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TRANSITION METAL CLUSTER COMPLEXES AS CATALYSTS FOR THE CONVERSION OF COAL-DERIVED SYNTHESIS GAS INTO ORGANIC FEEDSTOCKS AND FUELS. SEMIANNUAL RESEARCH REPORT

PENNSYLVANIA STATE UNIV., UNIVERSITY
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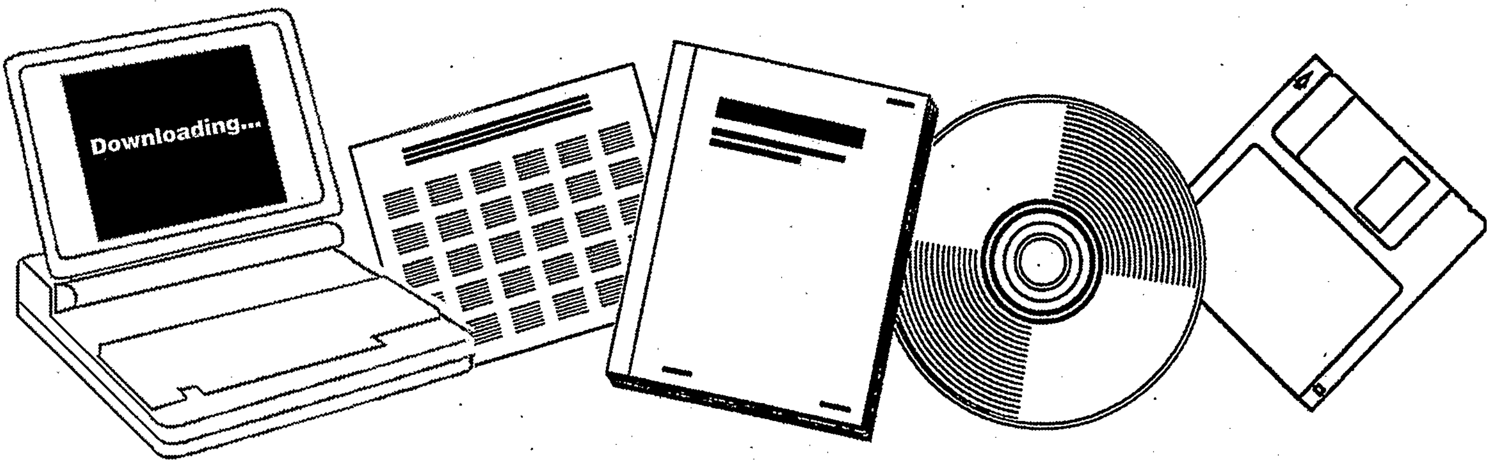

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February 26, 1979

Dr. Amy L. Simpson
Grants Office
U.S. Department of Energy
Operations, Division of Procurement
400 First Street, N.W.
Washington, D.C. 20545

Please file
Tab F

Dear Dr. Simpson:

Enclosed is one copy of my semi-anuual progress report on my grant entitled, "Transition Metal Cluster Complexes for the Conversion of Coal-Derived Synthesis Gas into Organic Feedstocks and Fuels - Grant No. EF-77-G-01-2740.

Sincerely yours,

Gregory L. Geoffroy
Associate Professor of Chemistry

Enclosure

GLG:cjh

Semiannual Research Report

for the Project

Transition Metal Cluster Complexes as Catalysts for the Conversion of Coal-Derived Synthesis Gas into Organic Feedstocks and Fuels

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March 1, 1979

I. Research Objectives

The overall goal of this research is to develop selective and efficient catalysts for the conversion of coal-derived synthesis gas into useful organic feedstocks and fuels. The specific objectives are to conduct a thorough evaluation of a variety of metal clusters for their ability to catalyze reduction of CO, to optimize the reaction conditions for these clusters which are identified as catalysts, and to develop a thorough understanding of the interactions of CO and H_2 on transition metal clusters.

II. Progress

Our initial efforts have been devoted to establishing the reaction conditions and analytical procedures necessary to evaluate the ability of specific metal carbonyl clusters to catalyze reduction of CO. The first level of evaluation involves heating 3×10^{-3} M isooctane solutions of each cluster to 100°C under one atmosphere pressure of a $3/1\text{-}H_2/CO$ gas mixture. The gases above the samples are periodically analyzed by gas chromatography to determine if any hydrocarbons or CH_3OH have been produced. The following clusters were found to decompose under these conditions and no organics were detected: $Fe_3(CO)_{12}$, $H_2FeRu_3(CO)_{13}$, $HCoRu_3(CO)_{13}$, $CH_3CCo_3(CO)_9$, and $PhCCo_3(CO)_9$. $H_4Ru_4(CO)_{12}$ appeared stable under these conditions but no organics were produced. This cluster will be reexamined at higher temperatures. As a check on our analytical procedures, we examined $Os_3(CO)_{12}$ which has been reported to catalyze CO hydrogenation [M. G. Thomas, B. F. Beier, and E. L. Muetterties, J. Am. Chem. Soc. 98, 1296 (1976)]. After heating this cluster to 100° for 24 h under the reaction conditions described above, substantial quantities of methane were observed with small amounts of ethane and other low-molecular weight hydrocarbons also produced. No color change or evidence of decomposition of $Os_3(CO)_{12}$ was observed during this period, but after heating for 5 days, the solution was noticeably deeper yellow in color.

We have assembled a reactor system which will allow us to study carbonyl clusters supported on SiO_2 and Al_2O_3 as heterogeneous catalysts for CO reduction. Our objective here is to avoid the high temperatures (400-500°C) generally used in the preparation of reduced metal catalysts and hence avoid the sintering which accompanies the reduction. Since the clusters we study are already in the zerovalent state and contain the substrate molecules CO and H_2, such high-temperature reduction is not necessary. We aim to take each supported cluster and slowly raise the temperature under a $3/1\text{-}H_2/CO$ atmosphere and observe when CO reduction beings to occur and the distribution of products formed. By beginning with well-defined metal cluster and especially mixed-metal cluster (e.g., $H_2FeRu_3(CO)_{13}$) precursors we should be able to study the effect of particle size at the lower limits and metal-composition on CO reduction. We have thus far only examined $Ru_3(CO)_{12}$ supported on SiO_2. When preheated to 200 or 250°C under an H_2 atmosphere and then placed under CO/H_2, methane and C_2 and C_3 hydrocarbons are produced. The catalyst activity decreases over a period of hours but may be regenerated by heating under H_2. No activity is observed at temperatures below 200°C.

III. Plans

In the coming months we intend to examine the following clusters for their ability to homogeneously catalyze CO reduction: $Ru_3(CO)_{12}$, In the coming months we intend to examine the following clusters for their ability to homogeneously catalyze CO reduction: $Ru_3(CO)_{12}$, $Co_4(CO)_{12}$, $Rh_4(CO)_{12}$, $H_3Re_3(CO)_{12}$, $H_3Mn_3(CO)_{12}$, $HFeCo_3(CO)_{12}$, $H_4Os_4(CO)_{12}$, $Fe_5C(CO)_{15}$, and $Fe_6C(CO)_{16}^{2-}$. Other clusters will be evaluated as they become available. Once clusters are found which catalyze the reaction, the conditions will be optimized and the selectivities of the catalysts determined.

In our study of supported catalysts, we intend to first vary the cluster size to determine if a critical number of metals are necessary to catalyze CO reduction. The series $Ru_3(CO)_{12}$, $H_4Ru_4(CO)_{12}$, $H_2Ru_6(CO)_{18}$, and $Ru_6C(CO)_{17}$ should present an interesting comparison. We will also evaluate the effect of metal composition on catalytic activity and will specifically examine the following mixed-metal clusters: $Fe_2Ru(CO)_{12}$, $FeRu_2(CO)_{12}$, $H_2FeRu_3(CO)_{13}$, $H_2Fe_2Ru_2(CO)_{13}$, $H_2FeRu_2Os(CO)_{13}$, $H_2FeRuOs_2(CO)_{13}$, $HFeCo_3(CO)_{12}$, $HCoRu_3(CO)_{13}$, and $HRuCo_3(CO)_{12}$.

We have also initiated a program to model the various steps which might occur during CO reduction on a metal surface by studying the reactivity of appropriately designed or selected metal clusters. Our initial efforts are devoted to studying the transformations of $HOs_3(CO)_{10}(OMe)$ and $Os_3(CO)_{10}(OMe)_2$ upon heating in the presence of H_2, studying the reactivity of a series of $YCCo_3(CO)_9$ ($Y = H, CH_3, Ph$) clusters under H_2, and attempts to force CO to become a 4 or 6 electron donor by inducing electron deficiency within clusters.