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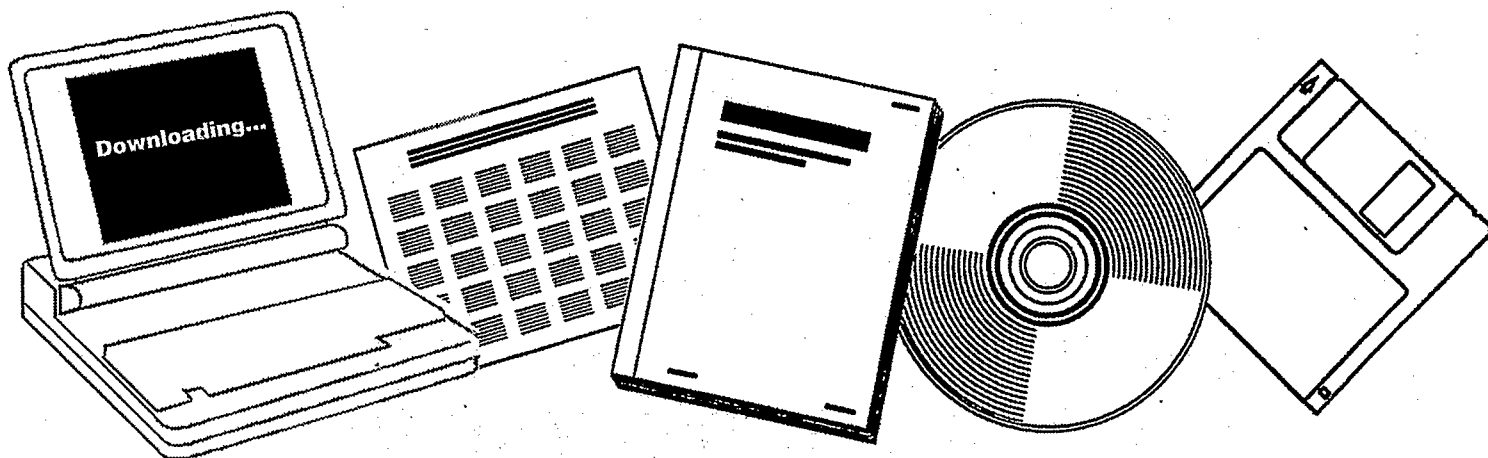
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**TRANSITION METAL CLUSTER COMPLEXES AS
CATALYSTS FOR THE CONVERSION OF
COAL-DERIVED SYNTHESIS GAS INTO ORGANIC
FEEDSTOCKS AND FUELS. FINAL TECHNICAL
REPORT**

PENNSYLVANIA STATE UNIV., UNIVERSITY
PARK. DEPT. OF CHEMISTRY

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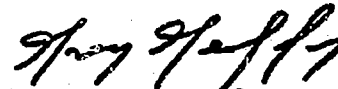
Dr. Amy L. Simpson
Grants Office
U.S. Department of Energy
Operations, Division of Procurement
400 First Street, N.W.
Washington, D.C. 20545

C/O 3/26/80

Dear Dr. Simpson:

Enclosed is one copy of my final technical 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

Enclosures

cc: M. McCracken

GLG:cjh

Final Technical Report
for the Project

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

Grant No. EF-77-G-01-2740

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May 13, 1980

I. Research Objectives

The overall goal of this research was to attempt to develop selective and efficient catalysts for the conversion of coal-derived synthesis gas into useful organic feedstocks and fuels. The specific objectives were 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 were identified as catalysts, and to develop a thorough understanding of the interactions of CO and H₂ on transition metal clusters.

II. Research Summary

Our initial efforts were 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 involved heating 3×10^{-3} M isooctane solutions of each cluster to 100°C under one atmosphere pressure of a 3/1-H₂/CO gas mixture. The gases above the samples were periodically analyzed by gas chromatography to determine if any hydrocarbons or CH₃OH had been produced. The following clusters were found to decompose under these conditions and no organics were detected: Fe₃(CO)₁₂, H₂FeRu₃(CO)₁₃, HCoRu₃(CO)₁₃, CH₃CCo₃(CO)₉, and PhCCo₃(CO)₉. H₄Ru₄(CO)₁₂ appeared stable under these conditions but no organics were produced. As a check on our analytical procedures, we examined Os₃(CO)₁₂ which had 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 $\text{Os}_3(\text{CO})_{12}$ was observed during this period, but after heating for 5 days, the solution was noticeably deeper yellow in color.

In an effort to understand why nearly all the clusters examined in this work are unstable under CO/H_2 atmospheres we undertook a study of the reactions of a series of mixed-metal clusters with CO. Reaction of the mixed-metal tetranuclear clusters $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$, $\text{H}_2\text{FeRu}_2\text{Os}(\text{CO})_{13}$, $\text{H}_2\text{FeRuOs}_2(\text{CO})_{13}$, $\text{HCoRu}_3(\text{CO})_{13}$, $\text{H}_2\text{FeRu}_3(\text{CO})_{12}\text{L}$ (L = PMe_2Ph , PPh_3), $[\text{HFeRu}_3(\text{CO})_{13}]^-$, and $[\text{CoRu}_3(\text{CO})_{13}]^-$ with CO under relatively mild conditions ($P_{\text{CO}} = 1 \text{ atm}$, $\text{temp} = 0\text{--}80^\circ\text{C}$) results in their fragmentation to give trimeric and monomeric products. The fragmentation reactions are generally quite selective: $\text{H}_2\text{FeRu}_2\text{Os}(\text{CO})_{13}$, for example, reacts with CO to give $\text{Ru}_2\text{Os}(\text{CO})_{12}$, $\text{Fe}(\text{CO})_5$ and H_2 with no $\text{RuOs}_2(\text{CO})_{12}$, $\text{FeRu}_2(\text{CO})_{12}$, or $\text{FeRuOs}(\text{CO})_{12}$ detected in the product mixture. This reaction and the corresponding fragmentation of $\text{H}_2\text{FeRuOs}_2(\text{CO})_{13}$ provide a convenient means of separating and isolating the mixed-metal trimers $\text{Ru}_2\text{Os}(\text{CO})_{13}$ and $\text{RuOs}_2(\text{CO})_{13}$. The reactivity of a particular cluster towards CO is greatly dependent on its metal composition and/or its structure. For example, $\text{H}_2\text{FeRu}_2\text{Os}(\text{CO})_{13}$ reacts slowly over a period of several days while the breakdown of $\text{HCoRu}_3(\text{CO})_{13}$ is complete within one hour. The tetrahydride clusters $\text{H}_4\text{FeRu}_3(\text{CO})_{12}$ and $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ first react with CO to displace H_2 and form the corresponding dihydride clusters which subsequently fragment under the reaction conditions. Kinetic measurements indicate that the fragmentation of $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ to produce $\text{Ru}_3(\text{CO})_{12}$, $\text{Fe}(\text{CO})_5$, and H_2 proceed largely by a second order, $[\text{CO}]$ -dependent path with activation parameters $\Delta H^\ddagger = 20.0 \pm 2.0 \text{ kcal/mole}$ and $\Delta S^\ddagger = -25.4 \pm 5.8 \text{ cal/mole-K}$. Likewise, fragmentation of $\text{H}_2\text{Ru}_4(\text{CO})_{13}$ to form $\text{Ru}_3(\text{CO})_{12}$, $\text{Ru}(\text{CO})_5$, and H_2 proceeds via a second order, $[\text{CO}]$ -dependent path with

$\Delta H^{\circ\dagger} = 12.5 \pm 0.5$ kcal/mole and $\Delta S^{\circ\dagger} = -36.6 \pm 1.6$ cal/mole-K. This work is described in detail in an article now in press in Inorganic Chemistry.

We also assembled a reactor system which allowed us to study carbonyl clusters supported on SiO_2 and Al_2O_3 as heterogeneous catalysts for CO reduction. Our objective here was 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 zero valent state and contain the substrate molecules CO and H_2 , such high-temperature reduction is not necessary. It was our aim to take each supported cluster and slowly raise the temperature under a 3/1- H_2 /CO atmosphere and observe when CO reduction begins to occur and the distribution of products formed. By beginning with well-defined metal clusters and especially mixed-metal cluster (e.g., $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$) precursors a study of the effect of particle size at the lower limits and metal-composition on CO reduction would be possible. Because of time constraints only $\text{Ru}_3(\text{CO})_{12}$ supported on SiO_2 has been examined. 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 were 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. Unfortunately, all experiments indicated that extensive sintering of the catalyst occurred during these reaction conditions and thus integrity of the Ru_3 framework was not maintained.

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