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**DESIGN OF A HIGH ACTIVITY AND
SELECTIVITY ALCOHOL CATALYST**

Final Status Report and Summary of Accomplishments

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Re: Grant No. DE-FG22-90PC90291
U of d No. 3-7-21-3119-12
Principal Investigator: Dr. Henry C. Foley

Dear Ms. Lebetz:

Enclosed please find the original final technical report for the above referenced grant for Dr. Henry C. Foley, Principal Investigator.

If you should have any further questions, please contact me at (302) 831-2060.

Sincerely,

Malinda Yarnell
Accountant

cc: Dr. Henry C. Foley
Principal Investigator

Susan Tkachick
Sponsored Programs Administration, UOD

Report Overview

This final DOE report for grant award number DE-FG22-90PC 90291 presents the results of our efforts to better understand the Rh-Mo/ γ -Al₂O₃ catalytic system for the hydrogenation of carbon monoxide and carbon dioxide to selectively form oxygenated products. The content of this report is divided into three major sections and a fourth, concluding section which addresses our major research accomplishments, as well as documents the most significant publications and presentations associated with this grant. The three main sections which make up the body of this report are presented in the in form of manuscripts which, in turn, summarize our progress in three areas of this project. The three body sections are organized as follows

Section I: Evidence for Site Isolation in Rh-Mo Bimetallic Catalysts Derived from Organometallic Clusters

Section II: Surface Chemistry of Rh-Mo/ γ -Al₂O₃: An Analysis of Surface Acidity

Section III: Comparative Study of Rh/Al₂O₃ and Rh-Mo/Al₂O₃ Catalysts

Again, following the main body sections, Section IV summarizes major accomplishments. The content of this final report is meant to generally highlight our progress in both characterizing the nature of the Rh-Mo/Al₂O₃ system and probing its reactivity for insight on the oxygenate synergy present in this class of catalysts.

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Section I

Evidence for Site Isolation in Rh-Mo Bimetallic Catalysts Derived from Organometallic Clusters

Research Context

The impetus for the work discussed in this section stems from (i) the proven synergy of Rh-Mo/Al₂O₃ for oxygenate formation and (ii) our working hypothesis in the global investigation of this catalyst system, namely that the Mo serves primarily as a textural promoter and stabilizes site-isolated Rh aggregates. Here, we hope to guarantee the close proximity of the Rh and Mo, and hence enhance the promotional effects of the Mo, in the catalysts derived from binuclear, homogeneous precursors. The catalysts prepared by coadsorption of RhH(CO)(PPh₃)₃ and [Mo(CO)₃Cp]₂ (molybdenum dimer) were synthesized essentially as control samples having similar chemical features to those in (PPh₃)₂RhMo(CO)(μ-CO)₂Cp; the monometallic precursors lacked the intimate metal contact—in the form of metal-metal bonds—found in the binuclear precursor. After the H₂ reduction of the catalyst during reactor testing and in transmission infrared studies, the metal-metal bond present in the binuclear precursor may have been disrupted, but the ultimately stable configuration of Rh and Mo in the binuclear-derived materials is indeed influenced by this initial intimate contact as evidenced by the data set forth below. Finally, in the context of discussing the effect of phosphorous in these materials, we highlight the potential to tailor the final properties of a supported metal catalyst through altering the nature of the ligands present on a homogeneous, organometallic precursor.

Section Abstract

The rhodium-molybdenum cluster, $(\text{PPh}_3)_2\text{RhMo}(\text{CO})(\mu\text{-CO})_2\text{Cp}$, has been employed as a precursor to alumina- and silica-supported catalysts; these catalysts have been applied in CO and CO₂ hydrogenation. When compared to catalysts made from the separate organometallic complexes, $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ and $[\text{Mo}(\text{CO})_3\text{Cp}]_2$, the catalysts derived from a binuclear precursor show superior selectivities towards oxygenates for both CO and CO₂ hydrogenation, namely, methanol, dimethyl ether and ethanol. To explore catalytic behavior of the samples more thoroughly, the kinetics of both CO and CO₂ hydrogenation were studied and global activation energies were determined. Fourier transform infrared spectroscopy studies indicate that CO chemisorbs on the cluster-derived catalysts mainly in the form of gem-dicarbonyl while on the catalysts made from separate rhodium and molybdenum complexes it is chemisorbed only in the linear-carbonyl configuration. This gem-dicarbonyl feature in the CO adsorption on the cluster-derived catalysts may imply enhanced site isolation of Rh by Mo.

Introduction

Since Fischer and Tropsch^{1,2} reported that CO could be catalytically hydrogenated to a broad range of organic compounds in 1926, great efforts have been made to develop a selective catalytic system to break down the so-called Anderson-Schulz-Flory distribution of the products. With more public attention focused on the reduction of petroleum dependence and on protecting the environment by producing synthetic components for gasoline blends, interest in CO hydrogenation to oxygenates by promoted rhodium catalysts has greatly increased. In contrast to traditional salt-derived bimetallic catalysts, bimetallic cluster-derived catalysts have several potential advantages: specifiable structural characteristics, adjustable metal skeletons, number and/or type of ligands, etc. The continued development of organometallic chemistry offers great opportunities and possibilities in this regard.

Recent investigations in the catalytic chemistry literature have focused on promoted rhodium catalysts with particular emphasis on the promotional effects of molybdenum and on organometallic-derived Rh-Mo catalysts.³⁻¹⁵ H. Miessner and M. Ichikawa et al.³⁻⁶ have published investigations of bimetallic cluster-derived Rh-Mo catalysts. These cluster-derived catalysts have shown significant oxygenate selectivity in CO hydrogenation when compared with bimetallic catalysts made from metal salts. There are various explanations for the strong promotional effects of the molybdenum on supported rhodium catalysts. Most such explanations tend to attribute the effects to coverage of large rhodium particles by a molybdenum suboxide or to the formation of mixed oxides of rhodium and molybdenum which are thought to be responsible for improved oxygenate selectivity.^{5,9,10} This kind of reasoning is probably true when applied to catalysts made from separate metal salts as initial materials and with high metal loading because of the aggregation of the metals during reduction. But this explanation can not account for the result that Rh-Mo bimetallic cluster-derived catalysts have even higher oxygenates selectivity than conventional bimetallic catalysts. The high oxygenate selectivity of such cluster-derived catalysts implies that intrinsic metal-metal interactions present in the catalyst precursor indeed result in different promoting behavior, as reported by Miessner and Ichikawa et al.³⁻⁶ as well as this paper. In their most recent paper,¹⁰ Miessner et al. also excluded molybdenum suboxide migration; instead they explained that the Mo promotion results in oxidative disruption of Rh_x particles and prevents the sintering of Rh. By reducing Rh sintering, the catalyst retains a high number of active sites on the boundary of small Rh particles even for the catalysts derived from separate complexes.

Similar structural arguments were put forth by us in earlier work on Rh-Mo catalysts derived from separate rhodium and molybdenum carbonyl precursors.¹² We concluded that the role of molybdenum on alumina was to "site isolate" rhodium in a highly dispersed form that was more proper to oxygenate production than larger rhodium particles. Site isolation can be taken as the limit of ultrahigh dispersion and textural promotion. Based on this investigation of Rh-Mo

bimetallic catalysts, particularly with regard to our infrared spectroscopic results, it seems reasonable to attribute the promotion of rhodium by molybdenum to a site isolation effect which is enhanced by synthesis of the catalyst with an organometallic cluster precursor.

Experimental

The bimetallic cluster, $(PPh_3)_2RhMo(CO)(\mu-CO)_2Cp$, was synthesized following the method reported by Preston et al.¹¹ Initial complexes, $RhCl(PPh_3)_3$, $Mo(CO)_6$, $NaCp/THF$, $RhH(CO)(PPh_3)_3$ and $[Mo(CO)_3Cp]_2$ were purchased from Strem and Aldrich and were used without further purification. Gamma-alumina (American Cyanamid, BET surface area= 250 m^2/g) and Silica (BET surface area=320 m^2/g) were heated at 200°C in air for 24 hours before catalyst preparation.

The impregnation method was employed for catalyst preparation. Calculated amounts of cluster or separate complexes were dissolved in dichloromethane and the solution was added to corresponding amounts of support under a N_2 atmosphere. The mixture was then stirred for 2 hours and finally the solvent was removed by vacuum evaporation. The calculated rhodium loading for all the samples presented in this study was 0.5%wt and the samples have a mole ratio of Rh to Mo of 1. Elemental analysis results of the samples are shown in Table 1.

All of the fresh and used catalysts are characterized by CO and H_2 chemisorptions, which are carried out in a classical chemisorption apparatus at room temperature. All of the samples are reduced at 350°C with H_2 flow for 4 hours and degassed at the same temperature under 10^{-5} torr (1 torr = 133.3 Nm^{-2}) for overnight. The chemisorption information of the catalysts can be seen from Table 2.

CO or CO_2 hydrogenation activities of the catalysts were tested in a fixed-bed high pressure reactor. Detailed descriptions of the reactor system, product analysis and pre-treatment of gases can be seen in elsewhere.¹² The reactor was charged with 1.0g of catalyst (approximately

60x100 mesh). The catalyst was oxidized at 200°C in flowing air (30 ml/min) for 4 hours and then reduced at 350°C for 6 hours in flowing H₂ (40 ml/min). After the catalyst reached its stable activity, reaction data were collected at different reaction conditions: 200 to 350°C; 1.0 MPa to 3.0 MPa; CO/H₂ or CO₂/H₂=2 to 0.33; GHSV= 1200 to 2400h⁻¹. Reaction rate is expressed as follow:

$$r = \frac{X \cdot F}{(22414 \cdot 60 \cdot W)} \quad (\text{mole of CO or CO}_2/\text{gRh/Sec.})$$

where, X is the conversion of CO or CO₂; F is flow rate of CO or CO₂ (ml/min) at NTP; W is weight (g) of Rh in sample.

The selectivity (S_i) toward product i is defined as:

$$S_i = \frac{(n_i \cdot C_i)}{(\sum n_i \cdot C_i)}$$

where n_i is the carbon number of the product i and C_i is the mole percentage of the component i detected.

Based on reaction rates and selectivity data, and their respective temperature dependencies, the natural log of the rate was plotted versus inverse temperature and activation energies for the total reaction and for each product formed were calculated from the slope of the fitted line. To determine the reaction orders for each component with respect to partial pressure of H₂ and CO (or CO₂), the total reaction rate and rates of formation for each product were measured while varying the partial pressure of both H₂ and CO (or CO₂). Total conversions of CO or CO₂ were maintained at less than 7%. These data were fitted by using least-square regression to a linearized power law rate expression as follows:

$$\ln(r_i) = \ln(k_i) + x_i \cdot \ln(P_{H_2}) + y_i \cdot \ln(P_{CO \text{ or } CO_2})$$

where k_i , x_i and y_i are the rate constant, and rate orders with respect to partial pressure of H_2 and CO (or CO_2), respectively, for the i th component.

In situ infrared spectroscopic studies of the catalysts were performed on a Nicolet 510 FT-IR spectrometer using a self-supported sample wafer in an *in situ* IR cell. All spectra were recorded at 50 scans with a resolution of 4 cm^{-1} . The mounted wafer was treated in a similar way to the pretreatment of catalyst sample in the reaction tests and then the cell was evacuated at 10^{-3} torr. after this 50 torr of CO was introduced to the wafer at room temperature. IR spectra were recorded after evacuating the IR cell at different temperatures.

Result and Discussion

The positive promotional effect of Mo on supported Rh catalysts for CO hydrogenation motivated us to develop a Rh-Mo cluster-derived catalyst which also includes phosphorous as a possible acidic promoter and/or selective inhibitor. In fact, as the results show Rh-Mo catalysts derived from supported $(PPh_3)_2RhMo(CO)(\mu-CO)_2Cp$ indeed behave differently from non-cluster-derived catalysts when tested in CO or CO_2 hydrogenation.

CO Hydrogenation Activity and Selectivity

The CO hydrogenation reaction conditions and results are summarized in Table 3. The results indicate that compared with the non-cluster derived catalysts, designated as Rh,Mo/SiO₂ and Rh,Mo/Al₂O₃, the bimetallic cluster-derived catalysts show superior selectivity towards oxygenates. In addition, the alumina-supported bimetallic cluster shows particularly high activity. Beyond the differences that arise from the different active metal phase precursors, the different supports also seem to alter oxygenate distribution: methanol is the main oxygenate on silica-supported catalysts while a much higher percentage of dimethyl ether is formed on the alumina-supported catalysts compared to other oxygenates. Methanol is dehydrated to dimethyl ether (i.e. dimethyl ether is a secondary product) on alumina-supported catalysts because of the significant Lewis acidity of the alumina surface.

CO₂ Hydrogenation Activity and Selectivity

Table 4 summarizes the reaction conditions and results for CO₂ hydrogenation testing of the catalysts. It can be seen that the activity of the catalysts for CO₂ hydrogenation is lower than that of CO hydrogenation, but again, the cluster-derived catalysts show distinctly higher selectivities toward oxygenates compared with catalysts derived from separate complexes. The differences in the product distributions from those of CO hydrogenation are that methanol is the main oxygenated component for both kinds of oxide-supported catalysts. Nevertheless, dimethyl ether was once again formed on the alumina-supported catalysts. As mentioned above, dimethyl ether is formed by secondary dehydration of methanol and the Lewis acidity of the support drives the dehydration. Therefore, the different dimethyl ether selectivities for CO and CO₂ hydrogenation on the same catalyst should originate from the difference in the basicity of CO and CO₂, i. e. the weak Lewis basicity of CO₂¹⁵ may block some of the Lewis acid sites thereby lowering the rate of dehydration. Another possible reason for the difference in the dimethyl ether formation is related to the reverse water-gas shift reaction. When a mixture of CO₂ and H₂ is fed to the reactor, the CO₂ can undergo the reverse water-gas shift reaction and produce both CO and H₂O. Water formed in this transformation will dissociatively adsorb on the Lewis acid sites of the support surface, and inhibit the dehydration of methanol. In contrast, when CO is fed to the reactor, the water-gas shift equilibrium is driven forward, consuming water which might otherwise inhibit dehydration of methanol, with the result that dimethylether is a more favorable product.

The Effect of Reaction Conditions on Selectivity

Temperature can dramatically change the selectivity of CO and CO₂ hydrogenation on both cluster-derived and mononuclear complex-derived catalysts. Although the changes are similar, the cluster-derived catalysts show higher activity and selectivity to oxygenates at lower temperatures compared with the corresponding mononuclear complex-derived catalysts. Figures 1 and 2 demonstrate the superior performance of the cluster-derived Rh-Mo catalyst by depicting

the product selectivity as a function of temperature. Methanol selectivity, for example, is approximately twice as high (80% compared to 45%) at 250°C over the RhMo/SiO₂ than over the Rh₃Mo/SiO₂.

The reaction rate and oxygenate selectivity increase, and hydrocarbon selectivity decreases, with increasing total pressure. The CO/H₂ or CO₂/H₂ ratio can effect the selectivity of oxygenates although this effect is not as strong as the effect of varying temperature. With higher hydrogen partial pressure, higher oxygenate selectivity is realized. (Fig. 3).

Finally, the cluster-derived catalysts are very stable after break-in (Figure 4), the CO hydrogenation rate and methanol selectivity for RhMo/SiO₂ are seen to remain stable for nearly 100 hours on stream.

Apparent Activation Energy of CO or CO₂ Hydrogenation

The apparent activation energy was determined according to the Arrhenus equation,

$$r = k \cdot \exp\left(\frac{-E_a}{RT}\right)$$

Where, E_a is the apparent activation energy; k is actually the product of the frequency factor of the rate constant, A₀, and the concentration terms maintained constant throughout the experiment. The results for the total reaction and for each product formed from CO and CO₂ hydrogenation are shown in Tables 5 and 6. Here the partial pressure of CO or CO₂ was maintained at approximately 0.5 and CO_x/H₂ ratio was 1.

Generally, apparent activation energy data show good agreement with the activity and selectivity trends implied by the data mentioned above. It can be seen that the global E_a for CO hydrogenation on the cluster-derived catalysts are significantly lower than that on separate complex-derived catalysts. The activation energies for oxygenate formation from CO on cluster-derived catalysts are lower than that of other catalysts. Similarly, for CO₂ hydrogenation, cluster-

derived catalysts exhibit lower global activation energies and significantly lower activation energies for oxygenate formation compared with the other catalysts examined. The most surprising result is the negative energy of activation for oxygenate formation from CO₂. This suggests a very strong heat of adsorption for CO₂ on these catalysts. Evidently, promotion by Mo of Rh for CO or CO₂ conversion and oxygenate formation is intrinsically more effective when the catalysts are made from Rh-Mo bimetallic clusters.

Another interesting result from the study of apparent activation energies, which does not appear in the Table 5, is the decline in activation energy for CO hydrogenation on the cluster-derived catalysts with the reaction time during the initial 50 hours on stream. For example, the global activation energy for CO hydrogenation on RhMo/SiO₂ decreased from 127 KJ/mol in the 3rd hour on stream to 88 KJ/mol at the 30th hour and stabilized at about 73 KJ/mol thereafter. The mononuclear complex-derived catalysts did not exhibit significant changes in global activation energy with the reaction time. This decrease in global activation energy with time for the cluster-derived catalysts suggests that the nature and number of active sites on this catalyst are transformed in the presence of the reactant gases at reaction conditions. All the E_a data included in the tables are reported when the reaction has reached its stable activity.

Reaction Orders with Respect to Partial Pressure of H₂ and CO or CO₂

In order to obtain the kinetic information for CO or CO₂ hydrogenation related to the total reaction and each component formed, the reaction rates were measured while changing partial pressures of H₂, and CO, or CO₂. Using the least-square regression method, the power law reaction orders were determined from the data and are listed in Tables 7 and 8.

It can be seen from Table 7 that reaction orders with respect to the partial pressure of H₂ are all positive for all components formed and that the reaction orders with respect to CO are mostly negative for hydrocarbon and oxygenate formation in the CO hydrogenation reaction. Although reaction orders of oxygenate formation with respect to H₂ on the cluster-derived catalysts are

slightly lower than that on the mononuclear complex-derived catalysts, the CO inhibition effect on oxygenate formation for the cluster-derived catalysts is significantly weaker than that for the mononuclear complex-derived catalysts. The oxygenate formation rate order with respect to CO is even positive for RhMo/SiO₂. Therefore, superior oxygenate selectivity of the cluster-derived catalysts in CO hydrogenation may be explained as the result of weak to zero inhibition of CO or the oxygenate formation rate by chemisorbed on the catalyst surface. Generally, the trends for promotion effects with respect to the partial pressure of H₂ and inhibition effects with respect to the partial pressure of CO on the Rh-Mo bimetallic catalysts reported here are in agreement with the results of the silica-supported Rh, Rh-Fe, Rh-Li, or Rh-Mn catalysts reported by Burch and Petch.^{14c}

Similarly, reaction orders with respect to H₂ for all products formed are positive in the CO₂ hydrogenation reaction, with the exception of total reaction and CO formation on Rh₃Mo/Al₂O₃, where the values are slightly negative. The reaction orders with respect to CO₂ for all product formations are negative. The stronger H₂ and the weaker CO₂ rate dependencies for oxygenate formation on the cluster-derived catalysts compared to that on the mononuclear complex-derived catalysts are in good agreement with the results described.

IR Evidence of Different Surface Features of the Catalysts

Fourier Transform infrared (FTIR) spectra were recorded *in situ* for all catalysts after reduction at 350°C, absorption of CO at 50°C and evacuation at room temperature. The spectra are shown in Figures 5 and 6.

The FTIR spectroscopy study indicates that CO chemisorption on the cluster-derived catalysts leads to mainly the gem-dicarbonyl, while in contrast it leads to principally linear-CO coordination on the mononuclear complex-derived catalysts. This interpretation of the observed IR for chemisorbed CO on these catalysts, is based upon those given by Olive and Olive in their extensive review.¹⁶ Accordingly, a doublet with component peaks at 2101 and 2031 cm⁻¹ was

assigned to the symmetric and antisymmetric vibration of dicarbonyls on an isolated Rh species, the broad band at 1855 to 1870 cm^{-1} and the band at 2056 to 2070 cm^{-1} were assigned to bridging CO, ($\text{Rh}_2(\text{CO})$), and linear CO, (RhCO) species on more "crystalline" island or rafts of Rh, respectively, in which reduced rhodium atoms form a close-packed array.

The carbonyl absorption characteristics of the IR spectra on the catalysts also show some variation with the oxide support used. For RhMo/SiO_2 , the strong gem-dicarbonyl absorption appeared at 2103 and 2033 cm^{-1} , broad weak-bridging absorption appeared at 1900 cm^{-1} and almost no linear-CO absorption was observed. In contrast, for $\text{RhMo/Al}_2\text{O}_3$, there was a distinct linear-CO absorption (2065 cm^{-1}) besides the similar gem-dicarbonyl (2096, 2026 cm^{-1}) and broad weak-bridging (1863 cm^{-1}) CO absorption. These differences in CO absorption are suggestive of the difference in oxygenate distributions on the cluster-derived catalysts supported for the two different oxides. The differences in CO absorption between the mononuclear complex-derived catalysts and the cluster-derived catalysts are evident in both the silica- and alumina-supported cases. Not only were there no gem-dicarbonyl bands on the mononuclear complexes-derived catalysts, but also the linear-CO peak positions are shifted from 2075 cm^{-1} to 2055, 2033 cm^{-1} for Rh,Mo/SiO_2 , and from 2065 to 2076 cm^{-1} for $\text{Rh,Mo/Al}_2\text{O}_3$.

It has been reported⁵⁻⁹ that the gem-dicarbonyl became the main species on the surface of supported rhodium catalysts only when the Mo/Rh ratio is high (>4). The gem-dicarbonyl feature also was thought to be a evidence of a high dispersion of rhodium.^{9, 17} However, strong gem-dicarbonyl absorptions were observed on the cluster-derived catalysts in this study, where the Mo/Rh ratio is only 1. After comparison with the IR spectra of mononuclear complex-derived catalysts with the same metal loading, it is evident that the gem-dicarbonyl feature of the cluster-derived catalysts is not a result of low metal loading in this work, though low Rh loading was found to give rise to gem-dicarbonyl on supported Rh catalysts.¹⁶ Therefore, the prominence of the gem-dicarbonyl feature in the CO absorption spectra of the cluster-derived catalysts points to more effective site isolation of rhodium by molybdenum on the alumina and silica surfaces. This

more effective site isolation arise from the fact that after chemisorbing the organometallic precursors, the next step is air oxidation prior to reduction. For the cluster-derived catalysts this is expected to leave more rhodium in the near vicinity of molybdenum than for the mononuclear-complex-derived catalysts for which other surface interactions may lead to less mixing of the metals. Hence due to the strong metal-metal bonds in the cluster precursor, rhodium-molybdenum proximity is maintained and rhodium site isolation is favored in the active form of the catalyst. This special surface feature of the cluster-derived catalysts may correlate to their superior oxygenate selectivity for CO_x hydrogenation.

Effect of Phosphorus

So far, no direct data demonstrate the effect of the presence of phosphorus on the catalysts, but it seems clear that phosphorus could potentially inhibit to some extent the activity of Rh-Mo bimetallic catalysts for CO or CO_2 hydrogenation. Nevertheless, the cluster-derived catalysts indeed show higher activity and superior oxygenate selectivity compared with mononuclear complex-derived catalyst even though both contain phosphorus. Phosphorus present on the surface, while often considered to be an inhibitor to metallic catalysts, may block some active sites on the surface for hydrocarbon formation and could actually decrease hydrocarbon selectivity in favor of oxygenate selectivity. In this way, the inhibitor could provide a useful means to controlling undesired side reactions. The key factor here is that the inhibitor would have to selectively obstruct some of the catalytic sites. Hence molecular modification of the cluster precursor could be a useful means for designing highly selective CO hydrogenation catalysts, not only from the standpoint of specific structural features of metals at the active site, but also from the standpoint of introducing certain ligands in the precursor that would lead to selective inhibitions on the active catalyst. The further development of this kind of surface organometallic chemistry offers some intriguing possibilities for the design of new catalytic materials.¹⁸

Conclusions

Rh-Mo catalysts derived from the bimetallic cluster, $(\text{PPh}_3)_2\text{RhMo}(\text{CO})(\mu\text{-CO})_2\text{Cp}$, show higher activity and superior oxygenate-selectivity in the CO and CO_2 hydrogenation reactions compared with catalysts derived from the mononuclear complexes, $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ and $[\text{Mo}(\text{CO})_3(\text{C}_5\text{H}_5)]_2$. The propensity for oxygenate formation on the cluster-derived catalysts also was confirmed by data derived from apparent activation energies and reaction orders. Gem-dicarbonyl was the main CO-absorbed species on the cluster-derived catalysts, and this implied that rhodium exist as +1 oxidation state. These IR results suggest that effective promotion of Rh by Mo in cluster-derived catalysts for CO hydrogenation might occur through enhanced "site isolation" of Rh by Mo.

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Table 1. Elemental Analysis of the Rh-Mo Bimetallic Catalysts

Catalysts	% Rh	% Mo	% P
RhMo/SiO ₂	0.51	0.47	0.28
Rh ₂ Mo/SiO ₂	0.36	0.38	0.25
RhMo/Al ₂ O ₃	0.58	0.66	0.39
Rh ₂ Mo/Al ₂ O ₃		0.31	0.39 0.33

Note: RhMo and Rh₂Mo represent catalysts derived from RhMo(CO)₃Cp(PPh₃)₂ and the mixture of RhH(CO)(PPh₃)₃ and [Mo(CO)₃Cp]₂, respectively.

Table 2. CO and H₂ Chemisorption Data of Rh-Mo Bimetallic Catalysts

Catalysts	State	Condition	CO/Rh	H ₂ /Rh
RhMo/SiO ₂	fresh	room temp.	1.06	0.08
	used	"	0.69	0.86
Rh ₂ Mo/SiO ₂	fresh	"	1.00	0.00
	used	"	0.00	0.00
RhMo/Al ₂ O ₃	fresh	"	1.19	0.02
	used	"	0.31	0.02
Rh ₂ Mo/Al ₂ O ₃	fresh	"	1.28	0.28
	used	"	0.66	0.08

Table 3. CO₂-free Selectivity of Rh-Mo Bimetallic Catalysts for CO Hydrogenation

Catalysts	H ₂ /CO	T°C	P(MPa)	CxHy	MeOH	Me ₂ O	EtOH	ΣOxy.	r ^a	TON ^b
RhMo/SiO ₂	2	300	2.0	21.6	73.5	0.3	4.4	78.2	9.80	9.52
Rh ₂ Mo/SiO ₂	2	300	2.0	48.0	41.5	/	10.5	52.0	12.5	12.9
RhMo/Al ₂ O ₃	2	250	1.87	24.8	17.8	44.9	12.4	75.1	55.2	47.8
Rh ₂ Mo/Al ₂ O ₃	2	300	2.0	37.4	19.9	42.7	/	62.5	3.87	3.11

a. Total reaction rate in the unit of 10⁻⁶xMol CO/gRh/Sec.

b. Turnover frequency, in the unit of 10⁻⁴/sec, calculated from CO chemisorption data.

Table 4. CO-free Selectivity of Rh-Mo Bimetallic Catalysts for CO₂ Hydrogenation

Catalysts ^a	H ₂ /CO ₂	T°C	P(MPa)	CxHy	MeOH	Me ₂ O	EtOH	ΣOxy.	r ^b	TON ^c
RhMo/SiO ₂	1	300	2.0	36.3	61.9	/	1.9	63.8	1.75	1.70
Rh ₂ Mo/SiO ₂	1	350	2.0	59.5	39.5	/	1.0	40.5	3.47	3.57
RhMo/Al ₂ O ₃	1	300	2.0	43.4	44.1	8.7	3.9	56.6	1.72	1.49
Rh ₂ Mo/Al ₂ O ₃	1	350	2.0	55.8	43.0	1.2	/	44.2	3.10	2.50

a. The catalysts are same with table 1.

b. Total reaction rate in the unit of 10⁻⁶xMol CO₂/gRh/Sec.

c. Turnover frequency in the unit of 10⁻⁴/sec, calculated from CO chemisorption data.

Table 5. Apparent Activation Energy of CO+H₂ on Bimetallic Catalysts (KJ/mol)

	RhMo/SiO ₂	Rh,Mo/SiO ₂	RhMo/Al ₂ O ₃	Rh,Mo/Al ₂ O ₃
Total reaction	73	93	85	102
CH ₄	92	104	129	129
C ₂ H ₆	100	105	152	122
C ₃ H ₈	88	100	133	113
C ₄ H ₁₀		108	123	83
MeOMe			63	67
MeOH	60	66	78	79
EtOH	56	71	69	

Table 6. Apparent Activation Energy of CO₂+H₂ on Bimetallic Catalysts (KJ/mol)

	RhMo/SiO ₂	Rh,Mo/SiO ₂	RhMo/Al ₂ O ₃	Rh,Mo/Al ₂ O ₃
Total reaction	54	68	64	67
CO	54	68	66	67
CH ₄	90	89	105	93
C ₂ H ₆	92	111	92	84
C ₃ H ₈	97	120	96	85
MeOMe	-17		-27	-31
MeOH	-24	19	-4.2	19
EtOH			-32	

Table 7. CO Hydrogenation Reaction Orders

Products	RhMo/SiO ₂	Rh ₂ Mo/SiO ₂	RhMo/Al ₂ O ₃	Rh ₂ Mo/Al ₂ O ₃
Reaction orders with respect to H ₂				
Total	0.54	0.73	0.08	0.06
CO ₂	0.49	0.84	0.01	0.33
CH ₄	0.75	0.97	0.76	0.81
C ₂ H ₆	0.47	0.55	0.73	0.56
C ₃ H ₈	0.42	0.53	0.61	0.09
C ₄ H ₁₀	0.26		0.08	
MeOMe			0.96	1.36
MeOH	0.73	1.15	0.69	0.76
EtOH	0.82	0.77	0.50	
Reaction orders with respect to CO				
Total	0.68	0.06	-0.11	-0.35
CO ₂	0.83	0.69	0.08	0.59
CH ₄	-0.48	-0.29	-0.76	-0.25
C ₂ H ₆	-0.33	-0.17	-0.27	-0.14
C ₃ H ₈	0.07	0.03	0.36	0.48
C ₄ H ₁₀	-0.45		0.49	
MeOMe			-0.84	-0.76
MeOH	0.49	-0.35	-0.24	-1.54
EtOH	0.37	-0.55	-0.94	

Table 8. CO₂ Hydrogenation Reaction Orders

Products	RhMo/SiO ₂	Rh ₂ Mo/SiO ₂	RhMo/Al ₂ O ₃	Rh ₂ Mo/Al ₂ O ₃
Reaction orders with respect to H ₂				
Total	0.46	0.3	0.29	-0.31
CO	0.28	0.3	0.29	-0.40
CH ₄	0.49	0.55	0.79	0.66
C ₂ H ₆	0.54	0.73	0.21	0.14
C ₃ H ₈	0.43	1.30	0.45	0.62
MeOMe			0.89	1.35
MeOH	0.35	1.42	0.35	1.23
EtOH	-0.47		0.36	
Reaction orders with respect to CO ₂				
Total	-0.06	-0.22	-0.13	-0.61
CO	-0.21	-0.22	-0.11	-0.68
CH ₄	-0.85	-1.30	-0.47	-0.80
C ₂ H ₆	-0.34	-1.50	-0.55	-1.42
C ₃ H ₈	-0.19	-1.76	0.25	-0.81
MeOMe			-1.84	-2.8
MeOH	-1.27	-1.67	-1.15	-0.81
EtOH	-1.74		-0.42

Figure 1. Temperature dependences of selectivities on RhMo/SiO₂ (300psi, CO/H₂=1/2).

Figure 2. Temp. dependences of selectivities of Rh,Mo/SiO₂. (300psi, CO/H₂=1/2).

Figure 3. Effect of CO/H₂ ratio on selectivity (RhMo/SiO₂, 350°C, 300psi).

Figure 4. Stability of RhMo/SiO₂ (350°C, 300psi, CO/H₂=1/2).

Fig. 5 A: CO-absorbed RhMo/SiO₂ evacuated at RT
B: CO-absorbed Rh₂Mo/SiO₂ evacuated at RT

Fig. 6 A: CO-absorbed RhMo/Al₂O₃ evacuated at RT.
B: CO-absorbed Rh,Mo/Al₂O₃ evacuated at RT.

Section II

Surface Chemistry of Rh-Mo/ γ -Al₂O₃: An Analysis of Surface Acidity

Research Context

In Section I, comparisons of catalyst materials centered on the significance of using a binuclear, homogeneous precursor. Substantially higher activities for CO conversion have been achieved with catalysts prepared with the *sequential* chemisorptive protocol outlined in the experimental section set forth below. Section III returns to the issue of the overall activity and selectivity of these sequentially adsorbed materials in the context of CO hydrogenation. In contrast, this section focuses on the nature of the metal-metal and metal-support interaction of significance in the synthesis of these sequentially adsorbed materials. The nature of the interactions of the Rh and Mo with the native γ -Al₂O₃ surface also influence the propensity of the catalyst, in its final form, to dehydrate first rank alcohol products produced in CO hydrogenation. This secondary, and in some cases, retrograde transformation to ethers takes place at the Lewis acid centers on the catalyst surface. Hence, the efforts set forth below focus on the nature of these Lewis acid centers, their relative strength and density across the catalyst materials which form the building blocks of the ultimate Rh-Mo/ γ -Al₂O₃ system, and the effect these sites have on the alcohol dehydration potential of the materials. In order to modify their Lewis acidity, KNO₃ was used to dope the surfaces of both native Al₂O₃ and the metal-loaded samples. The KNO₃ was applied to samples using both ion exchange and incipient wetness techniques, and as a matter of course, the ultimately achievable potassium loading using these two techniques offered further insight about the nature of catalysts' surface properties as set forth in the discussion below. The most significant findings reported here, concern the interplay between the Lewis acid sites on the Al₂O₃ surface and the chemisorbing Rh precursor.

Section Abstract

This study highlights the nature of the interactions between the transition metals in the Rh-Mo/ γ -Al₂O₃ system and the underlying alumina surface. The investigation was carried out in the context of exploring the retrograde dehydration to dimethyl ether of primary alcohols produced at active metal sites during CO hydrogenation. Both native γ -Al₂O₃ and Rh-Mo/ γ -Al₂O₃ samples were doped with KNO₃ in an attempt to create an alkaline-metal oxide layer on the support surface which would screen alcohols from underlying Lewis acidity. The samples were characterized by microreactor-based methanol dehydration studies, analysis of infrared spectra of adsorbed pyridine, and ammonia saturation and temperature-programmed desorption. As expected, the dehydration activity of the samples was strongly correlated to their potassium loading and, hence, their Lewis acidity. More intriguing however, are the insights gained in this analysis concerning the nature of the interactions between Mo, Rh, and the Lewis acid sites on the alumina surface. Our results are consistent with the principal, suggested in the Mo/ γ -Al₂O₃ literature, that our Mo(CO)₆ precursor interacts primarily with non-acidic hydroxyl groups on the dehydrated alumina surface. Furthermore, we provide strong evidence for the diminution of acidity brought on by the adsorption of Rh on Lewis acid sites of Mo/ γ -Al₂O₃.

Introduction

Past investigations of a series of alumina-supported bimetallic combinations of Group VI and noble transition metals identified synergistic characteristics of Rh-Mo/ γ -Al₂O₃ (1,2). Promoting rhodium with molybdenum oxide produced a catalyst with a significantly higher propensity for the production of oxygenates in the hydrogenation of CO than could be achieved using a monometallic rhodium catalyst at both atmospheric and moderate (~1.7 MPa) pressures. Other researchers have reported oxo-selectivity and activity enhancements on silica- and alumina-supported rhodium catalysts as a consequence of molybdenum promotion (3-6). Based on a combination of microreactor testing for CO hydrogenation, TEM and XPS analysis, and

H₂-chemisorption measurements, a qualitative model for the behavior of Rh in the presence of MoO_x was proposed wherein the oxidized Mo acts primarily as a textural promoter in small, bimetallic crystallites (~0.5 nm), site-isolating rhodium aggregates which would otherwise tend to sinter and agglomerate at comparable loadings. These site-isolated rhodium aggregates are thought to be primarily responsible for the oxygenate chemistry of the catalyst in the presence of synthesis gas. Larger, rhodium-rich bimetallic aggregates (~1.0 to 1.5 nm) were proposed to be primarily responsible for the dissociative adsorption of CO and subsequent hydrocarbon formation. Some infrared spectroscopic evidence in the literature (7,8) points to the partial oxidation of larger rhodium particles via migration of molybdenum oxide onto the surface of such larger rhodium aggregates. In contrast, Kip et al. (3), in an extended study of promoted Rh/SiO₂, employing temperature programmed reduction and oxidation, transmission electron microscopy, and CO hydrogenation probe reactions, as well as infrared spectroscopic analysis, found no evidence for molybdenum oxide migration onto rhodium aggregates (as opposed to the migration demonstrated by oxides of thorium and vanadium). More recently, in a study of Rh-Mo/SiO₂ derived from metal-carbonyl precursors, Trunschke et al. (6) suggest a textural promotion role for molybdenum oxide, wherein it stabilizes smaller rhodium aggregates—identified by their signature gem-dicarbonyl infrared doublets—against sintering and agglomeration upon exposure to reaction conditions.

Upon testing the Rh-Mo/ γ -Al₂O₃ catalysts at industrially relevant pressures, the oxygenated components of the product slate from CO hydrogenation shifted from predominantly methanol (MeOH), at atmospheric pressure, to predominantly dimethyl ether (DME) and ethanol (EtOH), at moderate pressures. We have ascribed the tendency to dehydrate primary alcohol products to secondary ether products to acidic features of the catalysts based on mechanistic evidence in the literature (9-13). For example, Parera (10) suggests the straightforward mechanism detailed in Figure 1, wherein MeOH encounters a Lewis acid site on native alumina and dissociatively adsorbs onto the site, ejecting an H⁺ ion onto an adjacent basic oxygen atom. The surface species

can then recombine to form the etherification products CH_3OCH_3 and H_2O . The chemistry governing Equation 1 of Figure 1 has been disputed in the literature (12,13). Notably, using ^{18}O -labeled alcohols, Decanio et al. (13) have demonstrated that the basic oxygen in a Lewis acid-base pair can cleave the carbon-oxygen bond in the alcohol in contrast to the electrophillic attach of the alcohol function by the Lewis site. While this reaction was detected using $\text{CH}_3^{18}\text{OH}$, the propensity of the surface toward basic attack was found to be a function of alkyl chain length. The net products in Equation 1 are the same in either case. Hence, for the purposes of this study we have focused our efforts on characterization efforts on measuring Lewis *acidity*.

In this study, we quantify and manipulate the Lewis acidity of $\gamma\text{-Al}_2\text{O}_3$ and $\text{Rh-Mo}/\gamma\text{-Al}_2\text{O}_3$ in order to obtain insight into alcohol etherification over the Rh-Mo catalyst during hydrogenation of CO and, more importantly, the bimetallic interactions of the Rh and Mo with the alumina surface and their effect upon the acidity of the underlying support. To study the influence of surface acidity, we have synthesized a series of potassium-promoted catalysts from both native and transition-metal-loaded starting materials. The catalytic materials were then characterized using the following techniques: (i) evaluation of microreactor results for the direct dehydration of MeOH, (ii) analysis of infrared (IR) spectra of adsorbed pyridine, and (iii) analysis of ammonia saturation and temperature-programmed desorption (TPD) spectra. By mapping the surface acidity of the various transition-metal-loaded samples, intriguing evidence concerning the nature of the interaction between the transition-metal precursors and the acidic surface features of the support became apparent. The implications of this evidence on the process by which transition-metal carbonyl precursors interact with the surface of alumina during chemisorption and calcination are also discussed herein.

Methods

Catalyst Synthesis

The support common to all the samples tested in this study was γ -Al₂O₃ (American Cyanamid, BET Surface Area = 250 m²/g). In all cases, the support was dehydrated in air at atmospheric pressure and 120 °C overnight for approximately 12 h prior to modification or testing. The dehydrated support was then used as the starting material for the series of samples synthesized in this study. The samples generated can be broadly divided into two categories: (i) doped, native alumina and (ii) doped Rh-Mo/ γ -Al₂O₃.

Native alumina was doped with KNO₃ (EM Science) via two methods. In the first method, the "ion-exchange" method, three separate batches of dehydrated alumina (~3 g each) were slurried and continuously stirred for 12 h in aqueous solutions of KNO₃ with the concentrations of approximately 0.12 M, 0.24 M, and 2.40 M, respectively. These samples were subsequently dried, filtered and calcined in air at 300 °C overnight for approximately 12 h. In the second method, the "aqueous impregnation" method, two separate batches of ~3 g of dehydrated alumina were impregnated with 2.63 M and 3.0 M aqueous solutions of KNO₃ to incipient wetness (0.79 ml/g) and calcined in air at 300 °C overnight for approximately 12 h. One of the aqueous impregnation samples was then reimpregnated with the 3.0 M KNO₃ solution and calcined a second time to achieve a higher potassium loading. The second impregnation was necessary due to the solubility limit of KNO₃ and the pore volume capacity of the alumina.

In order to prepare potassium doped Rh-Mo/ γ -Al₂O₃ samples, transition-metal loaded samples had to first be synthesized. Approximately 60 g of dehydrated alumina was slurried with 250 ml of anhydrous heptane (99+% pure, Aldrich). The heptane-alumina slurry was degassed by refluxing the heptane under flowing N₂ (dried and deoxygenated) for 1 h. The mixture was allowed to cool to room temperature and 11.0 g of Mo(CO)₆ (Strem) were added. The slurry was again brought up to reflux temperature under flowing N₂. Upon heating to reflux, the Mo(CO)₆

rapidly dissolved in the heptane, and almost immediately upon reaching refluxing temperature, the initially off-white alumina turned deep yellow. The color change in the alumina was associated with the chemisorption of Mo(CO)_6 on the support surface. IR analysis of a self-supporting wafer confirms this adsorption. The mixture was continuously stirred at reflux for 8 h, cooled to room temperature, and filtered and dried in air. The $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$ material was then slurried with 250 ml of fresh anhydrous heptane. The new slurry was again degassed by refluxing under flowing N_2 for 1 h and cooled to room temperature. Finally 5.0 g of $\text{Rh(I)(CO)}_2(\text{acac})$ (Strem) were added to the slurry and again stirred and refluxed under flowing N_2 for approximately 8 h, at which time the initially cloudy, brown supernatant had cleared, and IR analysis of the liquid phase indicated that no appreciable Rh carbonyls were present. The final material was again filtered and dried in air and the resultant catalyst was mildly calcined at 120°C overnight for approximately 12 h to both volatilize any residual heptane on the surface and oxidized the Mo and Rh.

Both the ion exchange and the aqueous impregnation methods described for the doping of alumina (*vide supra*) were employed to synthesize potassium promoted Rh-Mo/ $\gamma\text{-Al}_2\text{O}_3$ samples. Interestingly, however, the ultimately achievable potassium loading for the ion-exchanged Rh-Mo/ $\gamma\text{-Al}_2\text{O}_3$ was considerably lower than that achieved on doped, native alumina.

Methanol Dehydration Studies

The catalytic materials synthesized in this study have been tested for their propensity to dehydrate MeOH. In the MeOH dehydration experiments, approximately 0.15 g of sample was packed into a 5 mm I.D. Pyrex microreactor tube and loaded into a tube furnace (Lindberg 55031). In this reactor, the MeOH was fed directly to the packed bed by passing $25\text{ cm}^3/\text{min}$ of He carrier gas through a MeOH sparger, maintained at a constant temperature of 10°C with a circulating temperature bath. The MeOH-saturated carrier gas was fed to the packed bed which was maintained at temperatures of 180 to 250°C depending on the particular sample and

objectives of the reactor test. The reactor effluent was separated and analyzed by gas chromatography using a 12 ft, 1/8 in O.D. packed column containing 80 $\times$ 100 mesh Poropak T (Supelco) and a flame ionization detector to obtain conversion of MeOH to DME (or in the case of the Rh-Mo/ γ -Al₂O₃ series of samples, DME, light hydrocarbons, and formaldehyde). All rate data reported in this study are for conversions of less than 10% so that differential reactor conditions can be assumed.

Pyridine Adsorption and IR Analysis

The pyridine (99+% pure C₅H₅N, Aldrich) used in this study was refluxed over excess CaH₂ for 48 h under flowing N₂ and distilled and stored on 5Å molecular sieves prior to use in the surface characterization of catalyst samples. The dried pyridine was also degassed by repeated freeze-pump-thaw cycles before dosing the surface of a sample. The sample was ground to roughly 200 $\times$ 325 mesh (~60 μ m) and pressed into a self-supported wafer approximately 1.5 cm in diameter. The wafer was placed in a sealed quartz transmission infrared cell equipped with NaCl windows and 2 vacuum stopcocks for gas treatment and evacuation. The cell was then heated to 300 °C and simultaneously evacuated to approximately 3×10^{-3} Torr (1 Torr = 133.3 Pa) until the IR peaks associated with water on the wafer surface and CO₂ in the purged chamber surrounding the cell had diminished to insignificant levels. Following dehydration to 300 °C, the cell was cooled to 200 °C and the temperature was allowed to stabilize for approximately 30 min. An IR background spectrum was then collected, and all other spectra collected from the sample were referenced to this background (i.e., evacuated sample at 200 °C). Next, saturated pyridine vapor was allowed to equilibrate with the sample surface until repeated collection of IR spectra showed no increase in pyridine peak intensities (approximately 30 min). Finally, two sets of IR spectra were collected on the pyridine-saturated samples: (i) spectra for the samples in equilibrium with the saturated vapor, and (ii) spectra for the surface after the wafers had been evacuated to 3×10^{-3} Torr following pyridine dosing (evacuated for not less than 1 h). All

spectra discussed herein were recorded after 30 scans, have a resolution of 4 cm^{-1} and were collected on a Nicolet 510M Fourier Transform Infrared Spectrometer.

Ammonia Saturation and Temperature-Programmed Desorption

As an additional measure of the surface acidity of the samples examined in this study, we have collected ammonia saturation data and TPD spectra for the samples in Table 1. The ammonia used in the saturation and TPD analysis was 3.1% vol. NH_3 in a balance of He (certified, Matheson). Approximately 0.3 g of 60×100 mesh ($\sim 200\text{ }\mu\text{m}$) catalyst was packed in a 9 mm I.D. quartz microreactor tube between plugs of glass wool, and the tube was placed in a tube furnace (Lindberg 55035) and put on-line with flowing He at $10\text{ cm}^3/\text{min}$. The sample was allowed to equilibrate at $50\text{ }^\circ\text{C}$ and was then dehydrated by ramping to $400\text{ }^\circ\text{C}$ at a rate of $7\text{ }^\circ\text{C}/\text{min}$ and soaking at $400\text{ }^\circ\text{C}$ for 50 min under flowing He. Finally, the sample was cooled to $50\text{ }^\circ\text{C}$ (chosen to minimize the effects of ambient temperature fluctuations), the carrier gas stream was switched from He to NH_3 in He, and the gas eluted from the column was monitored with a thermal conductivity detector (TCD, Gow-Mac 40-250/252). When the baseline of the chromatogram had shifted and leveled off, indicating that the column was saturated with ammonia, the carrier was switched back to pure He and the temperature was ramped from 50 to $400\text{ }^\circ\text{C}$ at $7\text{ }^\circ\text{C}/\text{min}$ and then soaked for 50 min at $400\text{ }^\circ\text{C}$. The temperature program naturally led to the desorption of the NH_3 , and this was manifest as a peak or series of peaks in the chromatogram.

Results

K-Doped $\gamma\text{-Al}_2\text{O}_3$

Figure 2 depicts the steady-state conversion of MeOH to DME as a function of potassium loading on $\gamma\text{-Al}_2\text{O}_3$. The downward sloping trend in the data clearly indicates that as the potassium loading increases, the tendency to dehydrate MeOH is inhibited. The data shown for

8.2 and 11.9% potassium loadings resulted from samples made by the aqueous impregnation method.

The chemisorptive characterization data for this series of samples suggests that the decrease in methanol dehydration propensity with increasing potassium loading is due to a decrease in the surface acidity of the samples. Figure 3 contains two pyridine adsorption spectra: the IR absorbance of a self-supporting wafer of $\gamma\text{-Al}_2\text{O}_3$ maintained at 200 °C in a saturated atmosphere of pyridine vapor and the same wafer after the sealed IR cell has been evacuated to 3×10^{-3} Torr, following exposure to pyridine. The spectrum collected prior to evacuation contains the expected features for native $\gamma\text{-Al}_2\text{O}_3$. From the work of Parry (14), the intense peak at 1453 cm^{-1} , the strong peak at 1495 cm^{-1} , and that falling in the range 1600 to 1633 cm^{-1} can be assigned to vibrational modes of pyridine coordinatively bonded to the Lewis acid sites of the surface. Parry's analysis also suggests that the broad band between 1580 and 1600 cm^{-1} is attributable to the vibrational modes of pyridine molecules physisorbed on the surface through hydrogen bonding or other dispersion forces. As expected with native $\gamma\text{-Al}_2\text{O}_3$, the concentration of acidic surface hydroxyls is insignificant as evidenced by the lack of a strong signature Brönsted peak at $\sim 1540\text{ cm}^{-1}$. Note that after the cell is evacuated, the broad peak at $1580\text{--}1600\text{ cm}^{-1}$ has greatly diminished, indicating that the physisorbed pyridine has desorbed from the surface. In addition, the signature Lewis acid peaks, while slightly less intense, are well resolved and still present, indicating the existence of chemisorbed pyridine which is bonded strongly to the surface.

When the same pyridine adsorption protocol and IR analysis is carried out on the 8.2 and 11.9% K-doped $\gamma\text{-Al}_2\text{O}_3$, the spectra for the evacuated samples indicate that the Lewis acid sites on the surface coordinatively bond to pyridine more weakly than on native $\gamma\text{-Al}_2\text{O}_3$. This effect is apparent in Figure 4, where the spectrum for the evacuated 11.9% K sample lacks Lewis acid signature peaks and indicates that by doping the surface with potassium, the acidity has been quashed. The spectra for the 8.2% K-doped sample demonstrate the same trend and are not shown for the sake of brevity.

The ammonia saturation and TPD results for the potassium-doped alumina samples are consistent with the premise that increasing the potassium loading leads to decreased acidity. Table 1 lists the ammonia saturation results for selected catalyst samples synthesized for this study. As the first three entries of Table 1 indicate, the calculated number of reversible acid sites interacting with NH_3 below 400 °C drops considerably for the 8.2 and 11.9% potassium samples compared to native $\gamma\text{-Al}_2\text{O}_3$. "Reversible sites" are defined here as those which desorb NH_3 during the heating cycle of the sample which includes a maximum temperature exposure of 400 °C.

The reduction in acidity with increasing potassium loading is also demonstrated in Figure 5 which depicts the TPD traces for a series of alumina samples as a function of temperature. The TPD trace for native $\gamma\text{-Al}_2\text{O}_3$ has significant fine structure above 110 °C associated with convoluted peaks representing NH_3 desorbing from surface acid sites of increasing strength. This fine structure is greatly diminished when the loading is increased to 8.2 and 11.9% potassium. For the 8.2% potassium sample, only weaker acid sites are interacting with the NH_3 below 400 °C, and such sites desorb NH_3 very early in the temperature ramp. The 11.9% potassium sample again principally desorbs ammonia below 120 °C. The sites associated with the second broad peak in the 11.9% potassium trace between 150 and 250 °C may be an artifact of the synthesis protocol of this sample which required two impregnation and calcination steps, compared to the one required to make the 8.2% potassium sample. During the second impregnation, the surface may have been inadvertently rehydrated.

K-Doped Rh-Mo/ $\gamma\text{-Al}_2\text{O}_3$

Figures 6 and 7 detail the microreactor results for the K-doped Rh-Mo/ $\gamma\text{-Al}_2\text{O}_3$ samples. Figure 6 contains data for samples synthesized by both the ion exchange and aqueous impregnation methods and demonstrates that as the potassium loading increases, the rate of formation of DME from MeOH diminishes. Most of downward sloping trend in DME formation

as a function potassium loading is attributable to the first four points on this figure. These points represent the samples synthesized via the ion exchange method and hence have lower potassium loadings. This section of Figure 6 is expanded in Figure 7 which shows that for the sample with a 0.090% potassium loading, the rate of formation of DME has dropped by nearly a factor of 2 compared to the untreated Rh-Mo/ γ -Al₂O₃ surface.

The pyridine adsorption spectra for the transition-metal loaded samples are shown in Figures 8, 9, and 10. The spectra in Figure 8 for Mo/ γ -Al₂O₃ have essentially the same features as those in Figure 3 for native alumina, indicating the presence of significant Lewis acidity on the surface of this sample. In contrast, the spectra in Figure 9, the pyridine adsorption spectra for Rh-Mo/ γ -Al₂O₃, have features reminiscent of a highly K-doped alumina. While Lewis acid signature peaks are present when the Rh-Mo/ γ -Al₂O₃ sample is in equilibrium with pyridine vapor, these same peaks vanish when the sample is evacuated. Here, the process of chemisorbing the rhodium and oxidizing the catalyst has reduced the acidity of the surface. In Figure 10, which depicts the spectra for K-doped Rh-Mo/ γ -Al₂O₃, the evacuated sample again lacks Lewis acid signature peaks. The spectrum for the evacuated, doped sample is essentially unchanged from that of the undoped sample.

Ammonia saturation and TPD results are presented in Table 1 and Figures 11 and 12. The results presented in Table 1 indicate that the acid amount of sites interacting with NH₃ increases markedly upon addition of 2.5% molybdenum to the alumina surface. This increase can be related to the stoichiometry of the metals present on the surface, as will be discussed below. Figure 12, the TPD traces for the series of doped Rh-Mo/ γ -Al₂O₃ samples, suggests that while the total acid amount of reversible sites may be unchanged, the distribution of reversible sites shifts toward sites which interact *more* strongly with ammonia after the surface has been doped with potassium. This effect may be associated with both the ion exchange protocol used to synthesize these samples which may have rehydrated the surface and the relative basicity of NH₃ compared to pyridine.

Discussion

Past efforts to functionalize the alumina surface of rhodium-based catalysts focused on the role hydroxyl sites play in the sintering of monometallic, supported catalysts in high-temperature reactive environments. Yates et al. (15-17), in a series of investigations in 1991, demonstrated that in the presence of CO above 600K, Rh(0) is oxidized on fully or partially hydroxylated alumina to form rhodium gem-dicarbonyl, Rh(I)(CO)₂, by the following surface reaction:

Yates, as well as other researchers (18-21), contend that the formation of rhodium gem-dicarbonyl is correlated with rhodium's surface mobility and tendency to sinter and deactivate at high temperature. To combat this phenomenon, Yates first dehydroxylates the surface by evacuating Rh/ γ -Al₂O₃ at high temperature (475–900 K), and he later explores functionalizing the surface using both trimethyl silane and potassium (from K₂CO₃) to cap nucleophilic surface oxygen atoms and thus stabilize rhodium atoms in a highly dispersed array.

In contrast to the functionalization efforts of Yates, the bimetallic materials synthesized in this study are thought to employ molybdenum, in the form of highly dispersed molybdenum anhydrides, to stabilize a high dispersion of rhodium. The efforts to potassium dope the surface of both the metal-loaded and native support are aimed, in part, at addressing the reactivity of the underlying alumina and stemming its retrograde dehydration activity. The approach is meant to synthesize an alkaline-metal oxide layer on the alumina surface which effectively screens primary alcohol products of hydrogenation from the adsorptive sites of the support—believed here to be the Lewis acid-base pair sites of the support. Our microreactor results demonstrate, as expected, that the potassium loading is directly correlated with dehydration activity for both native alumina and the Rh-Mo/ γ -Al₂O₃. More intriguing, however, is the insight that can be

drawn from this study about the nature of transition metal chemisorption on the alumina surface during deposition from metal-carbonyl precursors.

Transition Metal Chemisorption Chemistry

The chemisorptive characterization of the samples with pyridine and ammonia supports our contention that the Lewis acid-base pairs play a key role in the dehydration mechanism, and the results are as expected for native alumina. The pyridine adsorption spectra in Figure 8 indicate that after the chemisorption of Mo subcarbonyl on the alumina surface and the mild oxidation of this Mo/ γ -Al₂O₃ sample, the surface acidity of the material is still significant. This result is in agreement with the work of Burwell and Brenner (22,23), which suggests that Mo(CO)₆ chemisorbs on alumina at hydroxyl sites rather than Lewis acid sites. If, upon oxidation of the material, the Mo subcarbonyl reacts with O₂ in the gas phase, the underlying Lewis acid sites of the support are left unmolested. The remaining Mo/ γ -Al₂O₃ would have the acid sites associated with the underlying support and perhaps Lewis acid sites associated with the molybdenum anhydride centers on the surface. Hence the spectra in Figure 8 indicate that considerable Lewis acidity is present on the surface of the 2.5% Mo/ γ -Al₂O₃. Because the pyridine adsorption technique is not quantitative, however, the increase in the acid amount, or number of pyridine-sensitive sites, cannot be accurately determined from the IR peak intensities given the degree of surface roughness in the self-supporting wafers used in this experiment.

Since the pyridine adsorption and IR analysis provided no quantitative measure of acid amount, we were motivated to use an adsorptive technique that could track the total amount of basic probe molecule adsorbed, namely NH₃ saturation and TPD. Upon examination of the second column of Table 1, the total ammonia adsorption of the samples tested, a jump in total acidity of the surface is evident when the results for native alumina and Mo/ γ -Al₂O₃ are compared. When the loading of Mo is increased from 2.5% to 3.4% in the 2.8% Rh-3.4% Mo sample, the total NH₃ capacity remains fairly constant. Essentially, the increase in Mo loading

and, hence, the number of Lewis acid centers is offset by the interaction of Rh with the surface and its titration of some of the acid sites present.

The spectrum for the evacuated sample in Figure 9, depicting the pyridine adsorption spectra for Rh-Mo/ γ -Al₂O₃, lacks Lewis signature peaks. This indicates that the process of chemisorbing the rhodium onto the Mo/ γ -Al₂O₃ material diminishes or otherwise weakens the acid sites on Mo/ γ -Al₂O₃. It is not surprising, then, that Figure 10 looks indistinguishable, within experimental uncertainty, from Figure 9. The addition of potassium to the surface of Rh-Mo/ γ -Al₂O₃ has no effect on the majority of acid sites sensitive to pyridine adsorption since these sites have already been weakened or eliminated by the presence of rhodium. This ameliorating effect of chemisorbed rhodium on the final acidic character of the Mo/ γ -Al₂O₃ is also the key to (i) interpreting the microreactor results of Figure 7 and (ii) the observation in the synthesis of the materials that the ultimate potassium loading achievable on Rh-Mo/ γ -Al₂O₃ using the ion exchange method is only a fraction of that for native alumina (as high as 3%) when both are exposed to the same concentration of KNO₃. The majority of the acidic character typically available for MeOH dehydration and available to interact with potassium cations has already been eliminated by chemisorbing rhodium.

The relation between the transition-metal loading and the acidity of the surface of the materials in this study can be tracked in a self-consistent fashion. On native alumina, the ammonia saturation data in Table 1 suggests that the amount of ammonia adsorbing sites is approximately 2450 μ moles/g. In Peri's model for the surface of dehydrated γ -Al₂O₃ (24), the hydroxyl site density is approximately 8 to 12 hydroxyl sites per 100 $\text{\AA}^2$. If we assume that (i) the MoO_x is present as the surface molybdate Mo(VI)O₄ (see Figure 13), as XPS analysis indicates (1) and Raman spectroscopic investigations by Stencel et al. (25) and Wachs and coworkers (26-29) suggest, (ii) the Mo has interacted with 2 hydroxyl sites per atom of Mo in chemisorbing and oxidatively binding to the surface, and (iii) each Mo center acts as a Lewis acid site in the presence of NH₃ which can adsorb 2 NH₃ molecules per Mo, then the

stoichiometry on the 2.5% Mo/ γ -Al₂O₃ sample suggests that it should adsorb approximately 2910 μ moles/g of NH₃. This simply calculated value deviates by only 3% from the experimentally measured NH₃ capacity on the 2.5% Mo/ γ -Al₂O₃, as reported in Table 1. In proceeding to consider the expected acid character of the 2.8% Rh-3.4% Mo/ γ -Al₂O₃, an adjustment must be made for the increase in Mo loading. Considering first only the influence of the Mo. Based on the assumptions above, the 2.8% Rh-3.4% Mo sample would be expected to adsorb approximately 3010 μ moles/g. If (i) the Rh present on the surface after oxidation of the catalyst is present as Rh(III), as XPS analysis indicates (1), (ii) the rhodium oxide screens 3 Lewis acid sites of the support per Rh atom, and (iii) each Rh atom is again capable of adsorbing 2 NH₃ molecules, then the implied stoichiometry suggests that the 2.8% Rh-3.4% Mo/ γ -Al₂O₃ should have an NH₃ capacity of 2738 μ moles/g. This value accounts for 96% of the NH₃ capacity measured experimentally. These results provide a systematic basis for interpreting the experimental observation that the presence of the Rh diminishes at least part of the acidity present on Mo/ γ -Al₂O₃.

The final issue which must be addressed in considering the adsorptive behavior of the transition-metal loaded samples considered in this study concerns the difference in their adsorptive behavior in the presence of ammonia versus pyridine. The evacuated pyridine IR spectrum in Figure 9 for the Rh-Mo/ γ -Al₂O₃ sample was similar to that of highly potassium-doped native alumina, yet the NH₃ saturation data of Table 1 suggest that the acid amount of the Rh-Mo sample is considerably larger than that of, say, doped 8.2% K on alumina sample. First, the pyridine adsorption study provided no measure of acid amount—technically, the acid *strength* of the Rh-Mo sample is comparable to that of highly doped alumina as measured by pyridine adsorption. Second, the relative tendency of NH₃ and pyridine to coordinate with transition-metal centers is strongly dependent on the π^* -backbonding ability, and hence, the oxidation state, of the transition-metal center. Shepherd and Taube (30) have calculated the relative ligand exchange rates for NH₃ and pyridine with [(NH₃)₅RuOH₂]²⁺ and

$[(\text{NH}_3)_5\text{RuOH}_2]^{3+}$, wherein the H_2O coordination site was replaced. In their study, Shepherd and Taube calculate that for Ru^{2+} , the affinity ratio of pyridine to NH_3 was approximately 2:1, and the greater affinity for pyridine resulted from the ~ 5.8 kcal/mol relative contribution to the free energy of association due to backbonding to the pyridine. In contrast, for the Ru^{3+} which was assumed to have no net backbonding to the pyridine, the pyridine to NH_3 affinity ratio was approximately 1:4 (1:24 after accounting for a statistical factor of six in the case of NH_3). In this study, the molybdenum and rhodium—like the Ru^{3+} of Shepherd and Taube's work—are present in a highly oxidized state prior to reduction. Hence, sites sensitive to strong NH_3 adsorption on the Rh-Mo and Mo on $\gamma\text{-Al}_2\text{O}_3$ surface may not bond as strongly to pyridine, and the adsorption results for NH_3 and pyridine should be expected to quantitatively differ.

Conclusions

The results presented for the series of K-doped alumina and Rh-Mo/ $\gamma\text{-Al}_2\text{O}_3$ samples synthesized in this study demonstrate that the MeOH dehydration propensity of these materials can be quantified and manipulated. This dehydration propensity has been correlated to the strength and amount of Lewis acid sites on the surface through analysis of the IR spectra of adsorbed pyridine and the NH_3 saturation and TPD data. The IR spectra of adsorbed pyridine and the NH_3 saturation and TPD data on the Rh-Mo/ $\gamma\text{-Al}_2\text{O}_3$ samples show that addition of rhodium diminishes surface acidity of Mo/ $\gamma\text{-Al}_2\text{O}_3$. This amelioration of acidity is evidenced by the observation that less than 6 wt% potassium doping is required on the Rh-Mo catalyst to completely quash the DME activity compared to more than 12 wt% on native $\gamma\text{-Al}_2\text{O}_3$ at temperatures of up to 250 °C. Furthermore, the chemisorptive characterization of the transition-metal loaded samples synthesized in this investigation is consistent with the contention of Burwell and Brenner (22,23) that the $\text{Mo}(\text{CO})_6$ interacts primarily with hydroxyl sites on the surface of the alumina. While the chemisorbing molybdenum subcarbonyls may not materially alter the Lewis acidity of the underlying support, such adsorbed and oxidized molybdenum centers seem to function as Lewis acid sites in the presence of NH_3 . The Lewis acid character of

the Mo centers is suggested by the dramatic jump in NH_3 capacity upon addition of Mo to the alumina surface. The process of chemisorbing and oxidizing a second, active transition metal from $\text{Rh(I)(CO)}_2(\text{acac})$ leads to a dramatic reduction in the strength of the Lewis acid sites on the surface and diminishes the number of sites which actively adsorb NH_3 . Additional chemisorptive characterization of transition-metal loaded samples is underway, and such studies are hoped to add more conclusive evidence to the stoichiometric arguments presented in the discussion section herein.

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Table Caption

Table 1. Ammonia Saturation Measurements Reflecting Surface "Acid Amount"

Sample	Reversible ^(a) NH ₃ Adsorption μmoles/g sample	Total NH ₃ Adsorption μmoles/g sample
γ-Al ₂ O ₃ (American Cyanimid)	594 ± 58	2450 ± 66
8.2% K on γ-Al ₂ O ₃	374 ± 37	2270 ± 75
11.9% K on γ-Al ₂ O ₃	349 ± 33	3080 ± 133
2.5% Mo on γ-Al ₂ O ₃	726 ± 71	2820 ± 83
2.8% Rh – 3.4% Mo on γ-Al ₂ O ₃	764 ± 71	2850 ± 75
2.8% Rh – 3.4% Mo on γ-Al ₂ O ₃ ; 0.03% K ^(b)	722 ± 66	2570 ± 62
2.8% Rh – 3.4% Mo on γ-Al ₂ O ₃ ; 0.08% K ^(b)	747 ± 71	2760 ± 75

(a) Reversible sites are defined as those NH₃-sensitive acid sites which desorb NH₃ upon heating to 400 °C.

(b) The 2.8% Rh – 3.4% Mo on γ-Al₂O₃ sample was used as the starting material for these potassium-doped catalysts. While elemental analysis was used to determine the potassium content, no analysis of transition metal content was conducted following the ion-exchange protocol.

Table 1. Ammonia Saturation Measurements Reflecting Surface "Acid Amount"

Figure Captions

- Figure 1. Methanol Dehydration Mechanism on Alumina, Adapted from Parera, J. M. and Figoli, N. S., *J. Catal.*, **14**, 303 (1969)
- Figure 2. Steady-State Conversion of Methanol to Dimethyl Ether as a Function of Potassium Loading on $\gamma\text{-Al}_2\text{O}_3$
- Figure 3. Pyridine Adsorption Spectra: Native $\gamma\text{-Al}_2\text{O}_3$
- Figure 4. Pyridine Adsorption Spectra: Potassium-Doped $\gamma\text{-Al}_2\text{O}_3$, 11.9% by Weight
- Figure 5. Ammonia Temperature Programmed Desorption for Series of Doped Alumina Samples
- Figure 6. Dimethyl Ether Formation as a Function of Potassium Loading on 2.8% Rh-3.4% Mo/ $\gamma\text{-Al}_2\text{O}_3$
- Figure 7. Dimethyl Ether Formation as a Function of Potassium Loading for Rh-Mo/ $\gamma\text{-Al}_2\text{O}_3$ Samples Doped via Ion Exchange
- Figure 8. Pyridine Adsorption Spectra: 2.5% Mo/ $\gamma\text{-Al}_2\text{O}_3$
- Figure 9. Pyridine Adsorption Spectra: 2.8% Rh-3.4% Mo/ $\gamma\text{-Al}_2\text{O}_3$
- Figure 10. Pyridine Adsorption Spectra: Potassium-Doped Rh-Mo/ $\gamma\text{-Al}_2\text{O}_3$, 0.03% by Weight
- Figure 11. Ammonia Temperature Programmed Desorption Tracing Acidity from Native Alumina to Final Bimetallic Catalyst
- Figure 12. Ammonia Temperature Programmed Desorption for Doped Rh-Mo/ $\gamma\text{-Al}_2\text{O}_3$ Series
- Figure 13. Mo(VI)O₄ Surface Species Adapted From Stencel, J. M. et al., *J. Catal.*, **90**, 314 (1984)

Figure 2. Steady-State Conversion of Methanol to Dimethyl Ether as a Function of Potassium Loading on $\gamma\text{-Al}_2\text{O}_3$

Figure 3. Pyridine Adsorption Spectra: Native γ -Al₂O₃

Figure 4. Pyridine Adsorption Spectra: Potassium-Doped γ - Al_2O_3 , 11.9% by Weight

Figure 5. Ammonia Temperature Programmed Desorption for Series of Doped Alumina Samples

Figure 6. Dimethyl Ether Formation as a Function of Potassium Loading on 2.8% Rh-3.4% Mo/ γ -Al₂O₃

Figure 7. Dimethyl Ether Formation as a Function of Potassium Loading for Rh-Mo/ γ -Al₂O₃ Samples Doped via Ion Exchange

Figure 8. Pyridine Adsorption Spectra: 2.5% Mo/ γ -Al₂O₃

Figure 9. Pyridine Adsorption Spectra: 2.8% Rh-3.4% Mo/γ-Al₂O₃

Figure 10. Pyridine Adsorption Spectra: Potassium-Doped Rh-Mo/ γ -Al₂O₃, 0.03% by Weight

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Figure 12. Ammonia Temperature Programmed Desorption for Doped Rh-Mo/ $\gamma\text{-Al}_2\text{O}_3$ Series

Figure 13. Mo(VI)O₄ Surface Species Adapted From Stencel, J. M. et al., *J. Catal.*, **90**, 314 (1984)

Section III

Comparative Study of Rh/Al₂O₃ and Rh-Mo/Al₂O₃ Catalysts

Research Context

In this section we return to the analysis of Rh/Al₂O₃ and Rh-Mo/Al₂O₃ catalysts synthesized via sequential chemisorption of mononuclear organometallic precursors, namely Rh(CO)₂(acac) and Mo(CO)₆. The focus of the investigations presented herein also return to the working hypothesis of our global efforts in the Rh-Mo system, i.e. the idea that Mo serves primarily as a textural promoter, site isolating small Rh aggregates. Here, the influence of the Mo is assessed directly through both CO hydrogenation and infrared spectroscopic analysis of the samples after exposure to room temperature and high temperature syngas environments. The comparisons center on testing Mo-promoted and unpromoted Rh catalysts of similar Rh loadings head-to-head and assessing their activity and oxygenate selectivity, as well as comparing the CO-active infrared frequencies of the samples. As discussed below, the microreactor analysis for CO hydrogenation and the insights gained from infrared spectroscopic characterization of the samples are well aligned with the idea that the Mo, indeed, stabilizes small, isolated Rh aggregates. The Mo-promoted samples tend toward higher oxygenate selectivity and enhance the intensity of the Rh "gem-dicarbonyl" infrared band, the primary marker for highly dispersed Rh. Again, Section I of this report explores an alternative synthesis approach to form Rh-Mo/Al₂O₃, and Section II traces the surface features of the catalytic materials during the synthesis process. In the investigations outlined in this section, we turn back to the origin of our interest in this catalytic system: the unique synergy of Rh and Mo for oxygenate synthesis.

The theme common to each proposal is that the rhodium active sites are isolated by molybdenum (oxide) and the site-isolated rhodium acts much like molecular rhodium complexes in homogeneous catalysis. Better understanding of this site-isolation effect is important for the design of new bimetallic catalysts—both rhodium and non-rhodium systems—for oxygenate synthesis from syngas. This work has focused on the comparative study of Rh/Al₂O₃ and Rh-Mo/Al₂O₃ catalysts using CO hydrogenation as a probe reaction and *in situ* infrared (IR) spectroscopic characterization of CO-pretreated catalysts.

Experimental

Catalysts preparation employs the method of non-aqueous sequential chemisorption of metal-carbonyl complexes on alumina, which was developed previously [Foley et al., 1990]. The metal-carbonyl precursors and support material are Mo(CO)₆, Rh(CO)₂acac, and gamma alumina (BET surface area = 250 m²/g), respectively. The catalysts are listed with their elemental analysis data in the following Table:

Table 1. Rh/Al₂O₃ and Rh-Mo/Al₂O₃ catalysts

Catalyst	Rh wt. %	Mo wt. %	Rh/Mo (mole ratio)
Rh-I	0.23	0	--
Rh-II	0.45	0	--
Rh-III	1.37	0	--
Rh-IV	2.66	0	--
RhMo-I	0.21	1.40	0.14
RhMo-II	0.41	1.42	0.27
RhMo-III	1.21	1.46	0.77
RhMo-IV	2.43	1.23	1.84

CO hydrogenation reactions were performed in a fixed bed, down-flow, high-pressure microreactor system, which consists of (i) high purity CO and H₂ gas sources, which were further purified by series of traps to exclude H₂O, O₂, Fe(CO)₅, etc. (ii) a stainless steel tubular reactor with capacity of 0.2-2.0g of catalyst, connected to the gas sources through high pressure

mass-flow controllers, (iii) a product analysis unit, in which the downstream mixture of reactants and products were sent to on-line GC's after releasing pressure through a back-pressure regulator. More detailed descriptions of the system can be seen elsewhere [Foley et al.,1990].

Each of the catalysts listed above was reduced at 300°C with H₂ for 3 h before introducing the reactant mixture. Reaction conditions are 473-623K, 2.0-6.6MPa, CO/H₂ = 1/1, and GHSV = 3500h⁻¹. Data comparing activity and selectivity were collected after the steady-state activity had been reached on the catalysts after about 10 h. on stream. In order to assure differential reaction conditions, CO conversions on all the catalysts are maintained below 10% by diluting the catalyst bed with inert, low surface area quartz chip.

In situ IR studies of the catalysts were performed on a Nicolet 510M FT-IR spectrometer using self-supporting sample wafers in a quartz cell equipped with NaCl windows. All spectra were recorded in flowing helium at room temperature after the sample was treated in CO at different conditions. Each spectrum was recorded using 50 scans with resolution of 4 cm⁻¹.

Results and Discussions

1. Activity and selectivity of the catalysts

To examine the effect of different rhodium loadings and different Rh/Mo ratios on catalytic performance, each catalyst was tested for CO hydrogenation under the same reaction conditions. The stability of the catalysts are shown in the Figures 1 and 2.

It can be seen that all the catalysts have reached relatively stable activities after approximately 8-10 h. But differences are apparent between the rhodium and the rhodium-molybdenum systems. Rh/Al₂O₃ catalysts exhibit gradually decreasing activities with increasing reaction time (Figure 1). In contrast, most of the molybdenum-promoted rhodium catalysts show stable or somewhat increased activities during the same reaction period (Figure 2).

Another significant difference is in the activities of the two series of catalysts. Rh-Mo/Al₂O₃ catalysts have approximately 5-fold higher activities compared with corresponding, unpromoted rhodium catalysts (Figure 1 and 2, Table 2). An interesting fact observed from this reaction data is that with the exception of Rh-I (lowest Rh loading in the group), Rh/Al₂O₃ catalysts have similar turnover frequencies (TOF) which may imply that the nature of the active site on these catalysts are the same or similar despite differences in Rh loading. The exception of Rh-I may be because the Rh loading is not high enough to form similar active sites to those in more highly loaded catalysts. For the molybdenum-promoted system, similar behavior is observed but with exception of both high and low rhodium loadings, RhMo-I and RhMo-IV (Figure 2). This may imply that RhMo-II and RhMo-III have similar active sites but the nature of the active sites are very different from that in the corresponding Rh monometallic system. The idea of probing the nature of active sites from TOF has been used extensively for iron catalysts in ammonia synthesis (see, for example, Topsoe et al 1980). For RhMo-IV the low Mo/Rh ratio may not provide enough physical promoter to form the active sites present in RhMo-II and RhMo-III for oxygenate formation, and hence, the inadequately promoted rhodium on RhMo-IV behaves more like a F-T and water gas shift catalyst with enhanced formation of CH₄ and CO₂. (Table 3). The behavior of the RhMo-I catalyst may be due to the low rhodium loading, as in Rh-I.

From the reaction testing, some broad distinctions can be made about these catalysts:

- (1) Mo-promotion significantly enhances oxygenate selectivity, as has been shown in previous investigations;
- (2) Oxygenate formation may require a minimum ensemble of rhodium sites as evidenced by the poor performance of Rh-I and RhMo-I samples;
- (3) Parity in the Rh and Mo concentrations seems to improve the oxygenate selectivity (compare the performance of RhMo-II and RhMo-III to the promoter-lean RhMo-IV).

Table 2. Summary of the reaction data*

	$\Sigma \text{C1-C6}$	ΣOxy	CO conv.	Rate
Rh-I	82.2%	17.8%	0.16%	1.21E-03
RhMo-I	83.0%	17.0%	0.12%	7.31E-03
Rh-II	93.3%	6.7%	1.59%	6.10E-03
RhMo-II	61.8%	38.2%	1.08%	3.32E-02
Rh-III	91.4%	8.6%	4.36%	6.96E-03
RhMo-III	58.8%	41.2%	1.53%	3.19E-02
Rh-IV	91.1%	6.7%	7.28%	7.41E-03
RhMo-IV	64.6%	25.6%	3.69%	3.85E-02

*Reaction condition: 300°C, 300psi, GHSV=3500/h. Rate: mol CO/mol Rh•sec.

Table 3. Product Selectivity (%) (300°C, 300psi, CO/H₂=1/1)

	CO ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	Me ₂ O	MeOH	C ₄	EtOH	MeOE	C ₅	C ₆
								t			
Rh-I	0.0	42.6	12.3	7.6	5.3	12.4	19.7	0.0	0.0	0.0	0.0
RhMo-I	0.0	39.4	24.1	14.6	7.8	9.2	4.9	0.0	0.0	0.0	0.0
Rh-II	0.0	69.4	4.6	4.2	1.3	5.4	9.8	0.0	0.0	3.6	1.7
RhMo-II	0.0	44.0	8.2	3.5	8.1	14.0	1.6	9.1	7.0	4.2	0.2
Rh-III	0.0	73.9	3.4	3.3	0.2	1.8	4.5	1.0	5.6	3.1	3.2
RhMo-	0.0	45.6	7.6	2.2	5.4	20.0	1.1	8.0	7.9	1.1	1.2
III											
Rh-IV	2.2	76.4	3.1	3.6	0.2	1.6	2.9	0.7	4.2	2.6	2.6
RhMo-	9.8	48.1	7.6	2.6	2.2	9.4	1.0	4.5	9.4	4.2	1.2
IV											

2. Effect of Temperature and Pressure on Selectivity

Generally, activities increases with increasing reaction temperature for both Rh/Al₂O₃ and Rh-Mo/Al₂O₃ catalysts. However, molybdenum promotion can greatly suppress hydrocarbon formation (principally CH₄) and enhance oxygenated product selectivity on rhodium catalysts. Figures 3 and 4 clearly show this difference for Rh-III and RhMo-III catalysts.

Pressure does not appear to strongly influence the selectivity of the reaction in the range of 2.0 MPa to 6.6 MPa. A slight increase in oxygenate selectivity was observed with increasing pressure. Figure 5 presents a representative example for RhMo-III.

3. In situ IR characterization of the catalysts

In situ IR studies focused on the characteristic carbonyl absorption of rhodium species, namely, gem-dicarbonyl (2100, 2025 cm⁻¹), terminal carbonyl (2050 cm⁻¹), and bridging carbonyl (~ 1850 cm⁻¹). It has been demonstrated on alumina-supported rhodium catalyst that the formation of gem-dicarbonyl, Rh(I)(CO)₂, is an indication of highly dispersed Rh(I) species, and terminal and bridging carbonyls are correlated to the formation of rhodium crystallites. [Yates et al., 1979, Wang and Yates, 1984]. It is also possible that rhodium species are intrinsically highly dispersed on Rh/Al₂O₃ and/or Rh-Mo/Al₂O₃. Comparison of the IR spectra of Rh/Al₂O₃ and Rh-Mo/Al₂O₃ (see below) indicate that the bimetallic catalysts generally show less terminal and bridging carbonyl intensity and more gem-dicarbonyl features than do the unpromoted catalysts. This distinction may imply that rhodium sites on Rh-Mo/Al₂O₃ are intrinsically more isolated.

All the catalyst samples, reduced exactly as in the reaction studies, had been treated by CO at different temperatures followed by *in situ* IR measurement at room temperature in flowing helium. Following room temperature CO-treatment, all samples show gem-dicarbonyl and terminal carbonyl absorption, and higher rhodium-loading catalysts also show bridging carbonyl features. (see spectra of room temperature CO treated samples, spectrum "A" in Figures 6-13)

These predominant gem-dicarbonyl features are expected because it has been concluded that CO treatment of Rh/Al₂O₃ in the presence of surface Al-OH leads to disruption of Rh(0) crystallites and to the formation of isolated Rh(I) sites [Basu et al., 1987, 1988, Van't Blik et al., 1983].

Following higher temperature treatment of the catalysts with CO, gem-dicarbonyl features are enhanced for low Rh-loading catalysts, namely, Rh-I, Rh-II, RhMo-I, RhMo-II (see Figures 6-9). Differences are minimal across these samples except that more terminal carbonyl absorption is seen in the unpromoted samples (Figures 6 and 8). Highly dispersed, gem-dicarbonyls are the predominate species on all the samples with low Rh loadings. In contrast, the difference between the Rh and RhMo series becomes more pronounced for the higher Rh-loading samples following high-temperature CO treatment. (Figures 10-13). Figures 10 and 11 for Rh-III and RhMo-III, respectively, demonstrate that molybdenum promotion stabilizes highly dispersed Rh(I) features. Terminal and bridging carbonyl species became significant on high-temperature, CO-treated Rh-III but not on RhMo-III. Similar rhodium agglomeration has been observed for CO-adsorbed rhodium catalysts at 423 K by Solymosi and Pasztor [Solymosi and Pasztor 1985]. Stabilization of the gem-dicarbonyl features on RhMo-III again suggests stabilization of isolated rhodium aggregates on the alumina surface and a suppression of rhodium agglomeration in the high-temperature CO environment. This difference between RhMo-III and Rh-III correlates with their different activities and selectivities. High-temperature CO treatment of Rh-IV and RhMo-IV promotes strong bridging carbonyl absorption on both samples although somewhat more intense gem-dicarbonyl features remain in RhMo-IV. The enhancement of bridging carbonyl features on RhMo-IV is probably due to the low Mo/Rh ratio, which is suggestive of the lack of sufficient molybdenum to keep rhodium active sites from agglomerating.

Summary

Molybdenum-promoted rhodium catalysts show high activity for CO conversion and much improved selectivity for oxygenates production. *In situ* IR characterization of the corresponding

catalysts reveals that molybdenum effectively hinders rhodium agglomeration. Therefore, molybdenum-promoted, site-isolated rhodium may be responsible for the observed high oxygenate selectivity on Rh-Mo/Al₂O₃ catalysts.

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13

Section IV

Summary of Major Accomplishments

Equipment and Instruments

During the period covered by this research grant, we have put in place and on-line the following equipment which was crucial to the progress made under this grant and continues to service research efforts in the departments of chemistry and chemical engineering here at University of Delaware:

- 1) Schlenk line for synthesis of air-sensitive materials under an inert environment. This apparatus was used in the synthesis of all the catalytic materials addressed in these studies.
- 2) Ammonia saturation and temperature programmed desorption unit. This apparatus was employed in the surface acidity characterization of many of the materials investigated in connection with this grant.
- 3) Transmission infrared (IR) cell. The cell was used in the pyridine adsorption infrared characterization of materials, investigation of the OH-region as a function of temperature, and investigation of the CO-region of the samples in high temperature CO and H₂ environments.
- 4) Low-pressure microreactor. The low-pressure reactor was employed in methanol dehydration probe reaction studies.
- 5) High-pressure reactor retrofitting. The high-pressure reactor was employed in all the CO hydrogenation testing of the catalytic materials.
- 6) Hydrogen chemisorption unit. This apparatus has been used throughout the course of the grant to quantify reactive surface area through H₂ and CO chemisorption on the catalytic materials synthesized in the course of our investigations

Scientific Progress

The three main sections of this report provide in-depth discussion of the scientific progress made during the period of this grant. In broad terms, (i) we have confirmed the synergy of the Rh-Mo combination for oxygenate production—both from materials in which the metals are sequentially chemisorbed and those in which the precursors are binuclear compounds containing rhodium and molybdenum, (ii) we have identified key features of the interactions between the transition-metal precursors and the alumina surface, and (iii) we have gathered evidence in support of our working hypothesis that the molybdenum in this system serves, primarily, to isolate and stabilize the active rhodium sites against agglomeration and consequent retrograde shifts in selectivity from oxygenates to hydrocarbons. More specifically, the following advances can be reiterated from the three manuscript sections of this report:

- 1) Bimetallic Rh-Mo/Al₂O₃ catalysts have been successfully synthesized from a homogenous, binuclear precursor, (PPh₃)₂RhMo(CO)(μ-CO)₂Cp, and tested for CO and CO₂ hydrogenation.
- 2) Catalysts derived from binuclear precursors show superior selectivities for oxygenates to those derived from coadsorption of mononuclear complexes.
- 3) Analysis of global activation parameters of the binuclear- and mononuclear-derived Rh-Mo/Al₂O₃ catalysts suggest that the activation energies for CO and CO₂ conversion are markedly lower for the binuclear-derived materials.
- 4) Infrared analysis of the binuclear- and mononuclear- derived materials confirms that the Rh is present in a more highly dispersed mosaic on the binuclear-derived materials, as evidenced by the gem-dicarbonyl intensities on these samples. The IR results imply enhanced site-isolation of the Rh in the binuclear-derived materials.

- 5) Surface acidity of both native and metal-loaded aluminas have been quantified and controlled through KNO_3 doping. These materials have been characterized via methanol dehydration probe reaction studies, pyridine adsorption infrared spectroscopy, and ammonia saturation and temperature programmed desorption.
- 6) Dehydration activity of the KNO_3 -doped samples was strongly correlated to their ultimate potassium loading and, hence, their Lewis acid character.
- 7) As has been suggested in the literature, Mo(CO)_6 precursors employed in this study appear to interact primarily with the non-acidic hydroxyl sites on the alumina surface during the sequential chemisorption used to synthesize these materials.
- 8) Upon adsorption of Rh subcarbonyls and their subsequent oxidation on the surface of $\text{Mo/Al}_2\text{O}_3$, the Lewis acidity of the materials is suppressed. This Rh-surface interaction suggests that the chemisorption of the active metal in this system occurs at Lewis acid centers of the surface.
- 9) Rh- $\text{Mo/Al}_2\text{O}_3$ catalysts, which have been prepared by sequential chemisorption (as opposed to coadsorption), have been tested for CO hydrogenation and compared directly to monometallic Rh/ Al_2O_3 catalytic samples.
- 10) Promotion of Rh with preadsorbed Mo dramatically improves the activity and oxygenate selectivity of the Rh-catalyzed CO hydrogenation.
- 11) *In Situ* IR characterization and comparison of the Rh- $\text{Mo/Al}_2\text{O}_3$ and the Rh/ Al_2O_3 materials, centering on analysis of the metal-carbonyl region, suggests that the Mo effectively hinders Rh agglomeration. This site-isolated Rh in the bimetallic system may, then, be responsible for the high oxygenate selectivity of these catalysts.

Major Presentations and Publications

Te, Mure, Lowenthal, Eric E., Foley, Henry C., "Comparative Study of Rh/Al₂O₃ and Rh-Mo/Al₂O₃ Catalysts", *Chemical Engineering Science*, submitted June 1994.

Te, Mure, Eric E. Lowenthal and Henry C. Foley, "Comparative Study of Rh/Al₂O₃ and Rh-Mo/Al₂O₃ Catalysts", poster to be presented at the 13th International Symposium on Chemical Reaction Engineering, Baltimore, Maryland, September 1994

Te, M., E. E. Lowenthal and H. C. Foley, "Evidence for Site Isolation in Rh-Mo Bimetallic Catalysts Derived from CpRhMo(CO)₃(PPh₃)₂", *Journal of Catalysis*, **146**, 591 (1994).

Lowenthal, E. E., S. Schwarz and H. C. Foley, "Surface Chemistry of Rh-Mo/ γ -Al₂O₃: an Analysis of Surface Acidity", *Journal of Catalysis*, submitted April 1994.

Lowenthal, E. E. and H. C. Foley, "Bimetallic and Metal-Support Chemistries on Rh-Mo/ γ -Al₂O₃", Presentation at Annual Meeting, American Institute of Chemical Engineers, St. Louis, Missouri, November 1993.

Lowenthal, E. E. and H. C. Foley, "Design of a High Activity, High Selectivity Alcohol Synthesis System: Secondary Dehydration and Site Isolation", Poster Presented at Biannual Meeting, North American Meeting of the Catalysis Society, Pittsburgh, Pennsylvania, May 1993.

Foley, H. C., M. Te and E. E. Lowenthal, "Rh-Mo Bimetallic Cluster-Derived Catalysts for CO Hydrogenation", Presentation at Annual Meeting, American Chemical Society, Petroleum Chemistry Symposium in Honor of Bruce C. Gates, Denver, Colorado, March 1993.