PNNL-16763

Pacific Northwest
National Laboratory
Operated by Battelle for the
U.S. Department of Energy

Mixed Alcohol Synthesis Catalyst Screening

M. A. Gerber
J. F. White
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September 2007

Prepared for the U.S. Department of Energy
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PACIFIC NORTHWEST NATIONAL LABORATORY
operated by

BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

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Richland, Washington

Summary

The 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 obtaining commercially available mixed alcohol or preparing promising mixed-alcohol catalysts and screening them in a laboratory-scale reactor system. Commercially available catalysts and the most promising experimental catalysts are provided to NREL for testing using a slipstream from a pilot-scale biomass gasifier.

After a review of the literature and conversations with companies that produce catalysts, it was determined that commercial, mixed alcohols synthesis catalysts are not currently available. One catalyst manufacturer did supply a modified methanol catalyst (MeOH-X). This catalyst was tested in the PNNL laboratory-scale system and provided to NREL for further testing. ICI Katalco (ICI) provided a commercially available methanol catalyst that was also tested at PNNL and provided to NREL to evaluate the performance of both catalyst testing systems

PNNL also prepared and tested the behavior of 10 other catalysts representing the distinct catalyst classes for mixed alcohol syntheses. The test conditions and the range of C_2+ oxygenate space-time yields (STYs) for these 10 catalysts plus the ICI and MeOH-X catalysts are shown in Table S.1.

Table S.1. Test Conditions

Catalyst	Promoters	Pressure (atm)	Temperature (°C)	GHSV ($L/L_{cat}/hr$)	STY of C_2^+ Oxygenates(a) ($g/L_{cat}/hr$)
ICI	NA	80	250	7,300–15,000	20–20
MeOH-X	Not Specified	80	250–325	3,300–10,000	10–90
$K/Cu/Zn/Mn/Co/Cr_2O_3$	K, Mn, Co	80	354–398	7,500	10–30
K/MoS_2	K	80, 53	325–375	6,700	40–50
$K/Co/MoO_2$	K, Co	80	317–381	6,700–15,000	2–180
$Rh/Mn/SiO_2$	Mn	80	255–305	3,300	110–150
$Rh/Mn/Fe/SiO_2$	Mn, Fe	80	257–402	7,400–15,000	170–400
$Rh/Zn/SiO_2$ $Rh/Zn/Pd/SiO_2$	Zn, Zn/Pd	80	375	3,300	0, 0
Modified F-T	Al_2O_3, K, Cu	80	304–386	25,000–98,000	80–670
Fischer-Tropsch FT-MeOH-Pd (mixture)	$K/Fe/Cu/Ga/Al_2O_3$ $Cu/Zn/Ga/Al_2O_3$, Pd/Al_2O_3,	80	300–413	25,000–74,000	50–830
(a) C_2+ oxygenates were predominantly C_2 to C_5 alcohols, acetic acid, acetaldehyde, and ethyl acetate.					

The $Rh/Mn/Fe/SiO_2$ catalyst and the two Fischer-Tropsch-based catalysts had significantly higher C_2+ oxygenate STYs than any of the other catalysts, including the MeOH-X catalyst. However, there are other considerations that must be used to fairly compare the catalysts. Specifically, it was found that in no cases were C_2+ oxygenates the major product. Methanol and/or Fischer-Tropsch liquids were major coproducts for all but the $Rh/Mn/SiO_2$ and $Rh/Mn/Fe/SiO_2$ catalysts. It was also found that the reactor system was subject to exothermic excursions under conditions that produced the high STYs for the two Fischer-Tropsch catalysts and nearly so for the rhodium catalyst. Tests that achieved the highest C_2+ oxygenate STY for each catalyst were compared in terms of the STYs of all liquid products, including C_1 oxygenates, C_2+ alcohols, other C_2+ oxygenates, and Fisher-Tropsch liquids, as shown in Figure S.1. Also shown are the liquid product STYs for the same Fischer-Tropsch catalyst under conditions that produce a lower C_2+ oxygenate STY that provides a fairer comparison to the other catalysts.

The MeOH-X catalyst can be economic because the high-methanol STY falls within the recommended range for commercial methanol plants that were selected according to Stiles et al. (1991). The $Rh/Mn/Fe/SiO_2$ catalyst produces high a C_2+ oxygenate STY but, because it does not produce other coproducts in significant quantities, it does not achieve the minimum recommended STY based on a methanol plant. The Fischer-Tropsch-based catalyst shown in the figure can achieve a C_2+ oxygenate STY that falls within the recommended STY range, but it exceeds that range when the Fischer-Tropsch liquids are included. Under these conditions, the reactor is thermally unstable. When conditions are selected that reduce the total organic liquid STY to within the range of stable operation for a commercial methanol plant (second from the right in the figure), the C_2+ oxygenate yield is below the recommended range although still greater than all but the rhodium-based catalyst shown in the figure.

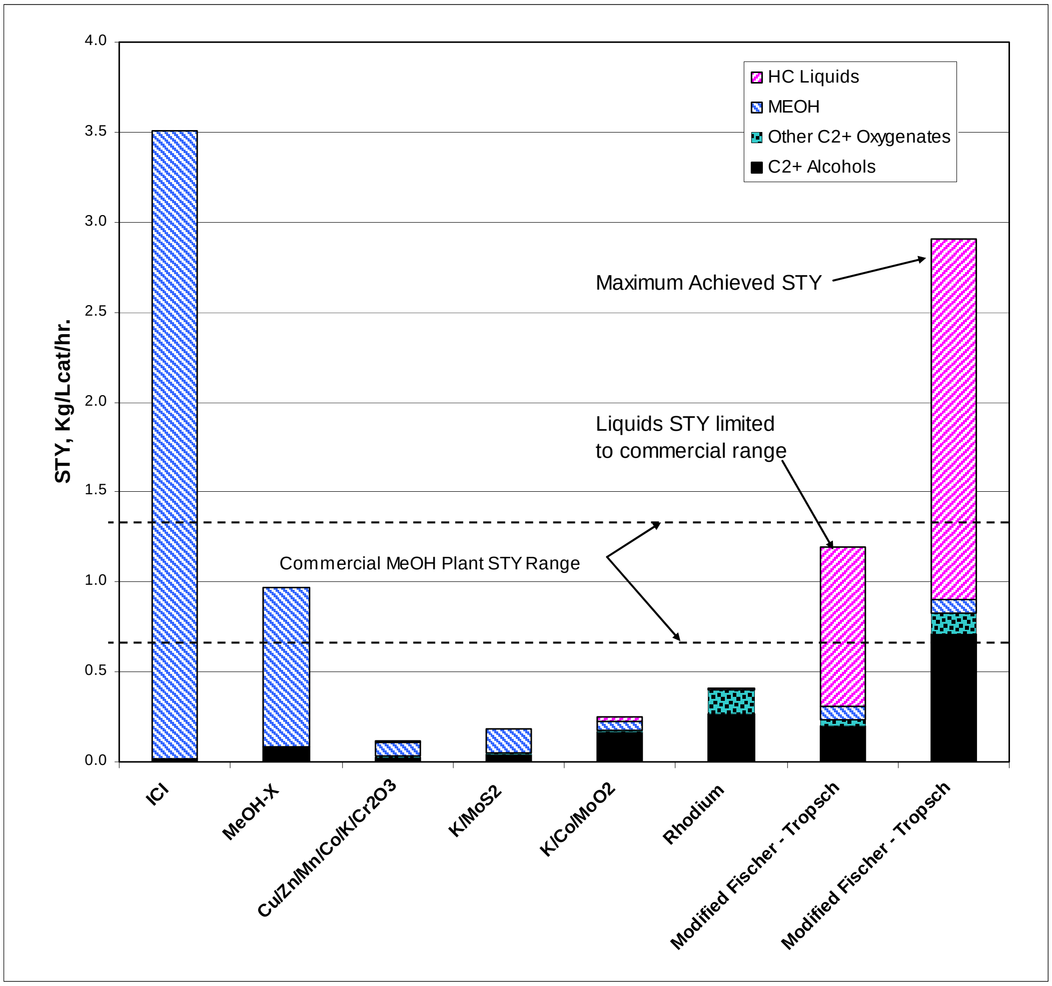

Figure S.1. Comparison of Tests to Achieve Highest STY

From the standpoint of producing C_2+ alcohols as the major product, it appears that the rhodium catalyst is the best choice in terms of both C_2+ oxygenate selectivity and STY. However, it can be seen from the figure that unless the rhodium catalyst can be improved to provide minimally acceptable STYs for commercial operation, mixed alcohol synthesis will involve significant production of other liquid coproducts. In this case, the modified Fischer-Tropsch catalyst shows the most promise for providing both an acceptable selectivity to C_2+ alcohols and total liquid STY. However, further optimization of the Fischer-Tropsch catalysts to improve selectivity to higher alcohols is highly desired. Selection of a preferred catalyst will likely entail a decision on the preferred coproduct slate. All other catalysts tested to date do not appear amenable to the significant improvements needed for acceptable STYs.

Further testing is recommended to optimize first rhodium and then Fischer-Tropsch catalysts to improve selectivity to higher alcohols and other C_2+ oxygenates. Further testing of other promising catalyst formulations could be warranted as they are identified. Testing is also needed to examine operational parameters such as:

- Lower system pressure to obtain data to evaluate the expected trade-offs between lower STYs, which affect capital costs, and lower pressures, which affect primarily operating costs.
- Lower H_2:CO ratios that would reduce or eliminate the need to adjust the H_2 and CO composition of the product gas from a biomass gasifier.
- Injection of methanol into the syngas feed to determine the ability of different catalysts to increase C_2+ oxygenate STYs by recycling methanol. This has been shown in the past with the MoS_2-based and some other catalysts.

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1.0 Introduction

The U.S. Department of Energy's (DOE) National Renewable Energy Laboratory (NREL) conducted technical and economic assessments of the feasibility of producing mixed alcohols as a primary product from biomass-derived synthesis gas (syngas) to complement alcohol fuel biosynthesis in an integrated biorefinery (Phillips, Aden, Jechura, Dayton, and Eggeman). The gasification process was based on a low-pressure, indirectly heated, entrained flow gasifier developed by Battelle. Downstream gas conditioning steps such as tar and light hydrocarbon reforming, sulfur removal, and gas compression were included to produce a syngas suitable for mixed alcohol fuel synthesis. After a review of the literature, the mixed alcohol synthesis process was based on the expected performance of a cobalt/molybdenum sulfide catalyst using methanol recycle in the synthesis reactor. The process increased the yield of higher alcohols and potentially recovered and recycled carbon dioxide from the product gas stream to a steam reformer to facilitate obtaining the desired syngas composition. Ethanol and higher alcohols were identified as the major products. Methane, light hydrocarbons, unreacted CO, and H_2 are recycled back to the synthesis reactor to maximize CO conversion. A purge stream taken from the recycled gas loop prevents excessive buildup of certain compounds.

1.1 Catalyst Performance Requirements

An integral part of the techno-economic assessment of this process was the assumption regarding the mixed alcohol fuel synthesis catalyst. The performance of the catalyst affects the capital costs of the 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.

The mixed alcohol synthesis catalyst forming the basis of the evaluation was based on a class of catalysts consisting of alkali-doped molybdenum sulfide with other metals such as cobalt added to promote the selective production of mixed alcohols. One purported advantage of this class of catalyst is its tolerance for sulfur in the syngas. Operating conditions and catalyst performance were based in part on the catalysts developed and tested by Quarderer (1986) and Quarderer and Cochran (1986) and patented by Dow Chemical Company and in part on typical values reported in the literature for similar catalysts in this class.

After review of the literature and conversations with selected catalyst manufacturers, it was determined that no molybdenum-based catalysts are commercially available. 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. The only other company found to have previously offered a commercial catalyst was Institut Francais du Petrole (IFP), who developed catalysts based on Cu/Co and Cu/Ni systems. Their work has been discontinued, and there is no longer any catalyst available for testing.

While testing was conducted using the MeOH-X catalyst, a review of prior research was also performed to identify other potential catalysts, including molybdenum-based catalysts that showed promise for mixed alcohol synthesis. The primary screening and selection criterion for catalyst performance was the space-time yield (STY) of C_2+ oxygenated hydrocarbons, with consideration given to the coproduction of methanol and liquid hydrocarbons. While the NREL techno-economic study cited an STY of 250 to 350 g mixed alcohol/L_{cat}/hr as a productivity rate typical of the molybdenum catalysts, this value was considered marginal based on the assessment made by Stiles et al. (1991), who stated that methanol synthesis plants ranged from approximately 670 to 1,340 g_{MeOH}/L_{cat}/hr. According to Stiles et al., higher methanol production rates create dissipation requirements that are difficult to manage. Production rates involving higher alcohol production create exothermic higher 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.

1.2 Catalyst Screening

In the absence of commercial catalysts having higher alcohol production rates at levels needed to achieve economic viability, this project was undertaken to identify the most promising catalysts and test them in a bench-scale system to determine which ones had the best performance. Potential catalysts were divided into six general classes:

- modified methanol catalysts (Cu/Zn and Cu/Mn based)
- modified molybdenum sulfide catalysts
- modified molybdenum oxide catalysts
- rhodium-based catalysts
- modified Fischer-Tropsch catalysts.

The approach taken in this study was to obtain or prepare catalysts that were either representative of each class of catalysts or that had the potential to achieve high STYs for C_2+ oxygenates and test them under conditions that would optimize C_2+ STYs at a common operating pressure (80 atm).

Table 1.1 lists the general characteristics of the catalysts in each class found in the literature, the typical range of operating conditions examined, and the range of C_2+ oxygenate STYs obtained. Not shown, but also important, are the types of catalyst supports, if any, that were used in preparing each class of catalysts, as well as the catalyst preparation methods.

The typical pressure ranges listed in Table 1.1 are illustrative only in that they provide the range of pressures examined for selected catalysts under what would be considered a typical operating pressure and provide a context for the corresponding ranges of STYs of C_2+ oxygenates listed. Many studies tested catalyst performance at near atmospheric conditions, usually to examine parametric changes to the catalyst or reaction conditions rather than to achieve commercially required productivities.

Table 1.1. General Characteristics, Typical Operating Conditions, and Productivity of Different Classes of Mixed Alcohol Synthesis Catalysts

Catalyst Class	Promoters	Pressure (atm)	Temperature (°C)	GHSV (L/L_{cat} /hr)	STY of C_2+ Oxygenates (g/L_{cat}/hr)
Modified Methanol (Cu/ZnO)	Alkali	50–150	275–400	1,000–10,000	26–49
Modified Methanol (Cu/ZnO/Mn)	Alkali, Co, Cr_2O_3	100–170	400	40,000	280–1,060
Modified Methanol (Cu/Mn)	Ni, Fe, Co	60–120	280–340	5,000	44–60
Molybdenum Sulfide	Alkali, Co,	70–200	250–330	1,000–6,000	35–200
Molybdenum Oxide	Alkali, Co	60–120	230–300	9,000–10,000	150–410
Rhodium	NA	70	300–320	13,000–27,000	120–240
Fischer-Tropsch (iron based)	Cu/Zn, Pd, Ga	80	330–350	20,000–70,000	280–780

The temperature and gross hourly space velocity (GHSV) ranges also provide an operating context for the STYs. For evaluating catalyst performance, all C_2+ oxygenates are considered because they can be further hydrogenated to the corresponding alcohols or recovered as byproducts.

Table 1.2 provides a qualitative comparison of the different catalyst classes found in the literature for the major reaction products and byproducts. For example, modified methanol catalysts generally produce high yields of methanol, much lower yields of C_2+ oxygenates and methane, and little if any higher hydrocarbons. The iron-based modified Fischer-Tropsch catalysts generally produce significantly higher yields of C_2+ oxygenates but much higher yields of hydrocarbon liquids. The molybdenum-based catalysts make moderate quantities of methanol, C_2+ oxygenates, and hydrocarbons, whereas the rhodium-based catalysts generally produce low quantities of methanol but comparable quantities of C_2+ oxygenates and hydrocarbons.

Based on the results reported in the literature, it can generally be concluded that a very high selectivity toward C_2+ oxygenates will be difficult to achieve. Instead, significant byproducts of methanol, methane, and/or higher hydrocarbons will accompany the production of the C_2+ oxygenates often resulting in the C_2+ oxygenates becoming a minor coproduct. Consequently, evaluation of selected catalysts must consider the potential value of these byproducts and how their yields contribute to overall product revenue, with the understanding that multiple products can make product recovery more costly.

Table 1.2. Comparison of Productivity and Carbon Selectivity to Byproducts for Various Classes of Mixed Alcohol Synthesis Catalysts

Catalyst Class	**STY C_2+ Oxygenates**	**Carbon Selectivity**		
		C_2+ Oxygenates	**C_1 Oxygenates (usually MeOH)**	**Hydrocarbons (HCs)**
Modified Methanol (Cu/ZnO)	Very low	Very low	Very high	Very low (mostly methane)
Modified Methanol (Cu/ZnO/Mn)	Moderately low to high	Moderately low	Moderately high	Moderate to moderately low
Modified Methanol (Cu/Mn)	Very low	Very low	Very high	Very low
Molybdenum Sulfide	Low to moderately low	Moderate	Moderate (can be < or > C_2+ oxygenates)	Moderately low (mixture of HC gases and liquids dominated by methane)
Molybdenum Oxide	Moderately low to moderate	Moderate	Moderate (can be < or > C_2+ oxygenates)	Moderate
Rhodium	Moderately low	Moderate	Low to very low	Moderate
Fischer-Tropsch (iron based)	Moderately low to moderately high	Low	Very low	High

2.0 Catalyst Testing

Catalyst testing at Pacific Northwest National Laboratory (PNNL) consisted of construction and shakedown of a bench-scale synthesis reactor system and evaluation of 12 catalysts. The synthesis reactor system and the catalysts tested are described in this section.

2.1 Synthesis Reactor System Description

A bench-scale tubular reactor system was designed to operate at pressures up to 1200 psig and temperatures up to 450°C. The catalyst chamber was 1.67 cm long (in selected tests the space was 0.215 cm long) and 1/4 in. in diameter. A 1/16-in. (0.159-cm) outer diameter thermocouple sheath extended through the center of the reactor, creating an annulus-shaped catalyst chamber. Two thermocouples inside the sheath were spaced so that one was at the center of the catalyst bed and the other just upstream.

Figure 2.1 is a simplified diagram of the reactor system. The reactor was oriented vertically in a furnace. Syngas was metered through a mass flow controller. The system also metered reducing gas (10% hydrogen in nitrogen) and nitrogen to the reactor during catalyst reduction. The raw product gas leaving the reactor was passed through a cold trap to condense liquids at 0°C and through a back-pressure regulator that controlled the system pressure. A separate bypass line containing a trap at ambient temperature was used during startup and initial aging of the catalyst.

The nominal feed rate to the reactor was determined by calibrating the mass flow controllers at system pressure before the tests, using a bubble flow meter downstream of the back-pressure flow regulator. Bubble flow-meter readings were corrected for standard pressure, temperature, and moisture content introduced by the bubble flow meter. The bubble flow meter downstream of the back-pressure regulator was also used to monitor product gas flow rate downstream of the liquid sample traps during each test.

Product gas grab samples were 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 were monitored during tests.

Gas cylinders containing a specified syngas mixture were used in the tests. The gas mixture consisted of hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2) and nitrogen (N_2). The nominal composition of the gas is shown in Table 2.1. Also shown are the measured concentrations of the feed gas used in the tests. The variation in the component concentrations in the feed gas are attributed to variations in the composition of the individual gas cylinder mixtures that were supplied for the tests.

During a typical test series, a catalyst was loaded into the reactor and its net weight determined. The reactor was placed in the reactor system and reduced in place at atmospheric pressure. The reactor was cooled after catalyst reduction, and the desired syngas feed rate and pressure were established. The reactor was heated up slowly to a temperature at which the reaction rate was significant and kept there for

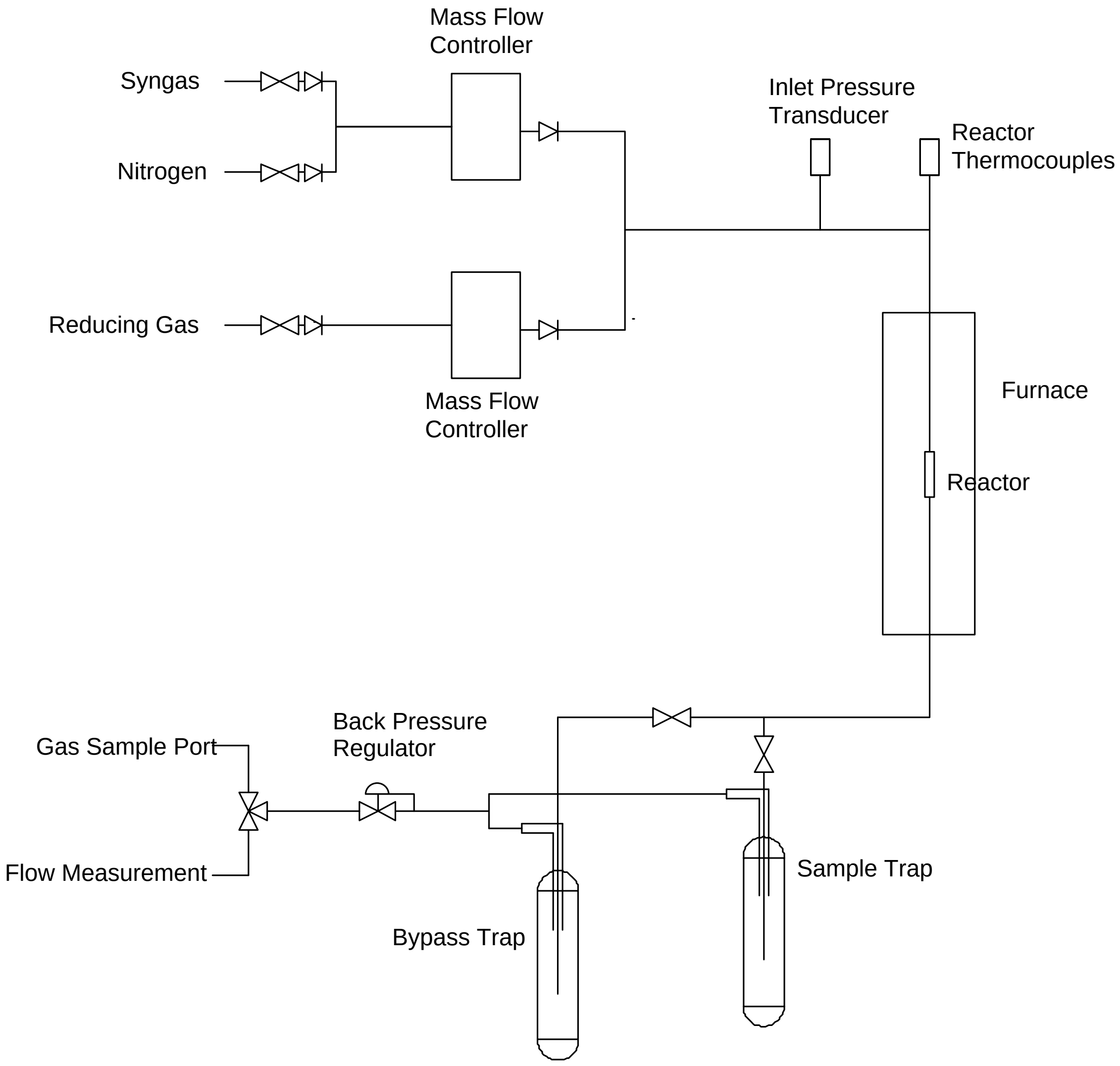

Figure 2.1. Simplified Diagram of Reactor System

Table 2.1. Nominal and Actual Composition of Syngas Used in Tests

Gas	**Nominal Concentration (%)**	**Measured Concentration (%)**
H_2	63	66.2–60.7
CO	29	25.4–30.5
CO_2	4	2.4–5.6
N_2	4	2.9–5.2

at least 24 hours to allow the catalyst to age. The product stream was directed through the bypass cold trap during this time. After aging the catalyst, the product stream was redirected through the sample 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 gas chromatograph (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 either using a GC (for the ICI Katalco and MeOH-X commercial catalysts), or a high pressure liquid chromatograph (HPLC) to quantify the C_1–C_4 oxygenates (principally alcohols, acids, aldehydes, esters, and any other significant peaks identified by the HPLC). After sampling, a new set of conditions (temperature and feed rate) was established and another cold trap sample 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 advanced to progressively higher temperatures with one or more space velocities examined during each test.

2.2 Catalyst Preparation

The 12 catalysts tested at PNNL are shown in Table 2.2, along with the labels used in this report.

Table 2.2. List of Catalysts Tested and Corresponding Labels

Catalyst	Label
ICI-Katalco 51-8PPT	ICI
Modified Commercial Methanol Catalyst	MeOH-X
$K/Cu/Zn/Mn/Co/CrO_2$	K/Cu/Zn/Mn/Co/Cr
$Rh/Mn/SiO_2$	$Rh/Mn/SiO_2$
$Rh/Mn/Fe/SiO_2$	$Rh/Mn/Fe/SiO_2$
$Rh/ZnO/SiO_2$	$Rh/ ZnO/SiO_2$
$Rh/ZnO/Pd/SiO_2$	$Rh/ZnO/Pd/SiO_2$
K/MoS_2	K/MoS_2
$K/Co/MoO_2$	$K/Co/MoO_2$
$K/Co/MoO_2/C$	$K/Co/MoO_2/C$
$K/Fe/Cu/Al_2O_3$	$K/Fe/Cu/Al_2O_3$
$K/Fe/Cu/Ga/Al_2O_3$ + $K/Cu/Ga/Al_2O_3$ + Pd/Al_2O_3 mixture	FT-MeOH-Pd

2.2.1 ICI and MeOH-X Catalysts

The first two catalysts listed are commercially available from catalyst manufacturers. The ICI Katalco methanol catalyst 51-8PPT (ICI catalyst) is a Zn/Al/Cu/Mg oxide catalyst that was used as a baseline to shake down the reactor system and verify the ability of the system to produce expected yields of methanol. The MeOH-X catalyst is a methanol catalyst modified to produce a mixture of alcohols. Its actual composition is not revealed. Both catalysts were ground and sieved to -60/+100 mesh and reduced according to the manufacturers' suggestions.

2.2.2 K/Cu/Zn/Mn/Co/Cr Modified Methanol Catalyst

The K/Cu/Zn/Mn/Co/Cr catalyst was based on a methanol catalyst formulation prepared by Stiles et al. (1991) that was modified with manganese, cobalt, and chromium to produce a catalyst with a Cu:Mn:Zn:Co:Cr atomic ratio of 0.4:0.1:0.1:0.003:0.06. The catalyst was prepared using appropriate quantities of the metals as nitrates dissolved in deionized (DI) water at a rate of 6.2 mL total nitrate solution/g $Cu(NO_3)_2 \cdot 6H_2O$. This solution was slowly added over a period of 1 hour to a second solution containing potassium carbonate at a ratio of 5.46 mL DI water/g $K_2(CO_3)$, with 1 mL of nitrate solution added to 1.67 mL of potassium carbonate solution. When the mixture achieved a pH of 10.5 during nitrate solution addition, a second solution of 6.67 mL DI water/g K_2CO_3 was added drop-wise as needed to maintain the pH between 10.5 and 10.6. The combined mixture was stirred for 2 more hours at 30°C and then 2 hours at 60°–65°C. The resultant slurry pH was readjusted to between 7.2 and 7.5 over an additional period of two hours to ensure precipitation of the copper in the solution. The precipitate was filtered, rinsed, and vacuum dried at 85°C. The dried precipitate was calcined for two hours at 350°C and sieved to -60/100 mesh.

2.2.3 Rhodium-Based Catalysts

Four rhodium-based catalysts were tested. The first, $Rh/Mn/SiO_2$, was used in previous alcohol synthesis studies at PNNL and consisted of 5.5% Rh and 2.3% Mn on silica. It was prepared using the incipient wetness technique with rhodium and manganese nitrate precursors. Davison 645 high surface-area SiO_2 (-60/+100 mesh) was pretreated by calcining at 500^{o}C for 2 hours (ramping up at 5^{o}C/min during heating and ramping down at 10^{o}C/min during cooling). The appropriate quantities of a rhodium nitrate solution (10 wt% Rh concentration in solution) and magnesium nitrate tetrahydrate were combined with enough DI 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 silica in drop-wise fashion and then dried overnight at 110°C. The dried catalyst was calcined at 400°C. The catalyst was reduced using a 10% H_2 in N_2 gas mixture, heating the catalyst to 220°C at 2.5°C/min, holding at that temperature for 1 hour, and then heating from 220°C to 260°C at 1°C/min and holding that temperature overnight.

A second catalyst ($Rh/Mn/Fe/SiO_2$) was prepared from the first before it was calcined by adding 0.3% Fe to the uncalcined catalyst, using the incipient wetness technique with ferric nitrate as the precursor. The preparation involved adding the appropriate quantity of iron to DI water to make a total ferric nitrate solution volume that was three times the pore volume of the catalyst to be impregnated. The silica was impregnated with one-third of the solution, then dried. This was repeated three times until all of the solution was used. The catalyst was then dried at 110°C overnight. The dried catalyst was calcined in an oven by heating to 400°C at 5°C/min, maintained at that temperature for 2 hours, and then cooled at 5°C/min. The catalyst was reduced in the same manner as the first rhodium catalyst.

A third rhodium-based catalyst ($Rh/ZnO/SiO_2$) contained 8.6% Rh and 17.6% ZnO on 5-mm-diameter Norpro high surface-area beads. It was prepared by adding an appropriate quantity of rhodium nitrate solution (Engelhard, Rh concentration 10.32%), an appropriate quantity of zinc nitrate hexahydrate crystals, and enough DI water to bring the total volume of the impregnation solution to twice the water adsorption pore volume of the support. After impregnation of one-half of the impregnation solution, the beads were dried while tumbling on a rotating coater dish with a flow of hot (about 150°C) air from a heat gun. They were then impregnated with the second half of the impregnation solution and aged for 2 hours before undergoing a second phase of tumble drying with a heat gun. Final drying was accomplished by heating in a vacuum oven at 80°C overnight. The dried catalyst was calcined in an oven at 350°C for 3 hours and subsequently ground and sieved to -60/+100 mesh. The catalyst was reduced using a 10% H_2 in N_2 gas mixture, heating the catalyst to 220°C at 2.0°C/min, and holding at that temperature overnight. In a second test using this catalyst, the catalyst was reduced using 2% H_2 in N_2, the catalyst heated to 220°C at 2.5°C/min, held at that temperature for 1 hour, heated from 220° to 250°C at 0.25°C/min, and held at that temperature overnight.

A fourth rhodium-based catalyst (Rh/ZnO/Pd/SiO_2 catalyst) contained 4.3% Rh, 4.45% Pd, and 17.6% ZnO. It was prepared in the same manner as the third catalyst except that an appropriate quantity of palladium nitrate solution (Engelhard, Pd concentration 20.74%) was also added to the impregnation solution and the quantity of rhodium nitrate solution was reduced to obtain the appropriate concentration that was lower than that in the third catalyst. The catalyst was reduced using a 10% H_2 in N_2 gas mixture, heating the catalyst to 400°C at 2.0°C/min and holding it at that temperature overnight.

2.2.4 Molybdenum Sulfide-Based Catalyst

The molybdenum sulfide catalyst (K/MoS_2) contained potassium carbonate and molybdenum sulfide at a weight ratio of 0.17 to 1. It was prepared by dissolving the appropriate quantities of ammonium tetrathiomolybdate [$(NH_4)_2MoS_4$] and potassium carbonate (K_2CO_3) in DI water [10 g water/g $(NH_4)_2MoS_4$], and evaporating the solution under vacuum in a roto-evaporator. The damp solids were removed from the roto-evaporator and dried overnight in an oven at 120°C. The catalyst was calcined in the reactor just before testing by heating to 450°C at 1.7°C/min in nitrogen and maintaining that temperature overnight.

2.2.5 Molybdenum Oxide-Based Catalysts

Two molybdenum oxide-based catalysts were tested. The first, K/Co/MoO_2, was prepared from ammonium heptamolybdate (AHM), cobalt nitrate hexahydrate, and potassium chloride to produce a mixture with a Co:Mo atomic ratio of 7.0:1 and a 0.95% KCl concentration, generally following the recipe of Zhang et al. (2001). AHM was dissolved in a 5% H_2O_2 solution at a ratio of 1 g AHM/mL H_2O_2 solution. Sufficient cobalt nitrate hexahydrate was dissolved in DI water at a ratio of 1 g $Co(NO_3)_2 \cdot 6\,H_2O$/1.5 mL H_2O and added to the AHM solution. Sufficient potassium chloride was dissolved in water at a ratio of 1 g KCl/25 mL H_2O and added to the mixture. The resulting mixture was allowed to completely gel in an oven set at 100°C. The dried gel was ground and subsequently washed 5 times in methanol, dried at 80°C in a vacuum oven, and calcined at 350°C for 3 hours. The calcined catalyst was screened to -60/+100 mesh and reduced overnight at 350°C in the reactor using a 10% H_2 in N_2 reducing gas mixture.

The second catalyst (K/Co/MoO_2/C) was also prepared from AHM, cobalt nitrate hexahydrate, and potassium carbonate to produce a mixture with a Co:Mo:K atomic ratio of 0.5:1.0:0.1, generally following the recipe of Bao et al. (2003). The AHM and cobalt nitrate hexahydrate were dissolved and combined like the previous catalyst. Sufficient potassium carbonate was dissolved in DI water at a ratio of 1 g K_2CO_3/10.4 mL H_2O and added to the AHM/cobalt nitrate solution. A citric acid solution containing 1 g citric acid/4.7 mL H_2O was added to the AHM/cobalt nitrate mixture at a ratio of 2 mL citric acid solution/g AHM, and the pH of the resultant mixture was adjusted to a pH of 3.5–3.6 using ammonia hydroxide or formic acid as needed. The solution was heated to 65°C overnight and then placed in an air oven at 100°C for two days, producing a lightweight, deep reddish-purple foam. The foam was calcined in a flow of nitrogen at 400°C for 4 hours, pelletized, and ground to a -60/+100 mesh. According to Bao et al. (2003), calcination of the citric acid produces an amorphous carbon, accounting for about 40% atomic concentration in the calcined catalyst. The catalyst was reduced in the reactor overnight at 400°C using a 10% H_2 in a N_2 reducing gas mixture.

2.2.6 Fischer-Tropsch Catalysts

An iron-based modified Fischer-Tropsch catalyst ($K/Fe/Cu/Al_2O_3$) that was used in previous studies at PNNL consisted of Fe/Cu/Al/K in the ratios 1.0/0.03/2.0/0.70. Preparation of this catalyst followed the recipe of Inui et al. (1997) and Inui and Yamamoto (1998) for their #2 catalyst, which uses a uniform gelation method to coprecipitate the corresponding metal nitrates from solution using NH_3 vapor. In this procedure, a concentrated mixed nitrate solution of the above metals was spread in a thin layer in a tray and placed inside a second tray that was partially filled with an aqueous NH_3 solution maintained at 60°C. The larger tray was covered with glass for 10 minutes to allow the gel to form. The gel was dried at 120°C overnight and ground to a powder. The powder was calcined in a flow of dry air while being heated to 350°C and held there for 30 minutes. After calcining, the catalyst was ground and sieved to -60/+100 mesh, then reduced in the synthesis reactor by heating at 2°C/min to 450°C in a 10% H_2 in nitrogen gas mixture and maintaining it at that temperature overnight.

A second catalyst mixture (FT-MeOH-Pd), also based on the work of Inui et al. (1997) and Inui and Yamamoto (1998), was prepared by physically mixing equal weights of three of their catalyst preparations. Used in this mixture are catalysts 4, 5, and 6, which had been used in previous alcohol synthesis studies at PNNL. Catalyst #4 was similar to the previously described catalyst #2 except that gallium was added to the recipe so that the atomic ratios of Fe/Cu/Al/K/Ga were 1.0/0.03/2.0/0.70/0.16. Catalyst # 5 was prepared using the uniform gelation method to coprecipitate the nitrates of copper, zinc, aluminum, potassium, and gallium so that the ratios of Cu/Zn/Al/K/Ga were 1.0/1.0/1.0/0.10/0.32. Catalyst # 6 consisted of γ-alumina impregnated with an aqueous solution of palladium nitrate to produce a 10.3 wt% concentration of Pd on alumina. All three catalysts were individually ground and sieved to -60/+100 mesh before being mixed. The catalyst mixture was reduced by heating the catalyst at 2°C/min to 450°C in a 10% H_2 in nitrogen gas mixture and maintaining it at a temperature of 450°C overnight.

3.0 Reactor System Performance

The reactor system was first used to evaluate the ICI-Katalco methanol catalyst to obtain comparative data for subsequent tests and to verify satisfactory operation. The system was operated at 1200 psig and 250°C at two flow rates corresponding to space velocities of 7,400 and 15,000 $L/L_{cat}/hr$. Two sets of data were collected at the lower space velocity; the first set was obtained during the 24-hour break-in period for the catalyst using the cold trap in the bypass line to collect the liquid sample. The cold trap was maintained at ambient temperature during this test. The second set of data was taken after the first set using the sample line cold trap to obtain the liquid sample. Both sets of data were very comparable. The C_1+ oxygenate STY ranged from 2,100 to 2,200 $g/L_{cat}/hr$ yield with 98.6% selectivity to methanol. No hydrocarbons were detected in the product gas. The operating temperature and gas flow rates were very constant during the 24-hour catalyst break-in period, and the liquid production rate was about 5% greater. This suggests that even the warm trap was efficiently collecting methanol, the most volatile alcohol, which gives greater confidence to the collection efficiency of the cold trap.

The third set of data was obtained at the higher space velocity and produced flow rates greater than expected. The nitrogen content in the product gas was also much greater than expected. However, if the measured flow rate and corresponding product CO and CO_2 gas concentrations were used, the carbon balance was comparable to those achieved for the first two data sets. It was concluded that the high nitrogen value was due to a slow leak in a globe valve in the nitrogen line used to backfill the sample trap after collecting a liquid sample. The reactor system was modified to back up all globe valves with ball valves between the nitrogen and hydrogen feed lines to reduce the chances of a similar leak in subsequent testing.

During testing it was determined that the measured outlet flow rate at a particular point in time was not always representative of the average flow rate during liquid sample collection in the cold trap because of slow fluctuations over irregular periods of several minutes to several hours. These fluctuations are attributed to relatively small fluctuations in the reactor pressure and transient changes in catalyst reactivity. For example, it was noted that the back-pressure regulator often cycled over relatively short periods of time (< 1 hour) and pressure changes (~5–10 psi). Flow rate was measured four or more times over a period of approximately 1 hour and averaged to mitigate this fluctuation. However, it was also noted that the ambient temperature, particularly during the summer months, cycled daily throughout the collection period, accompanied by a corresponding pressure change of the system. It was later determined that the temperature sensitivity of the back-pressure regulator was the likely cause of pressure changes that varied as much as 25 psi.

To calculate a representative average outlet flow rate during a sample collection period, a nitrogen 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 nitrogen balance. Carbon balances using this method were approximately ± 10%.

It was also found that when the more reactive catalysts were operated at reaction rates that approached the limits of the reactor furnace to remove excess heat, small changes in reactor temperature could cause large fluctuations in the catalyst bed temperature; in many cases it took many hours to return to a steady value. In these cases an average temperature was used for reporting the data. In some cases it was necessary to allow the catalyst bed to pass through the unstable region to a higher temperature where the CO conversion was nearly 100% to obtain a steady condition. One consequence of this phenomenon was that it was very difficult if not impossible to obtain steady flow conditions for some intermediate carbon conversions for some of the catalysts.

Slow aging of the catalysts during a test series could result in significant hot spot exotherm diminution over a period of several hours. Any effect on results was minimized by allowing the catalyst to stabilize for at least 24 hours before collecting liquid samples. Further aging of the catalysts likely occurred but was assumed to have a minor effect on comparisons of the performance of different catalysts.

4.0 Test Results

Sixty-five test conditions were evaluated using the 12 catalysts, including the ICI-Katalco catalyst used to shake down the system. Table 4.1 summarizes the test results. These results are discussed in this section according to the class of catalyst tested.

4.1 Methanol and Modified Methanol Catalysts

The methanol catalysts are very reactive and achieve high methanol STYs and nearly 100% carbon selectivity at relatively low temperatures (250° to 325°C). Carbon conversion to methanol is limited by equilibrium under typical operating conditions, with carbon conversion decreasing with increasing temperature. When methanol catalysts are modified by adding a small quantity of alkali, the catalysts are less reactive than the methanol catalysts and less selective to methanol. Instead, small quantities of higher alcohols are also produced.

The ICI-Katalco 51-8PPT (ICI) catalyst was operated at one temperature (250°C) and two space velocities (7,300 and 15,000 $L/L_{cat}/hr$) to shake down the reactor system and obtain baseline data representative of catalyst performance at a typical operating temperature. The MeOH-X catalyst was tested next over a range of temperatures typical for this catalyst (250° to 325°C) and space velocities (3,300 to 10,000 $L/L_{cat}/hr$) based on the manufacturer's suggestions. Both catalysts were very reactive at these temperatures, the ICI catalyst achieved carbon conversion greater than 50% at temperatures as low as 250°C and the MeOH-X catalyst at 275°C. At higher temperatures the MeOH-X catalyst achieved progressively lower carbon conversions, as shown in Figure 4.1, suggesting that the conversion rate was equilibrium driven with respect to methanol. The ICI catalyst showed similar behavior. Figure 4.2 shows the conversion of carbon in the feed gas to methanol predicted using the ChemCAD® chemical engineering process simulation software program, which is based on the composition of the feed gas used in the tests and the assumption that the product methanol achieved equilibrium in the product gas. Also shown in the figure are the calculated carbon conversions to methanol in the tests using the ICI and MeOH-X catalysts at various temperatures and inlet gas space velocities. It can be seen that at 275°C or higher catalyst temperatures, the carbon conversion to methanol by the MeOH-X catalyst is limited by equilibrium for space velocities ranging from 3,300 to 6,700 $L/L_{cat}/hr$, and at 300°C or higher temperatures, the catalyst is limited by equilibrium for space velocities as high as 10,000 $L/L_{cat}/hr$. At 250°C the carbon conversions for both the MeOH-X and the ICI catalysts are lower than that predicted by equilibrium at space velocities of 6,700 $L/L_{cat}/hr$ for the MeOH-X catalyst and 7,300 $L/L_{cat}/hr$ for the ICI catalyst. As expected, the carbon conversion rate to methanol is even lower at higher space velocities, as shown by the carbon conversion at 250°C for the ICI catalyst at a 15,000 $L/L_{cat}/hr$ space velocity.

The MeOH-X catalyst did not produce significant quantities of higher oxygenates (C_2+ oxygenates) until approximately 275°C and reached maximum selectivity at 325°C, the highest temperature examined (see Figure 4.3). As might be expected, carbon selectivity to the higher oxygenates was greater at the lower space velocities, but the STY of the higher oxygenates was lower due to lower gas feed rates. Oxygenates other than the alcohols were generally 1% or less at all of the conditions examined. Carbon selectivity to hydrocarbons was approximately 1% or less at temperatures below 300°C, but ranged from approximately 5 to 15% at 325°C over the range of space velocities examined. As might be expected, the selectivity to hydrocarbons decreased with increasing space velocity.

Table 4.1. Summary of Test Results

						Carbon Selectivity (Mol%)						STY (g/mL$_{cat}$/hr)						
Catalyst	**Space Velocity (L/L$_{cat}$/hr)**	**Temp. (°C)**	**Carbon Conv. (%)**	**CO Conv. (%)**	**CO Conv. to CO_2 (%)**	**MeOH**	**Other C_1 Oxygenates**	**C_2+ Alc.**	**Other C_2+ Oxygenates**	**CH_4**	**Other HCs**	**C_2+ Alc.**	**Other C_2+ Oxygenate**	**Total C_2+ Oxygenate**	**HC Liq.**	**MeOH**	**Total Liq.**	**Carbon Balance (C_{out}/C_{in}) (%)**
ICI	7300	250	64.5	66.8	2.2	98.57	0.88	0.55	0.00	0.00	0.00	0.01	0.00	0.01	0.00	2.07	2.08	102
ICI$^{(a)}$	15000	250	53.7	51.8	-2.0	98.42	0.74	0.74	0.10	0.00	0.00	0.02	0.00	0.02	0.00	3.49	3.51	107$^{(a)}$
MeOH-X	6700	250	66.0	63.8	-2.2	98.60	0.91	0.49	0.00	0.00	0.00	0.01	0.00	0.01	0.00	1.90	1.90	107
MeOH-X	6700	275	56.3	57.1	0.7	97.12	0.82	1.94	0.12	0.00	0.00	0.02	0.00	0.02	0.00	1.59	1.62	105
MeOH-X	3300	275	59.6	57.5	-2.1	95.49	0.80	3.20	0.42	0.00	0.09	0.02	0.00	0.02	0.00	0.83	0.85	109
MeOH-X	6700	300	37.8	42.3	4.5	90.39	0.54	7.59	0.43	0.85	0.21	0.05	0.00	0.06	0.00	1.00	1.05	103
MeOH-X	10000	300	37.5	39.7	2.1	91.72	0.55	6.78	0.36	0.59	0.00	0.07	0.00	0.08	0.00	1.50	1.58	104
MeOH-X	10000	325	24.7	28.8	4.1	81.47	0.29	12.32	0.26	2.46	3.20	0.09	0.00	0.09	0.00	0.88	0.97	105
MeOH-X	6700	325	25.0	33.0	8.0	78.06	0.00	14.21	0.00	3.17	4.56	0.07	0.00	0.07	0.00	0.57	0.63	103
MeOH-X	3300	325	27.4	39.1	11.6	68.76	0.00	16.42	0.00	4.56	10.26	0.04	0.00	0.04	0.00	0.27	0.32	102
MeOH-X	3300	300	40.1	45.0	4.9	87.13	0.49	9.57	0.54	1.11	1.16	0.04	0.00	0.04	0.00	0.51	0.55	104
MeOH-X	6700	275	51.4	48.4	-3.1	97.37	0.76	1.72	0.16	0.00	0.00	0.02	0.00	0.02	0.00	1.46	1.48	108
K/Cu/Zn/Mn/Co/Cr	7500	355	3.49	4.45	0.44	55.44	0.00	6.84	0.00	21.64	16.09	0.01	0.00	0.01	0.00	0.06	0.07	95.73
K/Cu/Zn/Mn/Co/Cr	7500	354	7.31	8.44	0.03	71.67	0.00	12.89	0.00	10.54	4.89	0.02	0.00	0.02	0.00	0.17	0.20	98.91
K/Cu/Zn/Mn/Co/Cr	7500	378	9.13	13.45	3.00	35.24	0.00	11.33	0.04	23.59	29.80	0.02	0.00	0.02	0.00	0.11	0.13	96.62
K/Cu/Zn/Mn/Co/Cr	7500	398	13.57	22.38	6.69	16.56	0.00	9.28	0.81	36.90	36.44	0.03	0.00	0.03	0.01	0.08	0.11	94.68
K/Cu/Zn/Mn/Co/Cr	7500	398	17.44	29.30	9.24	6.29	0.00	6.74	0.99	49.12	36.86	0.03	0.00	0.03	0.01	0.04	0.08	91.12
K/MoS_2	6700	325	8.2	11.1	2.9	56.02	0.00	22.48	0.50	21.00	0.00	0.04	0.00	0.04	0.00	0.14	0.18	100
K/MoS_2	6700	350	11.2	18.1	6.9	39.71	0.00	19.26	0.66	34.23	6.15	0.04	0.00	0.05	0.00	0.13	0.18	99
K/MoS_2	6700	375	12.1	20.3	8.2	24.68	0.00	19.27	1.10	39.16	15.78	0.05	0.00	0.05	0.00	0.09	0.14	99
K/$MoS_2^{(b)}$	6700	375	6.0	9.9	3.9	28.29	0.01	25.57	2.23	36.28	7.62	0.03	0.00	0.03	0.00	0.05	0.09	99
K/Co/MoO2	6700	352	26.38	49.25	19.05	1.70	0.00	0.39	0.02	61.26	36.62	0.002	0.000	0.002	0.003	0.014	0.019	98
K/Co/MoO2/C	6700	317	8.39	17.18	7.52	6.32	0.01	1.58	0.07	33.77	58.25	0.00	0.00	0.00	0.01	0.02	0.03	92
K/Co/MoO2/C	6700	335	13.81	26.62	10.70	5.35	0.00	14.31	0.24	31.67	48.42	0.04	0.00	0.04	0.01	0.02	0.08	90
K/Co/MoO2/C	6700	355	21.26	41.01	16.52	3.63	0.00	13.81	0.19	32.34	50.04	0.06	0.00	0.06	0.03	0.02	0.11	83
K/Co/MoO2/C	15000	358	15.43	31.11	13.29	4.20	0.00	17.84	0.34	30.50	47.13	0.13	0.00	0.13	0.02	0.04	0.20	94
K/Co/MoO2/C	15000	378	22.69	46.36	20.16	3.05	0.00	16.31	0.62	41.12	38.90	0.17	0.01	0.18	0.03	0.05	0.25	89
K/Co/MoO2/C	6700	381	33.65	62.16	23.46	1.47	0.00	10.67	0.41	51.18	36.27	0.08	0.00	0.08	0.03	0.02	0.12	79
Rh/Mn/SiO_2 (H_2:CO = 2)	3300	255	21.0	24.8	3.8	0.36	0.00	11.70	33.18	30.46	24.31	0.03	0.09	0.11	0.02	0.00	0.13	99
Rh/Mn/SiO_2 (H_2:CO = 2)	3300	280	37.1	39.3	2.1	0.29	0.00	9.75	22.56	33.37	34.03	0.04	0.11	0.15	0.07	0.00	0.22	103
Rh/Mn/SiO2 (H2:CO = 2)	3300	305	46.4	60.1	13.7	0.45	0.00	11.81	11.41	51.73	24.59	0.06	0.07	0.13	0.04	0.00	0.17	99
Rh/Mn/Fe/Al_2O_3	7400	257	21.8	28.7	6.9	0.24	0.08	14.24	24.79	37.17	23.48	0.07	0.14	0.21	0.00	0.00	0.21	98
Rh/Mn/Fe/Al_2O_3	15000	257	9.4	12.5	3.0	0.43	0.08	12.19	24.19	36.74	26.36	0.05	0.12	0.17	0.00	0.00	0.17	99
Rh/Mn/Fe/Al_2O_3	7400	285	36.3	53.9	17.6	0.17	0.08	13.55	19.92	47.56	18.72	0.11	0.18	0.30	0.00	0.00	0.30	91

Table 4.1 (contd)

Catalyst	Space Velocity (L/L/hr)	Temp. (°C)	Carbon Conv. (%)	CO Conv. (%)	CO Conv. to CO_2 (%)	Carbon Selectivity (mol%)					Other HCs	STY (g/mL_{cat}/hr)			HC Liq.	MeOH	Total Liq.	Carbon Balance (C_{out}/C_{in}) (%)
						MeOH	Other C_1 Oxygenates	C_2+ Alc.	Other C_2+ Oxygenates	CH_4		C_2+ Alc.	Other C_2+ Oxygenate	Total C_2+ Oxygenate				
Rh/Mn/Fe/Al_2O_3	11000	323	46.9	65.6	18.7	0.31	0.13	16.58	7.36	58.87	16.76	0.27	0.13	0.40	0.00	0.01	0.41	92
Rh/Mn/Fe/Al_2O_3	11000	326	45.4	61.2	15.8	0.38	0.00	15.56	5.52	63.62	14.91	0.25	0.09	0.34	0.00	0.01	0.35	95
Rh/Mn/Fe/Al_2O_3 (H2:CO = 2.0)	11000	326	39.0	49.4	10.4	0.33	0.00	15.04	8.08	59.06	17.49	0.22	0.13	0.35	0.00	0.01	0.36	97
Rh/Mn/Fe/Al_2O_3 (H_2:CO = 2.0)	15000	326	32.0	40.5	8.5	0.47	0.08	14.22	7.76	61.79	15.69	0.23	0.14	0.37	0.00	0.01	0.38	97
Rh/Mn/Fe/Al_2O_3	15000	354	26.8	35.4	8.6	1.00	0.00	8.76	2.91	82.90	4.43	0.11	0.04	0.15	0.00	0.02	0.17	98
Rh/Mn/Fe/Al_2O_3	15000	402	65.1	98.1	33.1	0.04	0.00	0.32	0.10	97.78	1.75	0.01	0.00	0.01	0.00	0.00	0.01	93
Rh/Zn/SiO_2	Not Active																	
Rh/Zn/Pd/SiO_2	Not Active																	
K/Fe/Cu/Al_2O_3	25000	304	17.3	36.1	18.8	0.33	0.00	2.99	2.93	12.80	80.94	0.04	0.05	0.09	0.41	0.01	0.51	92
K/Fe/Cu/Al_2O_3	49000	304	7.2	18.2	11.1	0.49	0.02	3.17	3.08	17.40	75.84	0.03	0.04	0.08	0.22	0.01	0.30	95
K/Fe/Cu/Al_2O_3	49000	323	11.7	19.2	7.5	0.57	0.01	4.25	2.96	13.26	78.95	0.07	0.07	0.14	0.51	0.01	0.66	99
K/Fe/Cu/Al_2O_3	49000	386	48.3	76.7	28.3	0.27	0.00	5.25	2.55	20.37	71.56	0.38	0.21	0.59	2.05	0.03	2.67	101
K/Fe/Cu/Al_2O_3	74000	386	32.3	49.3	17.0	0.38	0.00	5.39	3.21	19.96	71.06	0.39	0.27	0.66	1.86	0.04	2.55	103
K/Fe/Cu/Al_2O_3	98000	386	23.4	31.8	8.5	0.47	0.00	5.35	3.68	19.55	70.95	0.37	0.30	0.67	1.52	0.05	2.23	107
FT-MeOH-Pd	25000	300	3.8	16.9	13.1	3.53	0.02	12.61	4.07	18.65	61.12	0.04	0.01	0.05	0.02	0.01	0.09	93
FT-MeOH-Pd	25000	326	13.2	32.6	19.4	2.41	0.01	8.00	1.69	15.48	72.42	0.08	0.02	0.10	0.31	0.03	0.44	94
FT-MeOH-Pd	25000	350	30.5	50.3	19.8	2.28	0.00	8.72	0.99	10.68	77.34	0.20	0.03	0.23	0.89	0.08	1.20	101
FT-MeOH-Pd	49000	346	6.0	14.3	8.3	5.95	0.00	15.41	2.33	22.22	54.09	0.14	0.03	0.16	0.12	0.08	0.36	96
FT-MeOH-Pd	49000	413	51.4	92.1	40.7	0.62	0.00	9.30	1.30	24.59	64.18	0.71	0.12	0.83	2.01	0.07	2.91	89
FT-MeOH-Pd	25000	373	43.2	80.7	37.5	1.31	0.00	10.25	1.34	18.79	68.31	0.33	0.05	0.38	1.01	0.06	1.46	93
FT-MeOH-Pd	74000	364	6.1	10.0	3.9	6.76	0.03	13.46	4.73	28.12	46.90	0.19	0.07	0.26	0.18	0.14	0.57	99
FT-MeOH-Pd	74000	375	8.2	20.8	12.6	6.30	0.02	14.49	4.77	34.02	40.40	0.26	0.10	0.36	0.24	0.17	0.77	95

(a) Values based on using measured product gas flow rate instead of calculating product gas flow rate using a nitrogen balance.

(b) Test conducted at 800 psig instead of 1200 psig.

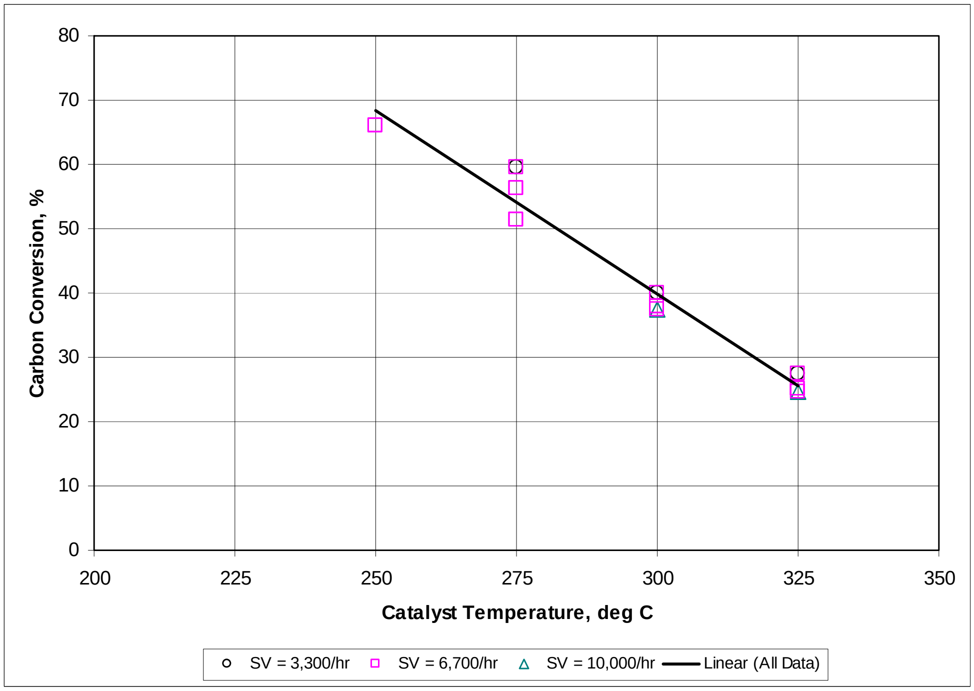

Figure 4.1. Carbon Conversion for MeOH-X Catalyst

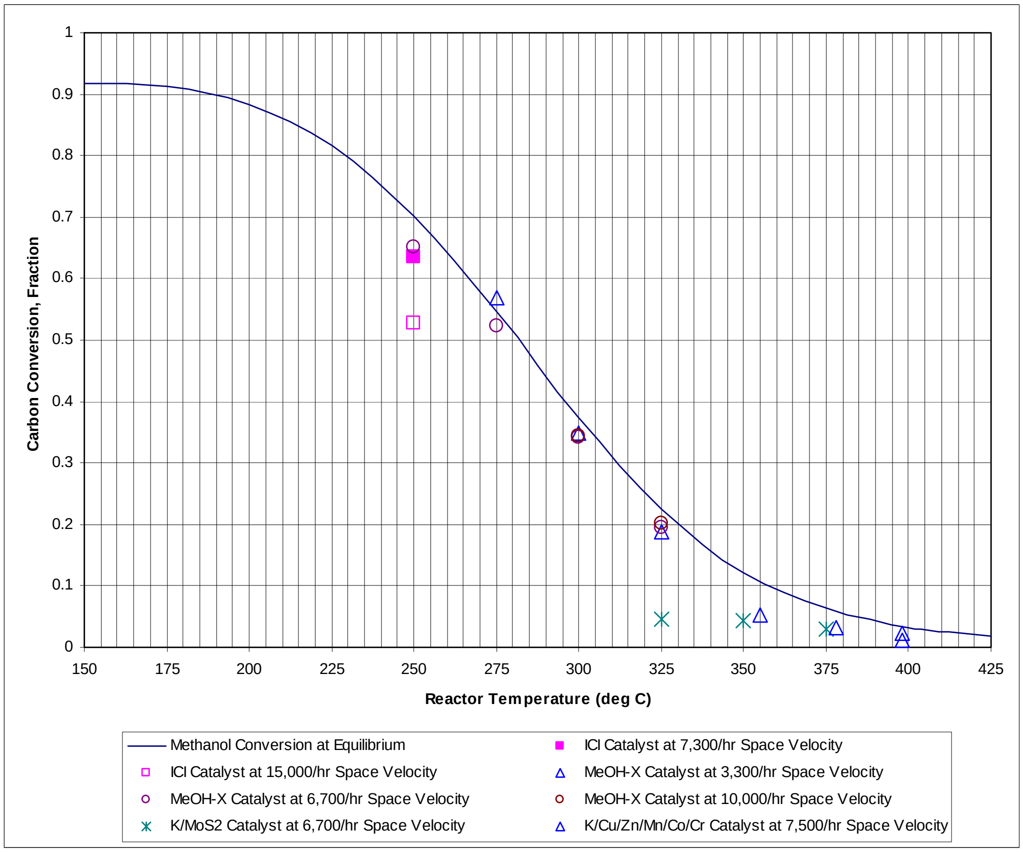

Figure 4.2. Comparison of Carbon Conversions to Methanol for the ICI, MeOH-X, and K/MoS_2 Catalysts Relative to the Equilibrium Carbon Conversions

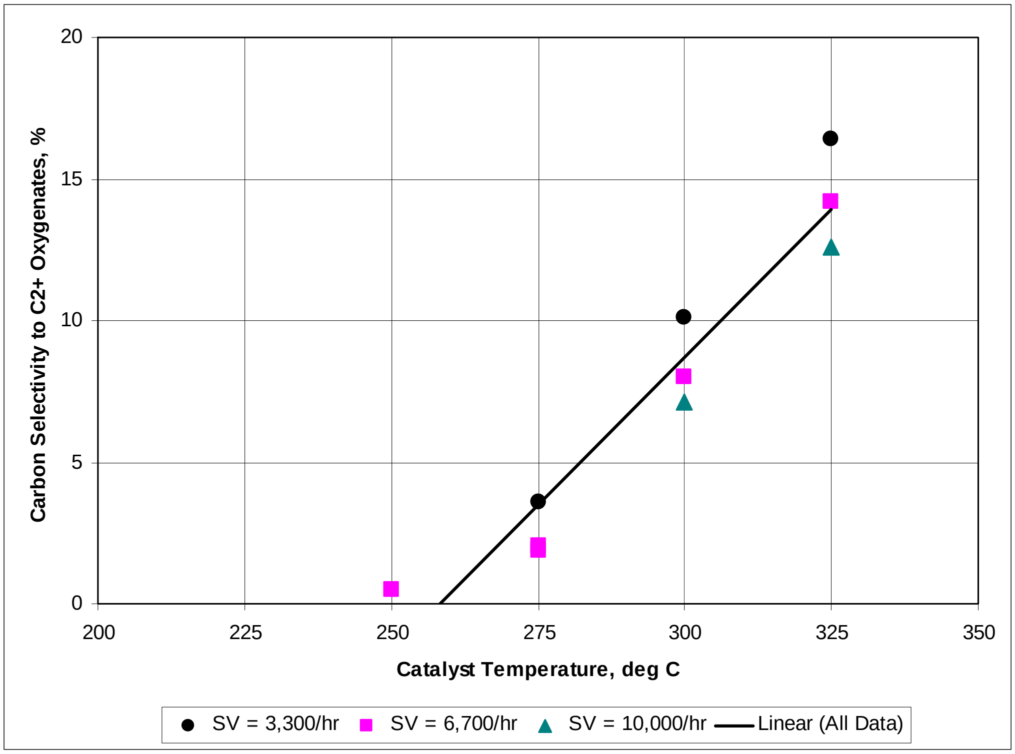

Figure 4.3. Carbon Selectivity to C_2+ Oxygenates for MeOH-X Catalyst

Figure 4.4 shows the effects of space velocity and temperature on the C_2+ oxygenate STYs and C_1+ oxygenates. It can be seen that while the C_2+ oxygenate STYs increase modestly with temperature, the C_1+ oxygenates decreased due to the equilibrium effects of temperature on methanol STYs. It can also be seen that increasing the space-time velocity produced minor increases in the C_2+ oxygenates STYs and much greater increases in the total oxygenate STY. The highest STY of C_2+ oxygenates was approximately 0.090 $g/g_{cat}/hr$ at 325°C and 10,000 $L/L_{cat}/hr$ space velocity. The total STY for all C_1+ oxygenates at these conditions was 0.970 $g/g_{cat}/hr$.

The K/Cu/Zn/Mn/Co/Cr catalyst was tested over a 355° to 398°C temperature range and a 7,500 $L/L_{cat}/hr$ space velocity. This catalyst was much less reactive than the MeOH-X and ICI catalysts, obtaining carbon conversions of 3.5% at 355°C and between 13.6 and 17.4% at 398°C, as shown in Figure 4.5. Carbon selectivity of C_2+ oxygenates was also low, as shown in Figure 4.6. While the carbon selectivity to methanol was high at 255°C (~ 72%) and decreased with increasing temperature, the amounts were not limited by equilibrium except possibly at the highest tested temperature, as shown in Figure 4.2. As would be expected for low carbon conversions and selectivities over the temperature range tested, the C_2+ oxygenates STYs were also much lower than those for the MeOH-X and ICI catalysts, as shown in Figure 4.7, achieving a maximum STY of about 0.030 $g/mL_{cat}/hr$ at 398°C.

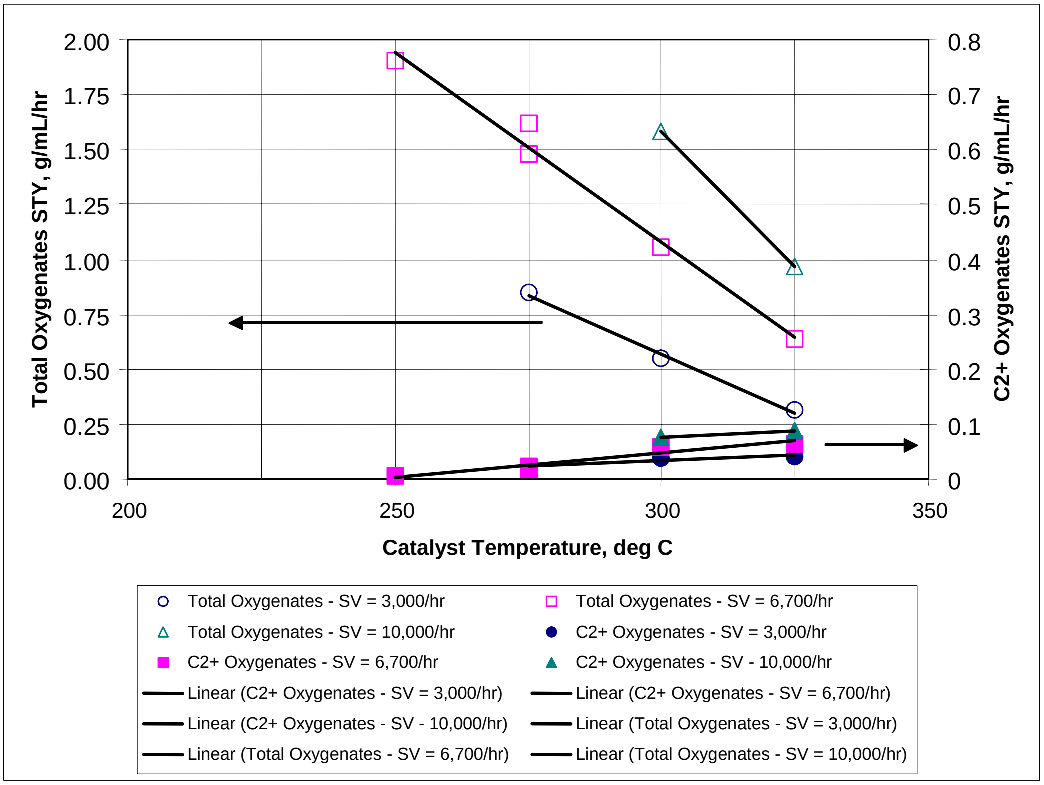

Figure 4.4. C_2+ and Total Oxygenate STYs for MeOH-X Catalyst

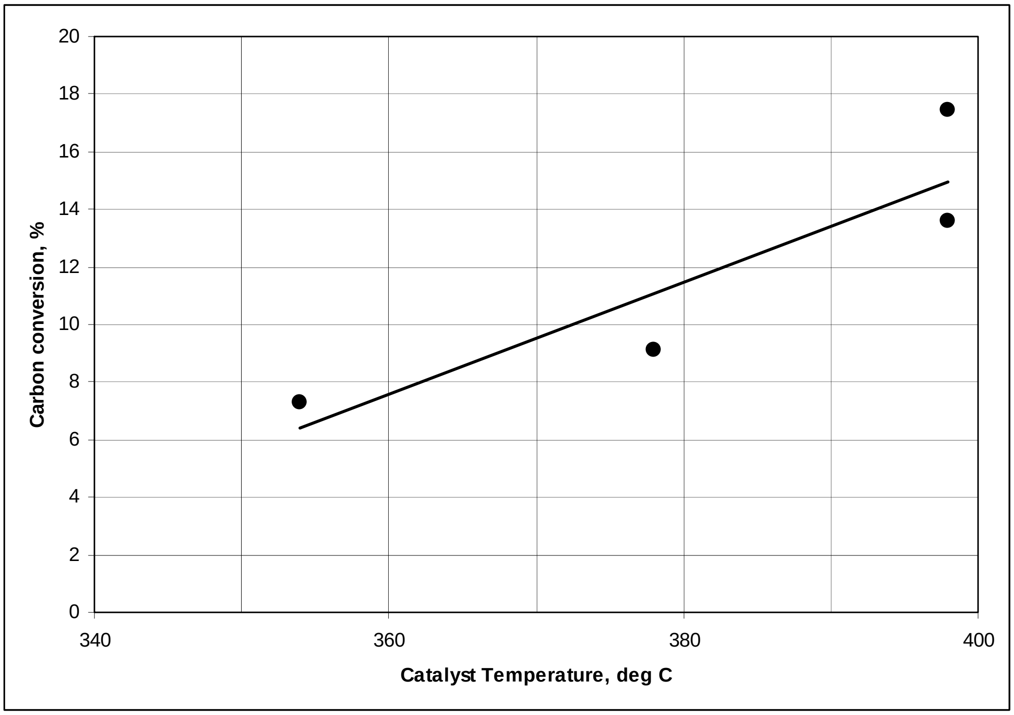

Figure 4.5. Carbon Conversion for K/Cu/Zn/Mn/Co/Cr Catalyst

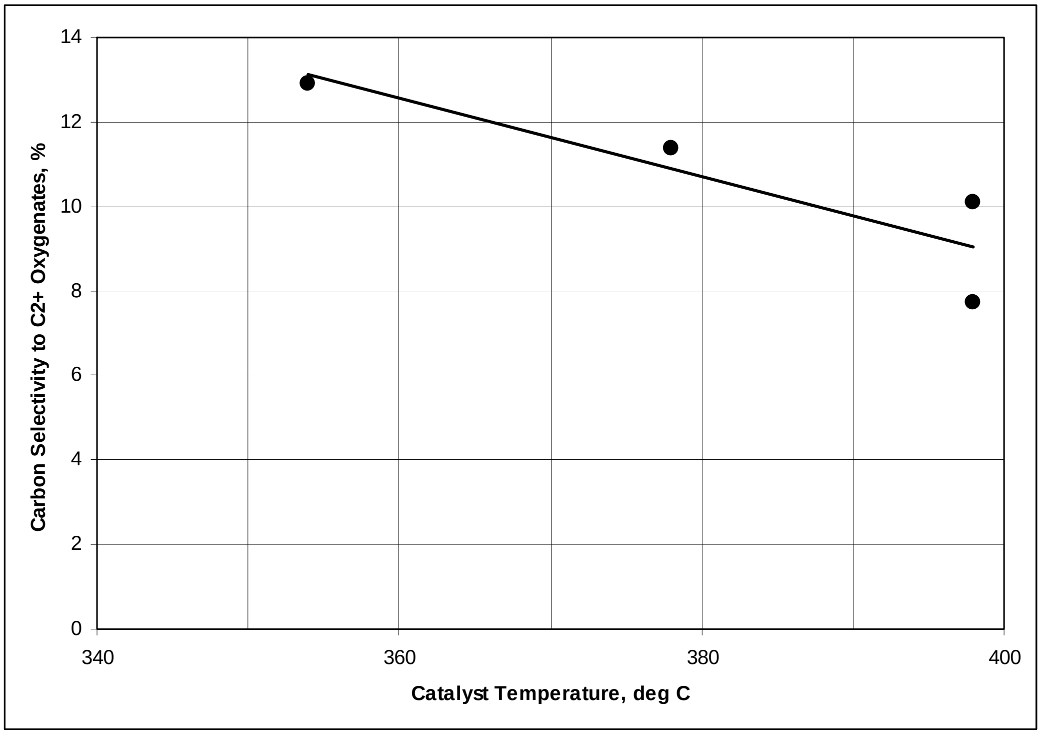

Figure 4.6. Carbon Selectivity to C_2+ Oxygenates for K/Cu/Zn/Mn/Co/Cr Catalyst

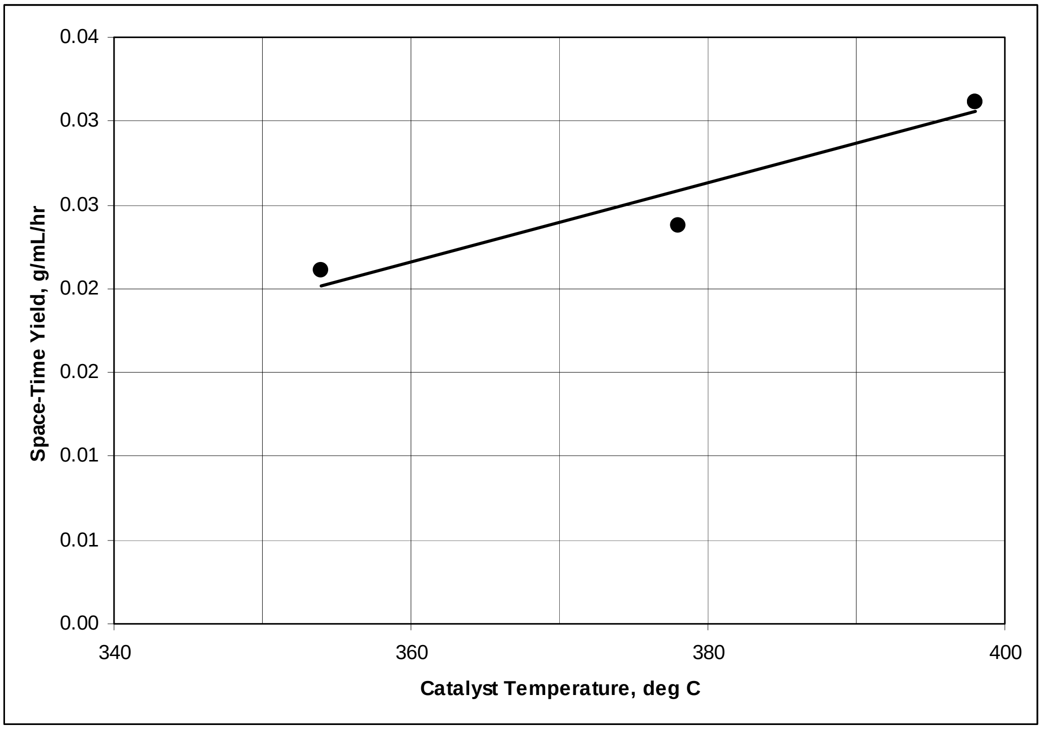

Figure 4.7. C_2+ Oxygenate STYs for K/Cu/Zn/Mn/Co/Cr Catalyst

4.2 Molybdenum Sulfide-Based Catalyst

The molybdenum sulfide-based catalyst (K/MoS_2) that was tested was fairly similar to other catalysts in the literature that were based on the decomposition of ammonium tetrathiomolybdate [$(NH_4)_2MoS_4$] to produce bulk MoS_2. The preparation used in this test relied on the coprecipitation of the potassium carbonate with the ammonium tetrathiomolybdate prior to calcination rather than first producing the MoS_2 and then adding the potassium by either physical grinding or impregnation with a K_2CO_3 solution. This catalyst was tested at temperatures ranging from 325° to 375°C and at a 6,700 L/L_{cat} /hr space velocity. An additional test was conducted at 375°C and 6,700 L/L_{cat} /hr but at 800 psig pressure.

The K/MoS_2 catalyst had carbon selectivities to all oxygenates, decreasing from about 79% at 300°C to about 45% at 375°C. Most of this decrease was attributed to a decrease in selectivity to methanol. The carbon selectivity to C_2+ oxygenates was fairly constant with increasing temperature, decreasing from about 23% to 19% over this temperature range, as shown in Figure 4.8. The decrease in selectivity to methanol with increasing temperature was not attributed to methanol equilibrium constraints, as shown in Figure 4.2, but to increasing yields of hydrocarbons. Figure 4.8 also shows that decreasing the system pressure increases selectivity to C_2+ oxygenates. In Table 4.2, it can also be seen that selectivity to all oxygenates increased with decreasing system pressure at the expense of the hydrocarbons.

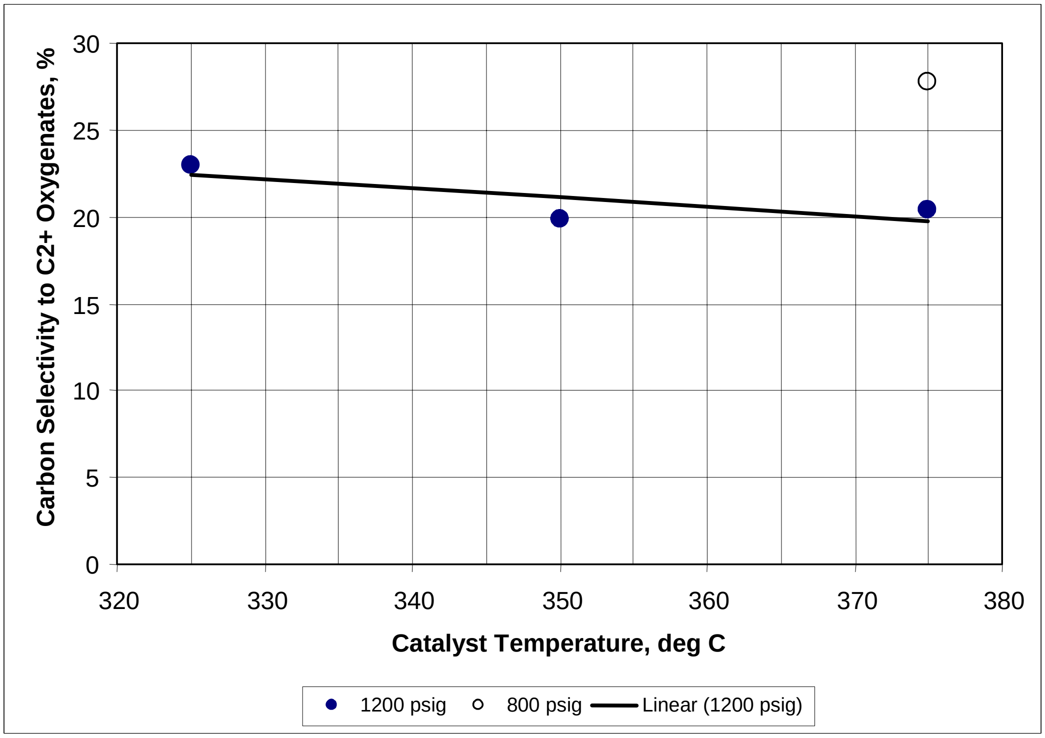

Figure 4.8. Carbon Selectivity to C_2+ Oxygenates for K/MoS_2 Catalyst

Table 4.2. Comparison of Bulk K/MoS_2 Catalyst Performance

Parameter	PNNL	Woo et al. (1991)	Liu et al. (1997)
Temperature, °C	325	300	325
Pressure, atm	80	80	50
GHSV, L/kg_{cat}/hr	7,900	3270	6000
Carbon Conversion, %	8.2	18.5	8–14 (est.)$^{(a)}$
C_1+ Oxygenate Selectivity, %	79	72	80
C_2+ Oxygenate Selectivity, %	23	29	40
C_2+ Oxygenate STY, kg/L_{cat}/hr	0.04	0.04	0.1
(a) Carbon conversion range estimated from STY and selectivity data for hydrocarbons and C_1 –C_4 alcohols.			

Figure 4.9 shows the effect of catalyst temperature on carbon conversion for the K/MoS_2 catalyst. It can be seen that this catalyst is not very reactive, even at temperatures as high as 375°C. Consequently, the C_2+ oxygenates and total oxygenates STYs for this catalyst were low, ranging from 40 to 50 g/L_{cat} /hr and 140 to 180 g/L_{cat}/hr, respectively, as shown in Figure 4.10. It can also be seen that decreasing system pressure significantly reduced carbon conversion for both C_2+ oxygenates and total oxygenate STYs.

A comparison of this catalyst's performance and similar bulk catalysts reported in Woo et al. (1991) and Liu et al. (1997) is shown in Table 4.2. While the test conditions for the three catalysts are not the same, it appears that the catalyst reported in this study has comparable reactivity. For example, the catalyst would be expected to have a carbon conversion close to that of Liu et al., whose work was performed at the same temperature and at a fairly comparable space velocity. The overall selectivity to oxygenates is comparable for all three catalysts, but the selectivity to C_2+ oxygenates appears to be lower than expected.

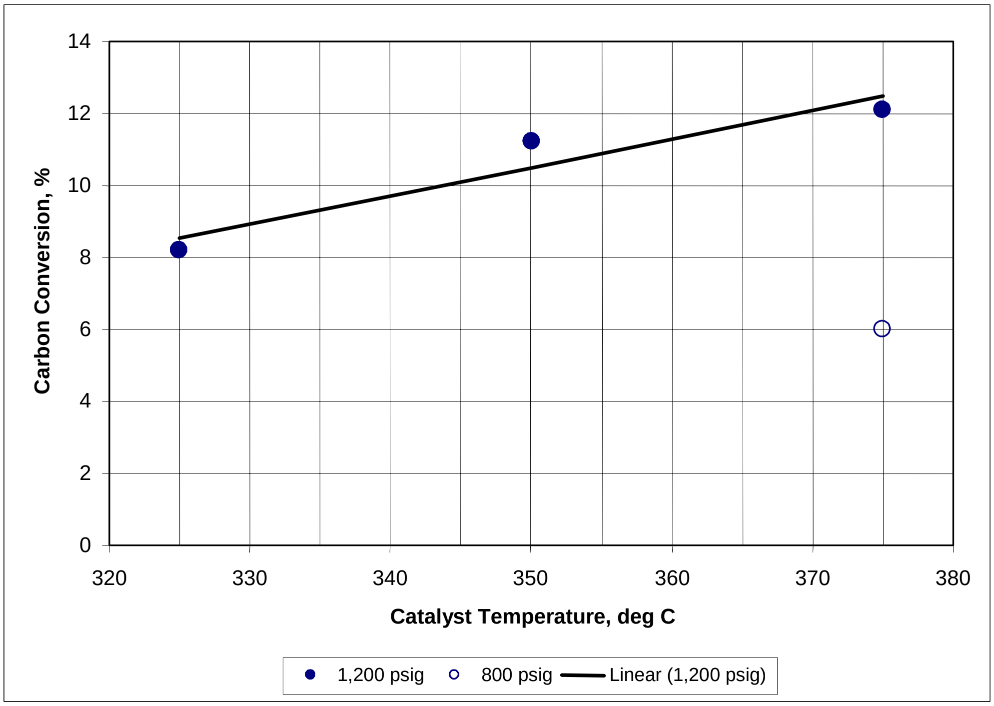

Figure 4.9. Carbon Conversion for K/MoS_2 Catalyst

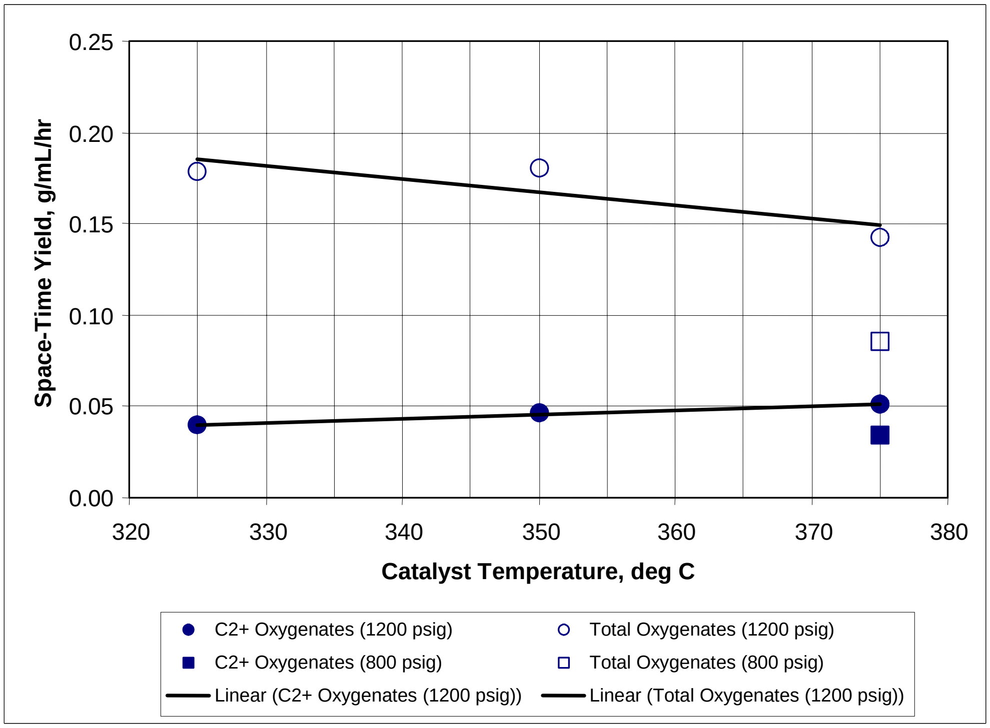

Figure 4.10. C_2+ and Total Oxygenate STYs for K/MoS_2 Catalyst

4.3 Molybdenum Oxide-Based Catalysts

Molybdenum oxide-based catalysts generally are expected to behave similarly to the molybdenum sulfide-based catalysts, producing a mixture of oxygenated organic liquids consisting primarily of C_1+ alcohols and minor amounts of other C_2+ oxygenates. They also produce significant quantities of methane and other higher hydrocarbons.

The K/Co/MoO_2 catalyst was only tested at 353°C and 6,700 L/L_{cat}/hr space velocity because it was making significant quantities of methane and higher hydrocarbon gases at this temperature and only a small quantity of alcohols. Carbon conversion was approximately 26% at this temperature, but carbon selectivity to methanol, C_2+ alcohols, and other C_2+ oxygenates was approximately 1.70, 0.39, and 0.02%, respectively. The STY of C_2+ oxygenates was only 0.002 g/mL_{cat}/hr. These results were much worse than expected based on the results of Zhang et al. (2001), probably due to our modifications to their preparation method that may not have produced a catalyst that was as well dispersed.

The K/Co/MoO_2/C catalyst tested at temperatures ranging from 317°–381°C at a 6,700 L/L_{cat}/hr space velocity and 355° to 371°C at a 15,000 L/L_{cat}/hr space velocity. The catalyst had carbon conversions ranging from 8.7 to 33.6% and 15.4 to 22.7% over these temperature ranges at the two respective space velocities, as shown in Figure 4.11. It can be seen that increasing the STY decreased the carbon conversion, as expected.

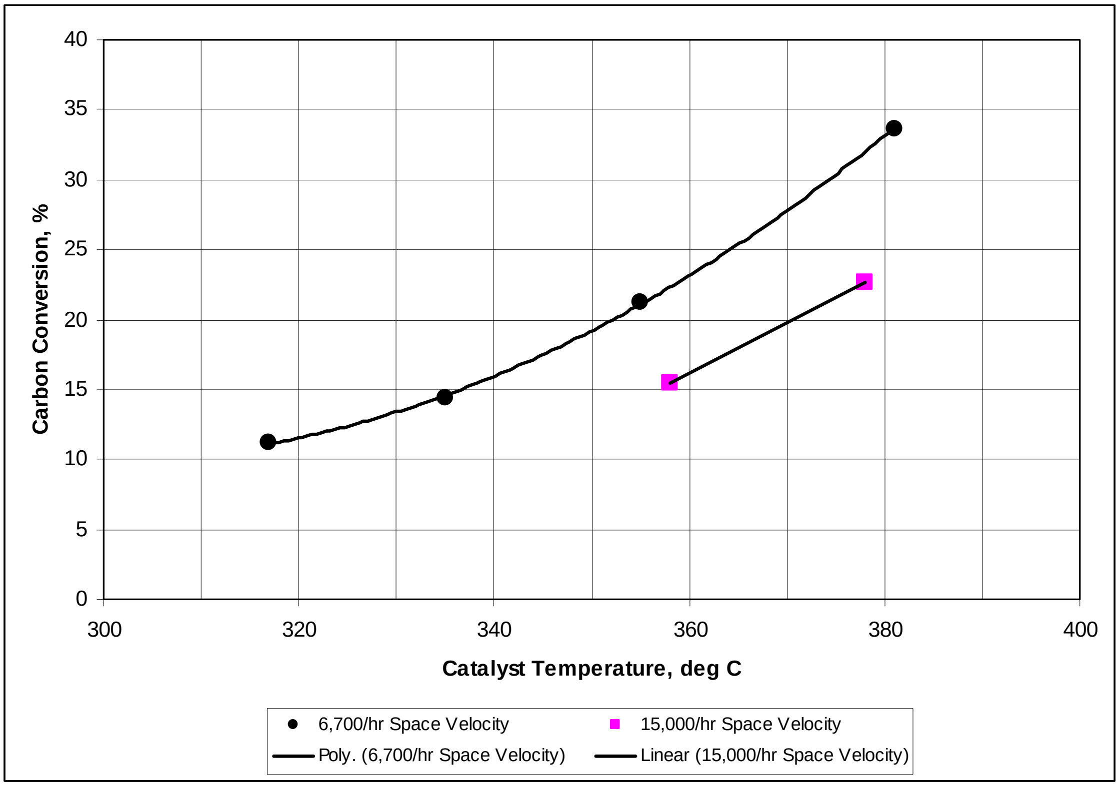

Figure 4.11. Carbon Conversion for K /Co/MoO_2/C Catalyst

Figure 4.12 shows the effect of temperature and space velocity on the carbon selectivity to C_2+ oxygenates. Increasing the catalyst temperature caused a decrease in selectivity to C_2+ oxygenates while increasing the space velocity increased selectivity. Table 4.1 shows that the major oxygenates were the higher alcohols, followed by modest amounts of methanol and only minor amounts of other C_2+ oxygenates. Figure 4.13 shows that the higher alcohol-to-methanol ratio increased with increasing temperature from 2.7 to 7.2 over the tested temperature range. Space velocity appeared to have only a minor effect on the ratio.

Figure 4.14 shows the effect of temperature and space velocity on the C_2+ oxygenate STY. It can be seen that the STY increases with temperature. Furthermore, the STY is higher and increases faster with temperature at the higher space velocities, suggesting an opportunity for further improvement in the STY by operating at even higher space velocities. The highest C_2+ oxygenate STY in the tests was 0.18 g/mL/hr, obtained at 378°C and 15,000 mL/mL/hr space velocity.

4.4 Rhodium-Based Catalysts

Rhodium-based catalysts are known to preferentially convert syngas to C_2 oxygenates relative to C_1 and C_3+ oxygenates. However, depending on the support and choice of promoters, if any, the catalysts may be even more selective to the production of hydrocarbons. Four rhodium-based catalysts were tested in FY 2006 to examine the effects of different promoters using a SiO_2 support.

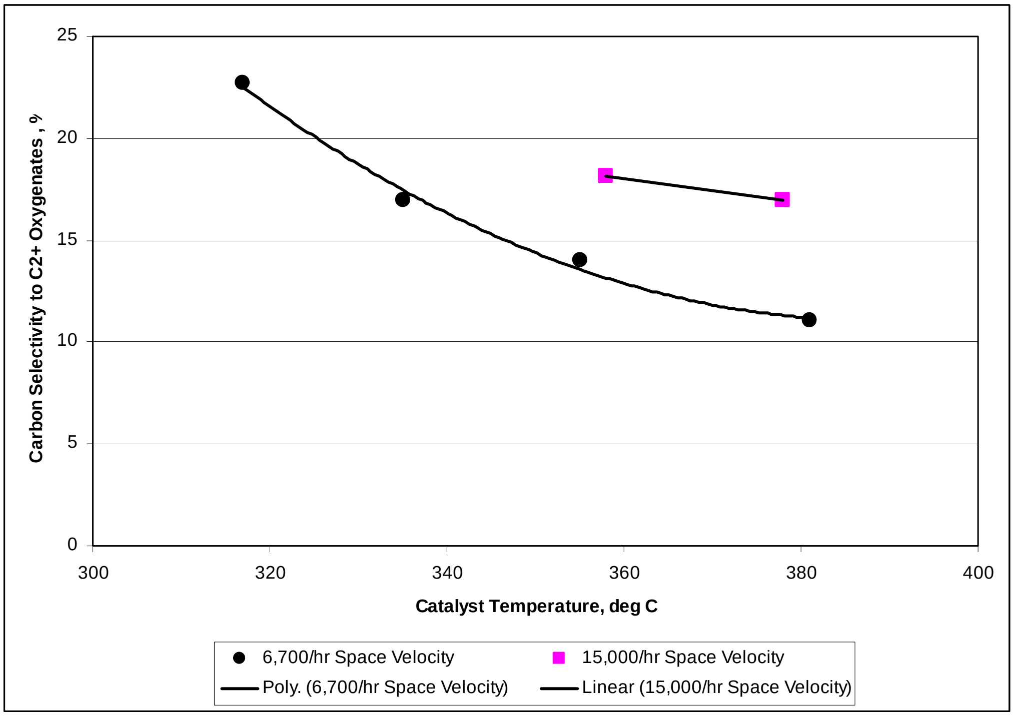

Figure 4.12. Carbon Selectivity to C_2+ Oxygenates for $K/Co/MoO_2/C$ Catalyst

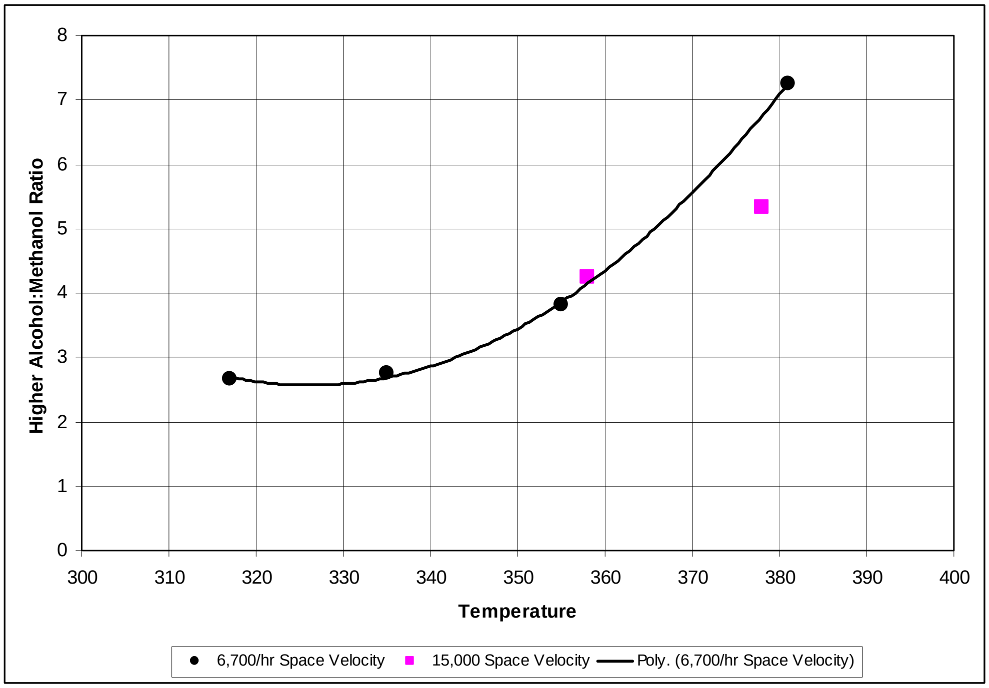

Figure 4.13. Effect of Temperature and Space Velocity on the Higher Alcohol to Methanol Ratio

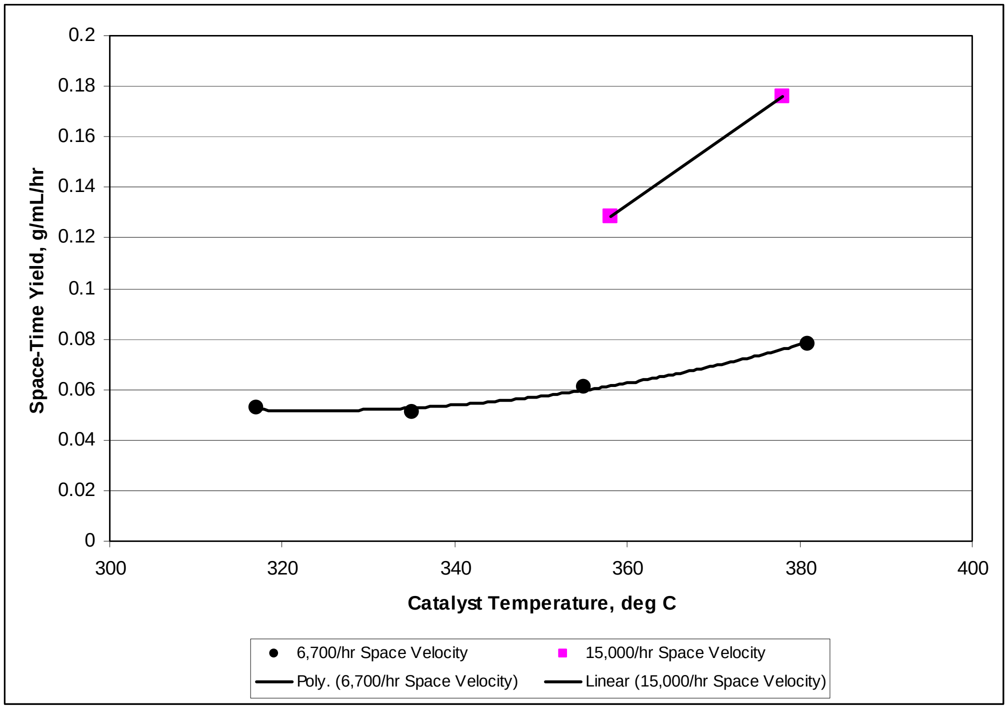

Figure 4.14. C_2+ Oxygenate STYs for K/Co/MoO_2/C Catalyst

4.4.1 Rh/Mn/SiO_2 and Rh/Mn/Fe/SiO_2 Catalysts

Two catalysts containing rhodium and manganese (Rh/Mn/SiO_2 and Rh/Mn/Fe/SiO_2) were tested. The Rh/Mn/SiO_2 was the first one tested over a 255° to 305°C temperature range and a 3,300 L/L_{cat} /hr space velocity to compare it to the MeOH-X catalyst. The H_2:CO ratio for these tests was about 2.0. The Rh/Mn/Fe/SiO_2 examined a broader temperature range (257°–402°C) and higher space velocities (7,400 to 98,000 L/L_{cat} /hr) to try to maximize the STY for C_2+ oxygenates. A small quantity of iron was added to the second catalyst to try to improve selectivity of C_2 oxygenates to ethanol and to possibly improve catalyst activity, based on the research of Bhasin et al. (1978), Gotti and Prins (1996), Nonneman et al. (1990), and Sachtler and Ichikawa (1986).

The test series using the Rh/Mn/Fe/SiO_2 catalyst encountered difficulties in obtaining stable operating conditions at temperatures above 300°C. Using careful control of the furnace temperature it was possible to maintain catalyst temperatures below about 333°C while establishing fairly steady average temperatures of 323° ± 6°C for one set of data and 326° ± 3°C for a second set of data. Two more sets of data were obtained at 326°C using a feed gas with a significantly lower H_2:CO ratio (H_2:CO ratio of 2.0 instead of about 2.5 for the other test conditions using this catalyst).

It was almost impossible to obtain steady-state conditions above 325°C because of the exothermic response of the catalyst bed to very small changes in the furnace temperature, and/or flow fluctuations, such as occurred when the flow was changed from the bypass line to the sample line and, in some cases, minor changes imposed by the mass flow controllers. The instabilities were attributed to poor heat transfer capabilities of the reactor and the high exothermicity of the reactions taking place. For example, when the furnace temperature was increased a few degrees (or in some situations tenths of a degree), the catalyst bed temperature would immediately increase by a significantly greater amount (such as 2 to 6°C for every degree of furnace temperature change), and then over a period of one or more hours, slowly decrease so that the final catalyst bed temperature increased by an amount approximately equal to the increase in the furnace temperature. By slowly increasing the furnace temperature in this manner it was possible to avoid a large temperature excursion and slowly raise the catalyst temperature by an amount comparable to the furnace temperature increase. However, it took many hours to increase the catalyst temperature significantly (on the order of 1°C/hr). This is the procedure that was ultimately used to obtain the steady-state conditions at ~325°C.

If the temperature of the furnace was increased too much or too fast, the increase in heat production rate of the reactions taking place significantly exceeded the ability of the reactor to remove the heat. The temperature continued to climb, causing even higher reaction rates, until the reactant (CO and H_2) concentrations were depleted to the point where incremental increases in heat production were matched by incremental increases in the heat removal rate, and the catalyst bed temperature would stop rising. For example, when the catalyst bed temperature was 325°C, the furnace temperature was about 70° lower at 255°C. Increasing the furnace temperature 15°, to 270°C, increased the catalyst bed temperature by 60°, to 385°C. However, over a few hours, the reaction rate slowly decreased at the new conditions, causing the catalyst bed to cool off and ultimately resulting in a reverse runaway condition that brought the temperature back to approximately the initial temperature (336°C). Once a thermal runaway occurred it was possible to take advantage of the subsequent runaway cooling that took place after several hours near the maximum temperature by increasing the furnace temperature to meet the catalyst temperature as the latter cooled (for example, increasing the furnace temperature from 270° to 290°C) so the new steady-state temperature was even higher. This had to be done with some care, or the reaction would undergo another thermal runaway. This latter method, which was used to obtain data at 354°C, is less desirable because it introduces uncertainty in the local temperatures of the catalyst during the thermal runaway that might not be fully reflected in the measured catalyst temperature and may have induced accelerated deactivation of the catalyst.

It was possible to obtain a pseudo steady-state condition at the maximum temperature by monitoring the cooling of the reactor and slowly raising the temperature of the furnace to maintain the temperature of the catalyst. After a few hours the cooling rate was slow enough that the reactor temperature decreased only a few more degrees over many hours, allowing data to be taken at a relatively constant temperature. This was the procedure used to obtain the last set of data at 402°C. Ultimately, however, the catalyst temperature would return to a new lower stable temperature that had been increased by an amount nearly equal to that of the furnace, and there was some risk that this occurred before sufficient time elapsed to obtain the pseudo-steady-state data. The relative stability obtained for the last two conditions at 354° and 402°C was achieved using this method and involved thermal runaways, with measured catalyst temperatures reaching at least 402°C and local temperatures possibly much higher. A comparison of the carbon conversion data at 354°C compared to that obtained at 326°C for the same space velocity of 15,000 L/L_{cat}/hr suggests that the catalyst may have become partially deactivated during the temperature transients.

Figure 4.15 shows the carbon conversion for the $Rh/Mn/SiO_2$ and $Rh/Mn/Fe/SiO_2$ catalysts. It can be seen that carbon conversion for the $Rh/Mn/SiO_2$ catalyst appears to increase fairly linearly between 250° and 305°C, for a constant space velocity of 3,300 L/L_{cat}/hr. The $Rh/Mn/Fe/SiO_2$ catalyst appears to show

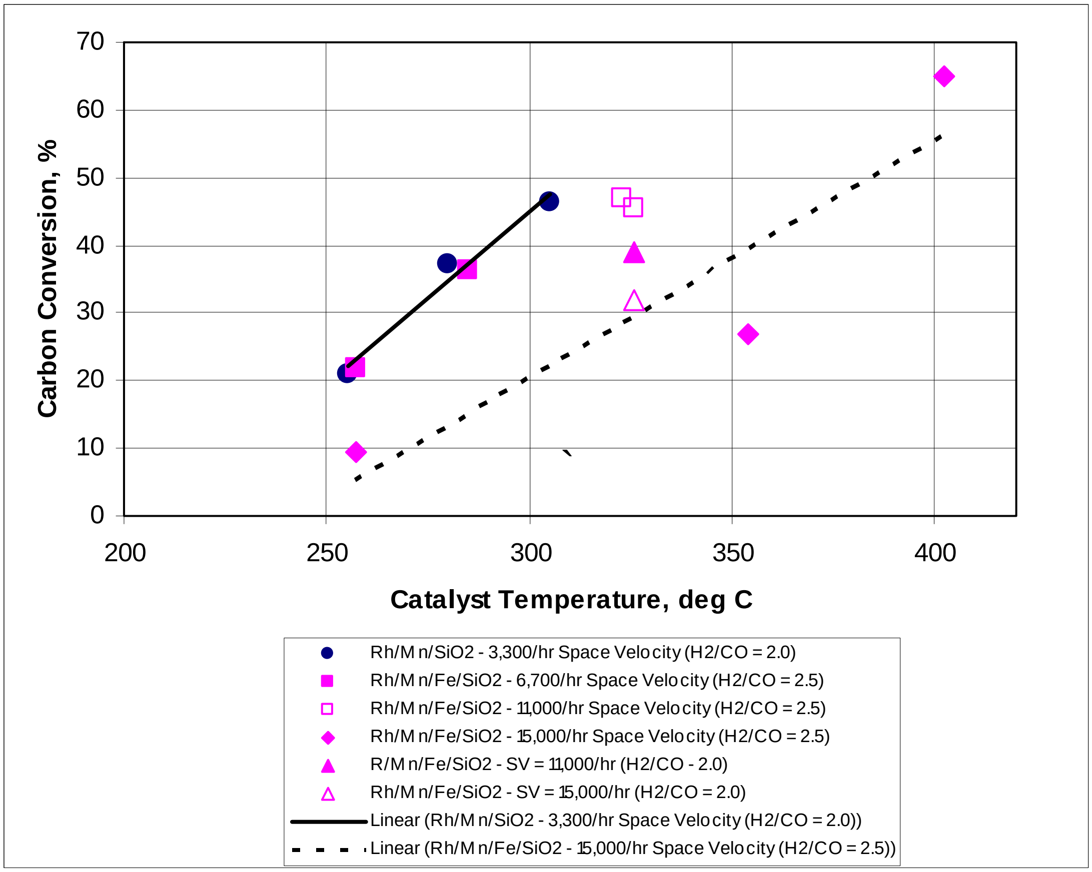

Figure 4.15. Carbon Conversions for Rh/Mn/SiO_2 and Rh/Mn/Fe/SiO_2 Catalysts

a similar trend over the same temperature range for a space velocity of 6,700 L/L_{cat}/hr. However, it is also clear that increasing the space velocity (such as at 257°C) reduced carbon conversion. This also occurred at 326°C for the same catalyst using a syngas with a 2.0 H_2/CO ratio. It also appears that carbon conversion decreased for lower H_2/CO ratios at 326°C and the same space velocity (11,000 L/L_{cat} /hr). Taken together, it appears that opposing effects of lower H_2/CO ratio and space velocity on the carbon conversion for the Rh/Mn/SiO_2 catalyst were largely off-setting, and the reactivity of this catalyst could be similar to the Rh/Mn/Fe/SiO_2 catalyst if both were tested under the same conditions.

Figure 4.16 shows the carbon selectivity to C_2+ oxygenates for the Rh/Mn/SiO_2 and Rh/Mn/Fe/SiO_2 catalysts. It appears that carbon selectivity depends primarily on the catalyst temperature and not the space velocity or the H_2/CO ratio.

Figure 4.17 shows the C_2+ oxygenates STYs for the Rh/Mn/SiO_2 and Rh/Mn/Fe/SiO_2 catalysts. The Rh/Mn/Fe/SiO_2 catalyst appears to have achieved significantly higher C_2+ oxygenate STYs for comparable conditions than the Rh/Mn/SiO_2 catalyst. The STYs also appear to have been relatively sensitive to the catalyst temperature but less sensitive to the space velocity or H_2/CO ratio over the temperature range of approximately 250° to 325°C.

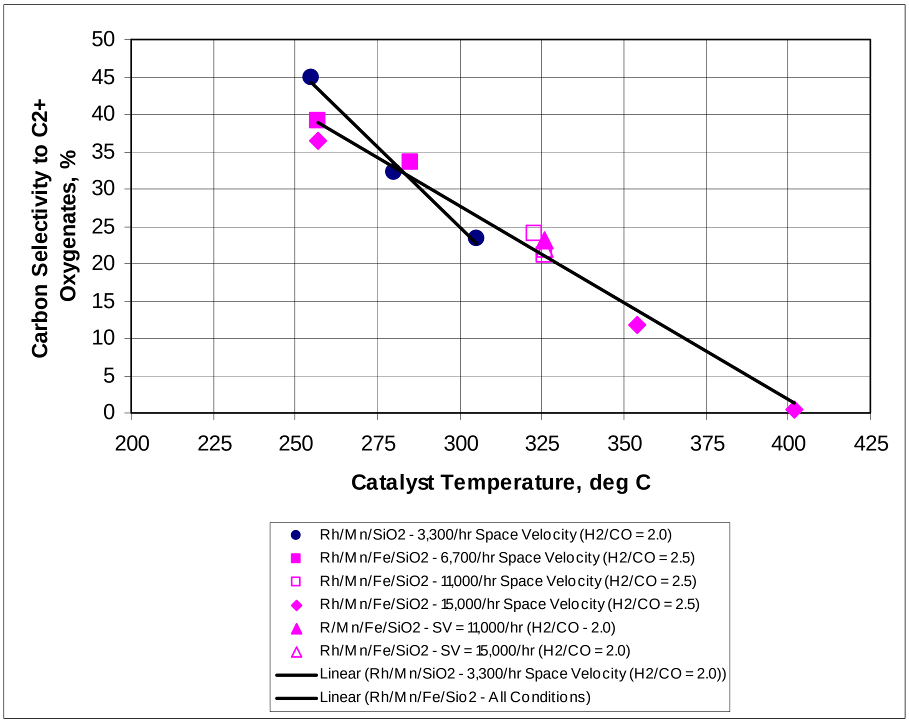

Figure 4.16. Carbon Selectivity to C_2+ Oxygenates for Rh/Mn/SiO_2 and Rh/Mn/Fe/SiO_2 Catalysts

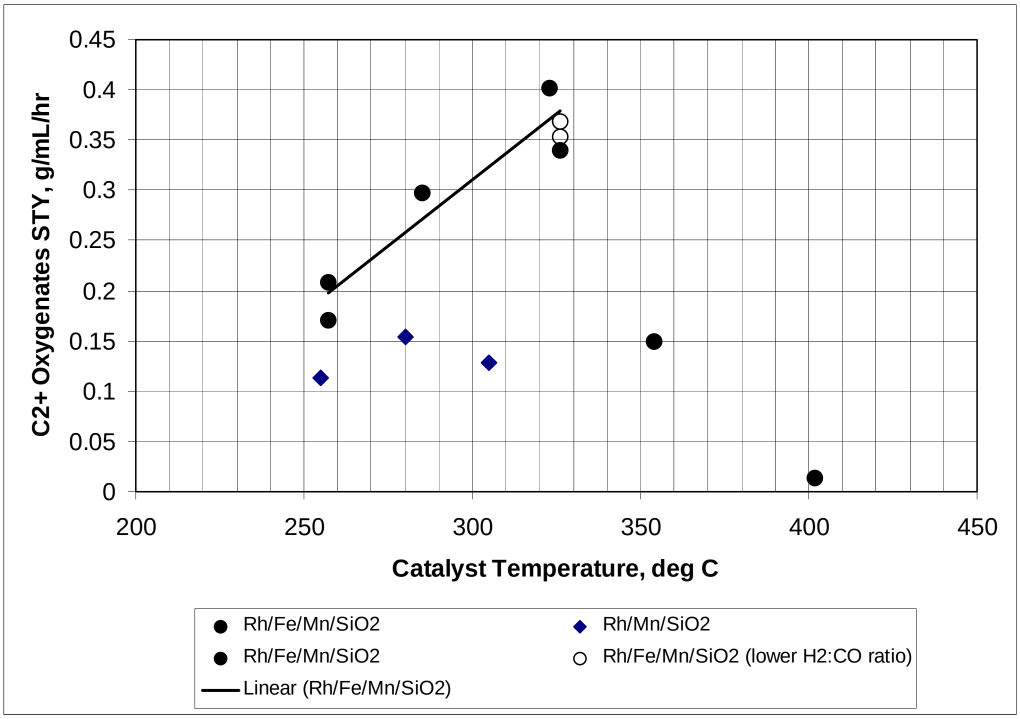

Figure 4.17. C_2+ Oxygenate STYs for Rh/Mn/SiO_2 and Rh/Mn/Fe/SiO_2 Catalysts

Examination of the specific composition of C_2+ oxygenated products produced by $Rh/Mn/SiO_2$ and $Rh/Mn/Fe/SiO_2$ catalysts did not show any major differences in the selectivity of either catalyst for specific C_2+ oxygenates, although there may have been a small improvement in the ethanol selectivity due to the addition of iron. However, in the absence of data for the two catalysts at identical test conditions, a firm conclusion cannot be made at this time. There was, however, a distinct difference in the yield of hydrocarbons. The product gases of the $Rh/Mn/SiO_2$ catalyst did not contain any C_2–C_4 alkenes, while the $Rh/Mn/Fe/SiO_2$ catalyst did. Furthermore, the $Rh/Mn/SiO_2$ catalyst produced a significant quantity of hydrocarbon liquids, whereas the $Rh/Mn/Fe/SiO_2$ did not.

It is clear that the C_2+ oxygenate STYs for the $Rh/Mn/Fe/SiO_2$ catalyst decreased significantly above 325°C. This is due, at least in part, to the increasing selectivity to methane at the expense of the C_2+ oxygenates. The apparent loss of catalyst reactivity, as evidenced by the unusually low carbon conversion at 354°C, is problematic at this point in that it suggests that the catalyst deactivated, whereas the higher carbon conversion at 402°C is more consistent with restored catalyst activity. The possibility that the catalyst deactivated is further supported by distinct differences in the composition of the hydrocarbon gases in the product gas. All product gases except those sampled for the tests at 354° and 402°C contained a mixture of C_1, C_2, C_3, and C_4 alkanes and alkenes. The product gases from the tests at 354° and 402°C contained only C_1, C_2, and C_4 alkanes (no alkenes or C_3 hydrocarbons detected). The temperature regime above 325°C would need to be further explored using care to establish operating conditions without undergoing a thermal runaway in order to fully explain the behavior of the catalyst.

4.4.2 $Rh/Zn/SiO_2$ and $Rh/Zn/Pd/SiO_2$ Catalysts

The two other rhodium-based catalysts tested were the $Rh/Zn/SiO_2$ and $Rh/Zn/Pd/SiO_2$. The $Rh/Zn/SiO_2$ catalyst was tested twice. Prior to the first test, the catalyst was reduced using 10% H_2 in N_2 at 220°C, while before the second test, the catalyst was reduced using 2% H_2 in N_2 at 250°C. The $Rh/Zn/Pd/SiO_2$ catalyst was reduced using 10% H_2 in N_2 at 400°C prior to its test.

During the first test with the $Rh/Zn/SiO_2$ catalysts, the temperature of the catalyst was slowly raised to 350°C at 3,300 L/L_{cat}/hr space velocity of the syngas while monitoring the product gas flow rate for signs of significant reaction. There was no indication that the catalyst was active, so it was left overnight at that temperature. The product gas was analyzed on the following day and indicated that only a trace amount of methane was formed. No liquid products were recovered from the sample cold trap. The test was repeated using fresh catalyst that was reduced at the higher temperature after achieving a temperature of 350°C at a syngas space velocity of 3,300 L/L_{cat}/hr without observing any significant change in the product gas flow rate. This time the reactor pressure was reduced to 800 psig at this temperature and maintained at these conditions overnight. Analysis of the product gas indicated that no gaseous hydrocarbon products were produced and no product was recovered from the sample cold trap.

The Rh/Zn/Pd/SiO2 catalyst was heated in syngas at 3,300 L/L_{cat}/hr space velocity to 350°C and maintained overnight. Analysis of the product gas showed only a trace of methane was produced, and there were no liquid products recovered from the sample cold trap.

4.4.3 Fischer-Tropsch Catalysts

The two Fischer-Tropsch-based catalysts were different from the others tested in that they were major producers of Fischer-Tropsch liquids but also produced significant quantities of alcohol as a byproduct. Both catalysts were based in whole or part on an iron-based Fischer-Tropsch catalyst consisting of Fe/Cu/Al/K in the ratio 1.0/0.03/2.0/0.70. According to O'Brian et al. (1996), the alumina support affects product selectivity toward more oxygenates and a higher alkene content of the hydrocarbon products. Potassium promotes the formation of longer chained hydrocarbons as well as selectivity to alkenes. Copper in the 1–4% range reduces the temperature for reducing iron in hydrogen but does not significantly affect product selectivity.

The two catalysts tested were the $K/Fe/Cu/Al_2O_3$ and the FT-MeOH-Pd catalysts, the latter consisting of a 1:1:1 physical mixture of the $K/Fe/Cu/Al_2O_3$ catalyst, a methanol catalyst based on an alkali-modified Cu/Zn catalyst and a palladium catalyst both supported on alumina ($K/Cu/Zn/Al_2O_3$). Both the Fischer-Tropsch and modified methanol catalysts used in the mixture were additionally promoted with gallium. The Fischer-Tropsch and methanol catalysts were combined to promote synergy between their major functions (i.e., chain growth of disassociated carbon and CO hydrogenation, respectively), hopefully to provide more opportunities for CO to insert into a carbon chain to produce a C_2+ oxygenate. Adding palladium and gallium was reported by Inui and Yamamoto (1998) to improve the yield of ethanol.

Both catalysts introduced significant operational challenges. Like the $Rh/Mn/SiO_2$, and $Rh/Mn/Fe/SiO_2$ catalysts, these catalysts are not constrained by methanol equilibrium but are limited by reaction kinetics. Also like the $Rh/Mn/SiO_2$, and $Rh/Mn/Fe/SiO_2$ catalysts, the Fischer-Tropsch-based catalysts are very reactive and selective to hydrocarbons. This introduces challenges associated with catalyst temperature (exotherm) control, similar to those experienced with the rhodium-based catalysts.

In addition, a large fraction of the hydrocarbons are liquids, and in some cases a smaller fraction are semi-solids (waxes). This creates a challenge for liquid hydrocarbon collection because a significant portion of the hydrocarbon liquids are solids at the cold trap temperature and can be difficult to recover.

There also appeared to be significant dissolution of light hydrocarbon gases into the cold trap liquids. When the trap was drained, care was needed to minimize spraying of the liquid product into the recovery bottle, causing a loss of sample because of gases coming out of solution. This was accomplished by only partially opening the drain ball valve until the liquid stopped flowing.

It is suspected that in some cases the presence of organic solids in the trap caused a portion of the hydrocarbon liquids and/or solids to remain in the cold trap, reducing the yield of hydrocarbons and resulting in lower-than-expected liquid hydrocarbon STYs. The unrecovered hydrocarbon liquids and solids were likely recovered in a later sample for different operating conditions and would have produced higher-than-expected STYs for hydrocarbon liquids. This problem was most apparent for the FT-MeOH-Pd catalyst, which was the first one tested that experienced this problem. In later testing of the $K/Fe/Cu/Al_2O_3$ catalysts, steps were taken to ensure that the trap valve was not plugged while recovering the last of the material collected in the bottom of the trap. Earlier tests with the $Rh/Mn/SiO_2$ catalyst also produced hydrocarbon liquids and, in one sample, a small quantity of hydrocarbon solids. However, the hydrocarbons made up a much smaller fraction of the total liquid samples, and they likely did not lead to drain valve blockage. The reactor system tubing downstream of the reactor for the Fischer-Tropsch-based catalysts and the Rh/Mn/SiO_2 catalyst was disassembled, cleaned with solvent to remove any solids retained in the tubing, and then reassembled for a new test. Solids were recovered from this tubing for the Fischer-Tropsch-based catalysts that were not accounted for in the data because they could not be assigned to specific test conditions.

The problems encountered with recovering the hydrocarbon liquids did not appear to affect recovery of the aqueous phase containing the alcohols significantly because this phase was the heaviest of the three and could be recovered once the trap began to gravity drain. In some cases, a small fraction of the aqueous phase was lost when the liquid sprayed into the sample bottle due to hydrocarbon gas evolution during sample recovery and was not accounted for in the reported alcohol yields. The lost quantities were not considered significant in the context of screening catalysts.

A significant portion of the dissolved gases in the liquid samples was likely lost during sample draining and in the sample bottle gas space during storage. These gases could not be quantified or accounted for in the product gas using the current method for sample collection and GC analysis downstream of the trap (gas samples were collected downstream of the back-pressure regulator valve). The quantities lost are not thought to be significant because the liquid sample volumes were small and the amount of gas passing through the traps was large. The dissolved gases remaining in the aqueous phase would not significantly affect alcohol yields, and remaining in the hydrocarbon liquid sample would only have a minor effect on the hydrocarbon liquid yield.

There was no effort to quantify any alcohols that partitioned to the hydrocarbon liquid phase, although significant partitioning of the higher alcohols (C_4+ alcohols) to the hydrocarbon phase will occur if a large quantity of hydrocarbon liquids is produced. That was the case for most of the liquid samples collected for both Fischer-Tropsch-based catalysts; thus, true STYs and carbon selectivities for the higher alcohols will be higher than the reported C_2+ oxygenate values, and the yields and selectivities for the hydrocarbons will be lower than the reported liquid hydrocarbon values.

Figure 4.18 shows the carbon conversion achieved for both catalysts. It appears that carbon conversion increased with increasing temperature and decreased with increasing space velocity, as might be expected. It also appears that the K/Fe/Cu/Al_2O catalyst was the more reactive of the two.

Figure 4.19 shows carbon selectivity for K/Fe/Cu/Al_2O_3 and Ft-MeOH-Pd catalysts to C_2+ oxygenates. The considerable scatter in the data for the FT-MeOH-Pd catalyst is attributed to the previously discussed difficulties in recovering liquid hydrocarbons for some samples, which causes an apparent increase in the yields of other products, including C_2+ oxygenates. This hypothesis is supported by the STYs of liquid hydrocarbons for this catalyst, as shown in Figure 4.20. Specifically, the tests performed at 350°C at 49,000 L/L_{cat}/hr space velocity and at 364°C and 375°C at 74,000 L/L_{cat}/hr space velocity at 74,000 L/L_{cat}/hr produced unusually high carbon selectivities to C_2+ oxygenates (Figure 4.19) and unusually low liquid hydrocarbon STYs (Figure 4.20). The trend is less apparent at 300°C and 25,000 L/L_{cat}/hr. However, a sample retrieved during the break-in period for the catalyst at the same conditions had a much higher yield of liquid hydrocarbons while producing the same yield of C_2+ oxygenates. Because of the effect of hydrocarbon liquid losses from some samples that were recovered in others, it is believed that the true carbon selectivities to C_2+ oxygenates for the FT-MeOH-Pd catalyst were about 10 to 13% for the conditions tested. The carbon selectivity to C_2+ oxygenates for the

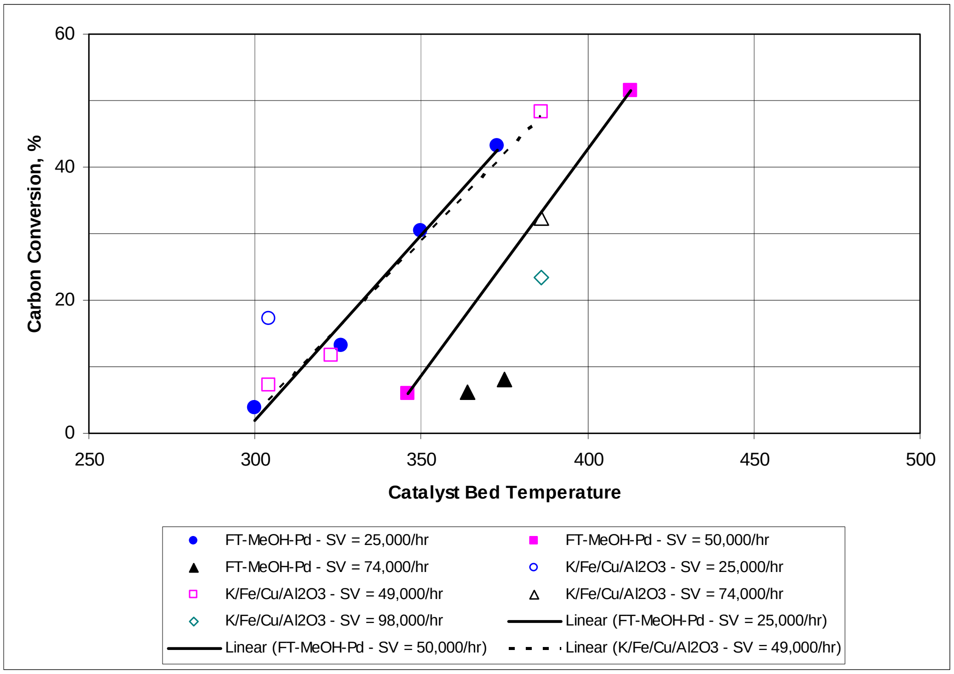

Figure 4.18. Carbon Conversions for K/Fe/Cu/Al_2O_3 and FT-MeOH-Pd Catalysts

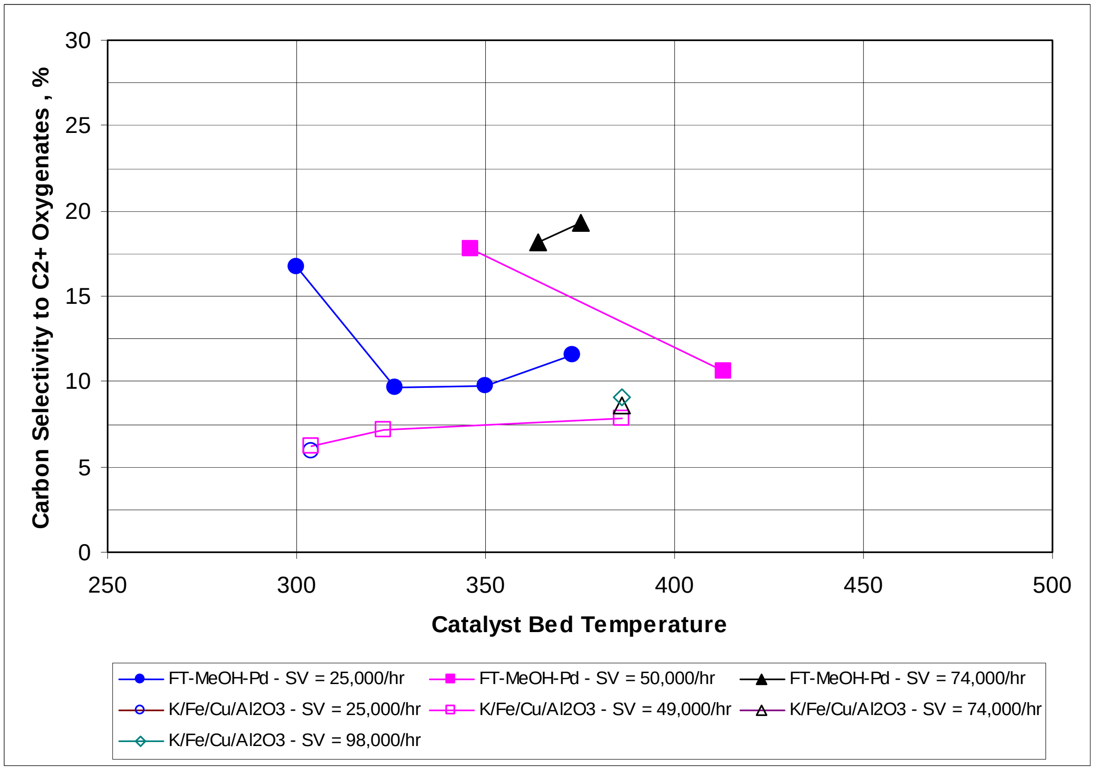

Figure 4.19. Carbon Selectivity to C_2+ Oxygenates for K/Fe/Cu/Al_2O_3 and FT-MeOH-Pd Catalysts

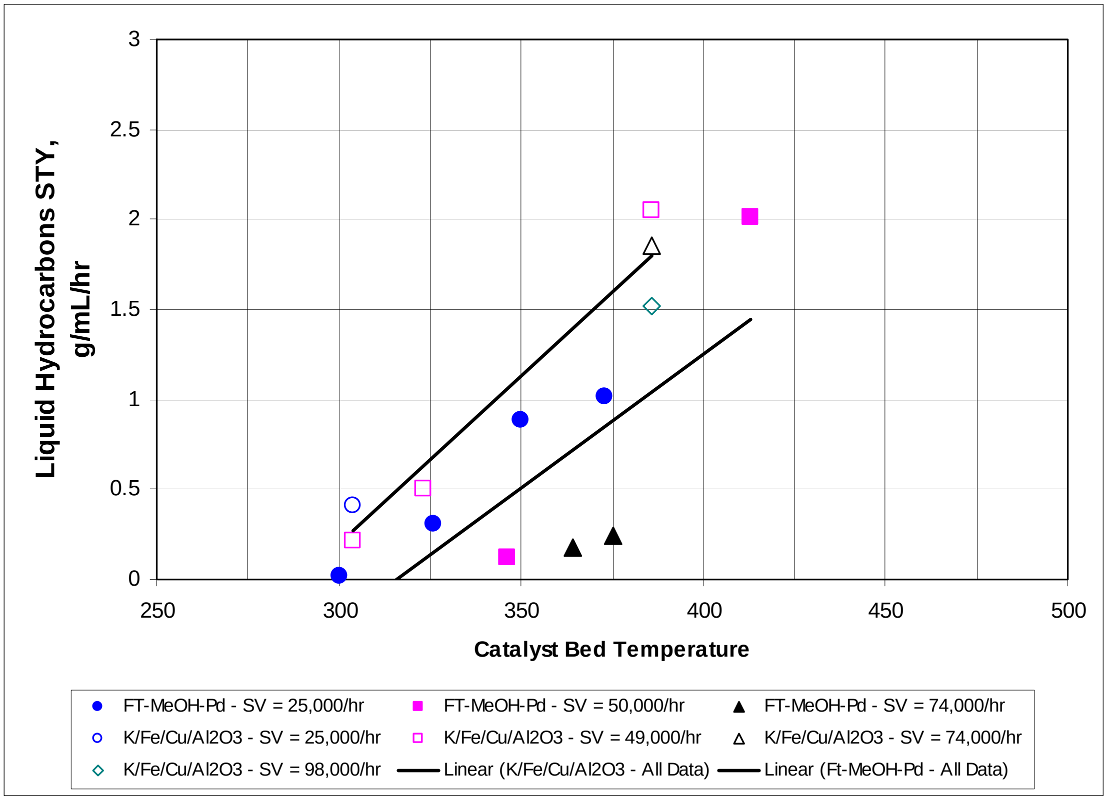

Figure 4.20. Liquid Hydrocarbon STYs for K/Fe/Cu/Al_2O_3 and FT-MeOH-Pd Catalysts

K/Fe/Cu/Al_2O_3 catalyst had much less scatter in the carbon selectivity to C_2+ oxygenates, ranging from about 6 to 9% for the conditions tested.

Figure 4.21 shows the effects of temperature and space-time velocities on the C_2+ oxygenate STYs for both catalysts. It appears that the space velocity has very little effect on the STYs relative to the effect of the catalyst temperature over the range of conditions evaluated. It also appears that the K/Fe/Cu/Al_2O_3 catalyst produces higher C_2+ oxygenate STYs than the FT-MeOH-Pd catalyst at the same operating conditions. Figure 4.22 shows the effects of temperature and space-time velocities on the total organic liquid product STYs for both catalysts. Again, the scatter in the data reflects that for the liquid hydrocarbons.

There were significant differences in carbon selectivity for various oxygenates for the K/Fe/Cu/Al_2O_3 and FT-MeOH-Pd catalysts. Table 4.3 shows that carbon selectivity ratios of methanol to C_2+ alcohols for the FT-MeOH-Pd catalyst, which ranged from 0.07 to 0.50, were significantly greater than those for the K/Fe/Cu/Al_2O_3 catalyst, whose ratios ranged from 0.05 to 0.11. Similarly, the carbon selectivity ratios of C_2+ alcohols to other C_2+ oxygenates, which ranged from 2.8 to 8.8 for the FT-MeOH-Pd catalyst, were significantly greater than those for the K/Fe/Cu/Al_2O_3 catalyst, whose ratios ranged from 1.0 to 2.1.

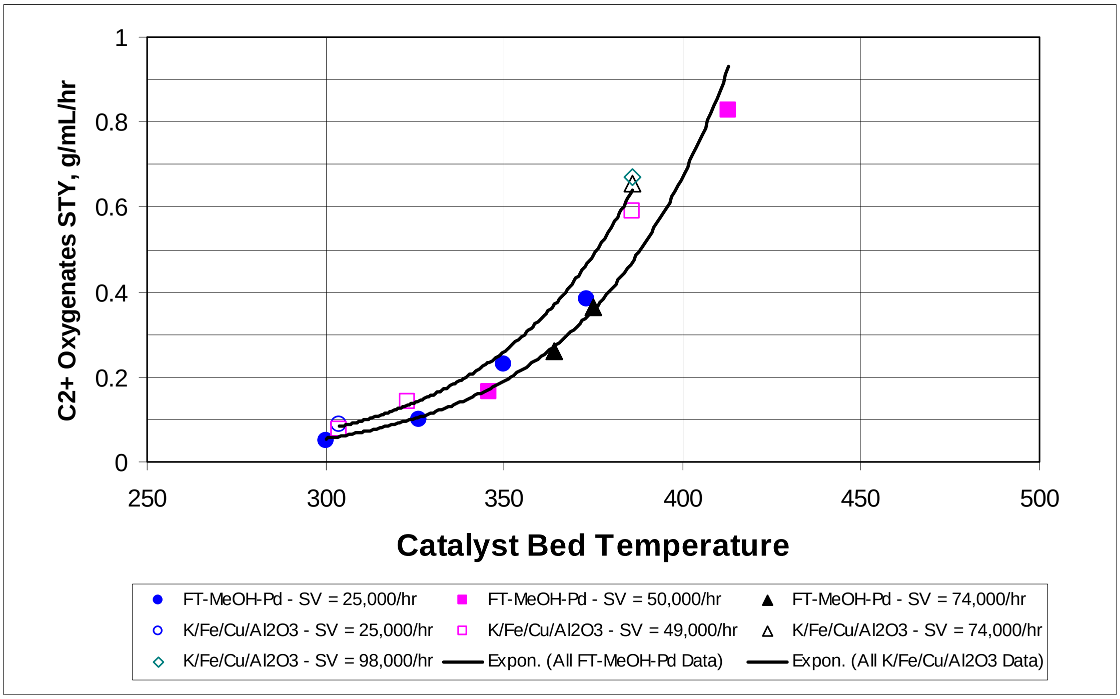

Figure 4.21. C_2+ Oxygenate STYs for K/Fe/Cu/Al_2O_3 and FT-MeOH-Pd Catalysts

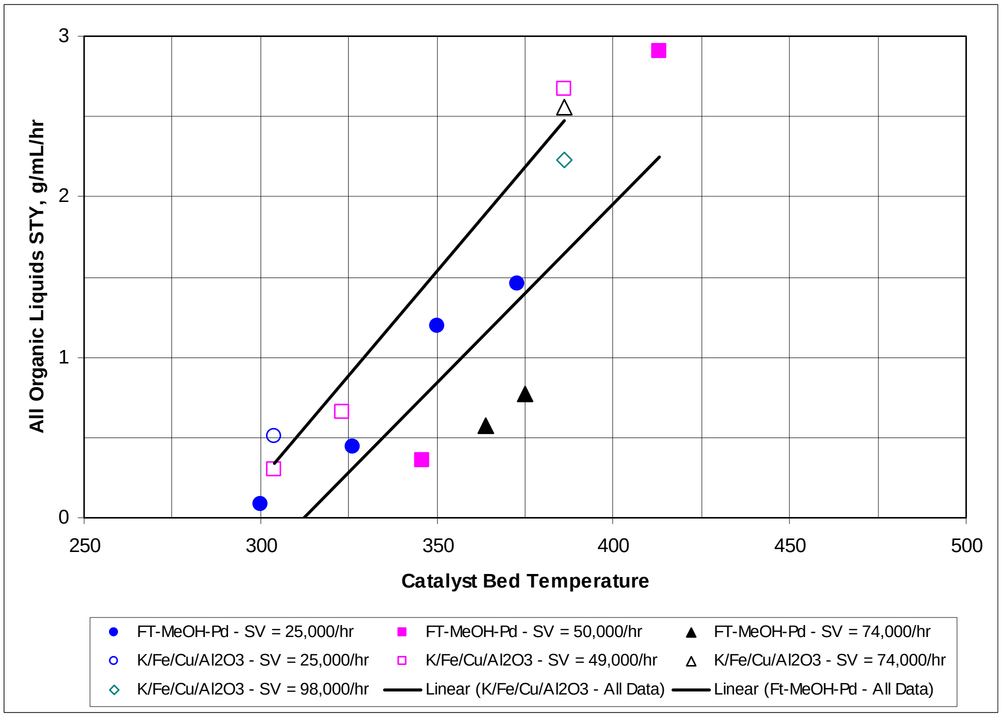

Figure 4.22. Liquid Hydrocarbon STYs for K/Fe/Cu/Al_2O_3 and FT-MeOH-Pd Catalysts

Table 4.3. Comparison of Carbon Selectivity to Various Oxygenates

Catalyst	**Space Velocity (L/L_{cat}/hr)**	**Temp. (°C)**	**Carbon Selectivity (Mol%)**				**Selectivity Ratios**	
			MeOH	**Other C_1 Oxygenates**	**C_2+ Alcohols**	**Other C_2+ Oxygenates**	**MeOH: C_2+ Alcohols**	**C_2+ Alcohols: Other C_2+ Oxygenates**
$K/Fe/Cu/Al_2O_3$	25000	304	0.33	0.00	2.99	2.93	0.11	1.0
$K/Fe/Cu/Al_2O_3$	49000	304	0.49	0.02	3.17	3.08	0.15	1.0
$K/Fe/Cu/Al_2O_3$	49000	323	0.57	0.01	4.25	2.96	0.13	1.4
$K/Fe/Cu/Al_2O_3$	49000	386	0.27	0.00	5.25	2.55	0.05	2.1
$K/Fe/Cu/Al_2O_3$	74000	386	0.38	0.00	5.39	3.21	0.07	1.7
$K/Fe/Cu/Al_2O_3$	98000	386	0.47	0.00	5.35	3.68	0.09	1.5
FT-MeOH-Pd	25000	300	3.53	0.02	12.61	4.07	0.28	3.1
FT-MeOH-Pd	25000	326	2.41	0.01	8.00	1.69	0.30	4.7
FT-MeOH-Pd	25000	350	2.28	0.00	8.72	0.99	0.26	8.8
FT-MeOH-Pd	49000	346	5.95	0.00	15.41	2.33	0.39	6.6
FT-MeOH-Pd	49000	413	0.62	0.00	9.30	1.30	0.07	7.2
FT-MeOH-Pd	25000	373	1.31	0.00	10.25	1.34	0.13	7.6
FT-MeOH-Pd	74000	364	6.76	0.03	13.46	4.73	0.50	2.8
FT-MeOH-Pd	74000	375	6.30	0.02	14.49	4.77	0.43	3.0

5.0 Comparison of Different Classes of Catalysts

5.1 General Performance

There were clearly differences between the different classes of catalysts in terms of the STYs for C_2+ oxygenates and total liquids, as well as the selectivities to different liquid products. The ICI catalyst (commercial methanol catalyst) performed as expected, achieving high carbon conversions and high selectivities to methanol at a relatively low temperature of 250°C and space velocities ranging from 7,300 to 15,000 L/L_{cat}/hr. The methanol STY ranged from 2.08 to 3.51 kg/L_{cat}/hr under these conditions.

The MeOH-X catalyst (modified copper catalyst) was operated over a temperature range of 250° to 325°C and appeared to have carbon conversions comparable to the ICI under comparable operating conditions. The MeOH-X catalyst also produced C_2+ oxygenates, predominantly ethanol. However, the selectivity to C_2+ oxygenates was less than 17% at the conditions evaluated, producing low C_2+ oxygenate STYs that were no higher than about 0.09 kg/L_{cat}/hr. The total organic liquid STY at the conditions producing the highest C_2+ oxygenate STY was 0.97 kg/L_{cat}/hr due to the high yields of methanol as a byproduct.

The K/Cu/Zn/Mn/Co/Cr catalyst, which was evaluated at temperatures ranging from 354° to 398°C and a 7,500 L/L_{cat}/hr space velocity, did not perform as well as expected, producing very few oxygenates, and those were dominated by methanol. The maximum C_2+ oxygenate STY of 0.03 kg/L_{cat}/hr was achieved at 389°C. The total C_1+ oxygenate STY at these conditions was 0.07 to 0.11 kg/L_{cat}/hr. The low yields may be attributed to difficulty in getting copper to precipitate simultaneously with the other metals during catalyst preparation.

The K/MoS_2 catalyst, which was evaluated at temperatures of 325° to 375°C at 6,700 L/L_{cat}/hr space velocity, was much less reactive than either the ICI or MeOH-X catalysts with only 20.3% CO conversion achieved at the highest temperature. The highest C_2+ oxygenate STY of about 50 g/g_{cat}/hr was also achieved at 375°C. This is lower than the highest STY achieved for the MeOH-X catalyst. The total STY for all C_1+ oxygenates at these conditions was 0.140 g/g_{cat}/hr, which is also much lower than for the MeOH-X catalyst. With the low CO conversion at these conditions, higher space velocities were not investigated at any of the conditions. Similarly, with a relatively low STY of C_2+ oxygenates, lower space velocities were not investigated.

The selectivity of the K/MoS_2 catalyst for C_2+ oxygenates over the range of temperatures evaluated ranged from about 20 to 23%, which was much better than the MeOH-X catalyst, but the selectivity to methanol was much lower, ranging from 25 to 56%. Examination of the carbon conversion to methanol for this catalyst at these temperatures suggests that equilibrium conditions did not constrain the selectivity to methanol except possibly at 375°C (see Figure 4.2). Higher reaction temperatures, however, would be expected to further reduce selectivity to methanol. Carbon selectivity to light (C_1 to C_3) hydrocarbons ranged from 21 to 55%, was much greater than that for the MeOH-X catalyst, and accounted for about half of the products produced. Higher reaction temperatures favor greater selectivity to hydrocarbons and limit the opportunity to achieve significant improvements in the selectivity to the higher oxygenates.

The K/Co/MoO$_2$/C catalyst, which was evaluated at temperatures ranging from 317 to 381°C and at 6,700 and 15,000 L/L$_{cat}$/hr space velocities, appeared to be much more reactive than the KMoS$_2$ catalyst under comparable operating conditions, according to Table 5.1. And while the selectivity to C$_2$+ oxygenates appeared to be lower under comparable conditions at the higher temperatures, the K/Co/MoO$_2$/C catalyst did not produce nearly as much methanol. The highest STY achieved by the K/Co/MoO$_2$/C was much higher than the K/MoS$_2$ catalyst and any of the modified methanol catalysts.

Table 5.1. Comparison of the CO Conversion and Selectivity of the K/MoS$_2$ and K/Co/MoO$_2$/C Catalysts at Comparable Conditions

Catalyst	Temperature °C	Space Velocity L/L$_{cat}$ /hr	Carbon Conversion	Carbon Selectivity %	
				C$_1$ Oxygenate	C$_2$+ Oxygenate
K/Co/MoO$_2$/C	358	6700	15.4	4.2	18.2
	378	15,000	22.7	3.1	16.9
	381	6,700	33.7	1.5	11.1
K/MoS$_2$	350	6,700	11.2	40.0	19.9
	375	6,700	12.1	24.7	20.3

The Rh/Mn/SiO$_2$ and Rh/Mn/Fe/SiO$_2$ catalysts appeared to be less reactive than the MeOH-X catalysts at temperatures up to ~ 280°C based on comparison of the carbon conversion rates shown in Table 5.2. At about 300°C the CO conversion rates are comparable. This is attributed to the major reduction in carbon conversion to methanol with increasing temperature by the MeOH-X catalyst due to equilibrium methanol concentration constraints at the higher temperatures without a commensurate increase in the carbon conversion to C$_2$+ oxygenates. The Rh/Mn/SiO$_2$ and Rh/Mn/Fe/SiO$_2$ catalysts, on the other hand, are very selective to C$_2$+ oxygenates and are not limited by equilibrium conditions at higher temperatures. Consequently, the C$_2$+ STYs for these two rhodium catalysts were much higher than those achieved with the MeOH-X catalyst, ranging as high as 0.11 g/L$_{cat}$/hr at 280°C and 3,300 L/L$_{cat}$/hr space velocity for the Rh/Mn/SiO$_2$ and 0.40 g/L$_{cat}$/hr at 323°C and 11,000 L/L$_{cat}$/hr space velocity for the Rh/Mn/Fe/SiO$_2$ catalyst.

Table 5.2. Comparison of CO Conversion and Selectivity of the MeOH-X, Rh/Mn/SiO$_2$, and Rh/Mn/Fe/SiO$_2$ Catalysts at Comparable Conditions

Catalyst	Temperature °C	Space Velocity L/L$_{cat}$ /hr	Carbon Conversion	Carbon Selectivity %	
				C$_1$ Oxygenate	C$_2$+ Oxygenate
MeOH-X	250	6700	63.8	99.5	0.5
MeOH-X	275	3300	59.6	96.3	0.4
MeOH-X	300	3300	37.8	90.9	8.0
Rh/Mn//Fe/SiO$_2$	257	7400	21.8	0.32	39.0
Rh/Mn/SiO$_2$	255	3300	21.0	0.36	44.9
Rh/Mn/SiO$_2$	280	3300	37.1	0.29	32.3
Rh/Mn/SiO$_2$	305	3300	46.4	0.5	23.2

The Rh/Mn/SiO_2 and Rh/Mn/Fe/SiO_2 catalysts also appeared to be both more reactive and more selective to C_2+ oxygenates than the MoS_2 catalyst, as shown in Table 5.3. At comparable catalyst temperatures (325° and 323°C), the carbon conversion for the Rh/Mn/Fe/SiO_2 catalyst is more than 5 times greater than the K/MoS_2 catalyst, while the carbon selectivity to C_2+ oxygenates is about the same (24% versus 23%). However, the Rh/Mn/Fe/SiO_2 catalyst produces almost no C_1 oxygenates, whereas methanol is the major product for the K/MoS_2 catalyst. Even at 257°C, carbon conversion for the Rh/Mn/Fe/SiO_2 catalyst is more than 2½ times greater than that for the K/MoS_2 catalyst at 325°C and comparable space velocity. Similarly, the Rh/Mn/SiO_2 catalyst at 305°C achieved a carbon conversion more than 5 times that of the K/MoS_2 catalyst at 325°C, though the space velocity for the rhodium-based catalyst was half that of the molybdenum-based catalyst.

The performance of the Fischer-Tropsch-based catalysts is difficult to compare with others. These catalysts produced Fischer-Tropsch liquids as the primary product and needed to be tested at higher space velocities to prevent plugging the catalyst bed with waxes (this occurred in an aborted test while breaking in the Rh/Mn/Fe/SiO_2 at 300°C catalyst bed temperature and 7,700 L/L_{cat}/hr). The previously discussed difficulties in obtaining good recovery of Fischer-Tropsch liquids from the sample cold trap also make comparisons more tentative in terms of product selectivity. The best comparisons of Fischer-Tropsch catalysts can be made between the Rh/Mn/Fe/SiO_2 (rhodium-based) and FT-MeOH-Pd (Fischer-Tropsch-based) catalysts, as shown in Table 5.4. The FT-MeOH-Pd catalyst appears to be less reactive than the

Table 5.3. Comparison of the CO Conversion and Selectivities of the K/MoS2, Rh/Mn/SiO_2, and Rh/Mn/Fe/SiO_2 Catalysts at Comparable Conditions

Catalyst	Temperature (°C)	Space Velocity (L/L_{cat} /hr)	Carbon Conversion	Carbon Selectivity (%)	
				C_1 oxygenate	C_{2+} oxygenate
K/MoS_2	325	6700	8.2	56	23.0
K/MoS_2	350	6700	11.2	40	19.9
Rh/Mn//Fe/SiO_2	257	7400	21.8	0.32	39.0
Rh/Mn//Fe/SiO_2	285	7400	36.3	0.25	33.5
Rh/Mn//Fe/SiO_2	323	11000	46.9	0.31	24
Rh/Mn//Fe/SiO_2	354	15000	26.8	0.29	11.7
Rh/Mn/SiO_2	305	3300	46.4	0.50	23.2

Table 5.4. Comparison of the CO Conversion and Selectivity of the Rh/Mn/Fe/SiO_2 and FT-MeOH-Pd Catalysts at Comparable Conditions

Catalyst	Temperature (°C)	Space Velocity (L/L_{cat} /hr)	Carbon Conversion	Carbon Selectivity (%)			
				C_1 oxygenates	C_2+ oxygenates	CH_4	Higher Hydrocarbons
Rh/Mn/Fe/SiO_2	323	11000	46.9	0.31	24	59	17
Rh/Mn/Fe/SiO_2	354	15000	26.8	0.29	11.7	83	4
FT-MeOH-Pd	326	25,000	13.2	2.4	9.7	15	72
FT-MeOH-Pd	350	25,000	50.3	2.28	9.7	11	77

$Rh/Mn/Fe/SiO_2$ catalyst at ~ 325°C and more reactive at 350°C, when the effects of space velocity on carbon conversion are accounted for (see Figures 4.15 and 4.18 for space velocity effects on carbon conversion).

The $Rh/Mn/Fe/SiO_2$ and FT-MeOH-Pd catalysts have similar selectivity to C_2+ oxygenates at ~350°C catalyst temperature, but the $Rh/Mn/Fe/SiO_2$ catalyst has a much higher selectivity at ~325°C. Figures 4.16 and 4.19 show that the selectivity to C_2+ oxygenates for $Rh/Mn/Fe/SiO_2$ decrease significantly with catalyst temperature, whereas the FT-MeOH-Pd catalyst selectivity to C_2+ oxygenates is relatively constant with temperature. Both catalysts also have relatively low selectivity to C_1 oxygenates, although the FT-MeOH-Pd catalyst has a distinctly higher selectivity than $Rh/Mn/Fe/SiO_2$. However, the $K/Fe/Cu/Al2O_3$ catalyst had selectivity to C_1 oxygenates similar to $Rh/Mn/Fe/SiO_2$ (see Table 4.1).

A major difference between the rhodium and Fischer-Tropsch catalysts is their selectivity to hydrocarbons. The rhodium catalysts produce methane as their major product, whereas the Fischer-Tropsch catalysts produce higher hydrocarbons as their major product.

5.2 Space-Time Yield Comparisons of Catalyst Classes Tested Under Optimum Conditions

For screening catalyst performance, STY was used as the primary criterion because it is directly related to capital costs (i.e., higher STYs result in lower reactor volumes to process a given feed-gas flow rate). If the STYs are too low, unit product capital recovery costs will be too high. It is clear from the test results that byproducts will be significant contributors to overall process economics because the carbon selectivity to C_2+ oxygenates never exceeded 45% for any of the catalysts tested, even under conditions producing less than optimum STYs. Therefore, the STYs of both the primary products of interest (C_2+ oxygenates and the more desirable C_2+ alcohols) and other liquid products (methanol and Fischer-Tropsch liquids) were considered in the comparing the catalysts.

Tests used to screen performance were selected from each of the catalyst classes that produced the highest STY of C_2+ oxygenates. In the case of the Fischer-Tropsch catalysts, the test with the highest C_2+ oxygenate STY occurred after a thermal runaway established a new stable condition at 51% carbon conversion and a 92% CO conversion. Therefore, a second test was selected that produced results under more stable operating conditions. This was done because of concern regarding the ability of a commercial reactor to control temperature at the much higher conversions achieved with these catalysts.

Table 5.5 summarizes the test conditions and corresponding STYs for the tests that were selected for comparison. Figure 5.1 compares the STYs of the potential liquid products for the optimum test conditions for each catalyst class. The ICI catalyst, which was tested under only two conditions during system shakedown, had the highest overall STY, consisting almost entirely of methanol. This STY is much higher than the recommended range of 0.67–1.340 $kg/L_{cat}/hr$ recommended for a commercial methanol plant, according to Stiles et al. (1991).

Table 5.5. Comparison of Catalysts at Conditions Maximizing C_2+ Oxygenate STYs

Catalyst	Space Velocity ($L/L_{cat}/hr$)	Temperature °C	Carbon Conversion (%)	CO Conversion (%)	**STY ($g/mL_{cat}/hr$)**				
					C_2+ Alcohols	**Other C_2+ Oxygenates**	**MEOH**	**HC Liquids**	**Total Liquids**
ICI	15,000	250	53.7	80.8	0.017	0.002	3.488	0.000	3.507
MeOH-X	10,000	325	24.7	28.8	0.085	0.002	0.881	0.000	0.968
Cu/Zn/Mn/ Co/Cr	7,500	998	13.6	22.4	0.028	0.003	0.075	0.008	0.114
$K/Mo/S_2$	6,700	350	11.2	18.1	0.045	0.002	0.134	0.000	0.180
$K/Co/MoO_2$	6,700	352	26.4	49.3	0.002	0.000	0.014	0.003	0.019
$K/Co/MoO_2/C$	15,000	378	22.7	46.4	0.169	0.007	0.047	0.031	0.253
Rh/Mn/Fe/ Al_2O_3	11,000	323	46.9	65.6	0.270	0.131	0.007	0.000	0.408
FT-MeOH-Pd	25,000	350	30.5	50.3	0.202	0.028	0.076	0.890	1.196
FT-MeOH-Pd	49,000	413	51.4	92.1	0.711	0.118	0.070	2.009	2.908

The STYs for methanol and total organic liquids for the MeOH-X catalyst were within the recommended STY range for methanol plants because the higher temperatures required to achieve a significant STY for C_2+ oxygenates caused the methanol STY to drop significantly due to methanol equilibrium limitations. However, even with the higher reaction temperatures, the STY for C_2+ oxygenates was low. Significantly higher C_2+ oxygenate STYs are not likely to be obtained with the MeOH-X catalyst because the catalyst was approaching its maximum recommended operating temperature, providing no margin for catalyst deactivation over time.

The K/Cu/Zn/Co/Cr catalyst was much less reactive than anticipated, achieving a maximum C_2+ oxygenate STY of only 0.031 $kg/L_{cat}/hr$ at 398°C and 7,500 $L/L_{cat}/hr$ space velocity. Based on the research of Stiles et al. (1991), the STY was expected to be closer to 0.5 $kg/L_{cat}/hr$. However, uncertainties in the preparation and difficulties getting the copper to coprecipitate with the other metals during preparation may have caused the poor catalyst performance. Further evaluation of this class of catalysts will require a more systematic development of the preparation procedure.

The $K/Mo/S_2$ catalyst had a much lower C_2+ oxygenate STY at its optimum conditions than the MeOH-X catalyst and a total organic liquid STY that was well below the recommended range. However, this catalyst was not considered to be the best catalyst in its class. For example, Qi et al. (2003) recently reported STYs for C_2+ alcohols and C_1+ alcohols of 0.18 and 0.33 $kg/L_{cat}/hr$, respectively, at 315°C catalyst temperature and 6,000 $L/L_{cat}/hr$ space velocity for a molybdenum sulfide catalyst containing Mn, Ni, and Mo in a 1:1:3 molar ratio. These STYs are more than double the STYs shown in Figure 4.10 and Table 5.5.

The $K/Co/MoO_2/C$ performed much better than the MeOH-X catalyst, achieving a maximum C_2+ oxygenate STY of 0.176 $kg/L_{cat}/hr$ at 378°C and 7,500 $L/L_{cat}/hr$ space velocity, which was twice the maximum STY achieved by the MeOH-X catalyst. However, this catalyst was more selective to the C_2+ oxygenates than the MeOH-X catalyst, so the total oxygenate STY was well below the commercially viable range.

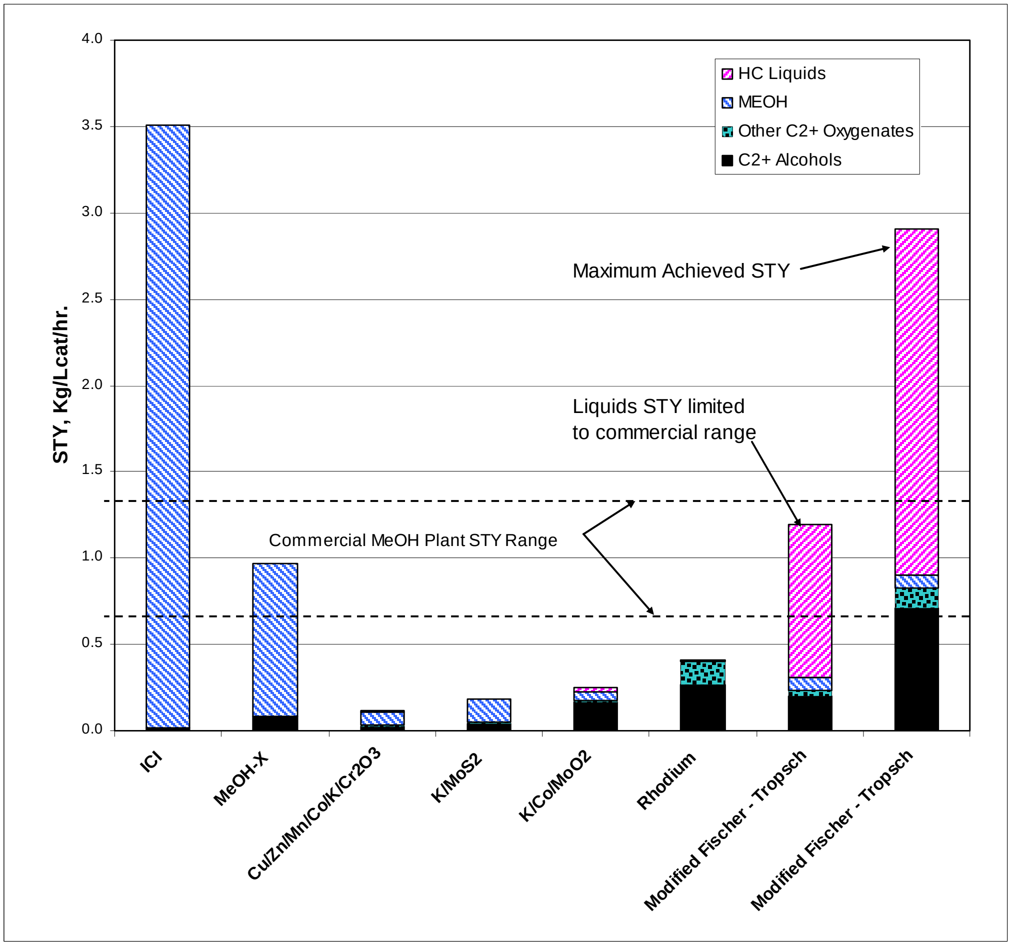

Figure 5.1. Comparison of Organic Liquid STYs for Catalysts Operated at Conditions Producing the Highest STY for C_2+ Oxygenates

The $Rh/Mn/SiO_2$ and $Rh/Mn/Fe/SiO_2$ catalysts were very selective toward producing C_2+ oxygenates; neither achieved more than 1% carbon selectivity to C_1 oxygenates and, in the case of the $Rh/Mn/Fe/SiO_2$ catalyst, no liquid hydrocarbons. Instead, carbon selectivity to C_2+ hydrocarbons ranged as high as 40%, with the balance consisting of methane and C_2 to C_5 hydrocarbon gases. The maximum C_2+ oxygenate STY was 0.400 kg/L_{cat}/hr, which is significantly higher that that achieved to date using the MeOH-X or the K/MoS_2 catalysts but still lower than the minimum recommended range for commercial processes.

$K/Fe/Cu/Al_2O_3$ and FT-MeOH-Pd catalysts produced Fischer-Tropsch liquids as the primary product, which is different from all other catalysts tested. The FT-MeOH-Pd catalyst had the highest C_2+ oxygenate STY at 0.83 kg/L_{cat}/hr, which is well above the minimum recommended range for commercial processes. However, the STY for total liquids, including hydrocarbon liquids and a relatively small quantity of methanol, was well above the recommended range. A second set of test conditions achieved a total organic liquid STY within the recommended range and (also shown in Figure 5.1) had a correspondingly lower C_2+ oxygenate STY of 0.23 g/L_{cat}/hr. This is significantly lower than the optimum yield achieved by the $Rh/Mn/Fe/SiO_2$ catalyst but significantly higher than that achieved by the other catalysts.

6.0 Conclusions and Recommendations

Based on a review of the literature and the results obtained to date, there are no known and readily available commercial mixed alcohol catalysts or laboratory-prepared mixed alcohol catalysts that produce C_2+ oxygenates as the main product and at space-time yields that are expected to be required for a commercially economic process. A modified, commercially available methanol catalyst provided by a catalyst company could achieve methanol plus C_2+ oxygenates STYs within the recommended range. However, its STY for C_2+ oxygenates is more than 7 times lower than the recommended minimum.

The molybdenum sulfide-based catalyst (K/MoS_2 catalyst) that was prepared and tested this fiscal year had even lower C_2+ oxygenate STY under optimum operating conditions than the MeOH-X catalyst, as well as a total organic liquid STY that was well below the minimum recommended range. Its performance was also less than might be expected based on the open literature. On the other hand, one of the molybdenum oxide-based catalysts (K/Co/MoO_2/C) had much better performance than the MeOH-X catalyst in producing C_2+ oxygenates, although total oxygenate production was much lower.

The two Fischer-Tropsch catalysts, modified to improve oxygenate yields, were prepared and tested this year. Both achieved C_2+ oxygenate STYs that were within the recommended range. However, because of their much higher selectivity to Fischer-Tropsch liquids, the STYs for total organic liquids exceeded the recommended range under optimum operating conditions. A test with the FT-MeOH-Pd catalyst under test conditions that produced a total organic liquid within the recommended range achieved a much lower C_2+ oxygenate STY, which, while higher than that achieved with the MeOH-X and K/Mo_2 catalysts, was still well below the recommended STY range.

The two rhodium-based catalysts, Rh/Mn/SiO_2 and Rh/Mn/Fe/SiO_2, that were experimentally prepared and tested this year were very selective to C_2+ oxygenates. They achieved higher C_2+ oxygenate STYs under optimum conditions than any of the modified methanol and molybdenum-based catalysts tested at their optimum conditions and Fischer-Tropsch catalysts at conditions that limited the total organic STYs to within the recommended range. The maximum achieved C_2+ oxygenate STY, however, was still below the recommended minimum. This class of catalysts is unique because it produces very little C_1+ oxygenate or Fischer-Tropsch liquids.

At present, only the MeOH-X and the modified Fischer-Tropsch catalysts achieve total organic liquid STYs that are within the recommended range. The MeOH-X catalyst depends on the production of MeOH as the major coproduct, while the modified Fischer-Tropsch catalysts produce Fischer-Tropsch liquids as the major coproduct. The choice between them depends on which major coproduct is desired. Currently, methanol is sold as a chemical, but it could be used as a fuel or converted into gasoline using Mobile's "Methanol to Gasoline" process. (This process was used in New Zealand from about 1977 until about 1996, when the gasoline synthesis section of the plant was decommissioned due to an unfavorable economic situation.) Fischer-Tropsch liquids are produced commercially outside the United States and refined to produce a high cetane, low-sulfur diesel fuel as a primary product along with a host of other hydrocarbon-based products. It can also be used as a feedstock to produce gasoline.

The rhodium catalyst is unique in its ability to produce primarily C_2+ oxygenates with low to very low yields of C_1 oxygenates and/or Fischer-Tropsch liquids. The best catalyst prepared and tested to date achieved an STY of 40 g/L_{cat}/hr, which is approximately 60% of the minimum recommended. A review of the literature revealed only a couple of studies using rhodium-based catalyst preparations tested under high-pressure conditions. However, several studies conducted at atmospheric pressure suggest that improvements are possible using other supports or promoters that improve catalyst dispersion and stabilize it against oxidation under the more oxidizing conditions that are experienced with higher levels of product water in the gas.

This screening also does not take into account the merit of recycling methanol to improve the yields of higher oxygenates. Quarderer et al. (1989) reported significant improvements in the yield of C_2+ oxygenates using a K/MoS_2 catalyst by injecting methanol into the feed syngas. They also showed that adding ethanol improved the yield of C_2+ oxygenates, though the effect was not as pronounced as it was with methanol addition. It is unknown whether other catalyst classes including molybdenum oxide-based catalysts are capable of similar performance improvements using methanol recycle.

Another opportunity for improving the STY of C_2+ oxygenates is the addition of promoters that enhance hydroformylation of olefins into oxygenates. Research reported by Sachtler and Ichikawa (1986) and Ichikawa et al. (1985) suggests that when small amounts of base metals such as zinc are added to a Rh/SiO_2 catalyst, the ethylene added to a H_2/CO synthesis gas is preferentially converted into predominantly propionic aldehyde instead of ethane. This suggests that there are opportunities to improve the yields of C_3+ oxygenates using the rhodium and Fischer-Tropsch catalysts by adding promoters that increase hydroformylation of olefins present in the product gas in significant concentrations.

It is recommended that additional screening tests be conducted to more completely evaluate catalysts based on molybdenum oxide and Fischer-Tropsch catalysts that are based on cobalt. Further screening of modified methanol-based catalysts may also be warranted.

It is recommended that research be conducted to improve the performance of rhodium catalysts. Research should focus on the use of promoters to improve the reactivity of rhodium at lower temperatures where hydrocarbon formation is not favored and/or suppressing the formation of hydrocarbons at higher temperatures. It is recommended that a limited number of tests be conducted to investigate the use of physical mixtures of the rhodium-based catalyst and a hydrogenation catalyst to improve the ratio of C_2+ alcohols to other oxygenates.

It is also recommended that limited tests be conducted with the addition of methanol to the syngas to examine whether methanol recycle is a viable alternative for the rhodium- and Fischer-Tropsch-based catalysts, as well as any new modified methanol- or molybdenum-based catalysts that show significant C_2+ oxygenate STY improvements over the one tested this year.

Finally, it is recommended that lower H_2:CO ratios and both higher and lower system pressures be examined to determine their effects on product STYs. Lower H_2:CO ratios favor C_2+ oxygenate production and could reduce or eliminate the need to adjust the untreated gasifier product gas H_2:CO ratio, which is already much lower than 2:1. Lower operating pressures are expected to reduce the C_2+ oxygenate STYs. However, lower operating pressures have a significant effect on the capital requirements and energy costs for compressing the feed gas. Conversely, higher pressures may be necessary to achieve acceptable STYs for C_2+ oxygenates. Knowing the effect of pressure on the product yields can help determine whether there is an overall economic benefit.

7.0 References

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