp while being shaken until a steady weight was achieved, and then dried overnight at 110°C in a drying oven. The dried catalyst was calcined at 400°C in air using a muffle furnace.

Prior to conducting the tests, the calcined catalysts were loaded into the reactor and reduced using a 10% H$_2$-in-N$_2$ gas mixture. All catalysts were heated in the reducing atmosphere to 220°C at a rate of 2.5°C/min and held that temperature for 1 hour, heated from 220°C to 260°C at a rate of 1°C/min and held at that temperature for 8 hours, and heated to approximately 350°C at a rate of 1.5°C/min and held at that temperature for 2 hours.

The testing sequence for the catalysts was generally the same except where noted. All catalyst were tested at sequentially higher temperatures with test conditions of approximately 256°C and 275°C at 7500 L/L$_{cat}$/hr GHSV and approximately 300°C, 315°C, and 325°C at 11,000 L/L$_{cat}$/hr GHSV (the V-promoted catalyst was not tested at 315°C). A repeat of the test condition at approximately 300°C was performed for the more active promoters La, Ce, Mg, B, and W, and the baseline RhMn catalyst. The Na- and V-promoted catalysts and the Rh catalyst were tested at approximately 345°C in lieu of testing at a repeat condition. Additional test conditions from certain catalysts are discussed below.

B.1 Unmodified RhMn/SiO$_2$ Catalyst

The unmodified Rh-Mn/SiO$_2$ catalyst was tested at all of the standard conditions up to approximately 325°C, and with a repeat condition at approximately 300°C. In addition, the test conducted at 315°C was repeated using a GHSV of 15,000 L/L$_{cat}$/hr, prior to testing at the standard condition at 325°C. There were problems with catalyst temperature control when setting the catalyst temperature at 300°C. It took nearly 5 hours to reach the desired set point without experiencing a significant thermal runaway of the catalyst bed and an additional 2 hours to stabilize at 300°C (catalyst temperature fluctuating between 298°C and 305°C during this period). The test condition was repeated to ensure that the data collected was representative of the condition. Temperature control was not a problem at the other test conditions.

Figure B.1 shows the carbon conversion for the unmodified Rh-Mn/SiO$_2$ catalyst. The Rh-Mn/SiO$_2$ catalyst achieves a regular increase in carbon conversion with temperature and a lower conversion at higher space velocities, as would be expected. The repeat condition suggests that there was some deactivation of the catalyst with respect to carbon conversion over the duration of the tests.
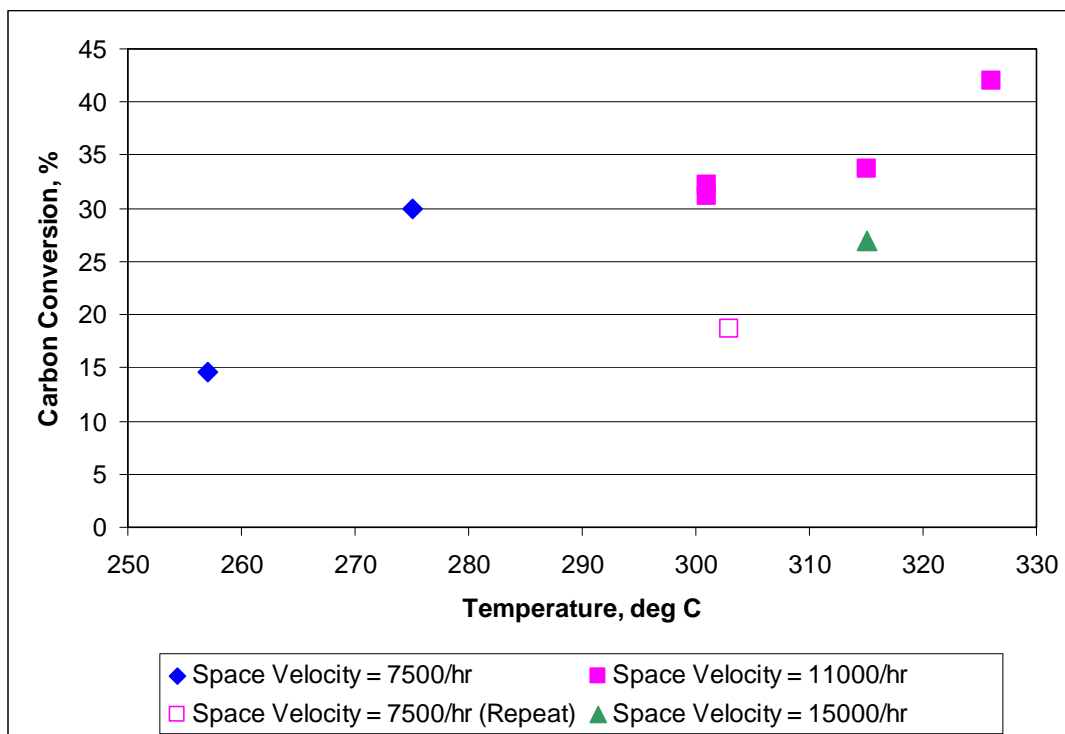
Figure B.1. Carbon Conversions for the Rh/Mn/SiO$_2$ Catalyst

Figure B.2 shows the C$_2$+-oxygenates STYs for both catalysts. It appears that while the STYs increased with increasing temperature up to about between 275°C and 300°C and then decreased at higher temperatures. Increasing the space velocity at 315°C to reduce carbon conversion did not improve the STY at that temperature, suggesting an overall deactivation of the catalyst at this temperature. Repeat of test conditions at lower temperatures for both catalysts confirmed this hypothesis.

Figure B.3 shows a regular decrease in the carbon selectivity to C$_2$+ oxygenates with increasing temperature. This trend did not appear to be affected by either the space velocity or deactivation of the catalyst.

Figure B.4 also shows a regular increase in carbon selectivity of all oxygenates to C$_2$+ alcohols with increasing temperature. Again, this behavior did not appear to be affected by either the space velocity or deactivation of the catalyst.
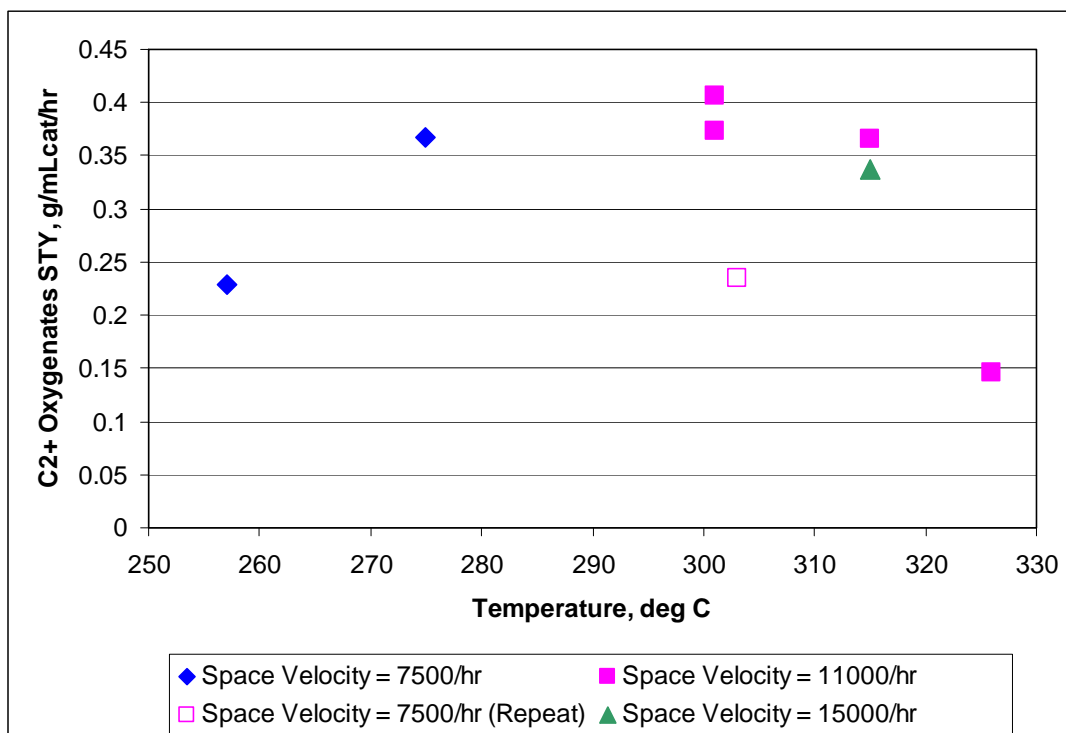
Figure B.2. C$_2$+ Oxygenate STYs for the Rh/Mn/SiO$_2$ Catalyst
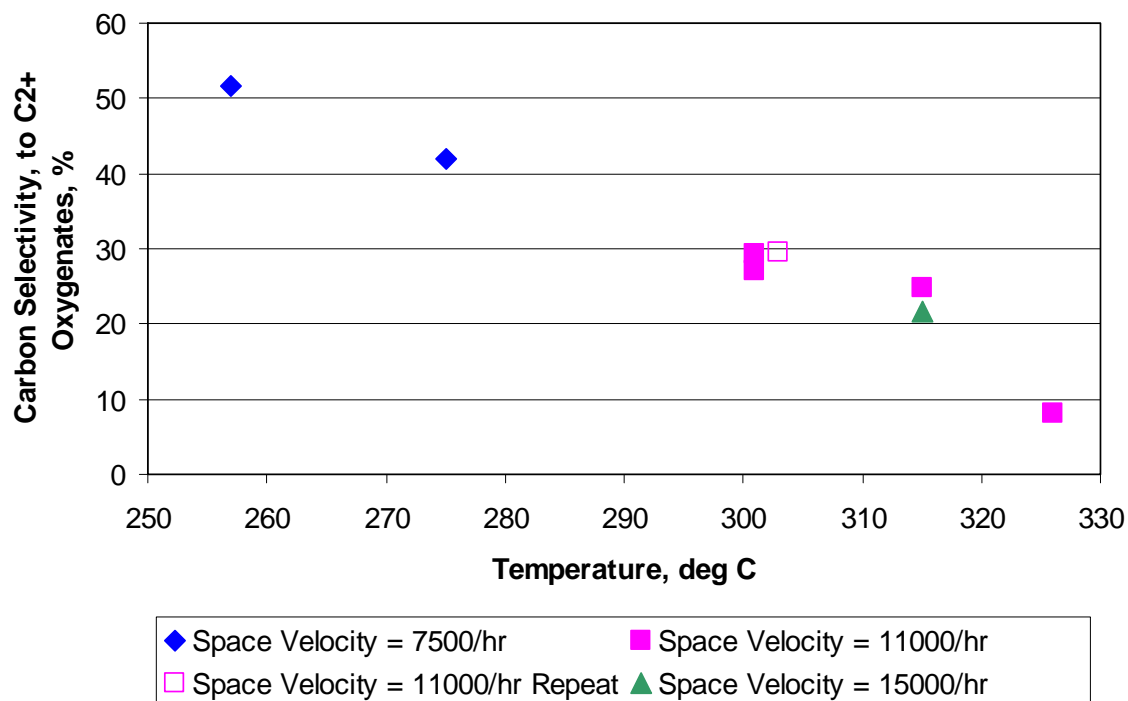
Figure B.3. Carbon Selectivity to C$_2$+ Oxygenates for the Rh/Mn/SiO$_2$ Catalyst
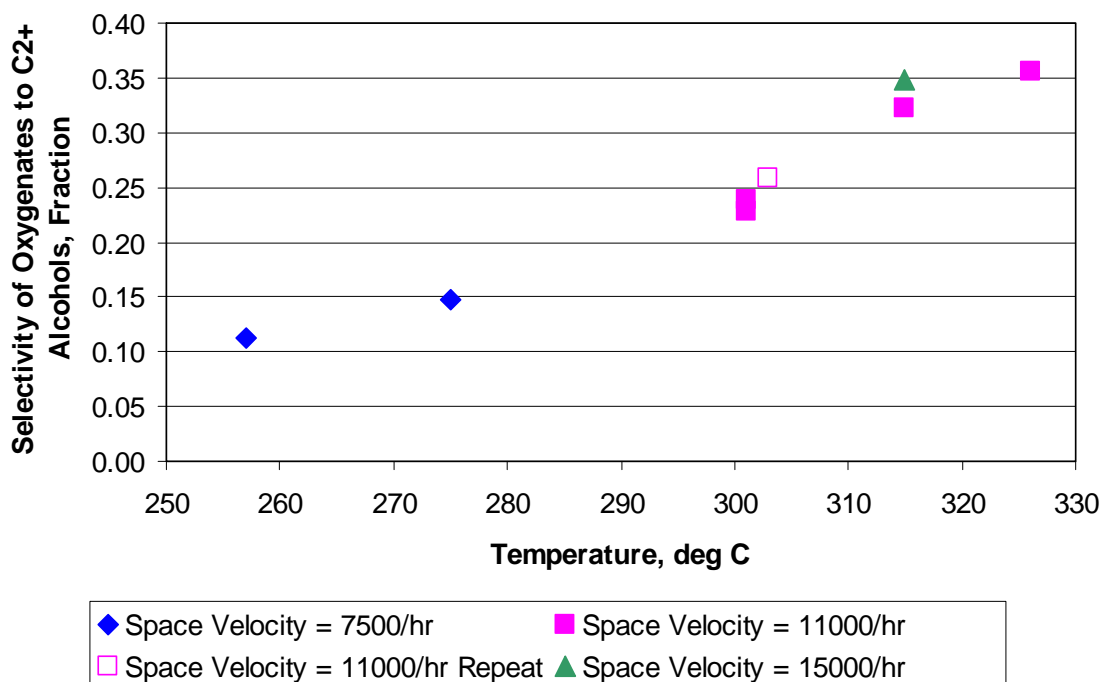
Figure B.4. Selectivity of the All Oxygenates to C_2+ Alcohols for the Rh/Mn/SiO$_2$ Catalyst

Figure B.5 shows the carbon selectivity of the catalyst to hydrocarbons. It appears that deactivation of the catalyst at about 300°C and at higher temperatures resulted in a greater selectivity to methane at the expense of the higher hydrocarbons. However, the repeat condition suggests that the overall selectivity to hydrocarbons was not significantly affected.
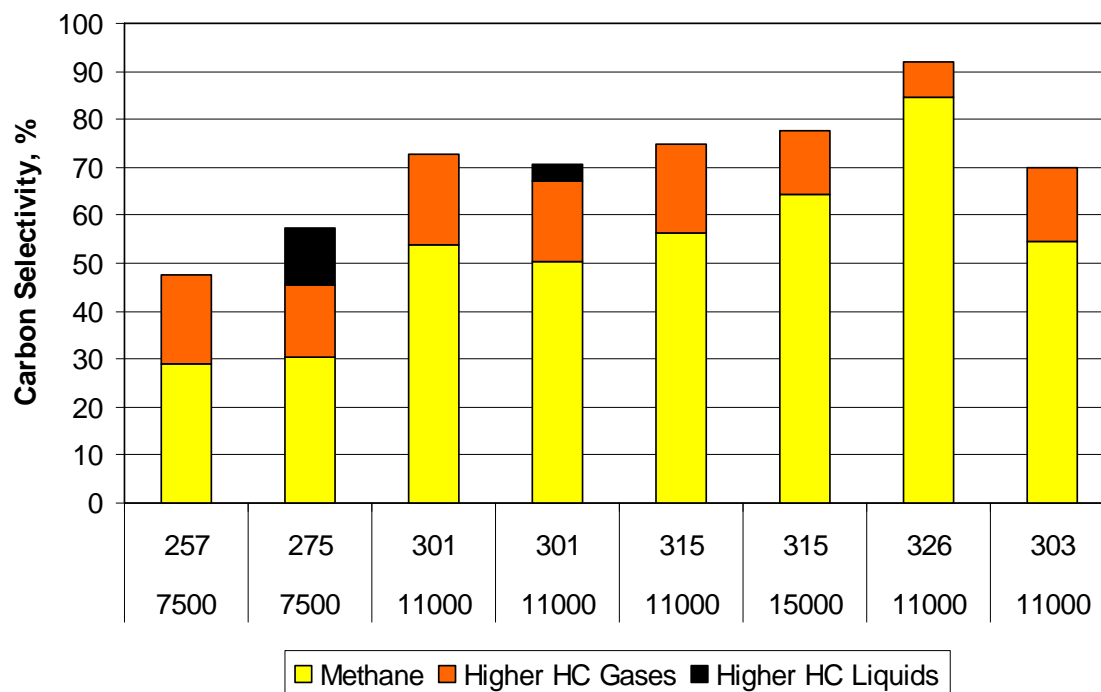
Figure B.5. Comparison of Hydrocarbon Selectivity for the Rh-Mn/SiO$_2$ Catalyst

B.4

B.2 Rh/SiO$_2$ Catalyst

The unmodified Rh/SiO$_2$ catalyst was tested at all of the standard condition. However, because the catalyst was not very active, it also was tested at approximately 345°C in lieu of a repeat test condition at 300°C. There were no problems with temperature control during the testing.

Figure B.6 shows that carbon conversion was less than 2% until the catalyst temperature was increased to 315°C. Carbon conversion achieved a maximum of about 8% at approximately 345°C.

Figures B.7, B.8, and B.9 show the C$_2$+ oxygenates STYs and carbon selectivity to C$_2$+ oxygenates and the selectivity of the C$_2$+ oxygenates to alcohols, respectively. Figure B.7 shows that there were small, but measurable, quantities of C$_2$+ oxygenates produced at temperatures as low as 255°C, but the STY only reached a maximum of 0.06 g/L$_{cat}$/hr at 345°C, which is very low. The carbon selectivity to the C$_2$+ oxygenates at the lower temperatures are misleading in Figure B.7 because the hydrocarbon concentrations in the product gas were below the detection limit and reported as zero concentrations. The low carbon selectivity to C$_2$+ oxygenates of about 25% at 300°C strongly suggests that comparable selectivity was probably occurring at the lower temperatures. Figure B.9 shows that the selectivity of the C$_2$+ oxygenates to alcohols increased significantly with temperature.
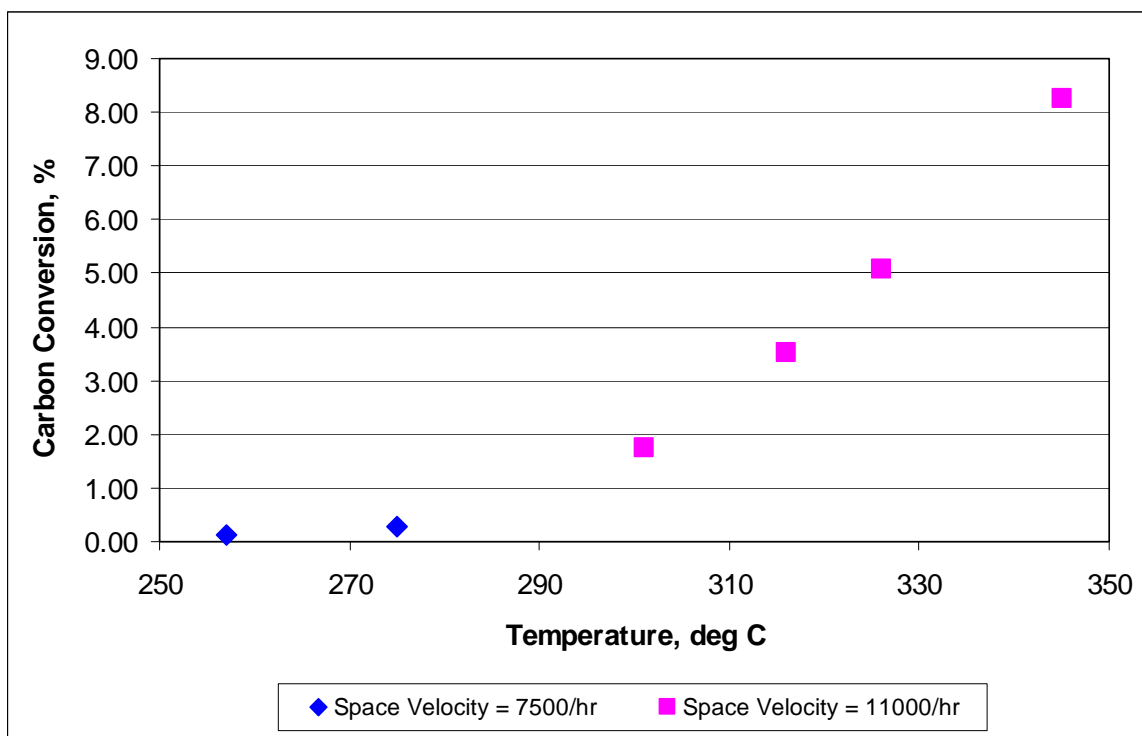
Figure B.6. Carbon Conversion for the Rh/SiO$_2$ Catalysts
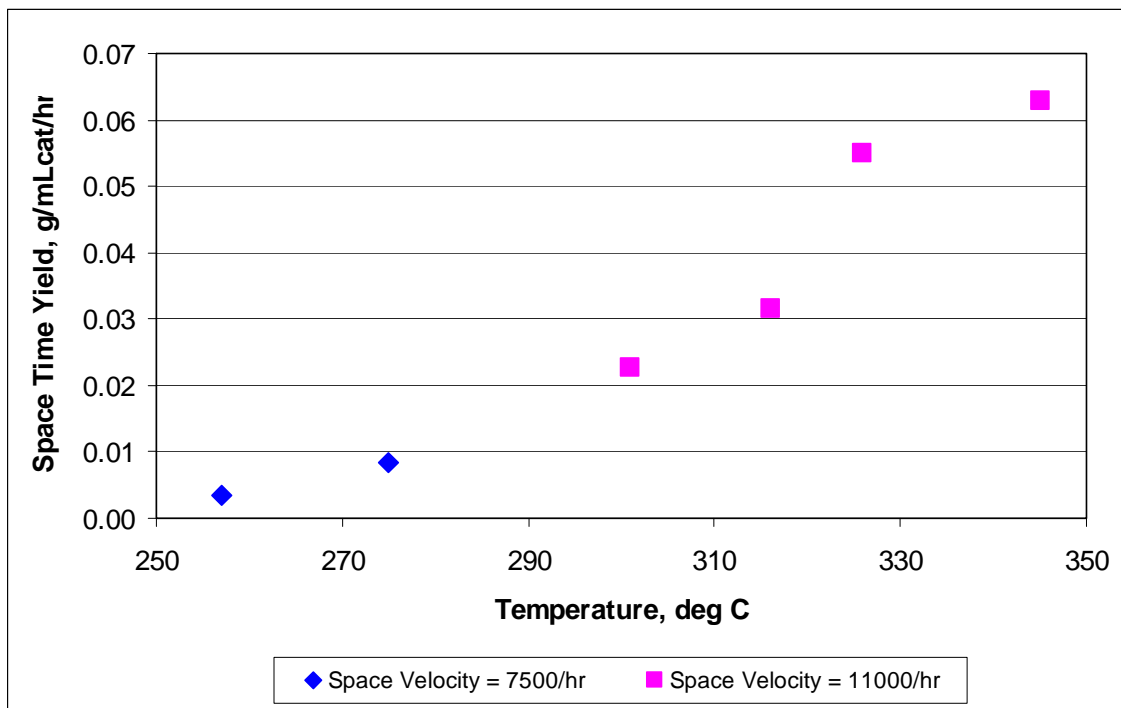
Figure B.7. C_2+ Oxygenate STYs for the Rh/SiO$_2$ Catalysts
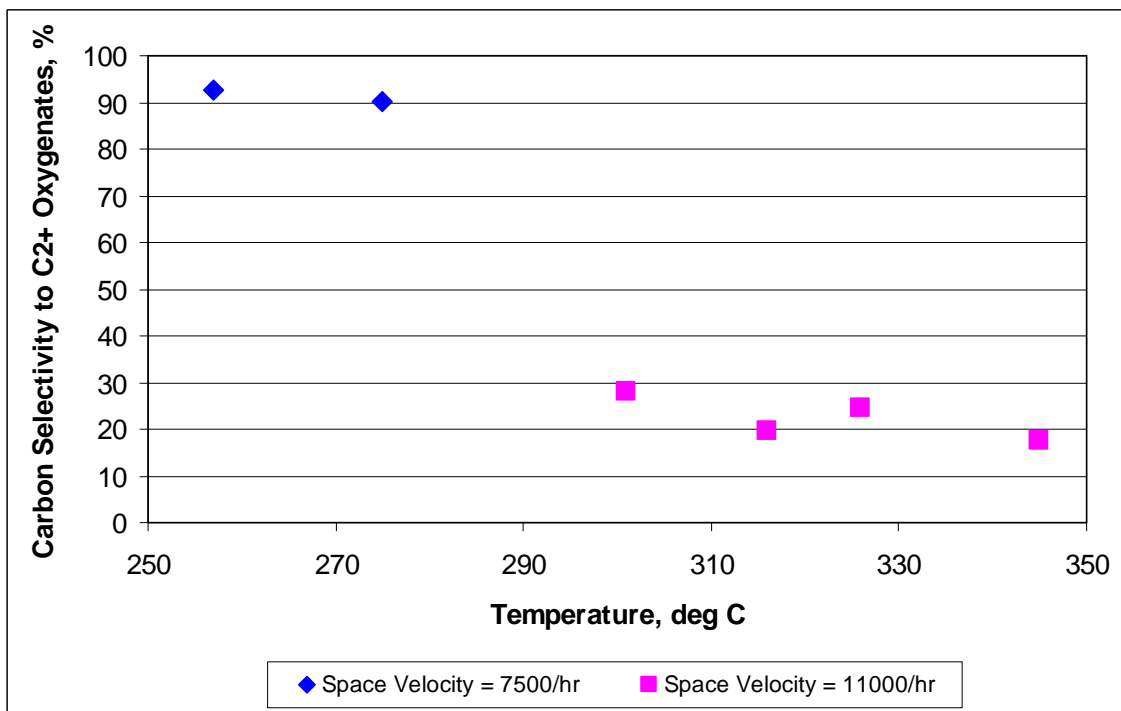
Figure B.8. Carbon Selectivity to C_2+ Oxygenates for the Rh/SiO$_2$ Catalysts
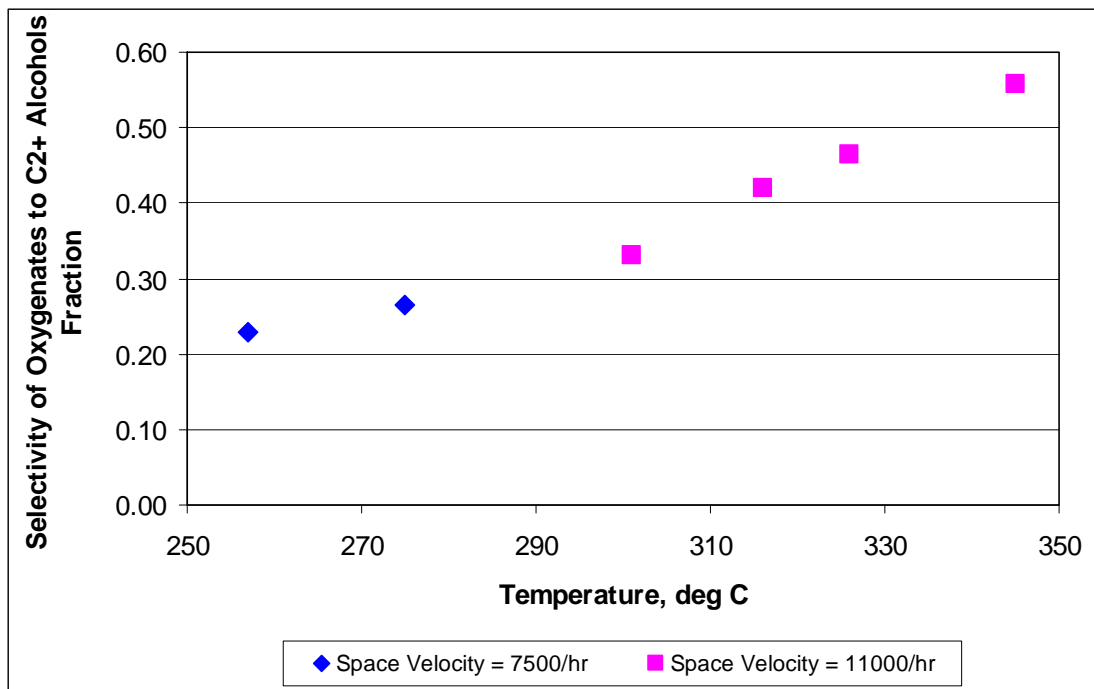
Figure B.9. Carbon Selectivity of All Oxygenates to C_2+ Alcohols for the Rh/SiO$_2$ Catalysts

Figure B.10 shows the selectivity of the Rh/SiO$_2$ catalyst to hydrocarbons. The selectivity of the catalyst to hydrocarbons was high at all temperatures where hydrocarbons were at concentrations above the detection limit. There also appears to be some deactivation of the catalyst at temperatures above 315°C. This deactivation resulted in a slight decrease in the selectivity to hydrocarbons.
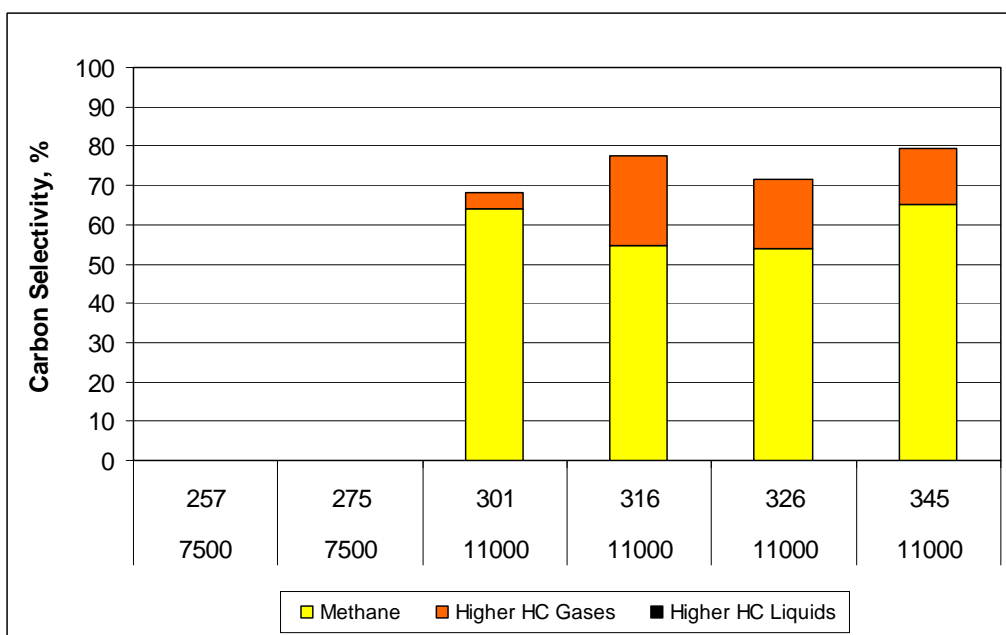
Figure B.10. Comparison of Hydrocarbon Selectivity for the Rh/SiO$_2$ Catalysts

B.3 La-Promoted Catalyst

The La-promoted catalyst (RhMnLa/SiO$_2$) was tested at all of the standard conditions up to approximately 325°C, and with a repeat condition at approximately 300°C. Further tests were conducted at 325°C (at both 7500 and 11,000 L/L$_{cat}$/hr) and at 345°C (at 11,000 L/L$_{cat}$/hr). A second repeat condition at 300°C to track deactivation of the catalyst also was run. There were no problems with temperature control during the tests.

According to Figure B.11, carbon conversion increased with increasing temperature and lower space velocities, as expected. There was some deactivation of the catalyst over time, however, as indicated by the repeat conditions.

The C$_2$+ oxygenates STYs also increased with increasing temperature up to 325°C, but decreased at 345°C as shown in Figure B.12. The first and second repeat conditions suggest that the catalyst deactivated at the higher temperatures. Catalyst deactivation masked any effect of the space velocity on the STY.
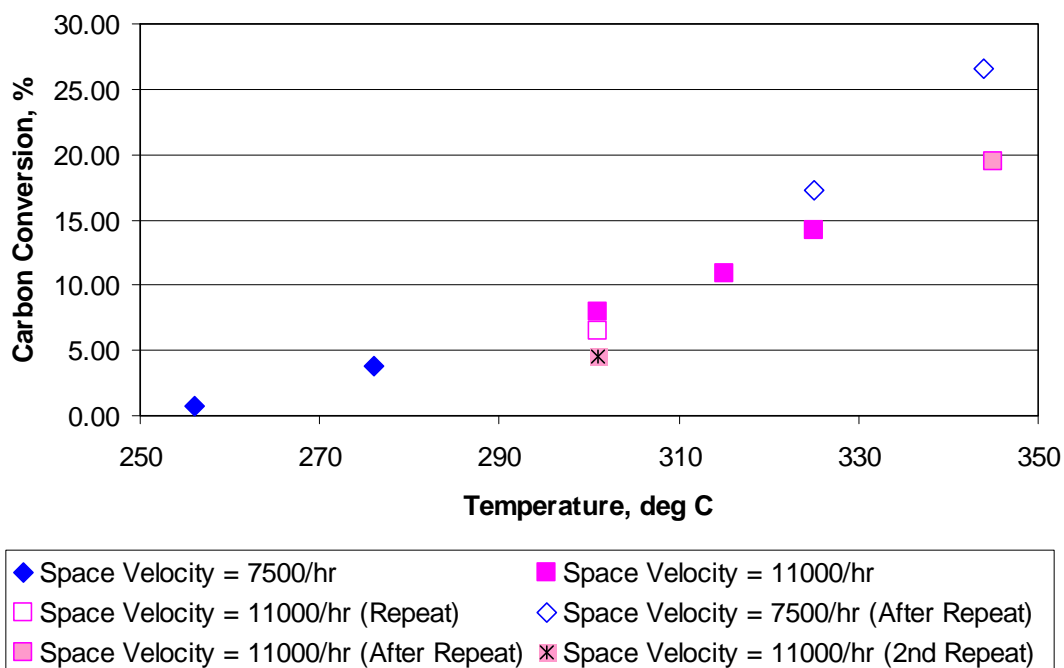
Figure B.11. Carbon Conversion for the La-Promoted Catalyst
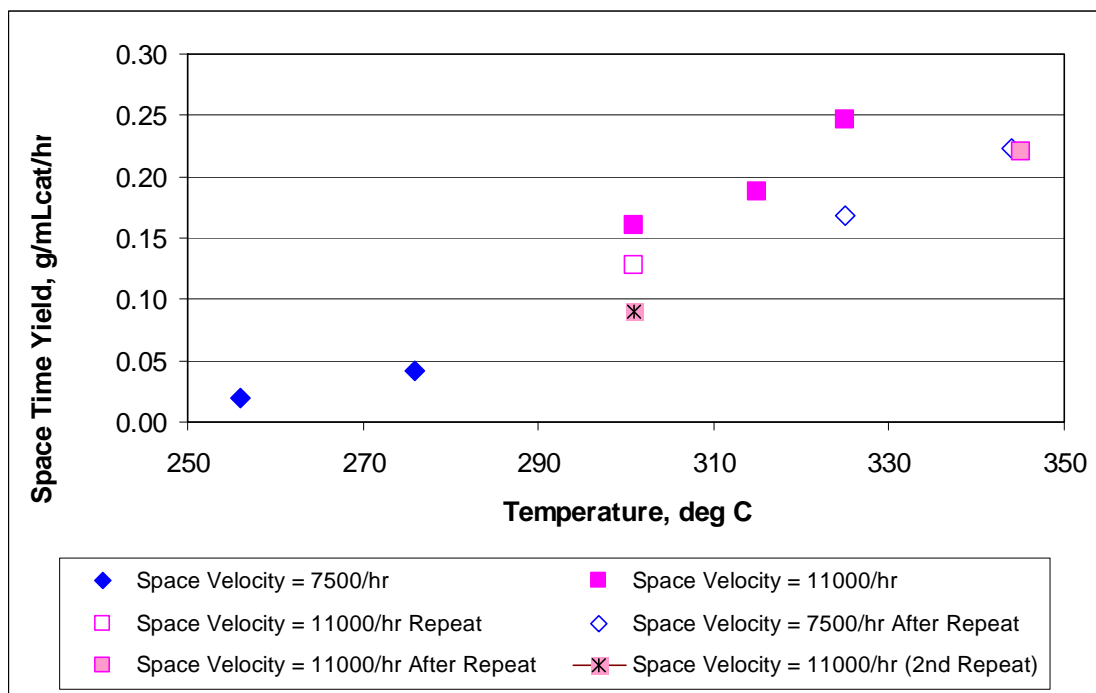
Figure B.12. C_2+ Oxygenate STYs for the La-Promoted Catalyst

The effects, of space velocity on carbon selectivity to C_2+ oxygenates and to C_2+ alcohols, are shown in figures B.13and B.14. The apparent high selectivity to C_2+ oxygenates at 256°C is misleading because there was a small quantity of C_2+ hydrocarbon gases measured in the product gas, but the methane concentration was below detection and reported as zero. Between 275°C and 325°C, carbon selectivity to C_2+ oxygenates remained relatively constant between 30% and 40%, possibly reaching a maximum at 300°C. The repeat conditions suggest that catalyst deactivation had little if any effect on the selectivity. The selectivity of oxygenates to alcohols was fairly high for this catalyst, and increased with increasing temperature. Results from tests performed at the repeat conditions suggest that the selectivity to alcohols increased as the catalyst deactivated.

Figure B.15 compares the carbon selectivity to hydrocarbons for the La-promoted catalyst. As previously discussed, there was no methane detected at 256°C, although it was likely present. Results from tests at the repeat conditions at 300°C suggest that the carbon selectivity to hydrocarbons decreased slightly as the catalyst deactivated, and the selectivity to methane increased at the expense of the higher hydrocarbon gases.
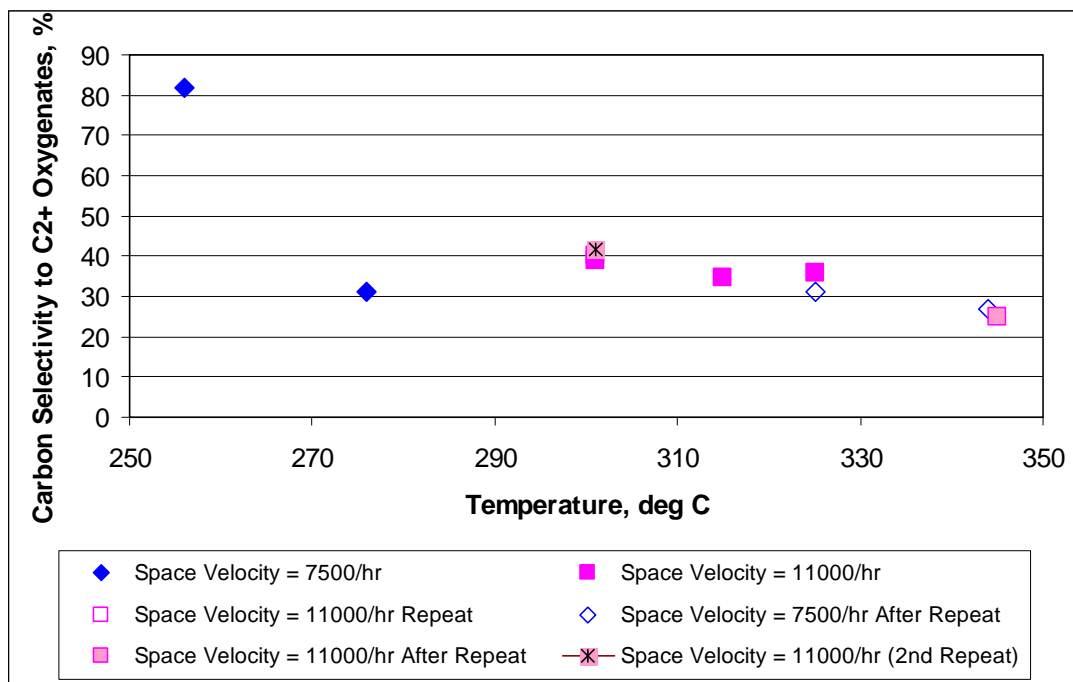
Figure B.13. Converted Carbon Selectivity to C_2+ Oxygenates for the La-Promoted Catalyst
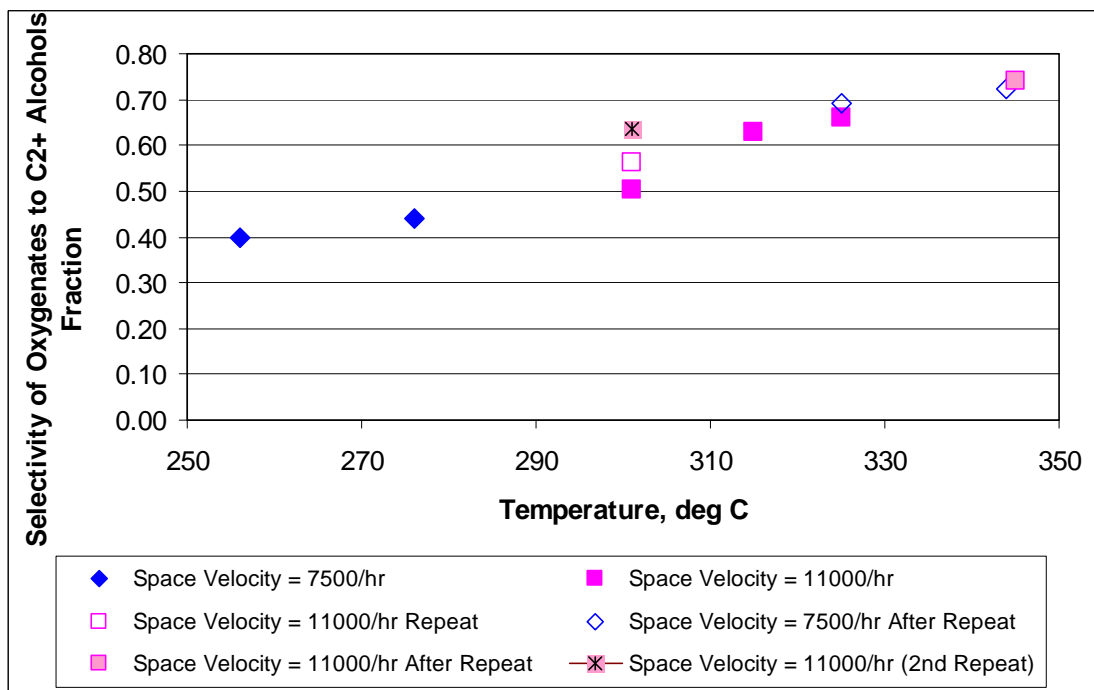
Figure B.14. Carbon Selectivity of All Oxygenates to C_2+ Alcohols for the La-Promoted Catalyst
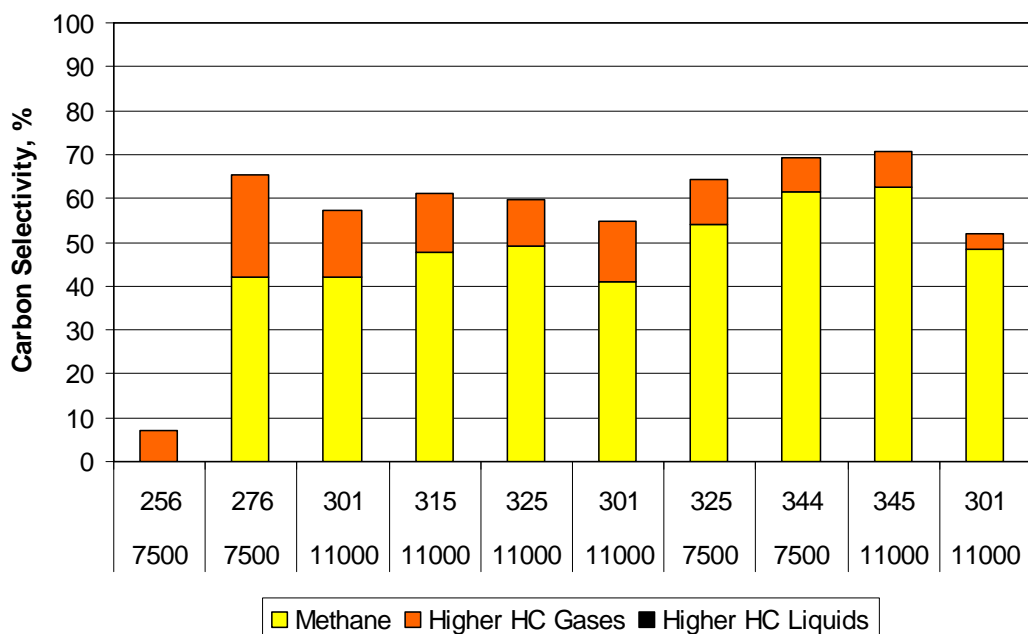
Figure B.15. Comparison of Hydrocarbon Selectivity for the La-Promoted Catalyst
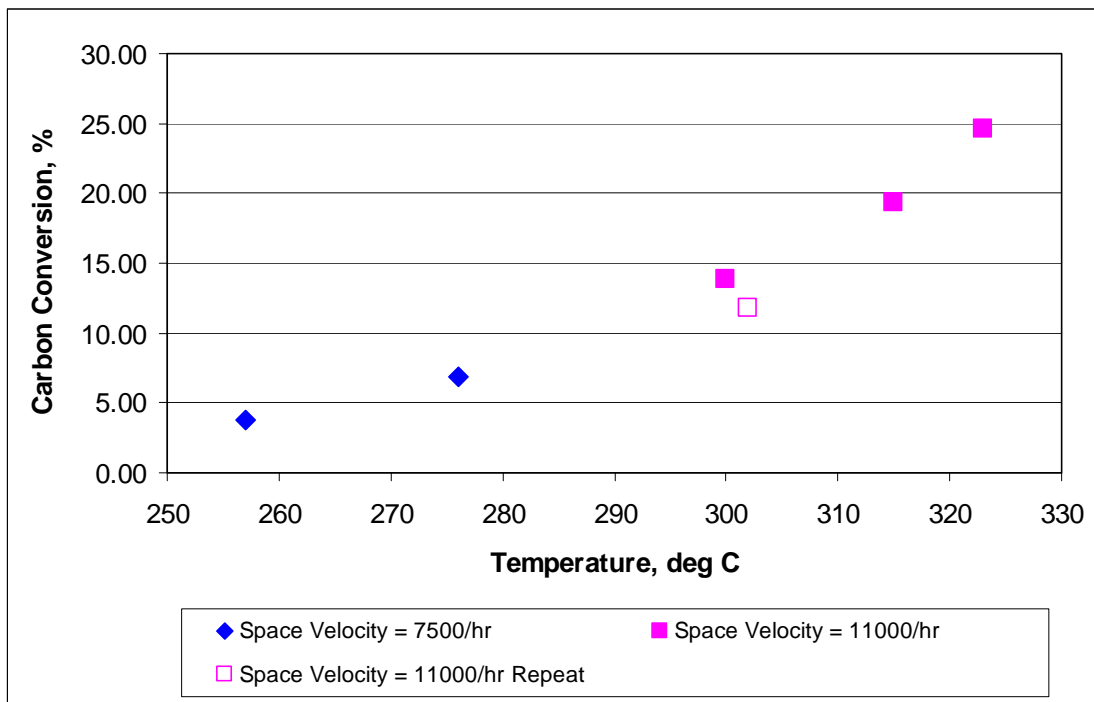
B.4 V-Promoted Catalyst

The V-promoted catalyst (RhMnV/SiO$_2$) was tested at the standard conditions up to approximately 325°C except for the condition at 315°C. It was skipped because carbon conversion and the C$_2$+ oxygenates STY were still relatively low at 300°C. Also, because the catalyst was still not very active at 325°C, it was also tested at approximately 345°C in lieu of a repeat test condition at 300°C. There were no problems with temperature control during the testing.

Figure B.16 shows that carbon conversion was less than 2% until the catalyst temperature was increased to 300°C. It reached a maximum of about 11% at approximately 345°C.

Figure B.17 shows that there were small, but measurable, quantities of C$_2$+ oxygenates produced at temperatures as low as 255°C, and the C$_2$+ oxygenates STY was only 0.10 g/L$_{cat}$/hr at 325°C, which was relatively low. The maximum STY achieved was 0.20 g/L$_{cat}$/hr at 345°C.

Carbon selectivity to the C$_2$+ oxygenates at the lower temperatures are misleading in Figure B.18 because the hydrocarbon concentrations in the product gas were below the detection limit and were reported as zero concentrations. A carbon selectivity to C$_2$+ oxygenates of about 45% at 300°C strongly suggests that the carbon selectivity were less than 90% at 275°C. Carbon selectivity to C$_2$+ oxygenates appeared to reach a minimum of about 35% at 325°C, and then remained about the same at 345°C. This behavior is different than most of the other catalysts tested, in which the selectivity continued to decrease as temperature increased. This phenomenon is consistent with the continually increasing C$_2$+ oxygenates STY at 345°C and suggests that the catalyst did not undergo significant deactivation at the higher temperatures. The selectivity of the oxygenates to C$_2$+ alcohols also appeared to reach a plateau at 325°C to 345°C at between 60% and 70% as shown in Figure B.19. Figure B.20 shows that there was a slight decrease in the carbon selectivity to hydrocarbons and, specifically, a lower selectivity to the C$_2$+

hydrocarbon gases as the temperature increased from 325°C to 345°C. Taken together, it appears that the catalyst is fairly stable up to 325°C and then undergoes minor deactivation at 345°C that results in improvements in the catalyst with respect to the selectivity to C_2+ oxygenates and possibly an accompanying increase in the C_2+ oxygenates STY. The latter is inferred mainly because the carbon conversion and the C_2+ oxygenates STY show no sign of reaching a maximum at 345°C, while the selectivity to the C_2+ oxygenates remains almost constant at the higher temperature.
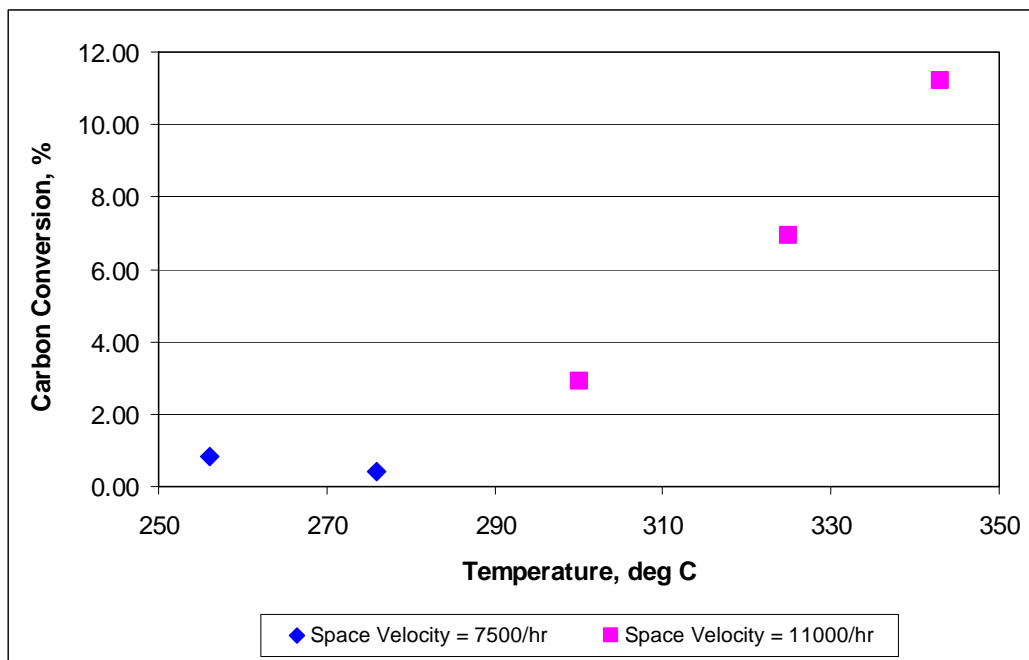

**Figure B.16**. Carbon Conversion for the V-Promoted Catalyst
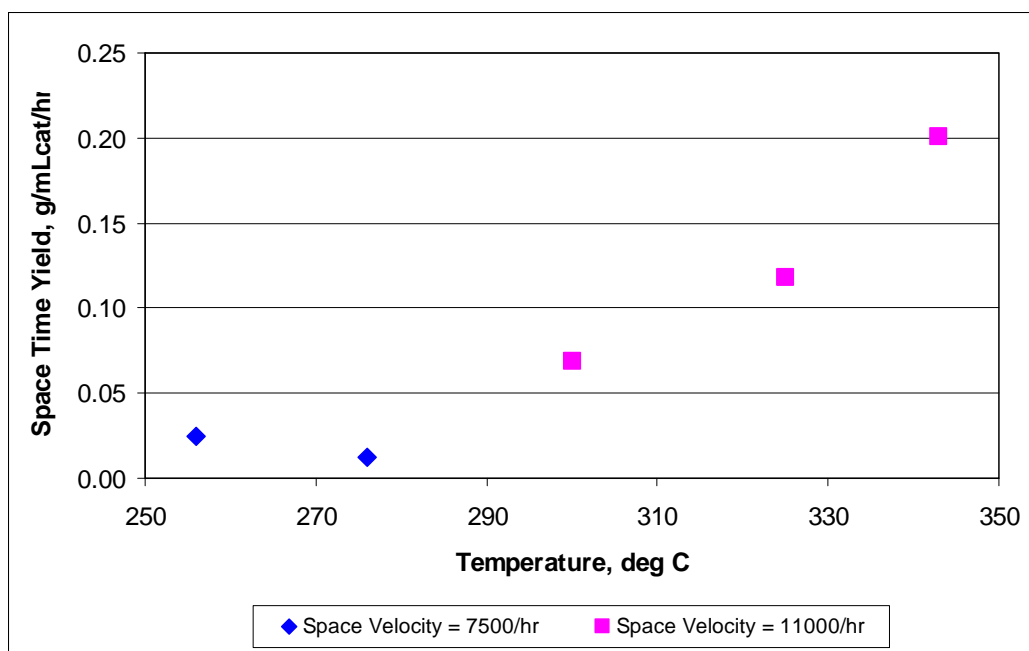
Figure B.17. C_2+ Oxygenate STYs for the V-Promoted Catalyst

B.12
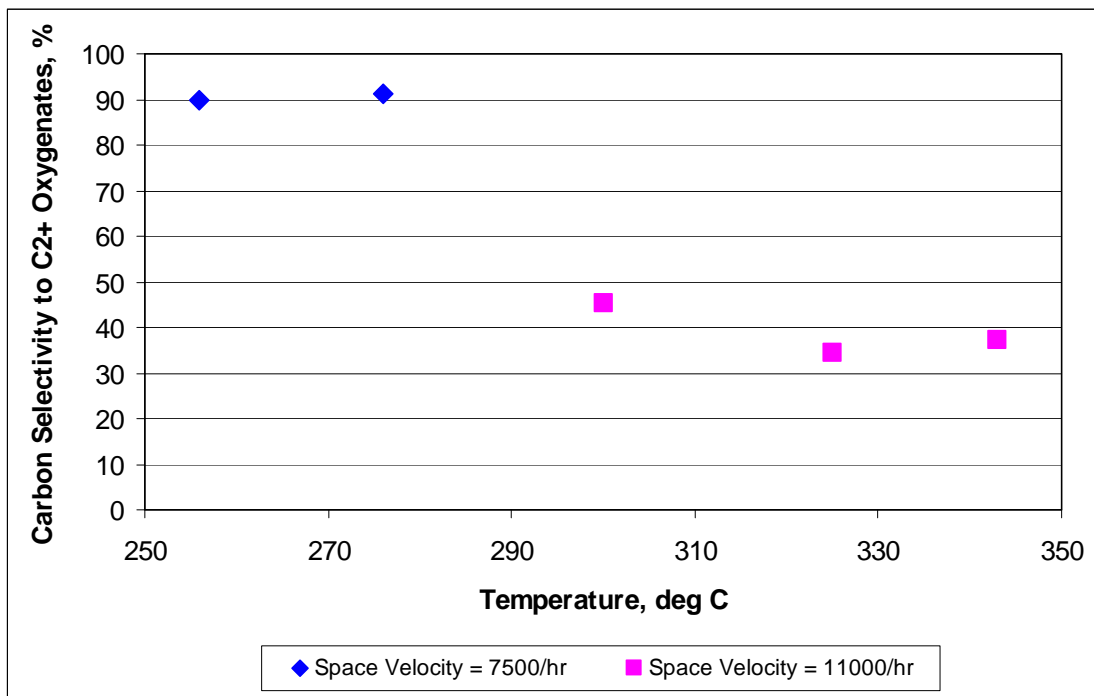
Figure B.18. Converted Carbon Selectivity to C_2+ Oxygenates for the V-Promoted Catalyst
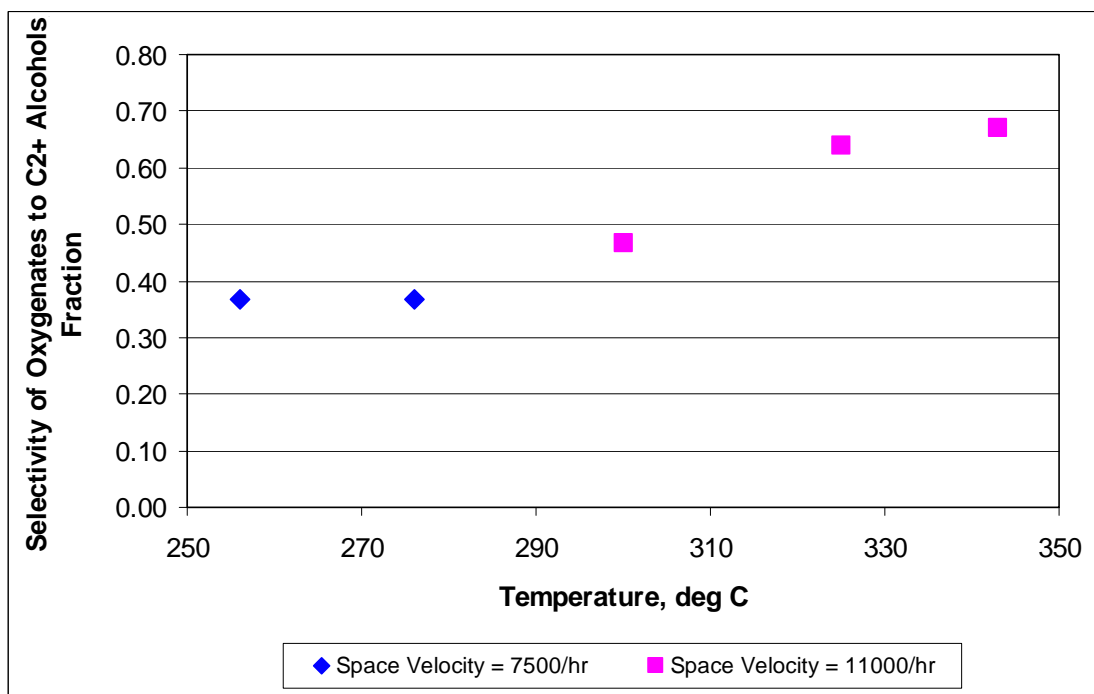
Figure B.19. Carbon Selectivity of All Oxygenates to C_2+ Alcohols for the V-Promoted Catalyst
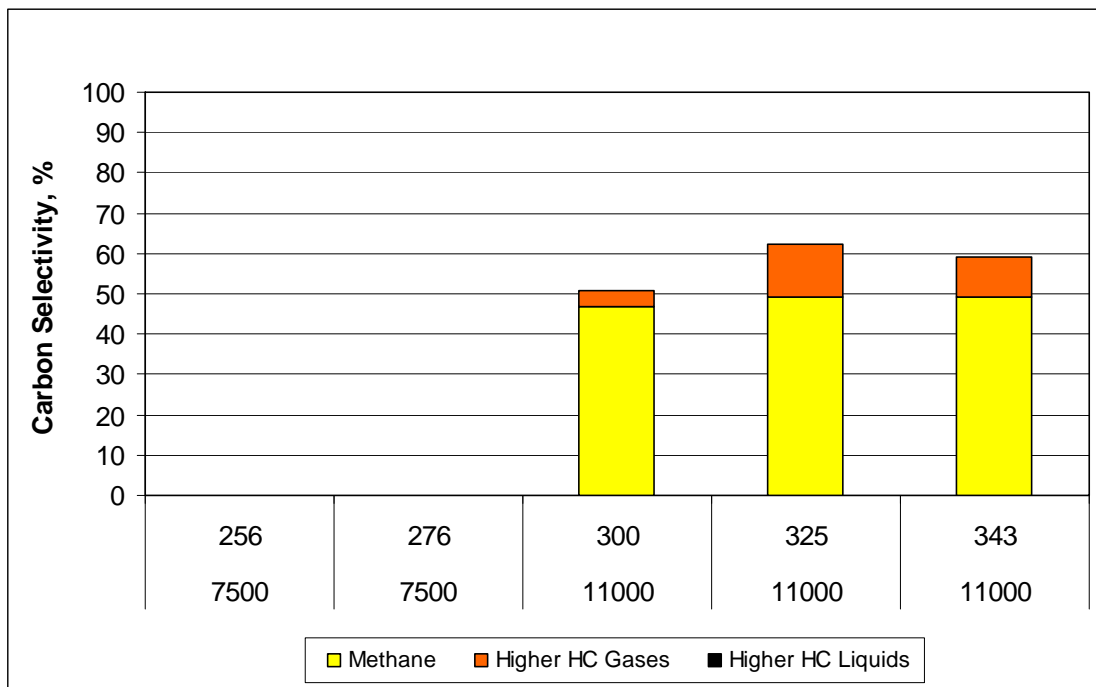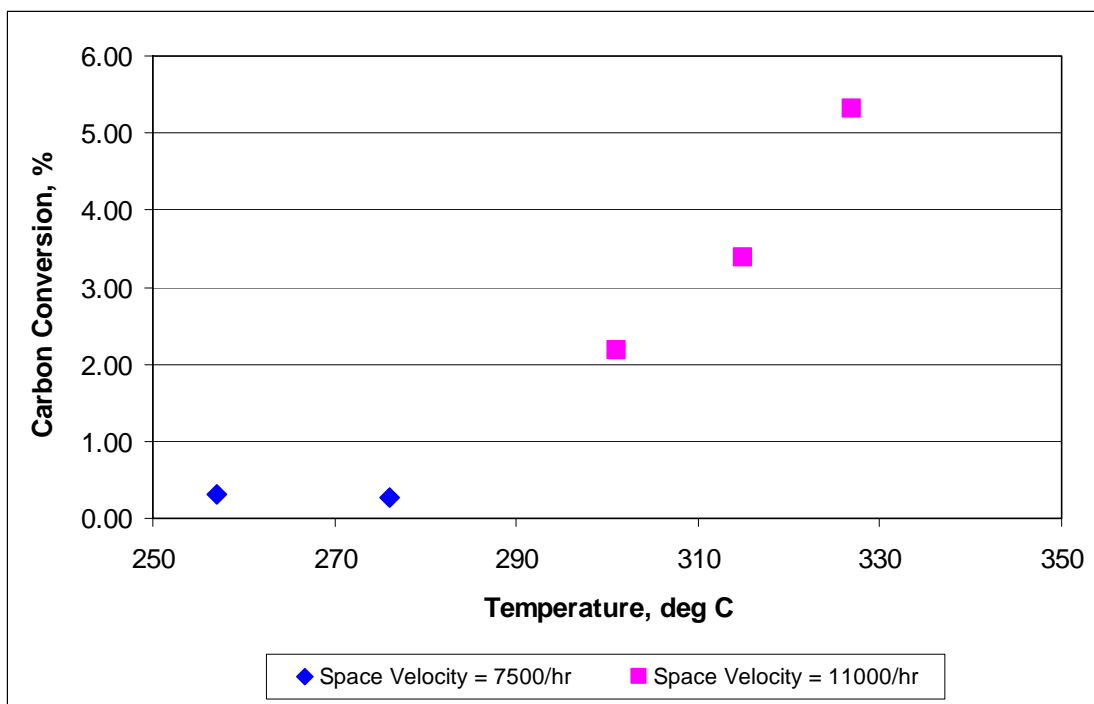
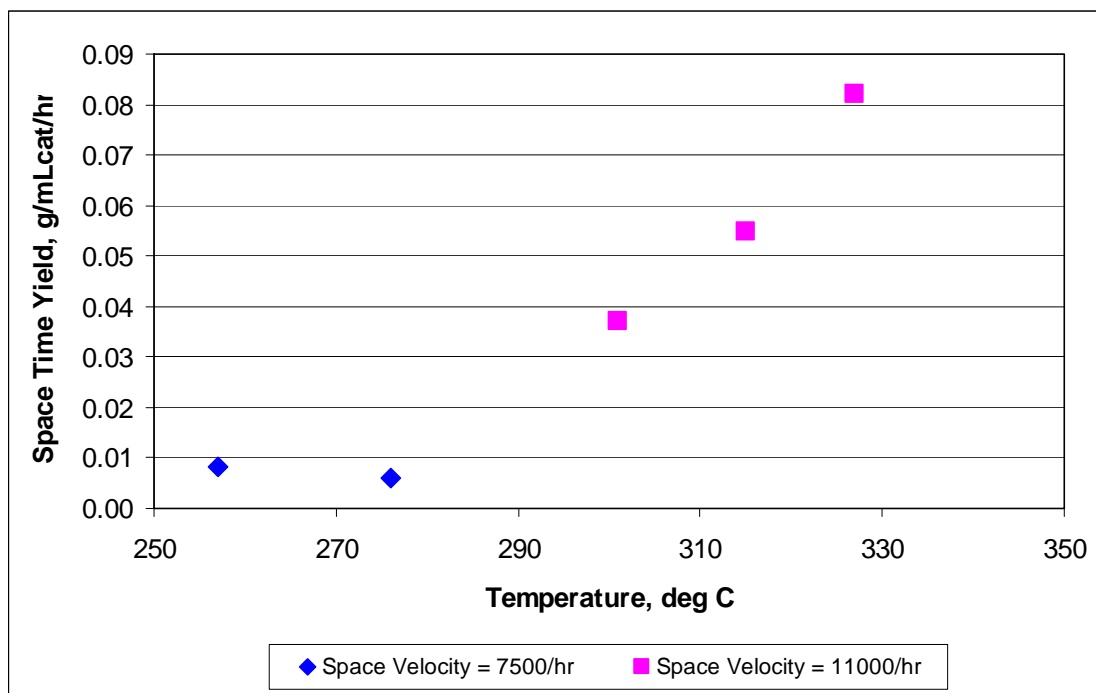**Figure B.20**. Comparison of Hydrocarbon Selectivity for the V-Promoted Catalyst

B.5 Mg-Promoted Catalyst

The Mg-promoted catalyst (RhMnMg/SiO$_2$) was tested at all of the standard conditions up to approximately 325°C, and with a repeat condition at approximately 300°C. There were no problems with temperature control during the tests.

Figure B.21 shows that carbon conversion increases with increasing temperature up to the maximum test temperature of 325°C. The repeat condition indicates that there was a slight deactivation of the catalyst at the higher temperatures.

The C$_2$+ oxygenates STY behaved in a similar manner as the carbon conversion except at 275°C, where the STY was slightly lower than it was at 256°C as shown in Figure B.22. This is attributed to a significant decrease in the carbon selectivity to C$_2$+ oxygenates when the temperature was increased from 256°C to 275°C as shown in Figure B.23. While the decrease in selectivity could have resulted at least in part to the detection limit of the GC to the various hydrocarbons, they were there in measureable quantities at 256°C, and the carbon conversion at this temperature was nearly 4%. However, the decrease in the C$_2$+ oxygenates STY does not depend on the amount of hydrocarbons measured, indicating that the catalyst behavior changed to making more hydrocarbons instead of oxygenates as the catalyst temperature was increased. At temperatures above 275°C, the selectivity to C$_2$+ oxygenates remained in a band between 30% and 40% even as the catalyst further deactivated as indicated by the results from the repeat condition shown in Figure B.23.

Figure B.24 shows that the selectivity of oxygenates to C_{2+} alcohols increased with increasing temperature. The maximum selectivity obtained at 325°C was intermediate between that achieved with the RhMn/SiO$_2$ and the La- and V-promoted catalysts.

Figure B.25 further illustrates the change in selectivity towards more hydrocarbons as the temperature increased from 256°C to 275°C. There also appears to be some further changes occurring between 275°C and 300°C. However, all of the total selectivity to hydrocarbons for the temperature range of 275°C to 325°C, including the repeat condition, remained within a band between 60% and 68%, suggesting that the catalyst selectivity was not particularly sensitive to temperatures above 275°C.


**Figure B.21**. Carbon Conversion for the Mg-Promoted Catalyst
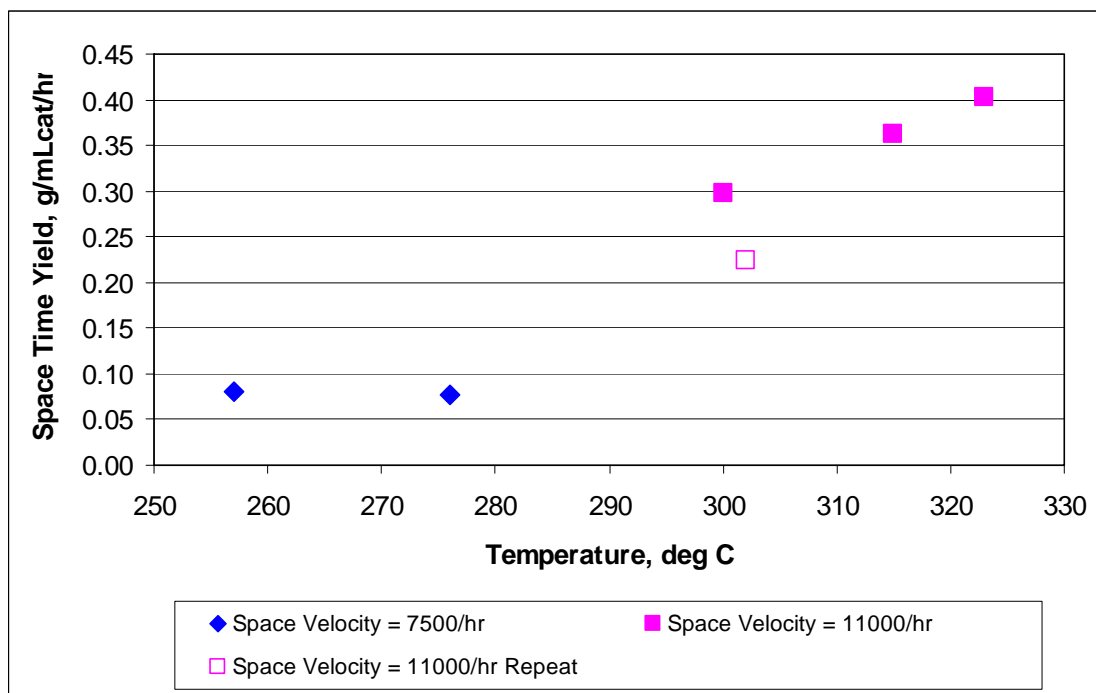
Figure B.22. C$_2$+ Oxygenate STYs for the Mg-Promoted Catalyst
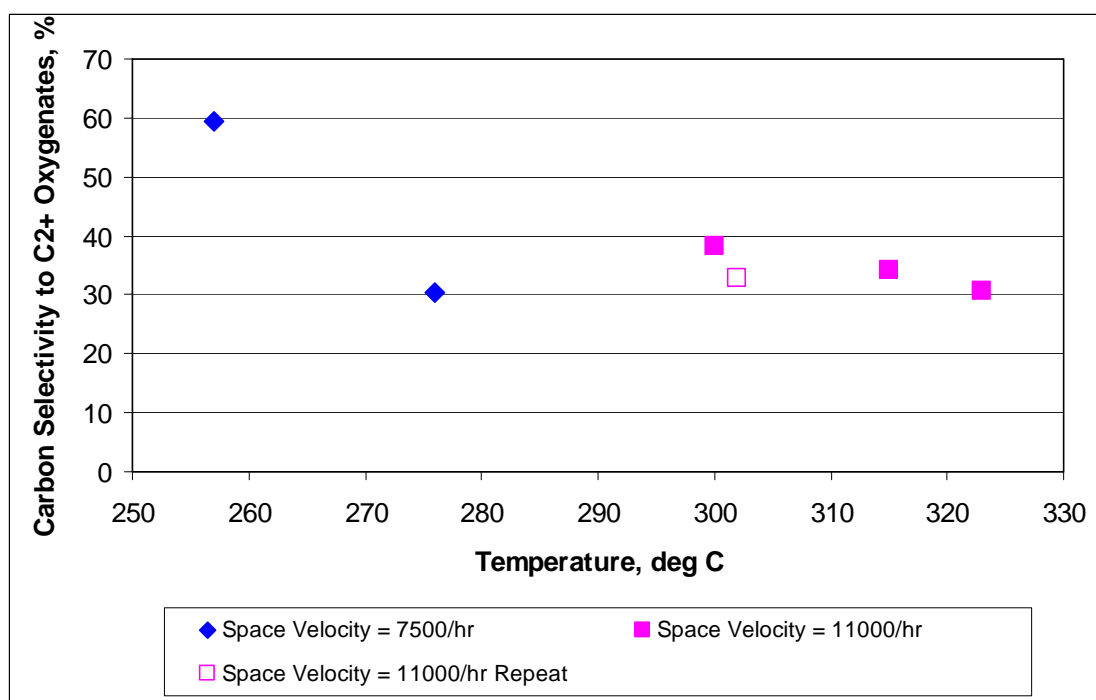
Figure B.23. Converted Carbon Selectivity to C$_2$+ Oxygenates for the Mg-Promoted Catalyst
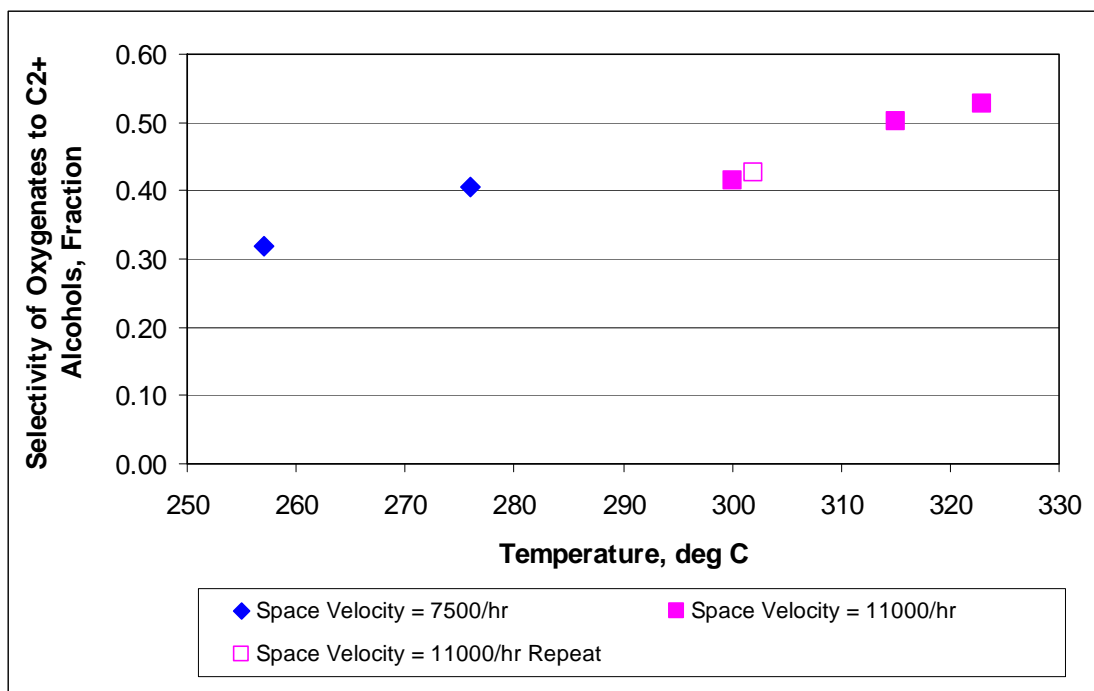
Figure B.24. Carbon Selectivity of All Oxygenates to C$_2$+ Alcohols for the Mg-Promoted Catalyst
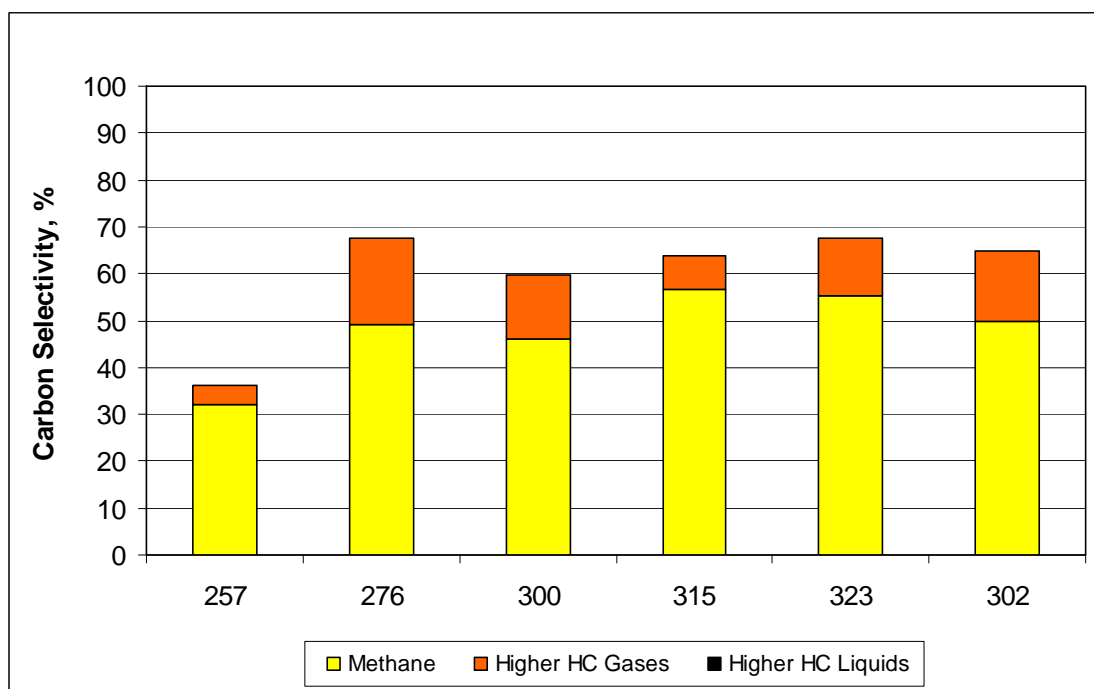
Figure B.25. Comparison of Hydrocarbon Selectivity for the Mg-Promoted Catalyst

B.6 Ce-Promoted Catalyst
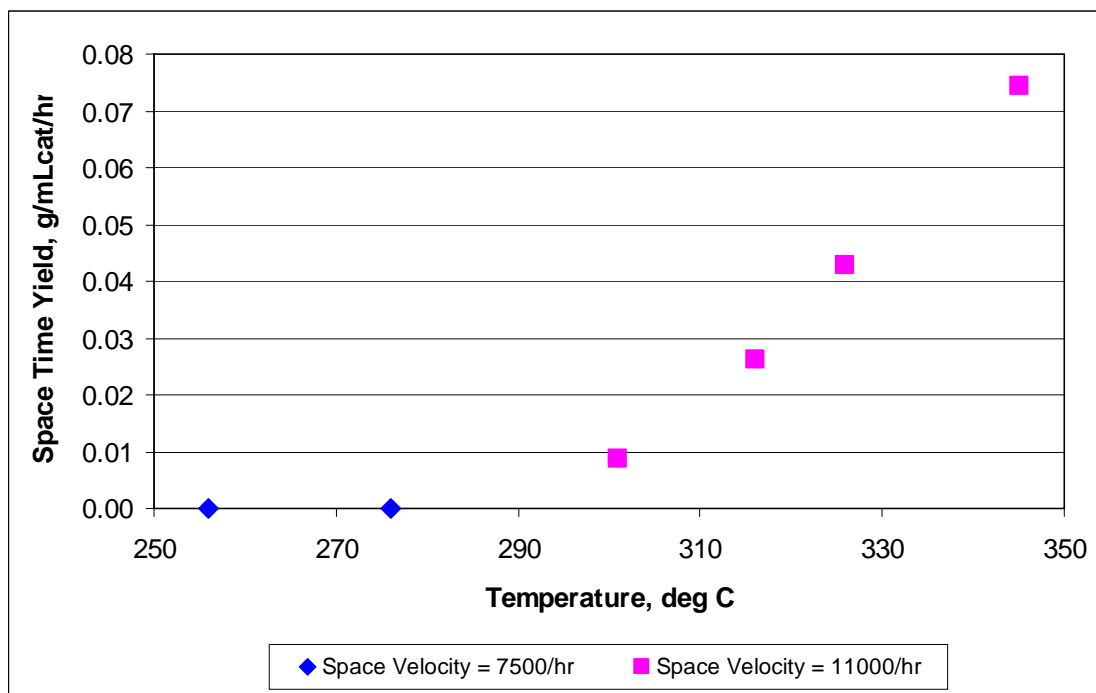
The Ce-promoted catalyst ($RhMnCe/SiO_2$) was tested at all of the standard conditions up to approximately 325°C, but no repeat condition was performed. There were no problems with temperature control during the tests.

The Ce-promoted catalyst was not very active at all conditions tested, achieving a maximum carbon conversion of a little over 5% (Figure B.26) and a C_2+ oxygenates STY of 82 g/L_{cat}/hr (Figure B.27) at the maximum temperature of 325°C. The carbon selectivity to C_2+ oxygenates shown in Figure B.28 are misleading at the two lowest temperatures tested because the hydrocarbon concentrations were below the detection limit and reported as zero as shown in Figure B.29. The selectivity to C_2+ oxygenates was relatively constant between 36% and 39% over the temperature range of 300°C to 325°C as shown in Figure 28. Similarly, the carbon selectivity to hydrocarbons was relatively constant at between 49% and 53% over the same temperature range. The selectivity of oxygenates to C_2+ alcohols increased with increasing temperature, reaching a maximum of about 58% as shown in Figure B.30.


**Figure B.26**. Carbon Conversion for the Ce-Promoted Catalyst

Figure B.27. C$_2$+ Oxygenate STYs for the Ce-Promoted Catalyst
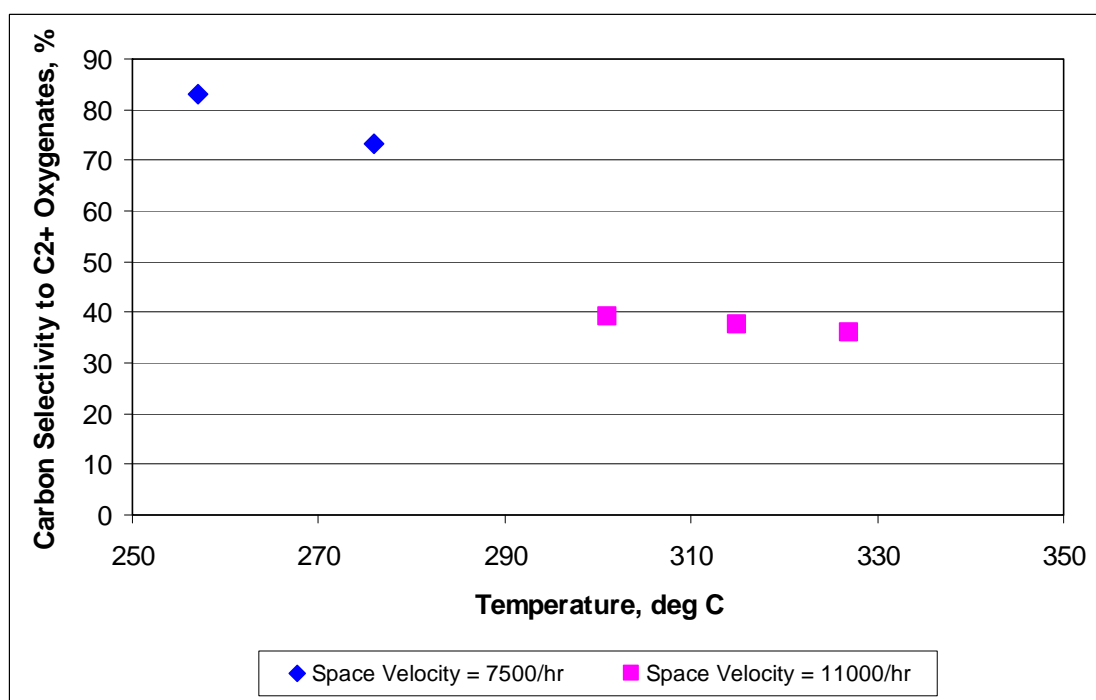
Figure B.28. Converted Carbon Selectivity to C$_2$+ Oxygenates for the Ce-Promoted Catalyst
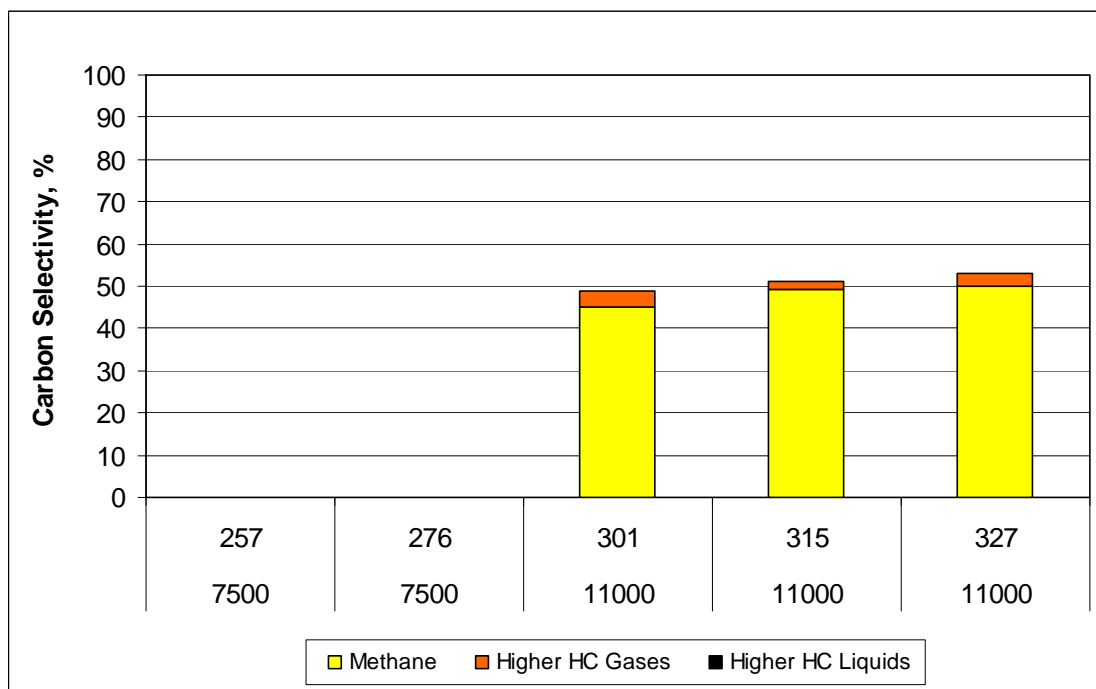
Figure B.29. Comparison of Hydrocarbon Selectivity for the Ce-Promoted Catalyst
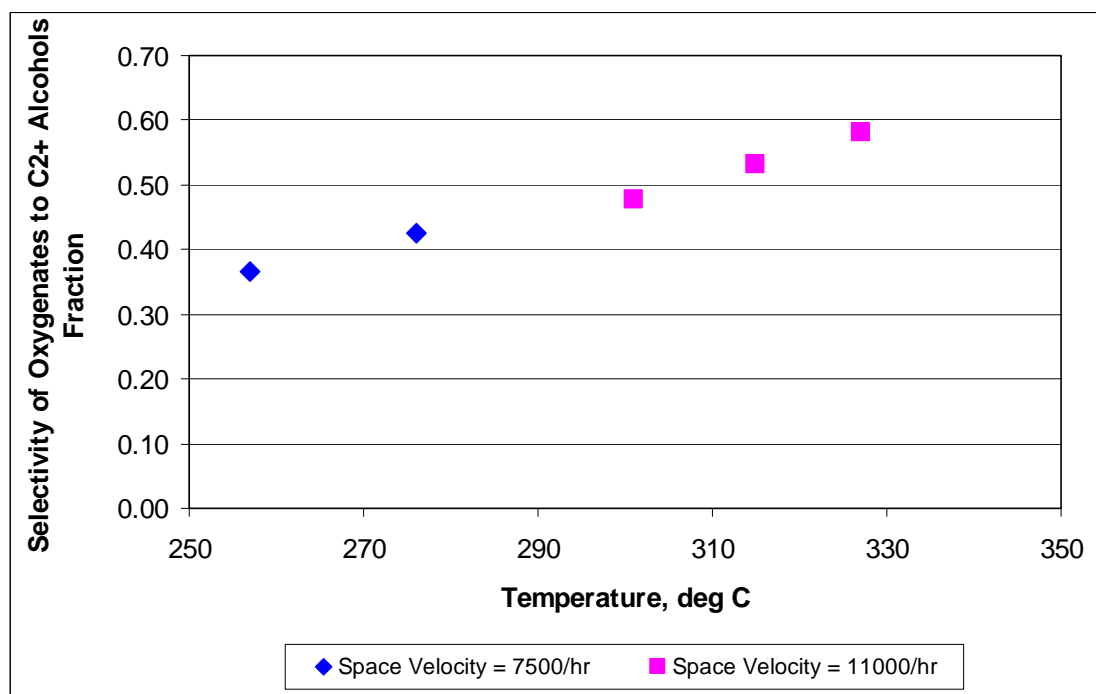
Figure B.30. Carbon Selectivity of All Oxygenates to C_2+ Alcohols for the Ce-Promoted Catalyst

B.7 Na-Promoted Catalyst

The Na-promoted catalyst ($RhMnNa/SiO_2$) was tested at all of the standard conditions up to approximately 345°C, but no repeat condition was performed. There were no problems with temperature control during the tests.

The Na-promoted catalyst was not active at temperatures up to 275°C and was barely active at the higher temperatures, achieving a maximum carbon conversion of a little over 4% (Figure B.31) and a C_2+ oxygenates STY of 74 $g/L_{cat}/hr$ (Figure B.32) at the maximum temperature of 345°C. The carbon selectivity to C_2+ oxygenates shown in Figure B.33 are misleading at all but the highest temperatures tested because the methane concentrations were below the detection limit and were reported as zero as shown in Figure B.34 (some higher hydrocarbon gases were detected at the 300°C test condition). Selectivity of oxygenates to C_2+ alcohols increased with increasing temperature as shown in Figure B.35, but were slightly lower than those achieved with the $RhMn/SiO_2$ catalyst at comparable temperatures.
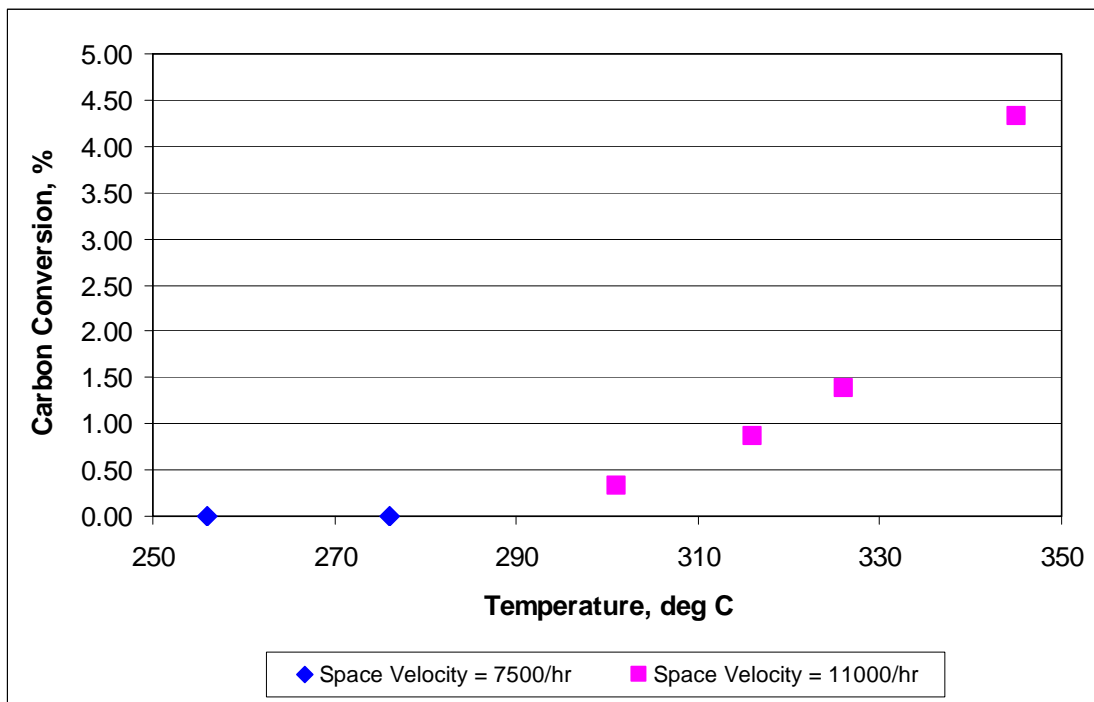
Figure B.31. Carbon Conversion for the Na-Promoted Catalyst

Figure B.32. C$_2$+ Oxygenate STYs for the Na-Promoted Catalyst
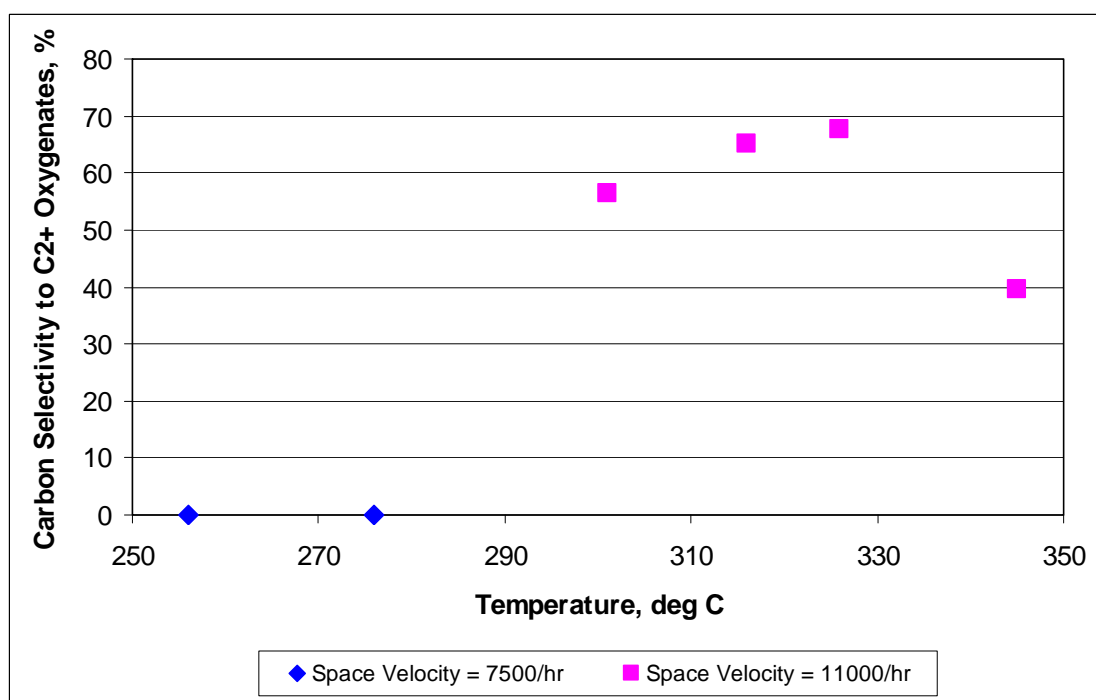
Figure B.33. Converted Carbon Selectivity to C$_2$+ Oxygenates for the Na-Promoted Catalyst
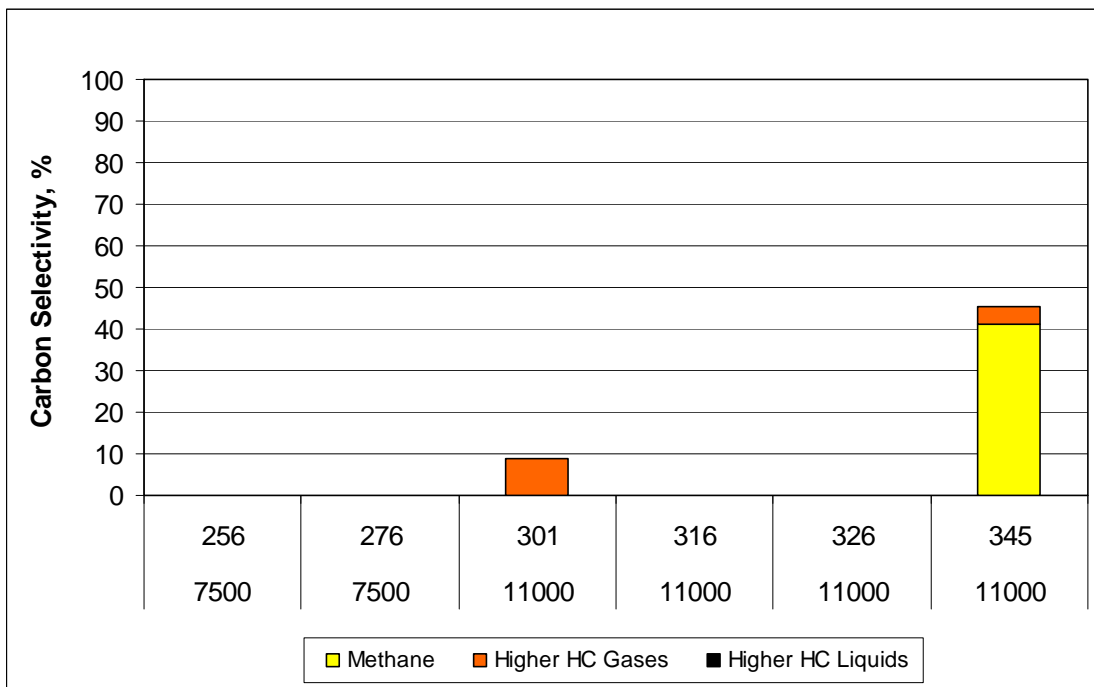
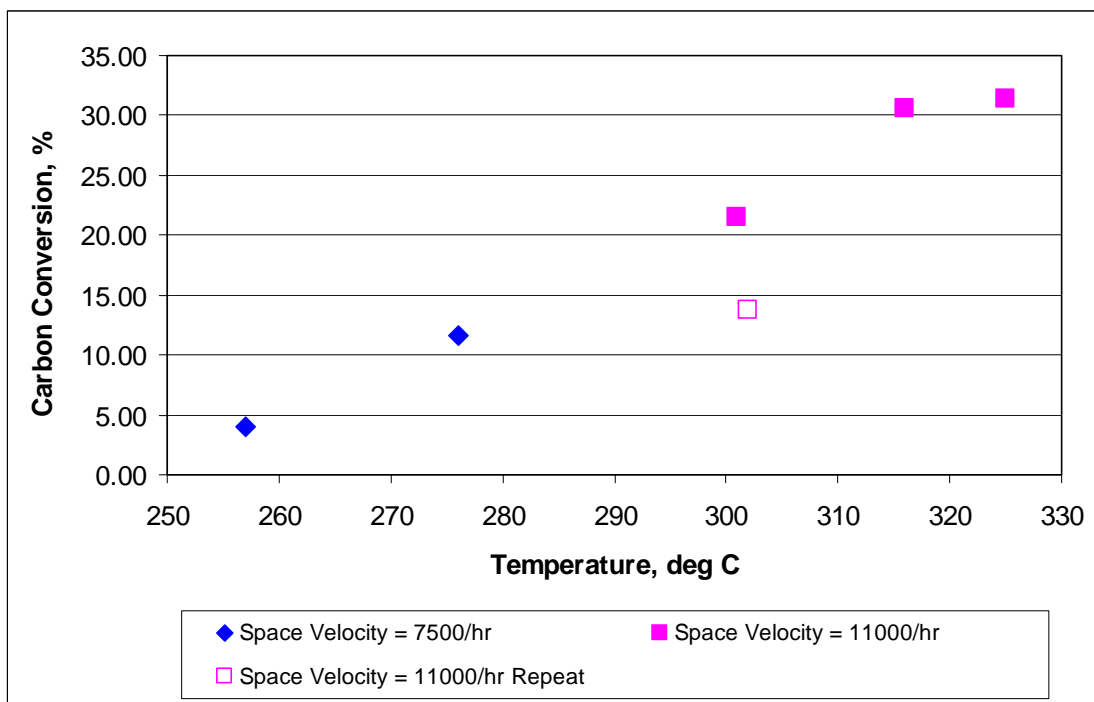**Figure B.34**. Comparison of Hydrocarbon Selectivity for the Na-Promoted Catalyst
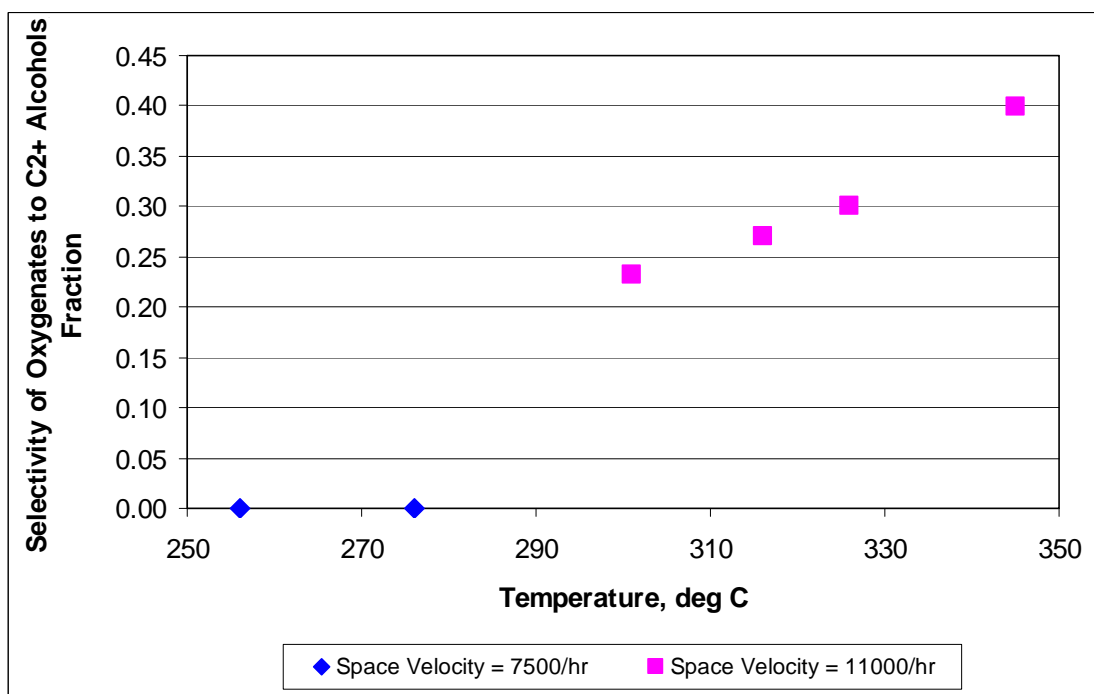
Figure B.35. Carbon Selectivity of All Oxygenates to C_2+ Alcohols for the Na-Promoted Catalyst
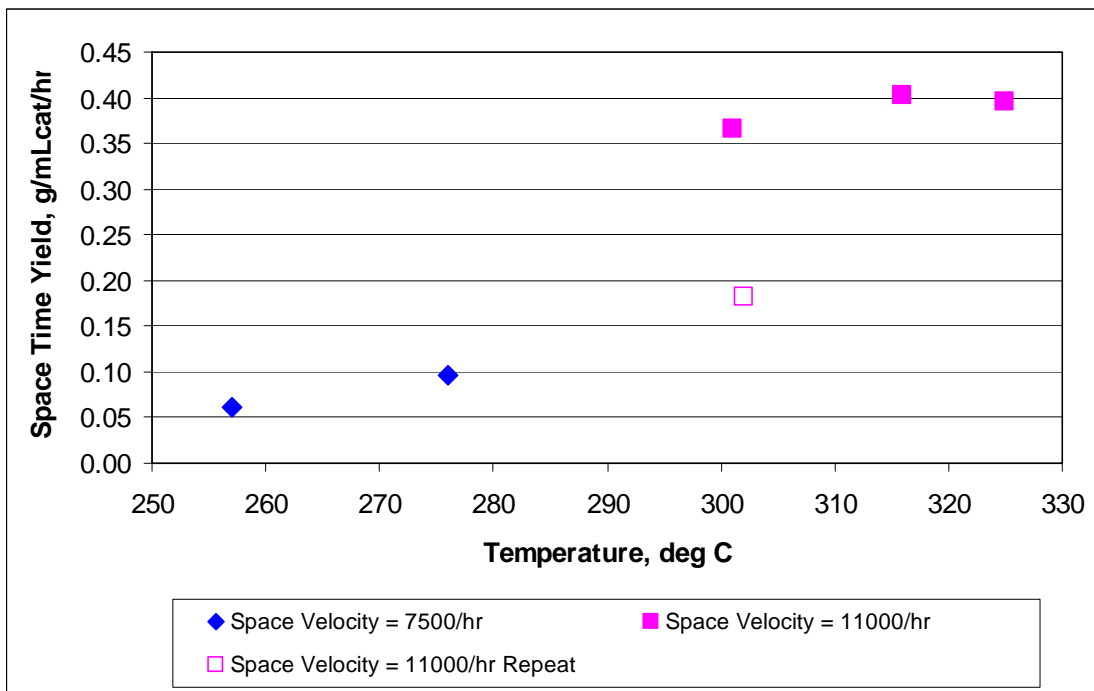
B.8 B-Promoted Catalyst

The B-promoted catalyst (RhMnB/SiO$_2$) was tested at all of the standard conditions up to approximately 325°C, and with a repeat condition at approximately 300°C. There were no problems with temperature control during the tests.

Figure B.36 shows that the carbon conversion increased with increasing temperature up to the maximum test temperature of 325°C. The repeat condition indicates that there was a significant deactivation of the catalyst at the higher temperatures.

The C$_2$+ oxygenates STYs behaved in a fairly similar manner with as the carbon conversion except that there was slight decrease in the STY as temperatures increased from 300°C to 325°C as shown in Figure B.37. This is attributed to the decrease in the carbon selectivity to C$_2$+ oxygenates when the temperature was increased (Figure B.38). The decrease in carbon selectivity offset any gains resulting from increased carbon conversion. Again, the repeat condition shows that there was considerable decrease in the activity of the catalyst. Data from the repeat conditions shown in Figure B.38 and Figure 39 also show that catalyst deactivation at the higher temperatures affected both the carbon selectivity to C$_2$+ oxygenates (selectivity decrease) and the fraction of oxygenates that were C$_2$+ alcohols (selectivity increase). Carbon selectivity to the various hydrocarbons shown in Figure B.40 suggests that the catalyst began deactivation between 275°C and 315°C. There was very little further effect of the higher temperatures on the selectivity to hydrocarbons.
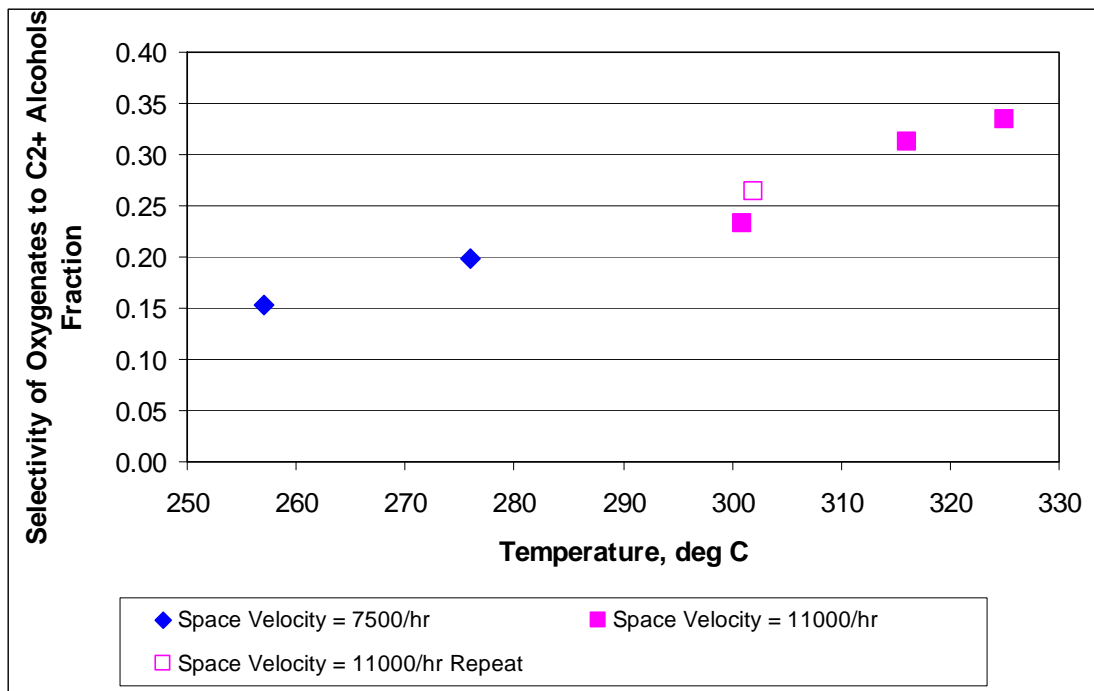

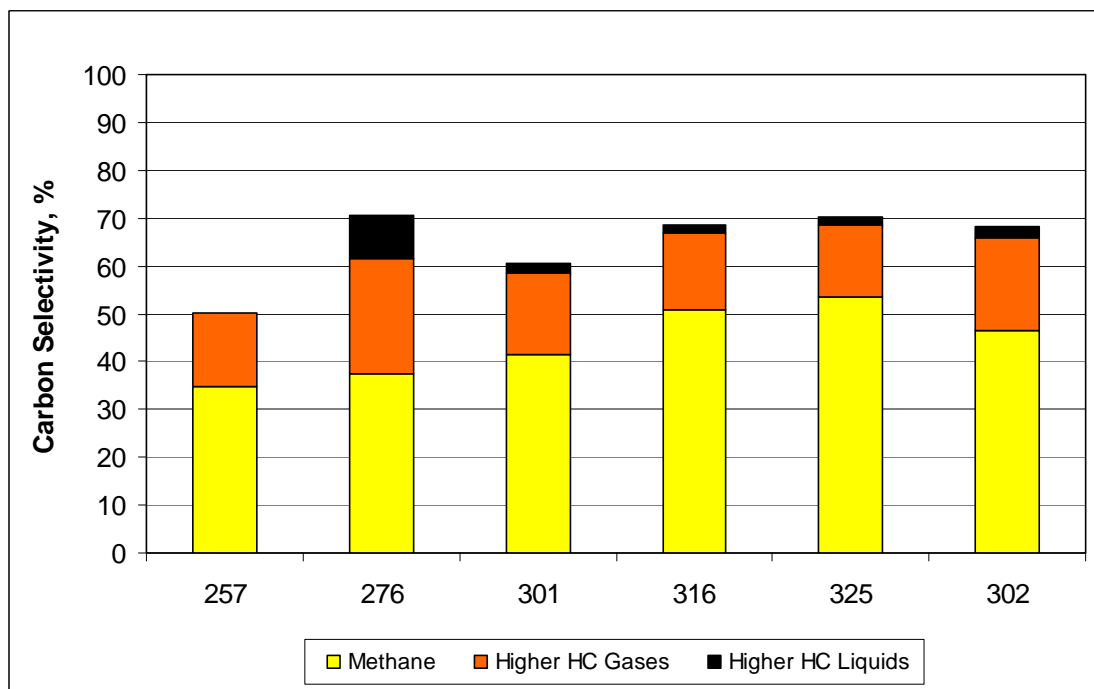**Figure B.36**. Carbon Conversion for the B-Promoted Catalyst

Figure B.37. C$_2$+ Oxygenate STYs for the B-Promoted Catalyst
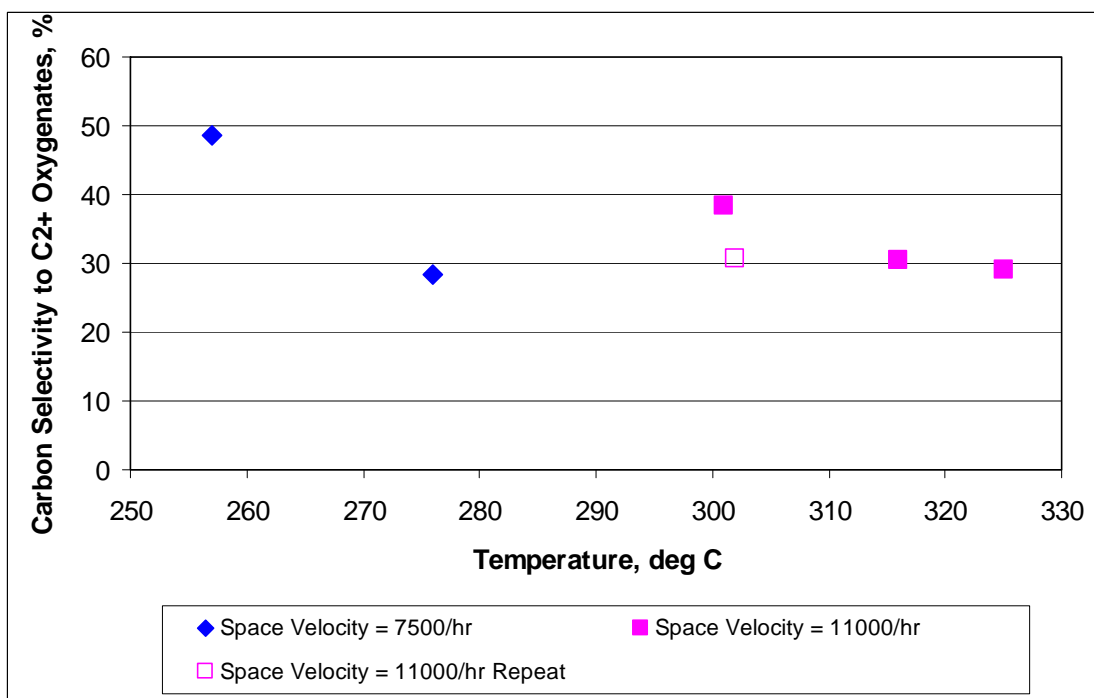
Figure B.38. Converted Carbon Selectivity to C$_2$+ Oxygenates for the B-Promoted Catalyst

Figure B.39. Carbon Selectivity of All Oxygenates to C_2+ Alcohols for the B-Promoted Catalyst


Figure B.40. Comparison of Hydrocarbon Selectivity for the B-Promoted Catalyst
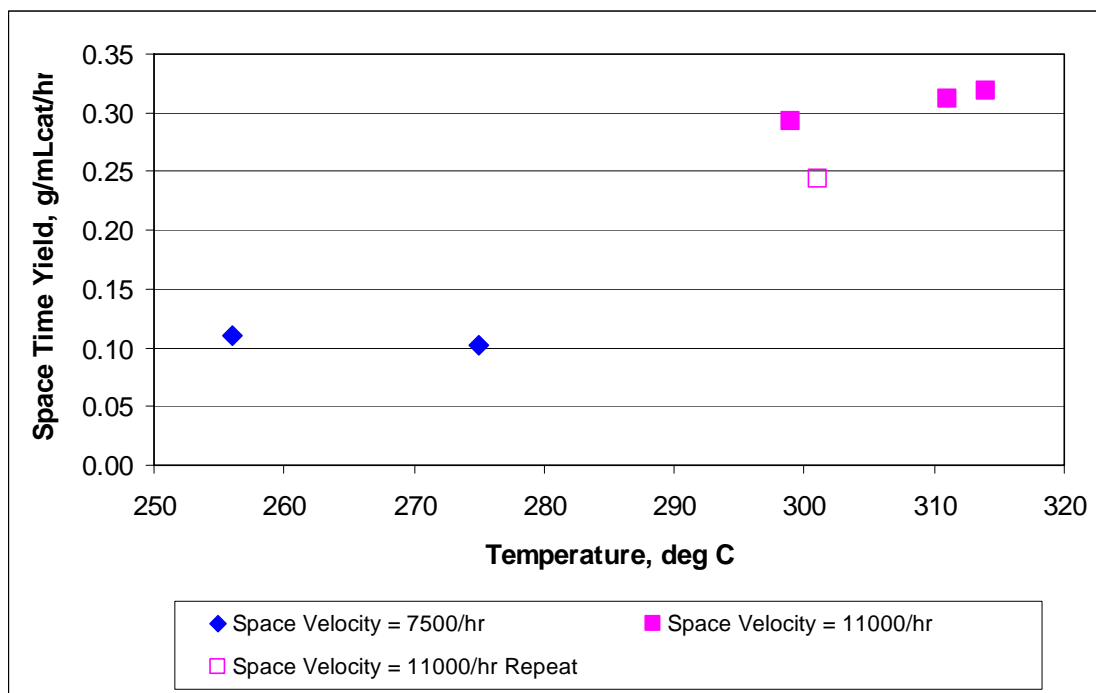
B.9 W-Promoted Catalyst

The W-promoted catalyst (RhMnW/SiO$_2$) was tested at all of the standard conditions up to approximately 315°C, and with a repeat condition at approximately 300°C. Higher temperatures were not investigated because of the poor selectivity to C$_2$+ oxygenates at the lower temperatures. The catalyst also was difficult to control when first attempting to conduct a run at 315°C. The catalyst temperature spiked several times while increasing the temperature from 275°C to 316°C and then it cooled 7°C overnight. The condition was repeated with a 4.5°C temperature drop overnight. No problems were encountered at repeated condition at 300°C.

This catalyst was fairly active with carbon conversion reaching about 30% at 314°C as shown in Figure B.41. However, carbon selectivity to C$_2$+ oxygenates was relatively low and constant (~ 20% to 27%) during tests at 275°C and higher as shown in Figure B.43). The resulting C$_2$+ oxygenates STYs appeared to reach a relatively constant level at 300°C, reaching a maximum of 320 g/L$_{cat}$/hr at 314°C as shown in Figure B.42. The STY at the repeat condition of 300°C was significantly lower, indicating catalyst deactivation at the higher temperatures. Figure B.44 shows that, with the exception of the test condition at 275°C, the selectivity of oxygenates to C$_2$+ alcohols was relatively constant between 27% and 33%. Figure B.45 shows that the selectivity to hydrocarbons was fairly unaffected from 275°C to 315°C.
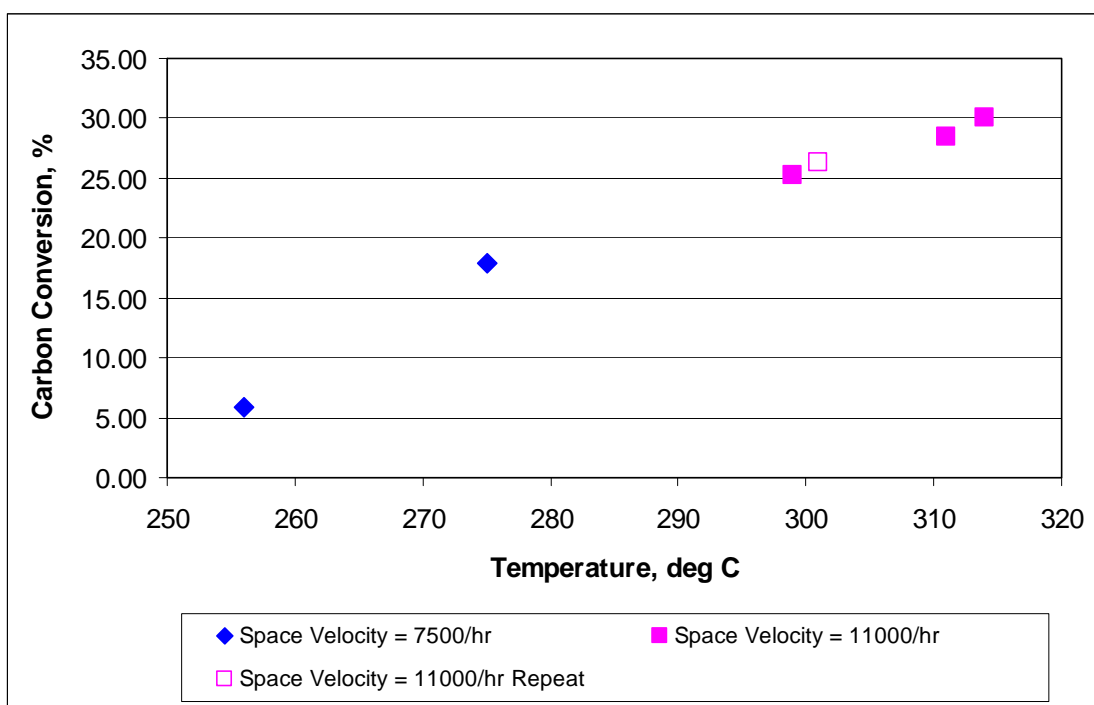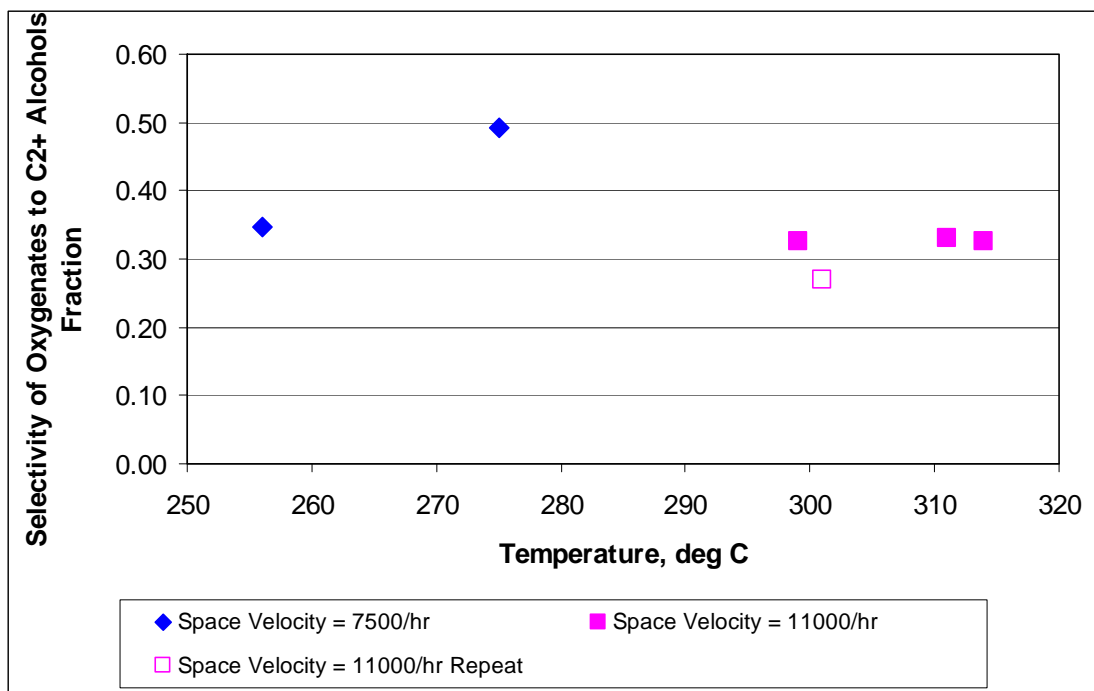

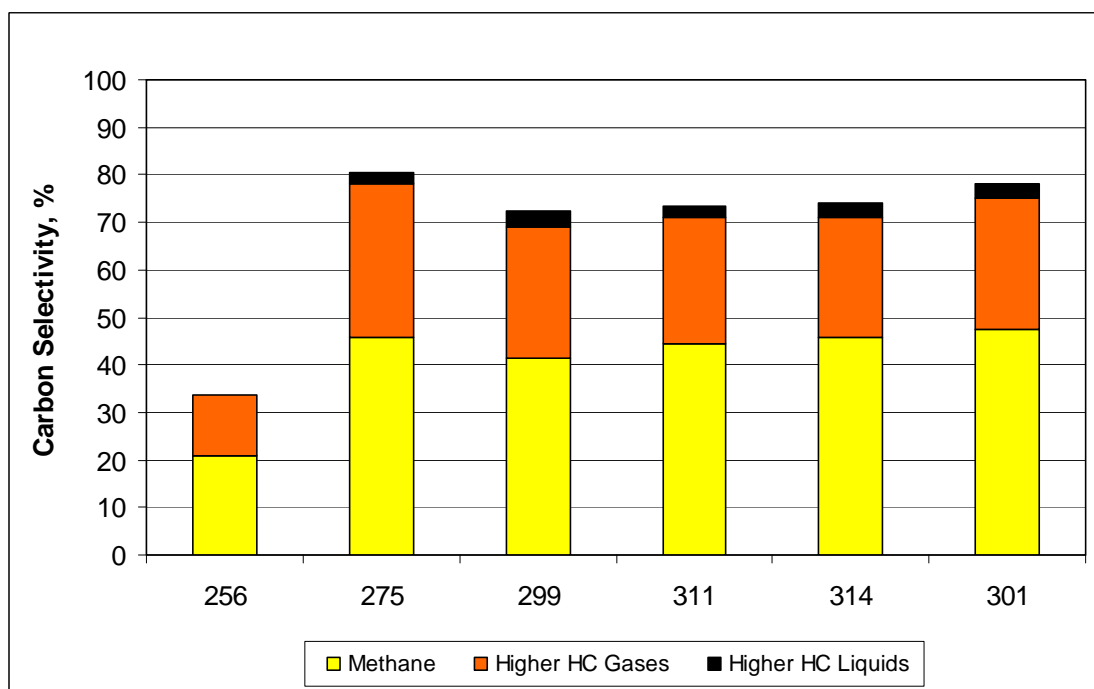**Figure B.41**. Carbon Conversion for the W-Promoted Catalyst

Figure B.42. C$_2$+ Oxygenate STYs for the W-Promoted Catalyst
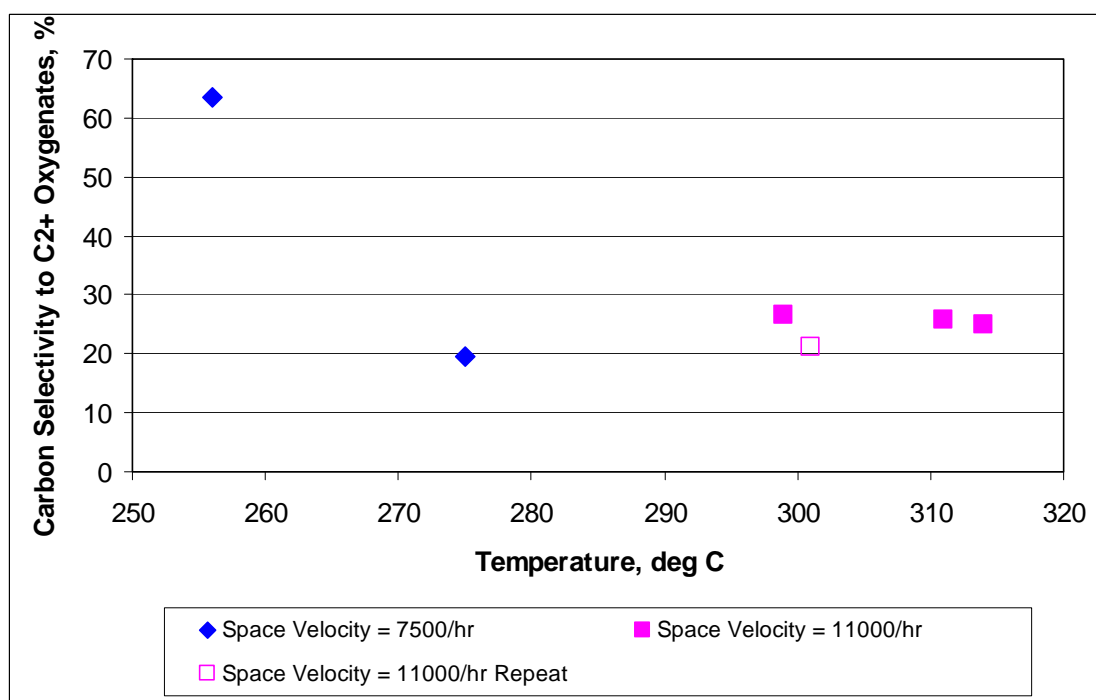
Figure B.43. Converted Carbon Selectivity to C$_2$+ Oxygenates for the W-Promoted Catalyst

Figure B.44. Carbon Selectivity of All Oxygenates to C_2+ Alcohols for the W-Promoted Catalyst

Figure B.45. Comparison of Hydrocarbon Selectivity for the W-Promoted Catalyst