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

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

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September 22, 1978

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Dear Dr. Simpson:

Enclosed is one copy of my annual 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

GLG:rl

Enclosure

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Annual Research 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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MASTER

September 1, 1978

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I. Research Scope and 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 though evaluation of a variety of metal clusters for their ability to catalyze reduction of CO, to optimize the reaction conditions for those clusters which are identified as catalysts, and to develop a better understanding of interactions of CO and H_2 on metal surfaces through model studies with metal clusters.

II. Progress

A. Evaluation of Clusters as Homogeneous Catalysts for Carbon Monoxide Reduction. In the initial phase of this research, we set out to evaluate the ability of specific metal cluster compounds to serve as homogeneous catalysts for reduction of carbon monoxide. We first established a set of reaction conditions and analytical procedures for evaluating each cluster. We initially heated 3×10^{-3} M isooctane solutions of each cluster to 100°C under 1 atm. pressure of a $3/1\text{-}H_2/CO$ gas mixture. The gases above the samples were periodically analyzed by gas chromatography to determine if any hydrocarbons or methanol were produced. The following clusters were found to decompose under these rather mild reaction 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 reaction conditions but no organics were produced. As a check on our analytical procedures, we examined $Os_3(CO)_{12}$ which has been reported to catalyze CO hydrogenation.[1]

After heating this cluster to 100°C 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.

B. Reaction of Metal Carbonyl Clusters with CO. The studies described above coupled with other observations which we had previously made in our laboratory indicated that many carbonyl cluster compounds are simply not very stable under an atmosphere of carbon monoxide or a mixed atmosphere of carbon monoxide/hydrogen. We thus decided to conduct a study of the reactivity of metal carbonyl cluster compounds with carbon monoxide. Obviously, if a cluster decomposes under an atmosphere of CO it will not be able to serve as a CO hydrogenation catalyst. Thus it seemed reasonable that the most efficient way to proceed in the research described above is to examine clusters first under CO and then carry out the catalytic evaluation only on those clusters which are relatively stable under a CO atmosphere.

The first cluster that we examined in this regard was $H_2FeRu_3(CO)_{13}$. We found that reaction of $H_2FeRu_3(CO)_{13}$ with CO gave quantitative production of $Ru_3(CO)_{12}$ and $Fe(CO)_5$ according to eq. 1.

$$H_2FeRu_3(CO)_{13} + 4CO \rightarrow Ru_3(CO)_{12} + Fe(CO)_5 + H_2 \qquad (1)$$

We subsequently observed that similar reactions occur with the three metal clusters $H_2FeRu_2Os(CO)_{13}$ and $H_2FeRuOs_2(CO)_{13}$, eqs. 2 and 3.

$$H_2FeRu_2Os(CO)_{13} + 4CO \rightarrow Ru_2Os(CO)_{12} + Fe(CO)_5 + H_2 \qquad (2)$$

$$H_2FeRuOs_2(CO)_{13} + 4CO \rightarrow RuOs_2(CO)_{12} + Fe(CO)_5 + H_2 \qquad (3)$$

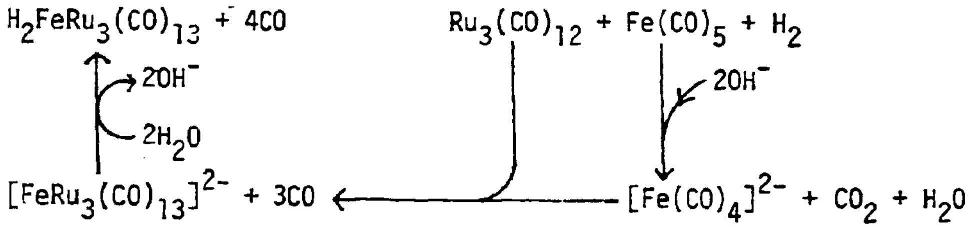
These latter two reactions provided a procedure for the separation and purification of $Ru_2Os(CO)_{12}$ and $RuOs_2(CO)_{12}$, which had never previously been separated from each other. These two trimers were completely characterized by their infrared and mass spectra and $Ru_2Os(CO)_{12}$ by its ^{13}C NMR spectra. Reactions of this type of cluster with CO has been extended to $H_2Ru_4(CO)_{13}$, $HCoRu_3(CO)_{13}$, $HCoRu_2Os(CO)_{13}$, and $HCoRuOs_2(CO)_{13}$. The reactivity is very dependent on the metals present. At room temperature, $H_2FeRu_3(CO)_{13}$, $H_2FeRu_2Os(CO)_{13}$, and $H_2FeRuOs_2(CO)_{13}$ react slowly over a period of several days, whereas the reaction is complete within minutes for $H_2Ru_4(CO)_{13}$, $HCoRu_3(CO)_{13}$, $HCoRu_2Os(CO)_{13}$, and $HCoRuOs_2(CO)_{13}$. The reaction rate increases with increasing temperature, and, for example, 90% of $H_2FeRu_3(CO)_{13}$ is converted to products after 90 h at 70°C. The reaction is also solvent-dependent. In the polar solvent system consisting of a 15:1 mixture of 2-ethoxyethanol and water, the rate of the reaction at 70°C increases by at least 8-fold. The overall mechanism of this reaction remains obscure. However, the absence of iron-containing trimers and the lack of ruthenium-osmium scrambling during formation of $Ru_2Os(CO)_{12}$ and $RuOs_2(CO)_{12}$ from $H_2FeRu_2Os(CO)_{13}$ and $H_2FeRuOs_2(CO)_{13}$, respectively, indicates that this portion of the cluster remains intact throughout the conversion. However, preliminary analysis or the reaction of $HCoRu_2Os(CO)_{13}$ and $HCoRuOs_2(CO)_{13}$ with CO shows that ruthenium-osmium scrambling does occur with these clusters and each gives a mixture of ruthenium-osmium trimers in addition to other products. The formation of $Ru(CO)_5$ and $Ru_3(CO)_{12}$ was observed in the reaction of $HCoRu_3(CO)_{13}$ with CO, but the cobalt-containing products were not conclusively identified.

The reactions of the clusters described above with carbon monoxide provide important insight into the mechanism of the metal cluster catalyzed water-gas shift reaction. Several carbonyl clusters have been demonstrated to catalyze the water-gas shift reaction, eq. 4

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (4)$$

and tetranuclear clusters have been implicated as key intermediates.[2-4] Ford and coworkers have shown that catalyst solutions prepared from $Ru_3(CO)_{12}$ and OH^- contain predominantly $[H_3Ru_4(CO)_{12}]^-$ and $[HRu_4(CO)_{13}]^-$.[2,3] The most active catalyst which Ford described was prepared from an $Fe(CO)_5/Ru_3(CO)_{12}$ mixture and alkaline solution, and infrared evidence indicated the formation of $H_2FeRu_3(CO)_{13}$.[3] Subsequent experiments showed that the same high activity could be obtained by direct use of $H_2FeRu_3(CO)_{13}$ as a catalyst.[3] We have suggested that this cluster functions as a catalyst in the water-gas shift reaction by the mechanism outlined below in Scheme 1.

Scheme 1 - Proposed Mechanism for the $H_2FeRu_3(CO)_{13}$ Catalyzed Water-Gas Shift Reaction



Net Reaction: $CO + H_2O \rightarrow CO_2 + H_2$

$Fe(CO)_5$ is known to react with hydroxide to produce CO_2 and either $[Fe(CO)_4]^{2-}$ or $[HFe(CO)_4]^-$ depending on pH. We previously showed that $[Fe(CO)_4]^{2-}$ reacts rapidly with $Ru_3(CO)_{12}$ to produce an apparent intermediate $[FeRu_3(CO)_{13}]^{2-}$ which gives $H_2FeRu_3(CO)_{13}$ upon protonation. This particular reaction is quite rapid giving an immediate color change upon combination of the reactants at room temperature and is essentially complete within 1 h. $[HFe(CO)_4]^-$ also reacts with $Ru_3(CO)_{12}$, albeit at a rate slower than $[Fe(CO)_4]^{2-}$ to yield $[HFeRu_3(CO)_{13}]^-$. The observation of $H_2FeRu_3(CO)_{13}$ in the $Fe(CO)_5/Ru_3(CO)_{12}$ catalyst solutions indicates that $[FeRu_3(CO)_{13}]^{2-}$ and $[HFeRu_3(CO)_{13}]^-$ are sufficiently strong bases to abstract hydrogen from water. Indeed, in the mechanism we proposed, Scheme 1, one of the key functions of the cluster system is to provide a means for abstracting hydrogen from water. Reaction of $H_2FeRu_3(CO)_{13}$ with CO subsequently liberates H_2 and produces $Fe(CO)_5$ and $Ru_3(CO)_{12}$. We would suggest that the relatively slow rate of the reaction of $H_2FeRu_3(CO)_{13}$ with CO is a rate-limiting step in the overall catalytic cycle. It is our belief that the other clusters which have been demonstrated to catalyze the water-gas reaction may also function via a catalytic cycle such as that shown in Scheme 4, and we aim to test this hypothesis in our subsequent research.

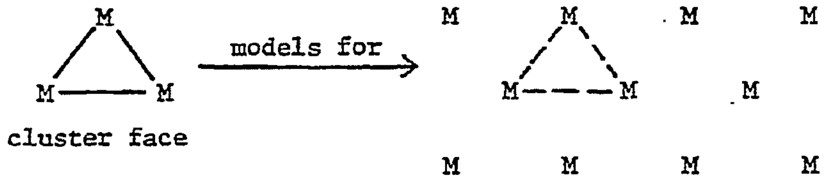
C. Metal Clusters as Precursors for Supported Heterogeneous Catalysts. We are currently examining the use of metal carbonyl clusters as precursors for supported heterogeneous catalysts for carbon monoxide reactions. Our objective in these studies is to avoid the high temperatures (400-500°C) generally used in the preparation of reduced Fischer-Tropsch catalysts and hence avoid the sintering which accompanies the reduction. Since the clusters we are studying are already in the zero valence state and contain the substrate molecules CO and H_2, such high temperature reduction is unnecessary. 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. We 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 precursors, we should be able to study the effect of particle size at the lower limit and metal composition on CO reduction.

We first studied $Fe_3(CO)_{12}$ supported on SiO_2 (2% loading by wt). This cluster, surprisingly, gave no detectable CO reduction at temperatures up to 400°C. Even when the $Fe_3(CO)_{12}/SiO_2$ sample was first reduced to metallic iron at 450°C for 24 h under an H_2 atmosphere and then evaluated for CO reduction at 250°C, no organics were detected. We intend to repeat these experiments at a higher metal loading level (10%).

The cluster $Ru_3(CO)_{12}$ supported on SiO_2 at a 5% metal loading level was then examined. We first found that when this sample was heated to 250°C under a 3/1-H_2/CO atmosphere, it initially produced methane and substantial quantities of ethane, propane and propylene. Over a period of several hours, its activity for the production of the higher hydrocarbons declined and after about 4 h only methane was being produced. The sample was then heated at 250° under a flowing H_2 atmosphere and it was noted that methane was continuing to be formed. When the gas stream was again switched to 3/1-H_2/CO, ethane, propane and propylene were noted in addition to the methane. Again, the higher molecular weight hydrocarbon activity declined over a period of hours. These results suggest that as the catalyst functions, it forms carbide deposits on the metal surface which are only hydrogenated to methane and that a bare metal surface is needed for the production of higher hydrocarbons.

We then repeated these experiments but at 100°C rather than 250°C. Under these conditions we saw no methane or other hydrocarbons produced under a flowing H_2/CO gas stream or under an H_2 atmosphere. We were able to recover the initial $Ru_3(CO)_{12}$ by washing the sample with hexane, and thus it appears that 100°C is not a sufficient temperature to activate the cluster for CO reduction. In the coming weeks, we intend to examine temperatures intermediate between 100 and 250°C to see what the minimum temperature necessary is for the reaction to occur.

D. <u>Metal Clusters as Models for Fischer-Tropsch and Methanol Synthesis Catalysts</u>. We have embarked on a research program in which we are attempting to gain a mechanistic understanding of the metal catalyzed Fischer-Tropsch and methanol synthesis reaction by using metal clusters to model the surface reaction. It is our contention that the triangular faces of clusters can serve as models for triangular metal sites on surfaces and hence that reactions which occur on cluster faces are analogs of reactions that occur on surfaces.



We have proposed mechanistic schemes for the surface catalyzed reduction of carbon monoxide to produce methanol and hydrocarbons and they are shown as Schemes 2 and 3, respectively. We are in the process of testing the likelihood of these mechanisms by attempting to synthesize clusters which resemble the surface intermediate and then intend to examine their reactivity in detail.

Our efforts to date have concentrated in two areas. In one study, we are attempting to prepare intermediates which resemble VIIA and VIIB in Scheme 2 by heating selected clusters in the absence of added ligand. Our hope is that these clusters will lose some of their initial carbon monoxide ligands and one of the remaining carbonyls will be induced to fold over to assume a bridging position such as that shown in VIIA and VIIC.

In the second study, we are attempting to prepare the intermediates VIC, VIE, VIE' and VIF shown in Scheme 3, by heating $Os_3(CO)_{10}H(OMe)$ and structurally analogous clusters in the absence of added ligand. We have preliminary evidence that several reactions occur and would like to think that the methoxy ligand folds over the cluster giving insertion of another metal into a carbon hydrogen bond and intermediates which resemble VIE or VIE'.

III. Future Research

A. Evaluation of the Ability of Metal Clusters to Homogeneously Catalyze Carbon Monoxide Reduction.

We now intend to proceed in this research by only evaluating those clusters which show a high stability under a pure carbon monoxide atmosphere as determined by the studies detailed in paragraph B below. We suspect that it will be necessary to employ clusters which are held together by bridging heteroatoms such as $H_3Ru_3(CO)_9(CMe)$ and $Ru_6C(CO)_{17}$ in order to prevent the clusters from falling apart under CO.

B. Reaction of Clusters with Carbon Monoxide.

We intend to examine the reactivity of a large number of clusters with CO. We will focus our attention on mixed-metal clusters such as $Fe_2Ru(CO)_{12}$, $FeRu_2(CO)_{12}$,

$H_2FeRu_3(CO)_{13}$, $H_2Fe_2Ru_2(CO)_{13}$, $H_2FeRu_2Os(CO)_{13}$, $H_2FeRuOs_2(CO)_{13}$, $HFeCo_3(CO)_{12}$, $HCoRu_3(CO)_{13}$ and $HRuCo_3(CO)_{12}$. The use of mixed-metal clusters will greatly facilitate analysis of the reaction products and a determination of the specific metal-metal bonds which are broken in fragmentation of the cluster. Such knowledge should point us in the direction of clusters which are more likely to be stable under carbon monoxide and which might be capable then of serving as Fischer-Tropsch catalysts. We also intend to measure the kinetics of these reactions and try to determine the rate equation in order to understand how the reactions proceed.

C. Metal Carbonyl Clusters as Precursors for Supported Heterogeneous Fischer-Tropsch Catalysts. 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 $HRuCo_3(CO)_{12}$.

D. Metal Clusters as Models for Fischer-Tropsch and Methanol Synthesis Catalysts. We are continuing the study described above and furthermore intend to prepare other intermediates which resemble the surface intermediates described in Schemes 2 and 3.

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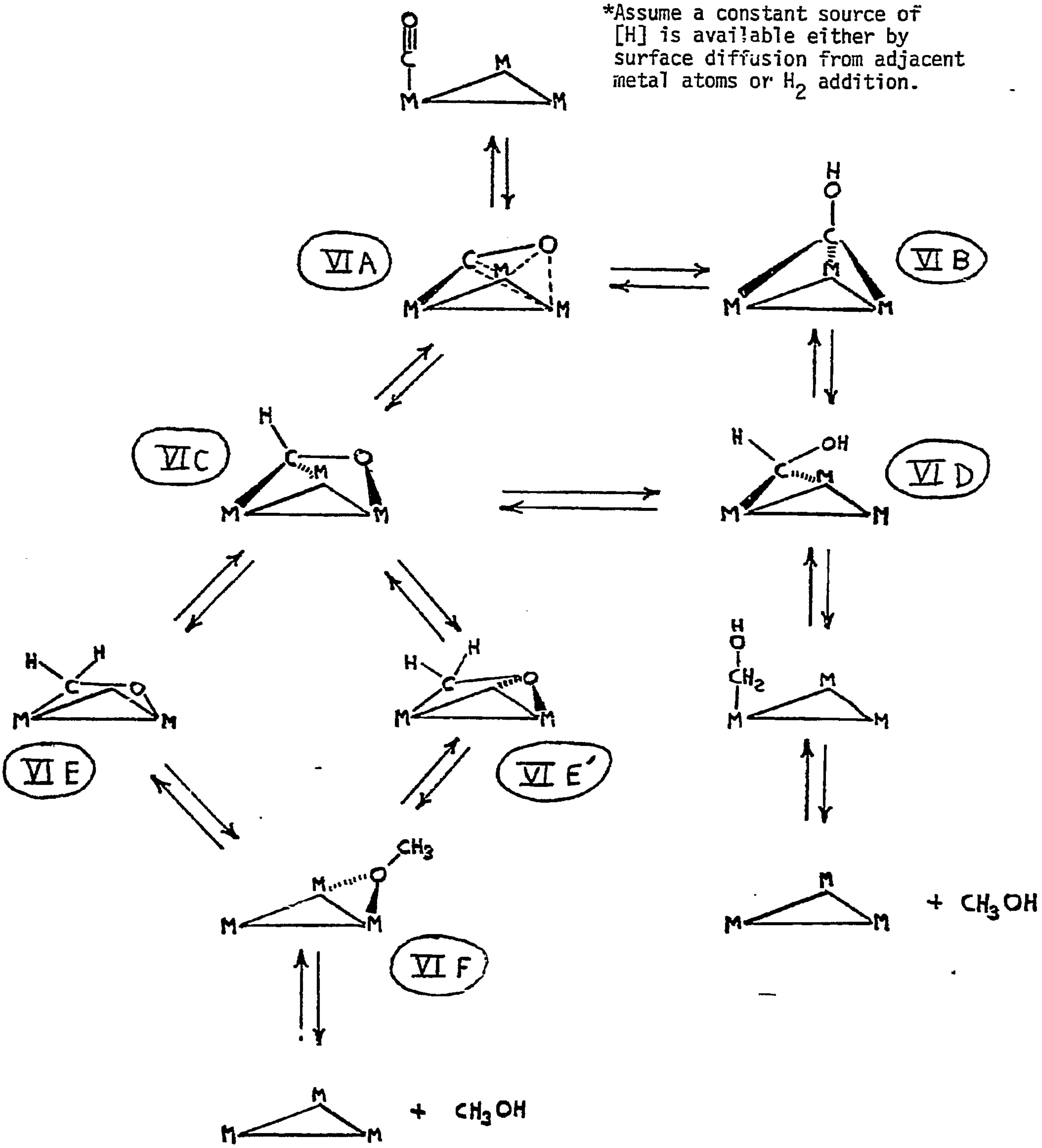
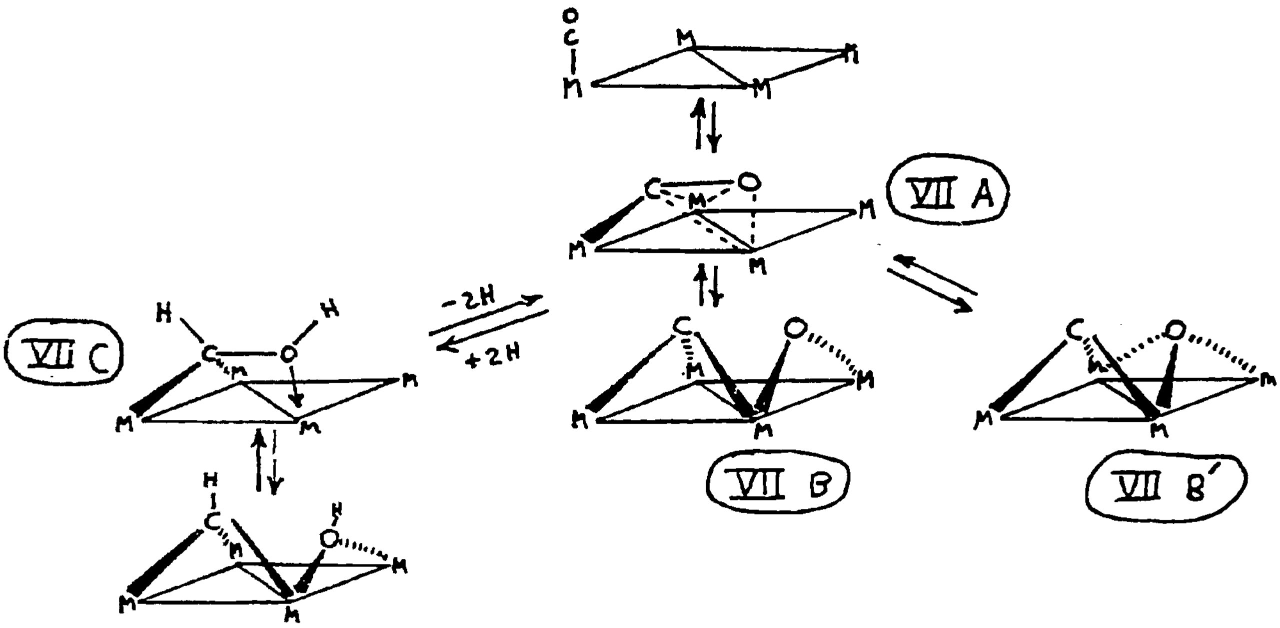
Scheme I - Model for Methanol Synthesis



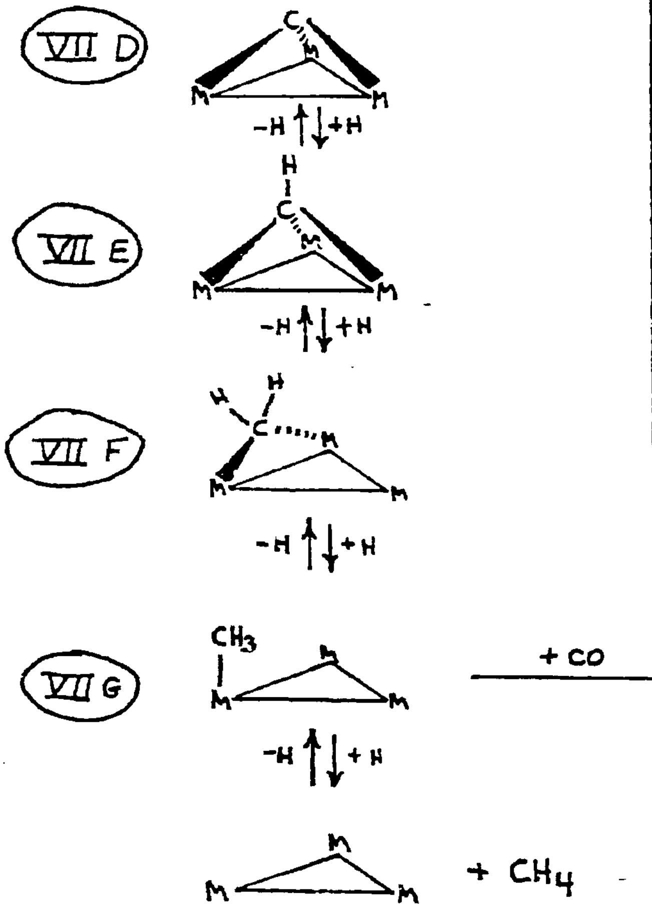
*Assume a constant source of [H] is available either by surface diffusion from adjacent metal atoms or H_2 addition.

Scheme II. - Model for Hydrocarbon Synthesis

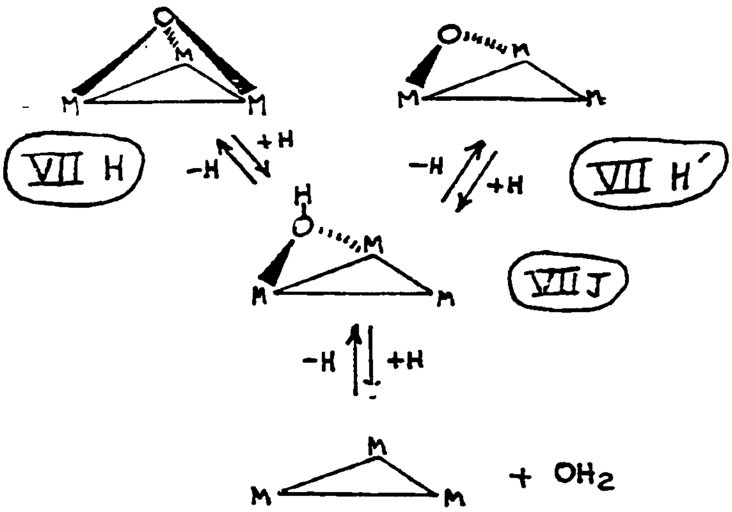
1. Dissociation of CO



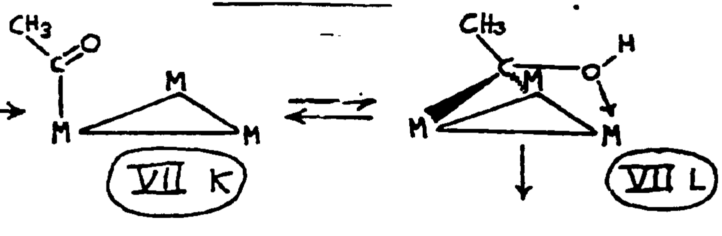
2. Hydrogenation of Carbon



3. Hydrogenation of Oxygen



4. Chain Growth



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