

Promoted Zinc Chromite Catalysts for Higher Alcohol Synthesis Semi-Annual Report

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Patent Information:

No patentable subject matter is disclosed in this report.

Abstract

During this reporting period, a “zinc chromite” catalyst promoted with 6 wt.% cesium (Cs) was evaluated at the following operating conditions: Temperature - 375°C and 400°C; Total Pressure – 13.6 MPa (2000 psig); Gas Hourly Space Velocity (GHSV) - 5000 standard liters/kg(cat)-hr; and H₂/CO feed ratio – 0.5, 1.0 and 2.0 mole/mole. Decahydronaphthalene (DHN) was used as the slurry liquid. The experiment lasted for twelve days of continuous operation. Unpromoted zinc chromite catalyst then was re-examined under the same operating conditions.

Reproducible data was achieved with a continuous liquid make-up. Compared with unpromoted zinc chromite catalyst, 6 wt.% Cs-promoted catalyst shifted the product distribution from methanol to higher alcohols, even though methanol was still the major product. The effect of operating conditions was less important than the addition of promoter. However, it was observed that higher temperature favors higher alcohol synthesis, and that a higher H₂/CO ratio leads to lower oxygenates selectivity and higher hydrocarbons selectivity. These trends showed clearly with the Cs-promoted catalyst, but were not as prominent with the unpromoted catalyst.

The slurry liquid did not decompose or alkylate to a measurable extent during either continuous, 12 - day experiment, even with the higher reactor temperature (400°C). There was a relatively significant loss of catalyst surface area during the experiment with the promoted catalyst, but not with the unpromoted catalyst.

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Executive Summary

The overall objective of this research project is to evaluate promoted "zinc chromite" catalysts for the production of higher (C_2^+) alcohols in a slurry reactor, using synthesis gas as the feedstock.

During this reporting period, a test of the newly purchased Maxpro gas booster (DLE 15/75) was carried out. Pure tetrahydroquinoline (THQ) was operated without catalyst at typical operating conditions. The evaporation rate of THQ was measured in order to determine a suitable liquid make-up rate when THQ is used as the slurry liquid.

Zinc chromite catalyst promoted with 6 wt.% cesium (Cs) was evaluated at variable operating conditions: Temperature: 375 and 400°C, Pressure: 2000 psig, H_2/CO – 1:2, 1:1, and 2:1 mole/mole, Gas Hourly Space Velocity (GHSV) - 5000 standard liters/kg(cat)-hr. Decahydronaphthalene (DHN) was the slurry liquid. Liquid was made up continuously during the experiments at a flow rate of 1.1 ml/hour. The experiment lasted for about two weeks of continuous operation. The gas product stream was analyzed using the on-line gas chromatographic (GC) system. Unpromoted zinc chromite catalyst then was re-examined under the same operating conditions.

Zinc chromite catalyst promoted with 6 wt.% Cs has a greater higher alcohol productivity and selectivity than unpromoted zinc chromite catalyst. However, methanol still was the major product using the promoted catalyst.

Higher operating temperature caused more higher alcohol and more hydrocarbon formation. When the H_2/CO feed ratio was changed from 0.5 to 2, hydrocarbon selectivity increased and oxygenate selectivity decreased. However, these trends were prominent only when the promoted catalyst was used. Carbon monoxide (CO) conversion was not affected significantly by either the promoter or the operating temperature.

"Spent" THQ liquid analyses were accomplished using a variety of analytical techniques. Identification of the components of the "spent" THQ may help us to understand the influence of the slurry medium on the methanol synthesis reaction. Silica gel liquid chromatography, HPLC (high performance liquid chromatography) and TLC (thin layer chromatography) were used to isolate the important compounds in the "spent" liquid, while GC/MS (gas chromatography/mass spectroscopy), FTIR (Fourier transform infrared) and NMR (nuclear magnetic resonance) analyses were applied to identify the structure of the compounds. No THQ was found in the "spent" THQ. However, one-methyl, di-methyl, and tri-methyl THQ, with one methyl group always attached to the N atom, were found to constitute more than 80% of the "spent" liquid.

A. Introduction

Branched higher alcohols, such as isobutanol (2-methyl-1-propanol) or isoamyl alcohol (2-methyl-1-butanol) could provide the raw materials needed to produce novel cetane enhancers for diesel fuel, e.g., methyl isobutyl ether (MIBE). Branched alcohols also could be of interest *per se* as oxygenated additives for motor gasoline.

With the exception of fuel-grade ethanol, current processes for producing higher alcohols are based primarily on imported petroleum. The objective of this research is to explore the synthesis of higher alcohols, using synthesis gas as the starting raw material. Synthesis gas is a mixture containing primarily hydrogen (H₂) and carbon monoxide (CO), which can be produced from a variety of domestically-available materials, e.g. coal, natural gas, and waste biomass.

Most previous attempts to produce branched higher alcohols from synthesis gas have been based on modified methanol synthesis catalysts, either the “low-pressure”, Cu/ZnO catalyst, or the “high-pressure”, ZnCrO (“zinc chromite”) catalyst. Either of these catalysts can be promoted with Group I elements such as potassium (K) and cesium (Cs) to shift the product distribution away from methanol towards higher alcohols.

Promoted “zinc chromite” catalysts are the focus of this research. All previous studies of this family of catalysts have been carried out in fixed-bed reactors. However, the highly exothermic character of higher alcohol synthesis (HAS) makes it difficult to control the temperature of a fixed-bed reactor, especially on a pilot-plant or commercial scale. A slurry reactor, by contrast, has excellent heat removal capability and many other advantages that make this type of reactor ideal for HAS.

The synthesis of methanol in a slurry reactor, using an unpromoted “zinc chromite” catalyst, was studied in depth by two previous students (1,2). Three slurry liquids were identified that appeared to have the necessary thermal and chemical stability at 375 °C, in the presence of the unpromoted “zinc chromite” catalyst (3,7). These liquids were: decahydronaphthalene (Decalin®, DHN), tetrahydronaphthalene (tetralin, THN), and tetrahydroquinoline (THQ). The rate of methanol synthesis was substantially higher in THQ than in the other two liquids. However, THQ was alkylated extensively during the reaction, raising questions about whether it participated in the catalytic cycle, and whether its composition would eventually stabilize. Details can be found in References 1 and 7. The present research involves the chemical analysis of the “spent” slurry liquid, i.e., the liquid in the reactor at the conclusion of experimentation, in order to understand the role of the slurry liquid in the catalytic process.

Some preliminary experiments were carried out with 3 wt.% Cs-promoted and 6 wt.% Cs - promoted “zinc chromite” catalysts by a previous M. Eng. student, and later by Ms. Xiaolei Sun under this contract (4,5). These prior experiments were qualitative in nature. However, they showed that the product contained significant concentrations of C₂⁺ alcohols, C₂⁺ olefins and C₂⁺ paraffins. An on-line gas chromatograph (GC) system was developed that appears to be capable of identifying and quantifying the broad spectrum of products obtained

with promoted zinc chromite catalysts. Details of this system are contained in previous Semi-Annual Reports (4,6,8,9).

The main objectives for this reporting period were:

1. To test the newly purchased Maxpro gas booster (DLE 15/75);
2. To evaluate a "zinc chromite" catalyst promoted with 6 wt.% Cs under variable operating conditions;
3. To re-examine unpromoted (0 wt.% Cs) zinc chromite catalyst under the same operating conditions as 6 wt.% Cs - promoted catalyst;
4. To continue the analysis of "spent" THQ liquid obtained from previous methanol synthesis experiments, and to propose mechanisms to explain the interaction between liquid and catalyst.

B. Results and Discussion

1. Test of New Gas Booster

A new Maxpro gas booster (DLE 15-75) was purchased because the existing Haskel gas booster developed a severe leak of synthesis gas, and was judged to be unworthy of repair. A test run was carried out after the booster arrived. No catalyst was involved. Two important questions were answered by this test run. First, did the new booster perform reliably under our typical operating conditions? Second, what is a suitable liquid make-up rate when THQ is chosen as the slurry liquid?

Details of operating conditions in this test run were as follows:

H₂ and CO feed = 1.67 l/min (total);

Temperature = 375°C

Pressure = 13.6 MPa (2000 psig);

Gas/Liquid separator temperature: 155°C;

Initial Liquid: THQ - 100 grams (94.25 ml);

Test time: 48 hours

This test run showed that the new booster provided 2000 psig operating pressure at the desired flow rate, with no CO leakage detected anywhere near the booster. After 48 hours, 41.5 ml THQ remained in the reactor, which meant that THQ evaporated at a rate of $(94.25 - 41.5)/48 = 1.1$ ml/hr. This rate would be a suitable liquid make-up rate when THQ is used as the slurry liquid.

2. Evaluation of Zinc Chromite Catalysts

A zinc chromite catalyst promoted with 6 wt% Cs was evaluated. The experiment was performed at variable operating conditions to investigate the effect of reaction temperature and H₂/CO feed ratio on the overall catalyst selectivity and productivity.

Unpromoted zinc chromite catalyst was re-examined under the same operating conditions as 6 wt % Cs - promoted catalyst. A comparison of the performance of promoted catalyst with that of unpromoted catalyst was carried

out to test the effect of promoter addition on HAS. The new experimental data for the unpromoted catalyst also was compared with earlier experimental data obtained with the same catalyst and under the same operating conditions.

a. Catalyst Preparation and Evaluation

- **Catalyst Preparation**

The 6 wt.% Cs-promoted zinc chromite catalyst (821A-2-36-1) was prepared by Engelhard Corporation using the incipient wetness technique. Reduced and stabilized Engelhard Zn-0312 catalyst (as described below) was impregnated with a solution of CsOH, and then dried at 125°C under N₂. The catalyst was not calcined after the drying process.

The unpromoted zinc chromite catalyst was a commercial, high-pressure methanol synthesis catalyst (Zn-0312 T1/8) from Engelhard Corporation, which was obtained in a reduced and stabilized form. The catalyst contained 60 wt.% Zn and 15 wt.% Cr, with ZnO and ZnCr₂O₄ phases detectable by X-ray diffraction. The as-received BET surface area was 145m²/g. The catalyst was received in tabletted form and was ground to less than 90 microns prior to use.

- **Catalyst Evaluation**

Each catalyst was evaluated at variable operating conditions for 12 days of continuous operation. The operating conditions were:

Temperature = 375°C and 400°C

Pressure = 13.6 MPa (2000psig)

GHSV = 5000 sl/kg(cat)-hr

H₂/CO molar feed ratio = 1:2, 1:1, and 2:1

Gas/liquid (G/L) separator temperature = 155°C

Mass of DHN in reactor = 80 gr

Mass of catalyst in reactor = 20 gr

Liquid make - up rate = 1.0 ml/hour at 375°C and at 400°C for 6 wt.% Cs promoted catalyst;
= 1.1 ml/hour at 375°C, and 2.0 ml/hour at 400°C for unpromoted catalyst

Experiments were carried out starting at 375°C. Three H₂/CO molar feed ratios, 0.5, 1, and 2.0, were examined at this temperature. Then, the operating temperature was increased to 400°C at the same pressure and the same three feed ratios were examined again. The reactor temperature then was decreased back to 375°C to re-examine catalyst performance at one feed ratio, normally H₂/CO = 1. The repeat run was performed to investigate whether the catalyst had deactivated during the experiments. Based on previous experience, the reaction was considered to reach steady state after 24 hours. Therefore, data collection started 24 hours after each new condition was set.

The purity of the feed gases, CO and H₂, and the properties of the slurry liquid, DHN, are contained in the fourth Semi-Annual Report (5).

Even though the catalyst was provided by Engelhard Corporation in a reduced and stabilized form, a reduction always was carried out on the first day of experiments to ensure that the catalyst was fully reduced. The procedure was a combination of the method for the reduction of copper chromite catalysts suggested by Engelhard and the procedure outlined by Tronconi et al. (12). Details can be found in the fourth Semi-Annual Report (5).

- **Data Collection**

The gas leaving the reactor was analyzed by the on-line GC system. Details of this system are available in References 6, 8, and 9. Liquid samples were collected from the liquid reflux line after the reactor temperature reached 400°C. The final liquid was obtained by filtering the catalyst slurry after the experiment. The volume and weight of the final liquid were measured.

BET surface areas of fresh and spent catalysts were measured with a Flow Sorb II 2300 instrument. Metal elementary analyses were performed by Galbraith Laboratories.

b. Results and Discussion

i. Gas Product Analysis

- **Data Reproducibility**

In the fourth Semi-Annual Report (5), several possible explanations were advanced to account for the lack of data reproducibility that was previously observed during catalyst evaluation experiments. These explanations were: variable Gas/Liquid (G/L) separator temperature, intermittent slurry liquid make-up, on-line GC analysis system, and catalyst deactivation. During the last Semi-Annual Report (4), we speculated that intermittent slurry liquid addition may have been the major reason for the variable gas outlet compositions. We suggested making up the slurry liquid continuously to minimize this effect.

In the two catalyst evaluation experiments performed during this report period, the liquid was made up continuously. Even though some scatter still remained, satisfactory data reproducibility was achieved, under good G/L separator temperature control. Normally four gas injections were made at each set of operating conditions. The final data was obtained by averaging these four sets of data. However, abnormal data was deleted before taking the average.

Gas product analysis was carried out to compare CO conversion, methanol productivity, methanol majority and carbon selectivity for the different catalysts and operating conditions. A summary of average gas outlet composition is provided in the Appendix.

- **CO Conversion**

The CO conversion is defined as the total moles of CO reacted divided by the total moles of CO fed:

$$\text{CO Conversion} = \frac{\sum_i \text{Outlet Mole Fraction of Product } i * \text{Number of Carbons in Product } i}{\text{CO Inlet Mole Fraction}}$$

Table 2.1 and Figure 2.1 show the CO conversion for promoted and unpromoted catalyst under different operating conditions. The CO conversion increased regularly as the H₂/CO feed ratio increased from 0.5 to 2.0. However, neither the operating temperature nor the presence or absence of Cs had a significant influence on the CO conversion.

Table 2.1 CO Conversion-Comparison of Promoted and Unpromoted Zinc Chromite Catalysts

CO Conversion					
6 wt% Cs promoted Zn/Cr			Unpromoted Zn/Cr		
H ₂ /CO	375°C	400°C	H ₂ /CO	375°C	400°C
0.5	3.5	3.3	0.5	3.7	4.8
1	6.3	7.0	1	7.8	6.3
2	7.6	12.2	2	9.6	9.6

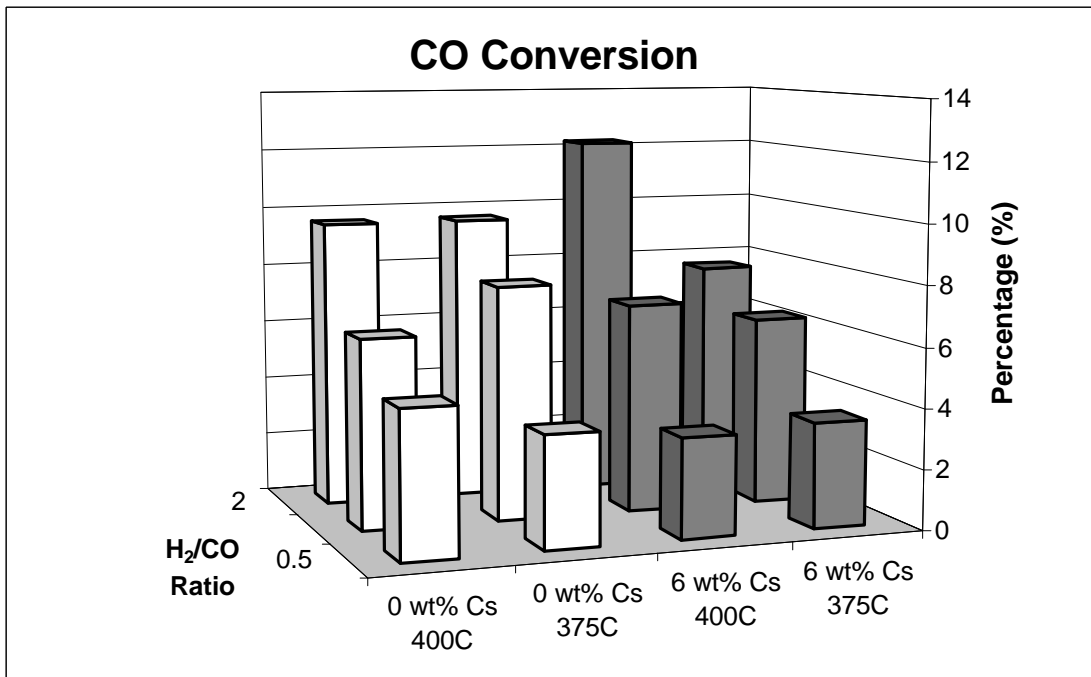


Figure 2.1: Carbon Monoxide Conversion for 6 wt.% Cs - promoted Zinc Chromite Catalyst and for Unpromoted Zinc Chromite Catalyst (T = 375°C and 400°C, GHSV = 5000 sl/kg(cat)hr, P = 2000 psig, DHN. The molar H₂/CO feed ratios are shown in the figure.)

Methanol Productivity

Methanol productivity is defined as:

$$\text{Methanol Productivity (gr./kg.(cat.)-hr.)} = \frac{\text{Rate of Methanol Production (gr./hr.)}}{\text{Weight of Catalyst (kg.)}}$$

The “Rate of Methanol Production” was calculated from the flow rate and the analysis of the outlet gas.

Table 2.2 shows a comparison of the performance of the 6 wt.% Cs - promoted catalyst with that of the unpromoted zinc chromite catalyst based on this parameter. Previous experimental data for the unpromoted catalyst and an equilibrium calculation also are shown in Table 2.2.

Table 2.2 Methanol Productivity - Comparison of Promoted and Unpromoted Zinc Chromite Catalysts

Methanol Productivity (g/Kg-cat/hr)						
	375°C			400°C		
Feed Ratio (H ₂ /CO)	0.5	1	2	0.5	1	2
6 wt% Cs promoted Zn/Cr	110	84	79	67	79	59
Unpromoted Zn/Cr (new)	128	210	130	143	130	126
Unpromoted Zn/Cr [1]	76	-	113	-	-	-
Equilibrium	197	338	410	107	184	220

The unpromoted catalyst has much higher methanol productivity than the promoted catalyst at all conditions. However, the equilibrium productivity was not achieved at the conditions evaluated. The new data for the unpromoted catalyst show a somewhat higher methanol productivity than the earlier data.

Unlike promoter concentration, which had a significant influence on methanol productivity, the operating conditions did not show a major effect.

- **Methanol Majority**

The Methanol Majority was defined as:

$$\text{Methanol Majority} = \frac{\text{Moles Methanol Production}}{\text{Moles of Total Alcohols Production}}$$

Table 2.3 shows a comparison of methanol majority for different catalysts and operating conditions. Unpromoted zinc chromite is almost exclusively a methanol synthesis catalyst. Methanol constitutes about 98% of the alcohols product. With the 6 wt.% Cs catalyst, methanol is still the major product, but there is a distinct shift from methanol to higher alcohols, especially at the higher temperature. On a preliminary basis, the highest higher alcohol fraction was achieved at a feed ratio of H₂/CO = 1.

Table 2.3 Methanol Majority - Comparison of Promoted and Unpromoted Zinc Chromite Catalysts

Methanol Majority					
6 wt% Cs promoted Zn/Cr			Unpromoted Zn/Cr		
H ₂ /CO	375°C	400°C	H ₂ /CO	375°C	400°C
0.5	0.94	0.89	0.5	0.99	0.99
1	0.84	0.82	1	0.99	0.97
2	0.93	0.86	2	0.98	0.98

- **Catalyst Selectivities to Oxygenates, Hydrocarbons and CO₂**

The carbon selectivity for a particular product is defined as the total number of carbons in that product divided by the total number of carbons in all of the products that are formed, i.e.:

Carbon Selectivity (Product A) =

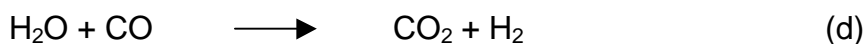
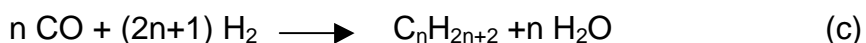
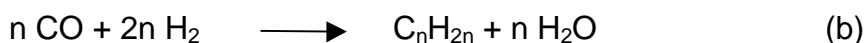
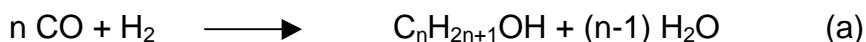
$$\frac{\text{Outlet Mole Fraction of Product A} \times \text{Number of Carbons in Product A}}{\sum_i \text{Outlet Mole Fraction of Product } i \times \text{Number of Carbons in Product } i}$$

Figures 2.2 and 2.3 show a comparison of carbon selectivity to total oxygenates, hydrocarbons and CO₂ for the two catalysts at 375°C and 400°C, respectively. For the unpromoted catalyst, oxygenates were the major component of the product stream at both temperatures. Hydrocarbon selectivity was relatively low. Neither selectivity showed a significant trend with either temperature or H₂/CO feed ratio.

For the Cs-promoted catalyst, the selectivity to oxygenates declined significantly as the H₂/CO ratio increased, at both temperatures. At a constant H₂/CO ratio, the oxygenates selectivity was lower at the higher temperature.

On balance, it appears that the main effect of the Cs promoters is to decrease oxygenate selectivity and increase the sensitivity of this parameter to the changes in operating conditions.

The CO₂ selectivity is directly related to the hydrocarbon and higher alcohol selectivities. When these products are formed, water is a by-product, as shown by Reactions a, b, and c below. This water forms CO₂ via the water gas shift (WGS) reaction, Reaction d.



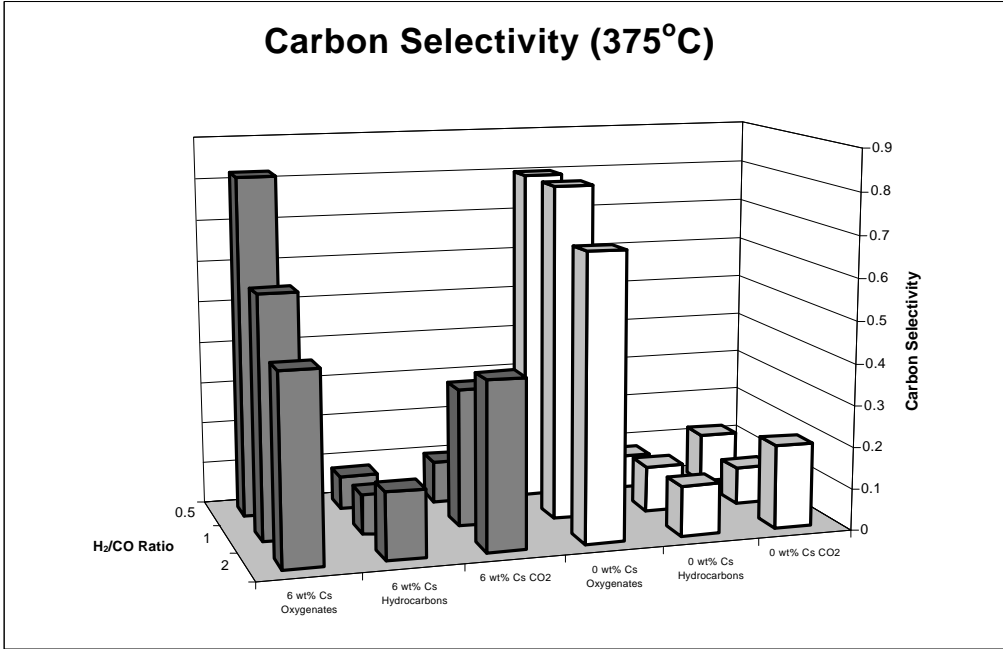


Figure 2.2: Carbon Selectivity 6 wt.% Cs - promoted Zinc Chromite Catalyst and for Unpromoted Zinc Chromite Catalyst (T = 375°C, GHSV = 5000 sl/kg(cat)hr, P = 2000 psig, DHN. The molar H₂/CO feed ratios are shown in the figure.)

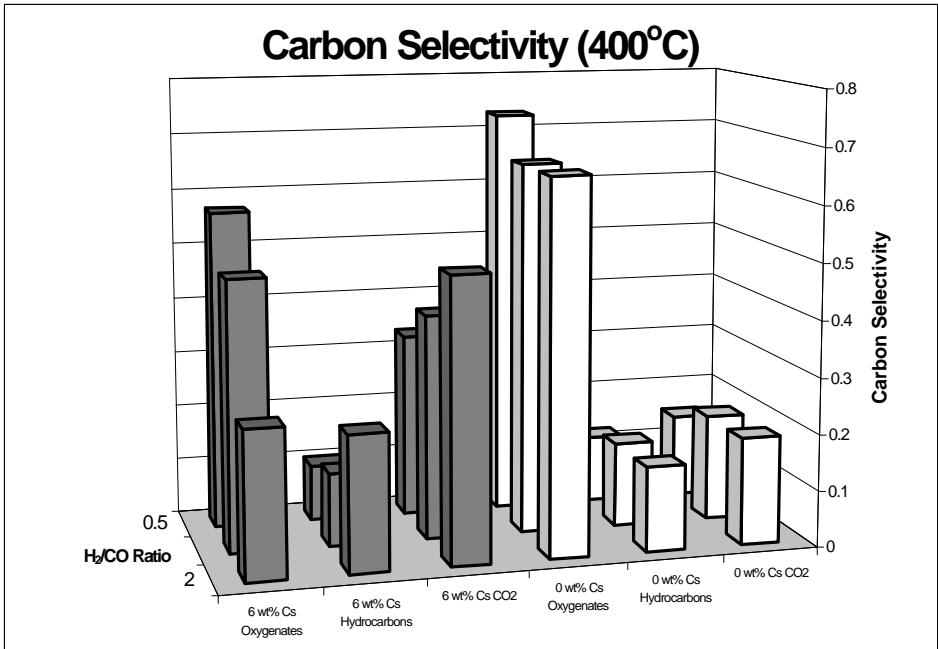


Figure 2.3: Carbon Selectivity for 6 wt.% Cs - promoted Zinc Chromite Catalyst and for Unpromoted Zinc Chromite Catalyst (T = 400°C, GHSV = 5000 sl/kg(cat)hr, P = 2000 psig, DHN. The molar H₂/CO feed ratios are shown in the figure.)

Table 2.4 shows the selectivity comparison for the promoted and unpromoted catalysts at the various temperatures and H₂/CO ratios.

Table 2.4: Total Oxygenates, Hydrocarbons and CO₂ Selectivities for Promoted and Unpromoted Zinc Chromite Catalysts

Carbon Selectivity						
6 wt% Cs promoted						
H ₂ /CO	375°C			400°C		
	Oxygenates	Hydrocarbons	CO ₂	Oxygenates	Hydrocarbons	CO ₂
0.5	0.82	0.080	0.10	0.57	0.10	0.33
1	0.58	0.094	0.33	0.48	0.13	0.40
2	0.45	0.16	0.40	0.26	0.24	0.50
Unpromoted						
H ₂ /CO	375°C			400°C		
	Oxygenates	Hydrocarbons	CO ₂	Oxygenates	Hydrocarbons	CO ₂
0.5	0.80	0.080	0.12	0.73	0.12	0.15
1	0.80	0.11	0.09	0.66	0.15	0.19
2	0.68	0.12	0.20	0.66	0.15	0.19

A detailed breakdown of the oxygenates, and a breakdown of the hydrocarbons into olefins and paraffins is shown in the Appendix.

ii. Liquid Analysis

The newly developed on-line GC analysis system is able to detect and quantify DHN. The system should also be able to detect and quantify any lower molecular weight compounds that might be formed by hydrocracking of DHN. The trans- and cis- DHN peaks were examined for every injected sample throughout the experiments described above. Based on the GC spectra, DHN did not appear to decompose during the experiments. Only trans- and cis- DHN peaks were detected.

Due to heavy use of the GC/MS in the Chemistry Department at North Carolina State University, the GC/MS analysis of the liquid samples obtained during this reporting period has not been carried out.

During the experiment with 6 wt.% Cs - promoted catalyst, fresh liquid was continuously made up at a constant rate of 1 ml/hr. Only about 10 ml liquid was found in the reactor after the experiment was shut down, which meant that the liquid makeup rate was lower than the liquid loss rate. Since the trans- and cis- DHN peak areas did not show a significant increase after the reactor operating temperature was increased from 375°C to 400°C, the evaporation rate of DHN did not appear to increase due to the higher temperature. Therefore, the makeup rate was not changed for the higher temperature. We adjusted the makeup rate in the second experiment to 1.1 ml/hr at 375°C, and to 2.0 ml/hr at 400°C. There was 130 ml of liquid left in the reactor after that experiment.

The liquid make-up rate for the next run will be 1.1 ml/hr at 375°C, and 1.5 ml/hr at 400°C. It is important to keep a constant liquid level in the reactor throughout the whole experiment. Too much or too little slurry liquid in the reactor may cause an undesirable situation, and therefore affect the measured catalyst activity.

iii. Catalyst Characterization

Catalyst recovered from the reactor was 8.65 gram (43%) for the first run (6 wt% Cs- promoted catalyst). Possibly due to the low liquid level in the reactor, the catalyst was distributed throughout the overhead system and liquid reflux line.

A total of 17.82 gram (89%) catalyst was recovered from the reactor for the second run. The overhead system, liquid reflux line, and filters were cleaned after each run.

Table 2.5 shows the measured BET surface areas of the fresh and spent catalysts. There was a relatively large surface area loss for the 6 wt.% Cs-promoted catalyst after the 12-day run. As noted previously, the 6 wt.% Cs-promoted catalyst was prepared without a final, high-temperature calcination, which might account for the larger surface area loss.

Table 2.5: Surface Areas of Fresh and Spent Catalysts

Fresh Zn/Cr (m ² /g)	Used Zn/Cr (m ² /g) (12-day run)	Fresh 6%Cs//Zn/Cr (m ² /g)	Used 6%Cs//Zn/Cr (m ² /g) (12-day run)
145	130	103	47

Metal elemental analysis was performed for the used 6 wt.% Cs-promoted catalyst. The Cs concentration was 5.79%. Iron was about 837 ppm. Nickel was less than 31 ppm.

iv. Charcoal Trap

The charcoal trap located immediately prior to the reactor was replaced before the last two experiments. Iron and nickel metal elemental analyses were performed on the spent charcoal, which has not been replaced for at least 3 years.

Table 2.6 shows the iron and nickel concentrations for several spent catalysts and the spent charcoal. The methanol synthesis run in March 1994 was carried out after the activated charcoal trap was installed (2). Compared with the September 1993 run performed before the charcoal trap installation, there was a marked decrease in metal deposition on the catalyst surface. The iron concentration dropped from 980 ppm to 364 ppm, and nickel concentration dropped from 527 ppm to 45 ppm. This proved that charcoal was effective for metal carbonyl removal. However, the iron concentration on the “spent” catalyst still was much higher than on the fresh catalyst (<100 ppm), and even on the

spent charcoal (100 ppm). Similar results were found for spent catalysts from the July 1999 and July 2000 runs.

According to Golden et al. (13), it is less likely for charcoal to reach its maximum adsorption capacity at such a low iron (100 ppm) and nickel (<36 ppm) concentrations. Therefore, another potential source for metal carbonyls was suspected to be the stainless steel reactor itself. Under the reactor conditions for these runs and based on the thermodynamic equilibrium of iron carbonyl formation, the reactor could have generated sufficient iron carbonyls to account for the iron present on the catalyst surface. A copper lined reactor would be the best option to ensure no iron carbonyl formation from the reactor. Experimental data did not show an obvious increase of methane productivity, even though spent catalysts contained such a high iron concentration. This is probably due to the low nickel concentration. This phenomenon further confirmed our suspicion that iron carbonyl was generated from reactor itself.

Table 2.6 Metal Elemental Analysis

Analyte	09/93 Spent Cu/ZnO (2)	03/94 Spent Cu/ZnO (2)	06/00 Spent Charcoal	07/99 Spent 3%Cs Zn/Cr	07/00 Spent 6%Cs Zn/Cr
Iron	980 ppm	364 ppm	110 ppm	1340 ppm	837 ppm
Nickel	527 ppm	45 ppm	<36 ppm	70 ppm	<31 ppm

c. Future Research

A new zinc chromite catalyst promoted with 3 wt.% Cs and prepared by the same method as the tested 6 wt.% Cs promoted catalyst will be evaluated under the same operating conditions.

A different slurry liquid, tetrahydroquinoline (THQ) will be evaluated as well. A detailed plan will be made after the 3 wt.% Cs-promoted catalyst evaluation. It is important to decide which catalyst will be the best choice to test the influence of THQ on HAS.

3. Analysis of Slurry Liquid

Substantial progress has been made on the analysis of “spent” THQ. We have used an array of analytical techniques, including silica gel liquid chromatography, HPLC, TLC, GC/MS, FTIR and NMR. It has been proved that the alkylated THQ in the “spent” THQ is composed of 1-methyl THQ, dimethyl THQ and tri-methyl THQ, with the N atom alkylated by one methyl group. These three compounds comprised more than 80% of the final liquid. A paper is being prepared based on this research. More details will be provided in the next Semi-Annual Report.

C. Conclusions

1. Zinc chromite catalyst promoted with 6 wt.% Cs has a greater higher alcohol selectivity than unpromoted zinc chromite catalyst. However, the methanol

productivity of the unpromoted catalyst is higher than that of the promoted catalyst, over the range of conditions tested.

2. With the 6 wt.% Cs-promoted zinc chromite catalyst, higher operating temperature caused more higher alcohol and more hydrocarbon formation. When the feed ratio of H₂/CO increased from 0.5 to 2, hydrocarbon selectivity increased at the expense of oxygenates selectivity. These trends were not obvious with the unpromoted zinc chromite catalyst.
3. With both catalysts, the CO conversion increased as the H₂/CO feed ratio was increased. However, the CO conversion was not affected significantly by either the presence or absence of promoter, or by the operating temperature.
4. "Spent" THQ analysis has been accomplished. A paper is being prepared.

D. References

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Appendix: Average Gas Outlet Composition (mol%) Obtained in Tests with Unpromoted and 6 wt.% Cs-promoted Catalyst:

With unpromoted Zn/Cr catalyst

Temperature	H ₂ /CO	H ₂	CO	CO ₂	Methanol	DME	Ethanol	1-Propanol	Isobutanol	Olefins	Paraffins	Total
375°C	0.5	29.4	66.7	0.30	1.79	0.093	0.0095	0.0083	0.0035	0.046	0.022	98.4
375°C	1.0	46.4	48.4	0.38	2.80	0.18	0.016	0.010	0.0025	0.11	0.046	98.3
375°C	2.0	66.1	30.6	0.66	1.82	0.14	0.022	0.013	0.0027	0.078	0.10	99.3
400°C	0.5	29.0	66.6	0.50	2.00	0.17	0.011	0.0089	0.0049	0.093	0.046	98.4
400°C	1.0	48.6	49.5	0.64	1.82	0.12	0.023	0.020	0.0064	0.11	0.12	100.6
400°C	2.0	66.8	31.0	0.62	1.76	0.15	0.018	0.014	0.0031	0.10	0.13	100.6

With 6 wt% Cs-promoted Zn/Cr catalyst

Temperature	H ₂ /CO	H ₂	CO	CO ₂	Methanol	DME	Ethanol	1-Propanol	Isobutanol	Olefins	Paraffins	Total
375°C	0.5	33.0	64.8	0.24	1.54	0.046	0.059	0.037	0.011	0.040	0.012	99.5
375°C	1.0	46.1	50.9	1.12	1.18	0.071	0.037	0.080	0.081	0.074	0.050	99.6
375°C	1.8	61.4	36.2	1.08	1.10	0.045	0.041	0.034	0.013	0.099	0.10	100.0
400°C	0.5	31.7	66.3	0.76	0.94	0.024	0.036	0.050	0.023	0.049	0.049	99.6
400°C	1.0	47.6	50.8	1.51	1.08	0.025	0.062	0.11	0.060	0.10	0.13	101.2
400°C	1.8	62.2	35.4	2.43	0.82	0.034	0.049	0.068	0.028	0.24	0.34	100.4