

DESIGN OF A HIGH ACTIVITY AND SELECTIVITY ALCOHOL CATALYST

Fourth Quarter (Yearend) Report for Period
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Background and Yearend Update

As specified in our original DOE grant proposal, the objective of this research is to design a new alumina-supported bimetallic catalyst for the selective hydrogenation of carbon monoxide to produce methanol and higher alcohols. A key feature of our research program is our intention to rationally design this catalyst based upon fundamental information about the structure, composition and reactivity of preliminary catalysts synthesized throughout the course of this work. During our first year, we have put in place many of the tools needed to synthesize and characterize our catalyst samples. Since this is a yearend report, a *brief* recapitulation of the progress set forth in the previous quarterly reports follows:

- (i) A high pressure flow microreactor, used in a previous project, has been reactivated and both the reactor and its associated instrumentation have been overhauled;
- (ii) A Ph.D. candidate, Mr. Eric Lowenthal, has been identified and selected to carry out the experimental work associated with this project as a basis for his thesis dissertation in chemical engineering;
- (iii) A Schlenk line and inert glove box have been assembled and installed for the synthesis, preparation, and handling of air sensitive catalyst samples;
- (iv) A low-pressure flow reactor for probe reaction studies has been constructed, and its associated instrumentation has been calibrated;
- (v) A volumetric chemisorption unit for use with hydrogen and carbon monoxide has been designed and constructed.

Following the significant equipment construction and retrofitting outlined above, subsequent experimentation has focused on both the synthesis of catalysts designed for high oxygenate activity and the suppression of the secondary dehydration of methanol to dimethyl ether on both native gamma-alumina and a bimetallic catalyst supported on gamma-alumina. The following report highlights our progress during the fourth quarter.

Catalyst Preparation and Characterization

Three bimetallic catalysts comprised of rhodium and molybdenum supported on gamma-alumina have been synthesized. The synthesis was conducted by sequential adsorption and intermediate oxidation of $\text{Mo}(\text{CO})_6$ and $\text{Rh}(\text{I})(\text{CO})_2(\text{acac})$ in an alumina-heptane slurry. The specific steps in the synthesis have been explained elsewhere¹, but the Schlenk line constructed early in the year provided the essential airless environment and dry, oxygen-free nitrogen need to carry out the synthesis procedure. Following the synthesis, each catalyst was dried for 24 hours at 125° C in air to remove residual heptane that may physically adsorb within the alumina pore matrix.

Following the synthesis, the catalysts were analyzed by inductively coupled plasma analysis to determine metal composition. The metal loading of rhodium varied significantly with slurry contact time and ranged from 2.1 to 2.8%. Molybdenum metal loading varied from 2.4 to 3.6% and was also dependant upon contact time but appears to reach a saturation level of approximately 3.6% on gamma-alumina when adsorbed from $\text{Mo}(\text{CO})_6$ in excess heptane.

In addition to characterization of the catalysts' metal content, preliminary adsorption studies have been conducted on both the native gamma-alumina support and on an existing 3% Rh/2.8% Mo on gamma alumina catalyst. The BET surface area measurement using argon adsorption is in good agreement with previous nitrogen adsorption measurements (N_2 BET S.A. = $250 \text{ m}^2/\text{g}$ and Ar BET S.A. = $247 \text{ m}^2/\text{g}$). Pore volume of the gamma-alumina as determined using argon adsorption is also in reasonable agreement with previous nitrogen adsorption studies which indicate a pore volume of approximately $1 \text{ cm}^3/\text{g}$. Furthermore, preliminary argon adsorption studies of the Rh/Mo catalyst indicate a BET surface area of $238 \text{ m}^2/\text{g}$, or less than a 10% deviation from the native support. This encouraging result suggests that the procedures used to absorb the metal carbonyls on the alumina neither lead to significant pore blockage nor mechanical collapse of the support surface. Finally, the first tests of our volumetric hydrogen chemisorption unit on the Rh/Mo catalyst are in good agreement with previous results indicating approximately 1.0×10^{-4} moles/g of active metal sites when the catalyst is reduced in flowing hydrogen for 4 hours at 420°C .

Probe Reaction Studies

In the catalytic synthesis of methanol from syngas over gamma-alumina supported metals, methanol produced at metal sites can subsequently adsorb or spill over as methoxy radicals on Lewis acid sites of the support. Adsorbed methoxy groups can then react in a secondary reaction to form dimethyl ether (DME). In some instances it may be desirable to suppress this dehydration since formation of DME reduces overall process selectivity for methanol and higher alcohol formation. In our system to study methanol dehydration directly, helium carrier gas is directed through a methanol bubbler maintained at constant temperature and approximately atmospheric pressure. This bubbler apparatus is used in conjunction with our low-pressure flow reactor to feed a mixture of helium and methanol to a packed bed of alumina or Rh/Mo on alumina maintained at reaction temperature by a tube furnace (see Second Quarter Report for a diagram of the low-pressure flow reactor). In this study, methanol—rather than syngas—is fed to our reactor as saturated vapor and dehydrated in the packed bed at sufficiently high temperatures ($>150^\circ \text{C}$).

As noted in our Third Quarter Report, we have completed experiments suggesting the role of Rh/Mo metallic crystallites in the secondary reactions of methanol. In these experiments, saturated methanol vapor in both He and, in a subsequent experiment, CO were fed to a fixed bed packed with an alumina-supported 2.8 % Rh/3.0 % Mo catalyst. In the presence of the inert He carrier, secondary light products were produced in the reactor beyond the DME formed on the native support. However, when CO was used as the carrier gas, almost no secondary products were formed, suggesting that the CO poisoned the active metal sites on the catalyst and thus limited a hydrogenolysis pathway otherwise available to the system.

Work during this last quarter regarding methanol dehydration was twofold. First, an attempt was made to establish a reactor regime which maintained conversions below 20% and was not complicated by interparticle mass transfer limitations. In this regime, the reactor may be assumed to be differential with respect to methanol conversion. In "differential mode", an otherwise plug flow reactor can be modelled as a perfectly mixed reactor in the sense that axial concentration gradients can be ignored and intrinsic kinetics information can be determined most directly.

As set forth in the section *Support Media Effects* of our grant proposal, we intended to examine the effect of doping the support surface with alkali metal oxides. In the second phase of this dehydration study, after a satisfactory reactor regime was established, several gamma-alumina samples were systematically doped with potassium: the samples were immersed in varying concentrations of potassium nitrate solution for six hours, filtered, and then dried for thirty-six

hours at 125° C. In this preliminary phase of the study, estimates of the surface concentration of hydroxide groups were determined based the empirical estimate of Anderson² that hydroxide groups are present in concentrations of 8 to 10 per square nanometer. Table 1 displays the relation between (i) the estimated K : OH ratio of the potassium in the contacting solution to the hydroxide surface sites and (ii) the activity for DME formation relative to an undoped gamma-alumina sample.

<u>Run</u>		<u>K's per H in OH's on Surface *</u>	<u>Relative DME Production</u>
Bare Alumina (Fresh Sample)		0	1.00
CASE 1		0.5	1.63
CASE 2		1	1.10
CASE 3		10	0.00

TABLE 1. Relation Between Dopant Concentration and DME Activity.

*Estimate based on Anderson's empirical values².

While our hypothesis is, as yet, unconfirmed, we anticipate that the potassium ions in the contacting solution displace the protons in the surface hydroxides. The surface protons play an intimate role in the mechanism for water formation during DME synthesis. This presence of the alkali oxide rather than the hydroxide should suppress DME formation. Our hypothesis appears to be born out in CASE 3 of Table 1, where the support surface was contacted with a large excess of potassium ions. The apparent increase in acidity of the alumina surface exhibited by CASE 1 and CASE 2 (K : OH of 0.5 : 1 and 1 : 1, respectively) are as yet unexplained, though surely some unanticipated surface modification is occurring. We will attempt to assess the acidity of our gamma alumina experimentally by (i) titrating the filtrate remaining upon separation from the alumina sample and (ii) possibly reacting the surface with n-butyl lithium and measuring the n-butane evolved. The n-butyl lithium experiment will once again employ the airless Schlenk line and glove box set up specifically in connection with this grant.

With regard to near term goals, we will attempt to explain the increase in acidity of the surface when contacted with low and moderate concentrations of potassium nitrate. Longer term goals involve both the assessment of the activity and selectivity of the catalysts recently synthesized for actual methanol synthesis as well as pursuing experiments establishing the structure sensitivity relationships of the supported metals as alluded to in both our grant proposal and the Third Quarter Report.

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