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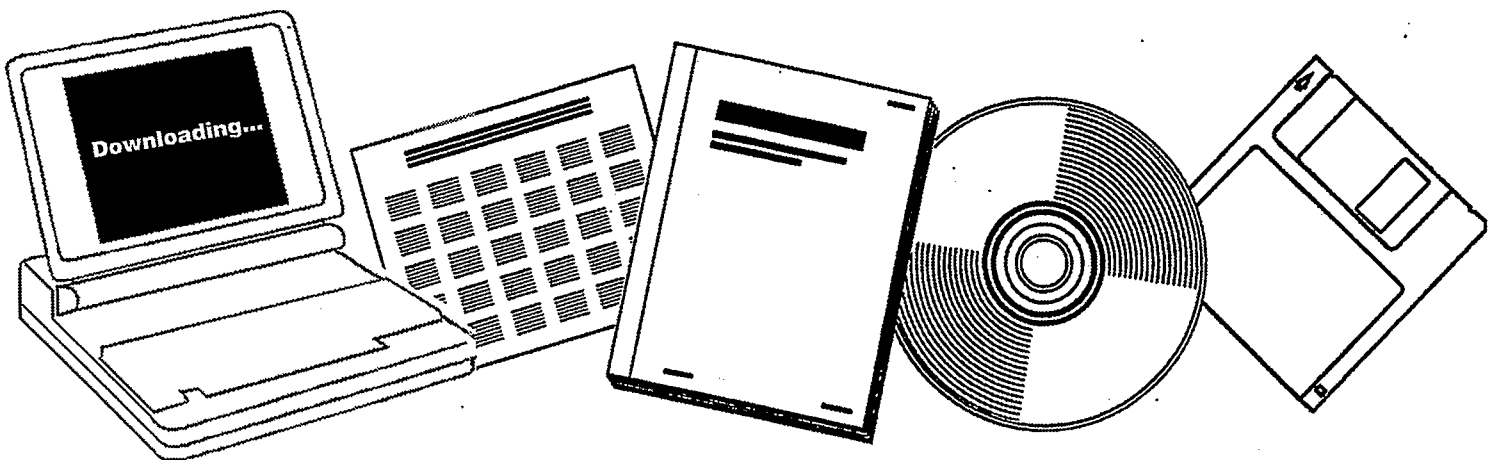
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**DESIGN OF A HIGH ACTIVITY AND SELECTIVITY
ALCOHOL CATALYST. THIRD QUARTERLY REPORT,
FEBRUARY 7, 1991-MAY 7, 1991**

**DELAWARE UNIV., NEWARK. CENTER FOR
CATALYTIC SCIENCE AND TECHNOLOGY**

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

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**Third Quarterly Report for Period
February 7, 1991 to May 7, 1991**

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**Design of a High Activity and Selectivity Alcohol Catalyst
DE-90PC 90291
Third Quarterly Report**

Improvements in the catalyst technology for the production of methanol (MeOH) from syngas have been limited since the introduction of the first commercial process by BASF in 1921 which employed a zinc oxide/chromia ($\text{ZnO/Cr}_2\text{O}_3$) catalyst. A major improvement in the economics of the original process was achieved by ICI in 1966 when they began commercial production of MeOH using a bimetallic catalyst comprised of Cu (reduced from CuO) and ZnO supported on alumina (Al_2O_3). With the greater activity and selectivity of the Cu/ZnO on Al_2O_3 catalyst, ICI was able to operate their system at 250°C and 50 to 100 bar, compared to the original BASF process which required temperatures on the order of 350°C and pressures of 250 to 350 bar.¹ The reduction in pressure of the process afforded the use of less costly compressor technology, and the catalyst used by ICI in 1966, with only slight variations, has remained the catalyst of choice for MeOH synthesis since its introduction. Nevertheless, the ICI process is still characterized by low per pass conversion, and relatively high pressures.

Recent systematic investigations by Foley et al.² concerning the hydrogenation of CO by bimetallic catalysts comprised of combinations of group VIB and VIIIB transition metals on gamma- Al_2O_3 have suggested the potential for a high selectivity, high activity catalyst for methanol and higher alcohol synthesis. In this study, Foley found that a 3 weight % rhodium (Rh)/2.8% molybdenum (Mo) catalyst had a high propensity for oxygenate formation at low, moderate and high pressures. Furthermore, this Rh/Mo catalyst produced MeOH and ethanol with a 40% selectivity at pressures on the order of 4 bar. Given the promise shown by this catalyst, studies were conducted at pressures up to 67 bar where the catalyst showed increased selectivity for oxygenate formation. At these higher pressures, however, the secondary dehydration of methanol to dimethyl ether became significant, most probably catalyzed by the latent acidity (in a Lewis acid sense) of the gamma- Al_2O_3 support. The primary *long-range* goal of this project will be to "tailor" a bimetallic catalyst comprised of Rh and Mo to achieve higher activity and selectivity for alcohol

production than has been realized in previous work. Rather than reformulating the catalyst by trial-and-error, we will rely on data garnered from various probe reaction studies (to be set forth below) and fundamental characterization techniques to lead us toward a *rationally* designed optimal catalyst.

Past characterization by Foley of the Rh/Mo catalyst has employed spectroscopic and microscopic techniques as well as hydrogen chemisorption. X-ray photoelectron spectra of the Rh/Mo catalyst indicate that the Mo is present as Mo (IV) even after vigorous in-situ reduction in flowing H₂ at 450°C. Hence, we expect that the Mo is present as MoO_x, where the subscript x indicates that the number of oxygen atoms which bind the Mo to the support surface is as yet uncertain. TEM micrographs and electron microprobe analysis of the catalyst indicate that it has an apparent bimodal distribution of metallic clusters wherein clusters of 1.0-1.5 nm contain Rh and Mo in a ratio of greater than 1.6 Rh atoms to Mo atoms, and clusters of approximately 0.5 nm contain the two metals in a ratio of less than 0.9 Rh atoms to Mo atoms. Based upon this dual cluster texture, Foley has proposed a model of the system which suggests that in the Mo rich clusters, rhodium atoms may be effectively "site-isolated" by the MoO_x, perhaps in the form of MoO₃. It has been suggested that this isolated Rh acts more like molecular rhodium in that its rate of carbon-oxygen bond cleavage is reduced relative to direct hydrogenation. The propensity for oxygenate formation exhibited by the Rh/Mo catalyst could be attributed to this shifting in the reactive character of the site-isolated Rh. Part of the emphasis of our initial research objectives will be to test the range of validity of this model and to further delineate the role of MoO_x in isolating Rh atoms.

With regard to our near-term research plans, three sets of probe reaction studies have been defined. First, pursuant to minimizing the problem of undesirable secondary dehydration of MeOH by the gamma-Al₂O₃ support surface, we will conduct a series of experiments to:

- (i) Quantify the extent of methanol dehydration over both the native support surface and the Rh/Mo supported catalyst;
- (ii) Explore the influence of the presence of the supported metallic crystallites on the dehydration;

- (iii) Attempt to mitigate this undesirable process by doping the support surface with metal oxides which will tend to titrate the latent acidity inherent in the near-spinel structure of the $\gamma\text{-Al}_2\text{O}_3$ without poisoning or otherwise diminishing the activity of the active hydrogenation sites on the catalyst.

In order to quantify the extent of dehydration, we will gather conversion versus temperature and conversion versus MeOH concentration data on the dehydration reaction with the goal of developing an apparent rate of reaction for this process. Recently conducted experiments indicate that the dimethyl ether formed from MeOH over the Rh/Mo loaded support appears to undergo carbon-oxygen bond cleavage and further dehydration to lighter products. We will analyze these lighter products using both an on-line gas chromatograph (GC) coupled with a flame ionization detector (FID) and off-line analysis of the reactor effluents using mass spectrometry. To confirm that the dopants that we introduce into the catalyst do not significantly diminish the number of active Rh sites we will continue to quantify the active metallic surface through hydrogen and carbon monoxide chemisorption studies as well as actual CO hydrogenation experiments. Finally, throughout the course of this probe reaction study as well as within the context of all future investigations, the size and composition of the metallic clusters on our various catalysts as well as the catalyst texture will be quantified by (a) SEM and TEM micrographs, (b) electron microprobe analysis, and possibly (c) x-ray photoelectron spectroscopy.

Our second probe reaction study concerns the goal of elucidating the influence of the MoO_x on the Rh atoms. To test the validity of the site isolation model outlined above, we will conduct a series of ethylene hydrogenation and ethane hydrogenolysis experiments wherein we will feed ethylene and hydrogen into a packed bed of Rh on $\gamma\text{-Al}_2\text{O}_3$ and Rh/Mo on $\gamma\text{-Al}_2\text{O}_3$ with increasing loadings of Mo. On the Rh/ $\gamma\text{-Al}_2\text{O}_3$ catalyst we expect significant hydrogenation to ethane at moderate temperatures (250°C to 300°C) and pressures near atmospheric. In addition, we expect the variation in Mo loading to have a negligible effect upon hydrogenation for a given active Rh surface area. In contrast, to the hydrogenation of ethylene,

Boudart³ suggests that ethane hydrogenolysis is structure sensitive due to a proposed dual site reaction mechanism involving both adsorbed ethyl radicals and adsorbed hydrogen. Studies by Sinfelt^{4,5} of silica supported Rh suggest that we should be able to observe significant ethane hydrogenolysis again at moderate temperatures and with the reactor feed stream diluted by He to partial pressures of ethane of 0.03 bar and hydrogen partial pressures of 0.20 bar. In the series of hydrogenolysis experiments, we expect to observe significant activity on the Rh/ γ -Al₂O₃ catalyst, but as the loading of Mo is increased the activity of the isolated Rh clusters for hydrogenolysis should diminish since, as Boudart suggests, the availability of large hydrocarbon "landing pads" with adjacent adsorbed hydrogen will be curtailed. Such a suppression of hydrogenolysis by site isolation of the Rh with MoO_x would be consistent with results of Sinfelt for an analogous study of unsupported copper nickel alloys where active Ni clusters were site-isolated by a Cu phase. The hydrogenolysis activity of the Ni was suppressed by a factor of 1,000 upon the addition of only 7.5 weight % Cu⁶. Again kinetic data will be obtained using an on-line GC/FID system, and characterization of active metal surface area will involve hydrogen chemisorption. As the issue of metal-support interactions could cloud the results of these experiments, we may attempt to establish that Rh site isolation is the dominant effect by executing a series of control experiments on a second support such as silica.

Finally, the third probe reaction study we have planned involves exploring alternative feed stocks for MeOH synthesis. Most syngas derived from coal gasification or methane steam reforming, contains a mixture of CO, CO₂, and H₂, yet past research by Foley on the Rh/Mo system has involved solely CO and H₂. In a study by Chinchin¹, isotopic labeling of CO₂ confirmed that the primary route for MeOH formation on the ICI Cu/ZnO catalyst was by preferential adsorption of CO₂, cleavage of one carbon-oxygen bond and subsequent formation of MeOH. Furthermore, Chinchin suggests that the principle route for MeOH formation from CO in syngas is once again via CO₂ through water-gas shift chemistry. Hence, our third probe reaction study will involve hydrogenating either pure CO₂ or a mixture of CO₂ and CO to explore the

possibility that our Rh/Mo/gamma-Al₂O₃ catalyst produces MeOH via a similar reaction pathway to that on the ICI catalyst and perhaps would achieve higher alcohol yields given the presence of CO₂.

Progress on this project to date has primarily involved equipment construction. We have completed the construction of a low-pressure microreactor system which was begun during the summer of 1990. This reactor provides precise control of the flow rates of up to 5 feed gases using Brooks 5850 series mass flow controllers. In addition, the reactor has the unique capability of feeding and vaporizing low boiling point liquid hydrocarbons should future experiments require such reactants. Reactions are carried out in a packed Pyrex or quartz reactor tube (depending on temperature) mounted in a tube furnace downstream from the mass flow controllers. Reactor effluent can be analyzed via an on-line GC/FID system. In addition to the construction of the low pressure microreactor system, we have mounted and equipped an Ace-Burlitch inert atmosphere system for inorganic synthesis of supported metal catalysts. This system provides a dry, oxygen-free nitrogen atmosphere for the synthesis of air sensitive materials.

Experimental progress to date concerns the methanol dehydration probe reaction study. Five reliable reactor runs have been completed using the low pressure microreactor system mentioned above. We have thus far quantified the conversion of methanol to dimethyl ether over the native gamma-Al₂O₃ used in the Rh/Mo/gamma-Al₂O₃ catalyst within a narrow temperature range. In addition, a series of qualitative experiments has been conducted which suggests that the presence of the metallic crystallites on the gamma-Al₂O₃ does not deter dehydration, at least at the 3.0% Rh and 2.8% Mo metal loading level. However, the metallic crystallites appear to catalyze secondary decomposition of either the dimethyl ether or the MeOH to lighter hydrocarbons. This effect was delineated by feeding saturated methanol vapor in both He and, in a subsequent experiment, in CO, over the Rh/Mo/gamma-Al₂O₃ catalyst. Table 1 below details the experimental conditions of two reactor runs using He and CO as a carrier gas; the associated figure, Figure I, plots the FID response ratio of DME to "Light Alkanes" versus time on stream. While the information in Figure I is somewhat qualitative in that response ratio shown is not directly equivalent to selectivity, it nevertheless demonstrates that with He as the methanol carrier (Run 1),

almost all of the reactor effluent consisted of lighter hydrocarbons with only trace amounts of dimethyl ether formed. In contrast, when MeOH vapor in excess CO was fed to the reactor (Run 2), the CO effectively saturated the active metallic sites and almost no secondary products were observed.

Table 1: Experimental Conditions

Carrier Flow Rate:	50 sccm
Reduction in excess H ₂ :	4hr at 250°C
Methanol entrained from bubbler:	Approximately 7.2 mole %
Reaction Temperature:	250°C
<i>Run 1:</i>	<i>He Carrier</i>
<i>Run 2:</i>	<i>CO Carrier</i>

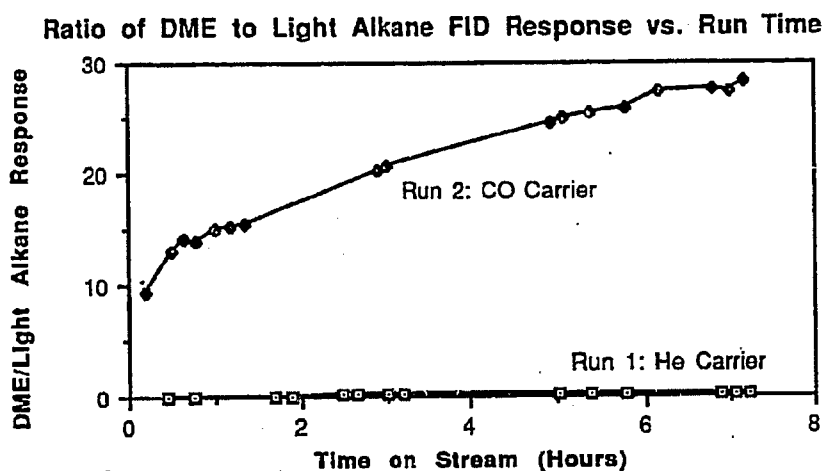


Figure I.

We are currently seeking to confirm that the lighter products observed using He as a carrier are light alkanes, CO₂, CO, and H₂O through off-line analysis of reactor effluents using mass

spectrometry. Two possible pathways exist for the formation of these lighter products, namely: (i) directly from MeOH or (ii) as second order products of the dimethyl ether formation in the sense of $A \rightarrow$ 1st order products (DME) \rightarrow 2nd order products (where "order" is not to be confused with reaction order). To determine which pathway is correct, we may attempt additional experiments such as feeding dimethyl ether in He, and separately CO, directly over the catalyst to assess whether the products of such an experiment coincide with those of the MeOH experiments. If the effluent of a DME in He experiment coincides with that of a MeOH in He experiment in both type of products and stoichiometric proportions, this would bolster the idea that the MeOH is first dehydrated by the γ -Al₂O₃ surface and then broken down on the metal sites.

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