2

DOE/PC/90043--T12 D-4

NOVEL APPROACHES TO THE PRODUCTION OF HIGHER
ALCOHOLS FROM SYNTHESIS GAS

Quarterly Technical Progress Report No. 11

For The Period April 1, 1993 to June 30, 1993

Contractor

NORTH CAROLINA STATE UNIVERSITY
DEPARTMENT OF CHEMICAL ENGINEERING
BOX 7905
RALEIGH, NC 27695-7905

George W. Roberts - Program Manager
Shirley Kow - Contract Coordinator

George W. Roberts

November 22, 1993

Prepared for the United States Department of Energy
Under Contract No. DE-AC22-90PC90043
Contract Period 25 September 1990 - 24 September 1993

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

175

DISCLAIMER

This report was prepared as an account of work sponsored by the United States Government. Neither the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed or represents that its use would not infringe privately owned rights.

NOVEL APPROACHES TO THE PRODUCTION OF HIGHER ALCOHOLS FROM SYNTHESIS GAS

Quarterly Technical Progress Report
April 1, 1993 to June 30, 1993

CONTRACT OBJECTIVES

- Task 1. Program Management.
- Task 2. Liquid-Phase, Higher Alcohol Process with Recycle of Lower Alcohols.
- Task 3. Novel Catalysts for Synthesis of Higher Alcohols.
- Task 4. Synthesis of Higher Alcohols via Acid-Base Catalysis.
- Task 5. Technology Evaluation.

SUMMARY

A set of four methanol synthesis runs was conducted. Significant catalyst deactivation was experienced, and essentially all of the oil was lost from the reactor over the course of two weeks of operation. Three screening runs of a potential high temperature oil were also conducted. However, essentially no oil remained in the reactor after completion of each run.

A 1% Rh/1.3%Re/Al₂O₃ catalyst was prepared from Re and Rh carbonyls with the objective of obtaining intimate contact between Rh and Re atoms. The CO hydrogenation activity of this catalyst was much lower than that of a 1%Rh/12%Re/Al₂O₃ catalyst derived from a Re salt. However, the total oxygenate selectivity of the cluster-derived catalyst was in excess of 60%.

Molybdenum (Mo) promoted Rh/Al₂O₃ catalysts are known⁽¹⁾ to give high oxygenate carbon efficiency in the CO hydrogenation reaction. In the work carried out this quarter, Mo was deposited on the catalyst from both molybdenum hexacarbonyl [Mo(CO)₆] and (NH₄)₆Mo₇O₂₄·4H₂O. The two catalysts (0.05%Mo/1%Rh/Al₂O₃ and 0.6% Mo/1%Rh/Al₂O₃) derived from the Mo cluster compound, Mo(CO)₆, had much higher oxygenate selectivities, over 60%, than the two catalysts derived from the salt, which had

oxygenate selectivities in the range of 25 to 35%. The activity of the cluster-derived catalysts was about half of the activity of the salt-derived catalysts.

The oxygenate selectivities of the 1%Rh/1.3%Re/Al₂O₃, 0.05%Mo/1%Rh/Al₂O₃ and 0.6%Mo/1%Rh/Al₂O₃ catalysts are the highest achieved to date under this contract. The activity of the two Mo catalysts is three to four times that of the Re catalyst.

TECHNICAL PROGRESS

- Task 2:

Methanol Synthesis Verification Runs

Four methanol synthesis verification runs were conducted with the commercial BASF S3-86 Cu/ZnO catalyst under the process conditions shown in Table 1. The feed gas contained 35% H₂, 51% CO, and 14% CO₂, typical of a Texaco coal gasifier exit gas.

Table 1
Process Conditions for the Methanol Synthesis Verification Runs

Run	Pressure (psig)	Reactor Temp. (°C)	GHSV (sl/kg cat - hr)
1	750	250	5000
2	750	250	10000
3	2550	250	16500
4	750	250	5000

The reactor was not shut down between each run. Instead, process conditions were changed and a new steady state was achieved. Run 4 was a repeat of Run 1 to detect any catalyst deactivation that might have occurred.

Results

The major problem encountered during these runs was loss of mineral oil; no oil was present in the reactor after shutting down. However, the liquid return line from the gas/liquid separator was plugged with a waxy material, and the separator itself contained some waxes. Apparently, sometime during the run (the data does not clearly indicate when), the liquid return line plugged, preventing oil recycle. Based on vapor pressure calculations, there was sufficient time for vaporization of all the oil from the reactor during the run. The oil may have collected in the gas/liquid separator, and then "distilled" overhead, leaving behind the waxy residue. Aggravating the situation was the fact that the thermocouples in the overhead system were reading as much as 200°C low, so that the actual temperatures in the condensor and gas/liquid separator were too high to

permit significant oil condensation. This situation will be discussed later, in the section on the oil screening runs. All of the catalyst was present in the reactor after run completion, indicating that a sudden "burp" of slurry from the reactor was not a likely cause of oil loss. The mineral oil probably left the reactor gradually, consistent with simple vaporization due to high temperatures in the overhead system and plugging of the liquid return line.

The data from these runs cannot be used as verification of the operation of the reactor since the slurry concentration was not constant throughout the run. Also, the vaporized mineral oil apparently condensed in the gas chromatograph lines and eventually in the columns, yielding poor analyses, especially with respect to differentiation of the alcohol products. However, some of the data can be used as a general indication of reactor behavior.

Catalyst Poisoning

As shown in Table 2, Inductive Coupled Plasma (ICP) analysis of the "spent" catalyst, sampled at the end of the run, revealed high levels of metal contaminants in the spent catalyst as compared with fresh catalyst. The 2280 ppm level of iron (Fe) on the spent catalyst from this run is higher than the 1550 ppm Fe present on the spent catalyst from the December, 1992 run. This suggests that carbonyl formation is still a significant problem, and the reactor carbonyl trap installed for this run did not perform as expected. ICP analysis of the alumina pellets inside the carbonyl trap showed no increase in iron content relative to fresh pellets, further illustrating the ineffectiveness of the carbonyl trap.

Table 2
ICP Analysis of the BASF S3-86 Cu/ZnO Methanol Synthesis Catalyst
from the April, 1993 Run

Component	Fresh Catalyst	Spent Catalyst
Iron	19 ppm	2280 ppm
Nickel	37 ppm	149 ppm
Chromium	1.6 ppm	65 ppm
Copper	71%	76%
Zinc	25%	22%
Aluminum	4%	2%

Further support for the hypothesis of catalyst poisoning is provided by CO conversion data from Runs #1 and #4, shown in Figure 1. Note the large decrease in CO conversion between the two runs. These two runs were conducted at the same process conditions except, as mentioned earlier, most of the mineral oil probably had disappeared by the time Run #4 was carried out. Some of the decrease in conversion between Run #1 and Run #4 may be due to the oil loss, but most is probably attributable to catalyst deactivation through poisoning. Note also the steady downward trend in CO conversion for all the runs.

Figure 1
CO Conversion Data for Methanol Synthesis Runs

The initial (short time) CO conversions shown in Figure 1 are much greater than the equilibrium conversions calculated for the methanol synthesis reaction at these operating conditions. In some cases, the conversion exceeded the stoichiometric maximum based on the amount of H_2 available. However, at longer times, the calculated CO conversion was negative. This suggests inaccurate analytical data, as noted earlier.

High Temperature Mineral Oil Screening

Three high temperature runs were conducted in the stirred autoclave to test the compatibility and stability of the Drakeol® 34 mineral oil for alcohol synthesis purposes. No catalyst was present in the reactor. All three runs had the same result: < 5 mL oil was present in the reactor upon shutdown. However, in all cases, plausible explanations for the oil disappearance are available. A summary of each run in chronological order is provided below, along with the process modifications made to correct the perceived cause of the oil disappearance.

Oil Screening Test #2

The process modifications made prior to this run, after the last screening run (Oil Screening Test #1) in November, 1992, included:

- The mineral oil condensing/recycle loop (overhead system) was redesigned, as outlined in the previous Quarterly Report.
- The liquid return line from the gas/liquid separator to the reactor was heat traced.

Table 3
Conditions for Oil Screening Test 2

REACTOR CONDITIONS					
DATE	Press (psig)	Temp (°C)	Slurry	Oil Left (mL)	GAS FEED
5/11 - 5/14	1000	250, ramp to 400 over 3 days	175 mL Drakeol 34; no catalyst	< 5 mL	H ₂ /CO = 1; 1650 sccm each

Results/Explanations

- No significant oil remained in the reactor at the end of the run.
- The liquid return line from the gas/liquid separator was not plugged with wax, as in the previous methanol synthesis run, nor did the gas/liquid separator itself contain any oil or waxes.

- Some carbon was present on the reactor surfaces and in the reactor exit lines, but there was significantly less carbon than in the previous run .

Results of ICP analysis of the carbon collected at the end of Oil Screening Test #2 are shown in Table 4. Concentrations from the previous oil screening run are shown for comparison. The metal contamination is reasonably similar in both cases, indicating carbonyl formation is still a significant problem. The most recent carbon analysis suggests that the reactor carbonyl trap was not performing as expected.

Table 4
Metal Contamination in Carbon from Oil Screening Runs

Component	11/92	5/93
Iron	22400 ppm	31900 ppm
Nickel	4240 ppm	5160 ppm

Based on heat transfer calculations performed on the thermowells for the internal thermocouples in the overhead system, the gas inlet and outlet thermocouples (T/C's) in the gas/liquid separator could have been reading as much as 200° C lower than the actual gas temperature. The discrepancy is due to the thermowells acting as "cooling fins", allowing heat transfer to the atmosphere . Also, the T/C at the outlet of the gas/liquid separator was not in contact with the end of the thermowell, aggravating the problem further. Since the outlet temperature from the gas/liquid separator was controlled at 130°C, and so in actuality was about 300°C, the oil probably never condensed in the gas/liquid separator, accounting for the oil loss.

Oil Screening Test #3

The equipment modifications made prior to this run included:

- All internal thermowells were eliminated; only the bare thermocouple sheath was inserted.
- The liquid drain line from the gas/liquid separator was enlarged from 1/8" diameter to 1/4" diameter. This accommodates the anticipated oil return rate of 3 mL/min with minimal pressure drop, and discourages plugging as experienced in earlier runs.

As shown in Table 5, only H₂ was fed in order to determine whether previous experience with carbon formation during high temperature runs was due to CO disproportionation or mineral oil decomposition. No carbon was found at the end of the run, so the carbon formed in previous runs probably originated from CO disproportionation, not mineral oil decomposition.

Table 5
Conditions for Oil Screening Test 3

DATES	REACTOR CONDITIONS				
	Press (psig)	Temp (°C)	Slurry	Oil Left (mL)	GAS FEED
6/13 - 6/17	1000	250 ramp to 400 over 3 days	175 mL Drakeol 34; no catalyst	< 5 mL	H ₂ only, 3300 sccm

Results/Explanations

- No process lines were plugged, so the liquid drain line enlargement apparently succeeded.
- The internal thermocouples were not centered in the tube, and contacted the tube wall, again probably giving a gas temperature reading that was lower than actual.
- No oil remained in the reactor.

Again, the oil probably did not condense or collect in the gas/liquid separator due to thermocouple inaccuracies i.e., high overhead system temperatures, and the lack of "mist" collection apparatus (like steel wool) in the separator. Also, if the pressure drop in the gas line between the reactor and the gas/liquid separator exceeded 1 psi, then the liquid drain line from the separator to the reactor would be the preferred gas flow route, allowing bypassing of the cooling loop and not allowing oil condensation.

Oil Screening Test #4

Based on the above explanations for the oil disappearance, the equipment modifications made prior to this run included:

- Steel wool was installed in the gas/liquid separator to trap oil mist.

- A check valve was added on the liquid drain from the gas/liquid separator to permit flow only from the separator to the reactor, i.e., to prevent gas flow up through the liquid drain line.
- The tips of all internal thermocouples were coated with cement to center them in the tube.
- Traps submerged in liquid N₂ were added after the wet test meter to capture any mineral oil in the exiting gas stream.

Table 6
Conditions for Oil Screening Test 4

REACTOR CONDITIONS					
DATE	Press (psig)	Temp (°C)	Slurry	Oil Left (mL)	GAS FEED
6/28 - 6/30	1000	400 (no ramping)	175 mL Drakeol 34; no catalyst	< 5 mL	H ₂ only, 3300 sccm

Results/Explanation

- No oil remained in the reactor.
- The check valve was wet with oil and not plugged, suggesting that oil did flow through the valve at some point during the run.
- The gas/liquid separator was wet with oil, but no significant amount was present at the end of the run.
- Some mist or vapor was observed leaking from the NPT fittings in the 400°C portion of the overhead system. Based on oil vaporization calculations, a gas leak of only 3% of the total flow is required in the 400°C portion of the overhead system to account for the entire oil loss.
- Less than 1 mL of oil was captured in the liquid N₂ traps.

Thermodynamics of Higher Alcohol Synthesis

A paper describing the thermodynamics of higher alcohol formation from synthesis gas was published during the quarter in the American Chemical Society's journal *Energy & Fuels*. A copy of the paper is in Appendix A.

- **Task 3:**

A. Niobium Promoted Rh/Al₂O₃ Catalysts

Results of Extended X-Ray Absorption Fine Structure (EXAFS) analysis of Rh and Nb edges on 1 wt.% Rh/Nb/Al₂O₃ catalysts containing various niobium levels are summarized in Table 7. The preparation procedure and the reaction results for these catalysts were previously reported in the October-December, 1992 Quarterly Report.

On "as synthesized" 1%Rh/Nb/Al₂O₃ samples, Rh had between 2 and 3 Rh next nearest neighbors. The Rh-Rh coordination number decreased from 2.7 to 2.2 with increasing Nb concentration. Upon heating these catalysts in 50 cc/min He at 200°C for 1 hr, the Rh-Rh coordination number increased to between 4 and 5, indicating agglomeration of Rh atoms. Further heating of the 1%Rh/Al₂O₃ catalyst at 250°C for 1 hr in 50 cc/min of 1:1 H₂:CO mixture increased the Rh-Rh coordination number to 5.6.

The Rh-C/O coordination number of the heated samples was approximately 1. The measured Rh-C/O bond distance was between 1.90 and 1.95, between the Rh-O bond distance of 2.05 and the Rh-C bond distance of 1.85. This result suggests that carbon, possibly resulting from disproportionation of CO in the Rh₄(CO)₁₂, may be present on the catalyst surface.

EXAFS of Nb edges showed that Nb did not have either Rh or Nb next nearest neighbors. These observations are consistent with our Rh/Nb/Al₂O₃ catalyst model, where Al₂O₃ is covered by NbO_x patches on which the Rh clusters reside.

Table 7

***Cluster Configuration and Geometry by EXAFS Spectroscopy on
Nb Promoted Rh/Al₂O₃ catalysts***

Catalyst	Rh-Rh		Rh-C/O	
	N*	R*	N*	R*
1%Rh/Al ₂ O ₃ :				
as synthesized	2.7	2.74		
200°C, He, 1hr	4.3	2.67	1.16	1.94
250°C, 1:1H ₂ :CO, 1hr	5.6	2.71	0.87	1.90
1%Rh/3%Nb/Al ₂ O ₃ :				
as synthesized	2.6	2.74		
200°C, He, 1hr	4.2	2.67	1.7	1.95
1%Rh/6%Nb/Al ₂ O ₃ :				
as synthesized	2.2	2.77		
200°C, He, 1hr	4.8	2.67	1.2	1.94
1%Rh/9%Nb/Al ₂ O ₃ :	2.2	2.76		

*N : coordination number; R : bond distance

B. Rhenium Promoted Rh/Al₂O₃ Catalysts

MI-307 gamma-alumina (170m²/g surface area) obtained from the W. R. Grace Company was used as a catalyst support. Five g of Al₂O₃ was heated to 500°C for 4 hr in 50 cc/min of oxygen, evacuated for 1 hr and stored in a dry, oxygen-free environment.

About 2 wt. % Re was adsorbed on 5 g alumina using 0.179 g Re₂(CO)₁₀ dissolved in 75 cc hexane that had been dried by refluxing over a sodium-benzophenone mixture. The alumina support was stirred in this solution for 1 hr. The support was filtered and washed with fresh, dry hexane. The amount of Re adsorbed was determined to be 1.3 wt.% using Fourier Transform Infrared Spectroscopy (FTIR), as the difference between the intensity of the CO bands of the initial and final [Re₂(CO)₁₀]/hexane solutions.

The FTIR spectra of Re₂(CO)₁₀ adsorbed on Al₂O₃ and then heated to different temperatures are shown in Figure 2. At low temperatures, up to about 125°C, four CO bands at 2076, 2019, 1980, and 1923 cm⁻¹ wavenumbers are discernable. At higher temperatures, bands are observed at 2028 and 1924 cm⁻¹, with possibly a very weak peak at 1862 cm⁻¹. We speculate that these bands are associated with the specie [Re(CO)₃{OAl}{HOAl₂}] based on the following analogy. In earlier, published studies based on EXAFS and FTIR evidence, i.e., CO bands at 2028, 1924, and 1862 cm⁻¹ wavenumber, the structure of Re clusters on MgO after heating in hydrogen at 80°C was formulated as [Re(CO)₃{OMg}{HOMg₂}]^(2,3,4). Therefore, we speculate that [Re(CO)₃{OAl}{HOAl₂}] was formed by heating Re₂(CO)₁₀ adsorbed on Al₂O₃ in helium at 150°C. Based on Figure 2, this structure is stable in He up to 250°C. However, heating in 50cc/min O₂ above about 225°C removed all carbonyls, as shown in Figure 3.

Rh was deposited on the 1.3%Re/Al₂O₃ support using [Rh₄(CO)₁₂] dissolved in hexane which had been dried by refluxing over a sodium-benzophenone mixture. Five grams of the 1.3%Re/Al₂O₃ support was heated in vacuum at 150°C for 1 hr. to form the structure that we have hypothesized to be [Re(CO)₃{OAl}{HOAl₂}]. The support was stirred for 1 hr. in 0.093 g [Rh₄(CO)₁₂] dissolved in 75 cc of hexane. The slurry was filtered and washed with fresh, dry hexane. The amount of Rh adsorbed was determined to be 1 weight % from the difference between the FTIR intensities of the CO bands of the initial and final [Rh₄(CO)₁₂]/hexane solutions.

Figure 2
FTIR Spectra of 1.3% Re/Al₂O₃ Derived from Re₂(CO)₁₀
At Various Temperatures

Figure 3:
FTIR Spectra of 1.3%Re/Al₂O₃ After Heating in Oxygen
At Various Temperatures

Wave Number
(cm⁻¹)

The FTIR spectra of 1%Rh/1.3%Re/Al₂O₃ at different temperatures are shown in Figure 4. Up to 100°C, six CO bands, at 2096, 2062, 2034, 1924, 1862 and 1832 cm⁻¹ wave numbers, are evident. The bands at 2096 and 2034 are attributed to Rh-gem dicarbonyl, with a Re band at 2028 probably reinforcing the Rh-CO band at 2034 cm⁻¹. The band at 2062 cm⁻¹ results from the linear Rh-CO species and the band at 1832 cm⁻¹ is attributable to the bridged Rh-CO complex. The bands at 1924 and 1862 cm⁻¹ result from the presumed [Re(CO)₃{OAl}{HOAl}₂].

At 100°C, the linear and bridged Rh-CO species have disappeared, leaving the Rh-gem-dicarbonyl species and the [Re(CO)₃{OAl}{HOAl}₂] species. The CO bands due to Rh-gem-dicarbonyl decrease in intensity with a further increase in temperature and are gone completely at 250°C. However, the intensity of the CO bands due to [Re(CO)₃{OAl}₂] did not change up to 250°C.

By way of contrast, CO was completely removed from Rh₄(CO)₁₂/Al₂O₃ (1 wt. % Rh) at 200°C. Therefore, the presence of Re appears to stabilize adsorbed rhodium carbonyls, indicating interaction between Rh and Re clusters.

The catalyst 1%Rh/1.3%Re/Al₂O₃ was heated at 250°C in 50 cc/min He for 1 hr. and then was cooled to 50°C, after which it was exposed to CO at 100 torr. The FTIR spectra of adsorbed CO at different temperatures are shown in Figure 5. The spectra at lower temperature suggest contributions from both Rh-gem-dicarbonyl and (Re(CO)₃{OAl}{HOAl}₂). At 200°C, most of the CO had desorbed from Rh, but the Re-CO bands were hardly diminished relative to their low-temperature values.

The results of catalyst testing are shown in Table 8. The CO conversion was 0.11% for the sequentially-impregnated 1%Rh/1.3%Re/Al₂O₃ catalyst. The C₁ oxygenate carbon efficiency was 48% and the C₂⁺ oxygenate carbon efficiency was 14%, giving a total oxygenate efficiency of 62%. The methane selectivity for this catalyst was only 22%.

The performance of the 1%Rh/1.3%Re/Al₂O₃ catalyst is compared with that of two earlier Rh/Re/Al₂O₃ catalysts in Table 8. The oxygenate carbon efficiency was much lower on the 1%Rh/1.5%Re/Al₂O₃ catalyst prepared by co-adsorption of [Rh₄(CO)₁₂] and [Re₂(CO)₁₀], perhaps due to insufficient interaction between Rh and Re clusters. The CO conversion, however, was significantly higher for the co-impregnated catalyst.

Figure 4
FTIR Spectra of 1%Rh/1.3%Re/Al₂O₃

Figure 5
FTIR Spectra of CO Adsorbed on 1%Rh/1.3%Re/Al₂O₃ as a
Function of Temperature

Table 8
Activity and Selectivity of 1%Rh/Re/Al₂O₃ Catalysts
Derived from Re₂(CO)₁₀

Catalyst		Yield, based on carbon efficiency				alcohol to aldehyde ratio
	Conversion	<u>Hydrocarbons</u>		<u>Oxygenates</u>		
No. Composition	% CO	C ₁	C ₂ ⁺	C ₁	C ₂ ⁺	
1. 1%Rh/1.5%Re/Al ₂ O ₃ (co-adsorption); reaction at 200°C						
	0.25	49	13	26	12	2.1
2. 1%Rh/1.3%Re/Al ₂ O ₃ (sequential adsorption); reaction at 200°C						
	0.11	22	16	48	14	1.9
2a. Catalyst 2 after 250°C for 1 hr. in He, reaction at 250°C						
	1.0	52	14	18	16	1.7
3. 1%Rh/12%Re/Al ₂ O ₃ (impregnation with NH ₄ ReO ₄ followed by adsorption of Rh ₄ (CO) ₁₂); reaction at 200°C						
	0.6	23	25	35	18	2.1

Note: The results for catalysts 1 and 3 were reported previously in the Monthly Report for February 1, 1993 to February 28, 1993 and in the Quarterly Report for January 1, 1993 to March 31, 1993.

The total oxygenate selectivity of the catalyst derived from the Re salt, NH_4ReO_4 , was somewhat lower than that of the $\text{Rh}/1.3\%\text{Re}/\text{Al}_2\text{O}_3$ catalyst, 53% versus 62%, but the activity of the salt-derived catalyst was much higher. The alcohol-to-aldehyde ratio was similar for all three catalysts.

C. Molybdenum Promoted Rh/Al₂O₃ Catalysts

$\text{Rh}/\text{Mo}/\text{Al}_2\text{O}_3$ catalysts were also studied. To obtain the Mo promoter in a lower oxidation state, Mo was deposited from $\text{Mo}(\text{CO})_6$ instead of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}^{(1)}$, which is traditionally used. For catalysts derived from ammonium heptamolybdate, the desired structure was patches of polymeric MoO_3 (MoO_x) on alumina, surrounding the Rh clusters attached to alumina. For the catalysts prepared from molybdenum hexacarbonyl, intimate contact between Mo and Rh was desired. Most of the Mo was expected to attach to alumina in the vicinity of Rh clusters, with a small fraction of Mo forming a Rh-Mo alloy.

Catalyst Preparation

The four $\text{Rh}/\text{Mo}/\text{Al}_2\text{O}_3$ catalysts used in this work are listed in Table 9. Aluminum oxide-C (gamma-alumina with $100\text{m}^2/\text{g}$ surface area) from Degussa Corporation was used as a catalyst support. A thick slurry of 5 g alumina in distilled water was heated at 70°C for 12 hr. The powder was ground and an aliquot of size range 90-250 micron was selected.

Catalysts 1 and 2 in Table 9, containing 5.5 and 11 wt.% Mo respectively, were prepared by impregnation of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ using the incipient wetness technique. According to the results of Wachs et al.(5), 11 wt.% Mo gives a monolayer coverage on $100\text{ m}^2/\text{g}$ Al_2O_3 . Hence 5.5% Mo corresponds to about half a monolayer. The supports: Al_2O_3 , 5.5% $\text{Mo}/\text{Al}_2\text{O}_3$ and 11% $\text{Mo}/\text{Al}_2\text{O}_3$, were dried at 70°C for 12 hr, calcined at 500°C for 4 hr in 50 cc/min of oxygen and evacuated for 1 hr. During calcination, some MoO_3 desorbed from the catalysts as evidenced by white deposits at the exit of the calcination tube. After calcination, the supports were transferred to a dry, oxygen-free environment.

Table 9
Activity and Selectivity of Rh/Mo/Al₂O₃ Catalysts

Catalyst	Conversion	Yield, based on carbon efficiency				alcohol to aldehyde ratio
		Hydrocarbons		Oxygenates		
No. Composition	% CO	C ₁	C ₂ ⁺	C ₁	C ₂ ⁺	
1a 0.96%Rh/5.5%Mo/Al ₂ O ₃	0.52	44	29	12	15	1.3
1b 0.96%Rh/5.5%Mo/Al ₂ O ₃ reaction at 250°C	4.4	54	30	6	10	0.68
2a 0.91%Rh/11%Mo/Al ₂ O ₃	0.88	39	26	16	19	0.3
2b 0.91%Rh/11%Mo/Al ₂ O ₃ reaction at 250°C	7.3	53	28	9	10	0.19
3a 0.05%Mo/1%Rh/Al ₂ O ₃	0.38	28	11	35	26	2.2
3b 0.05%Mo/1%Rh/Al ₂ O ₃ reaction at 250°C	3.5	53	11	12	25	1.5
4a 0.6%Mo/1%Rh/Al ₂ O ₃	0.47	27	11	36	26	2.7
4b 0.6%Mo/1%Rh/Al ₂ O ₃ reaction at 250°C	4.3	54	11	11	24	1.6
4c 0.6%Mo/1%Rh/Al ₂ O ₃ pretreatment: pressurize in syngas and heat to reaction temperature of 200°C	0.29	53	17	21	9	1.9
4d 0.6%Mo/1%Rh/Al ₂ O ₃ pretreatment: pressurize in syngas and heat to reaction temperature of 250°C	2.1	54	21	9	16	1.3
4e 0.6%Mo/1%Rh/Al ₂ O ₃ pretreatment: pressurize in syngas and heat to reaction temperature of 300°C	13.3	75	13	4	8	0.5
4f 0.6%Mo/1%Rh/Al ₂ O ₃ pretreatment: pressurize at 18 atm in syngas and heat to reaction temperature of 250°C	1.1	60	19	3	19	0.8

Roughly 1% Rh was adsorbed onto the support using 5 g of support and 0.092 g $[\text{Rh}_4(\text{CO})_{12}]$ dissolved in 75 cc hexane that had been dried by refluxing over a sodium-benzophenone mixture. The support was stirred in $[\text{Rh}_4(\text{CO})_{12}]$ /hexane solution for 1 hr. The slurry was filtered and washed with fresh, dry hexane. The amount of Rh adsorbed was determined using FTIR, as the difference between the intensity of the CO bands of the initial and final $[\text{Rh}_4(\text{CO})_{12}]$ /hexane solutions. Thus, catalysts consisting of 1%Rh/ Al_2O_3 , 0.96%Rh/5.5%Mo/ Al_2O_3 , and 0.91%Rh/11%Mo/ Al_2O_3 were synthesized.

Catalysts 3 and 4, consisting of 0.05%Mo/1%Rh/ Al_2O_3 and 0.6%Mo/1%Rh/ Al_2O_3 respectively, were prepared by adsorbing $\text{Mo}(\text{CO})_6$ on 1%Rh/ Al_2O_3 . In the preparation of Catalyst 3, 1%Rh/ Al_2O_3 was heated to 200°C in 10^{-6} torr vacuum for 1 hr and then exposed to 100 torr H_2 for 30 min. The catalyst was then cooled to 50°C and exposed to an amount of $\text{Mo}(\text{CO})_6$ equivalent to 1% Mo at 30°C for 30 min. The rest of the apparatus was maintained at 70°C. The catalyst was then evacuated at 50°C and stored under a dry, oxygen-free environment. The Mo uptake measured by Auger spectroscopy was 0.05 wt. %. Catalyst 4 was prepared following a similar procedure. However, the $\text{Mo}(\text{CO})_6$ was slowly heated such that all of it vaporized and was adsorbed by the catalyst. Mo uptake was estimated to be 0.6 wt. %.

Reaction Results

In a typical reaction study, the catalysts were pretreated by heating in 50 cc/min of He at 200°C for 1 hr. The CO hydrogenation reaction i.e., the synthesis of higher alcohols from CO and H_2 , was carried out at 200°C, 30 atm, 2:1 H_2 :CO, 75 cc/min gas flow rate, 0.5 g catalyst and 9000 1/kg/hr GHSV. The results are listed in Table 9. Any changes in the pretreatment procedure or the reaction conditions are listed in the table.

Catalysts promoted by cluster-derived Mo showed higher oxygenate selectivity than those derived from Mo salts. The 0.6%Mo/1%Rh/ Al_2O_3 catalyst gave 36% C_1 oxygenate carbon efficiency and 26% C_2^+ oxygenate carbon efficiency at 200°C. Syngas conversion activity and oxygenate selectivity were comparable on 0.6%Mo/1%Rh/ Al_2O_3 and 0.05%Mo/1%Rh/ Al_2O_3 catalysts, indicating that only a small amount of Mo, intimately associated with Rh, is necessary as a promoter.

The oxygenate selectivity was lower on the catalysts promoted by Mo derived from salts. However, the CO conversion increased as the Mo loading approached monolayer

coverage. The highest conversion at standard conditions, 0.88%, was given by a catalyst with 11% Mo, which is equivalent to a monolayer coverage.

The effect of operating conditions was also studied on the 0.6%Mo/1%Rh/Al₂O₃ catalyst. When this catalyst was directly activated in syngas, the conversion and oxygenate selectivity decreased. A change in pressure from 30 atm to 18 atm had little effect on oxygenate selectivity, but the syngas conversion decreased. The oxygenate selectivity decreased sharply on all the catalysts as the temperature was increased from 200 to 250°C, mainly because of the increase in CH₄ carbon efficiency.

The alcohol to aldehyde ratio increased concurrently with the increase in oxygenate carbon efficiency, suggesting that CO insertion may be a rate determining step on Rh/Mo/Al₂O₃ catalysts.

References

1. Bhore N. A., Sudhakar C., Bischoff K. B., Manogue W. H., Mills G. A., Proceedings of the 9th International Congress on Catalysis, Phillips M. J. et al. eds., Vol.2, pp. 594-602, 1988.
2. Kirlin P. S., DeThomas F. A., Bailey J. W., Gold H.S., Dybowski C., Gates B.C., J. Phys. Chem., Vol. 90, p. 4882, 1986.
3. Kirlin P. S., Van Zon F. B. M., Koninsberger D. C., Gates B. C., J. Phys. Chem., vol. 94, p. 8439, 1990.
4. Chang J. R., Gron L. U., Honji A., Sanchez K. M., Gates B. C., J. Phys. Chem., Vol. 95, p. 944, 1991.
5. Vuurman M. A., Wachs I. E., J. Phys. Chem., Vol. 96, pp. 5008-5016, 1992.

Appendix A
A Reprint of "Thermodynamics of Higher Alcohol Synthesis" from *Energy and Fuels*.

DATE

FILMED

3 / 22 / 94

END

10

10