CHEMICAL TRAPPING OF CO/H SUB 2 SURFACE SPECIES. QUARTERLY REPORT, SEPTEMBER 1986

PITTSBURGH UNIV., PA. DEPT. OF CHEMICAL AND PETROLEUM ENGINEERING

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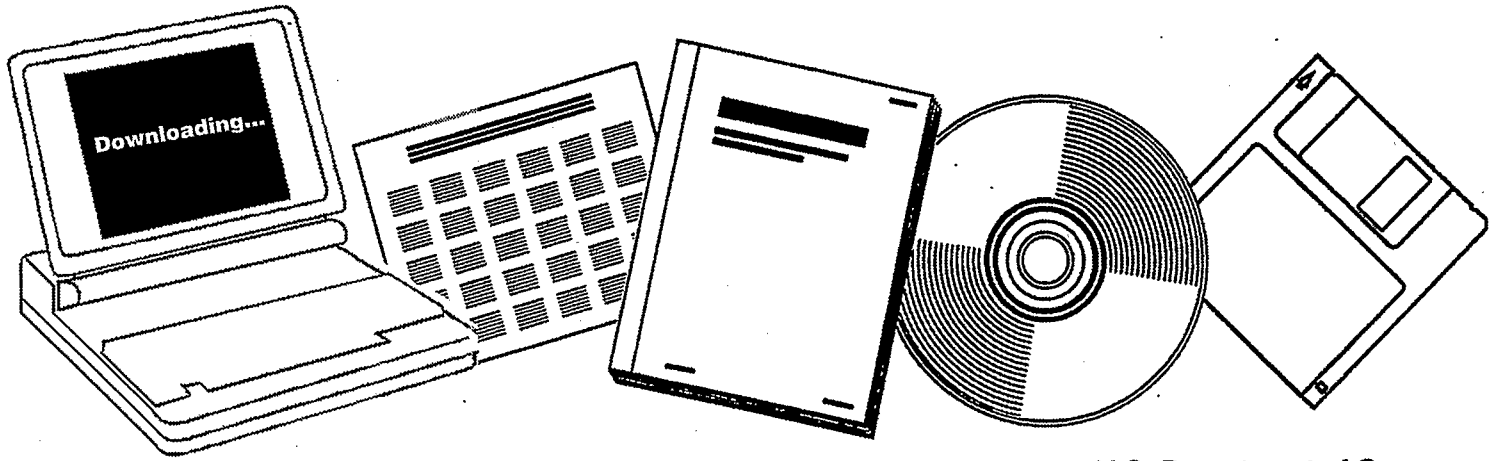

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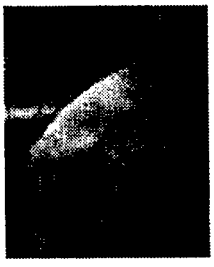

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DOE/PC/80526--T5

DE87 000637

Chemical Trapping of CO/H_2 Surface Species

Quarterly Report

September 1986

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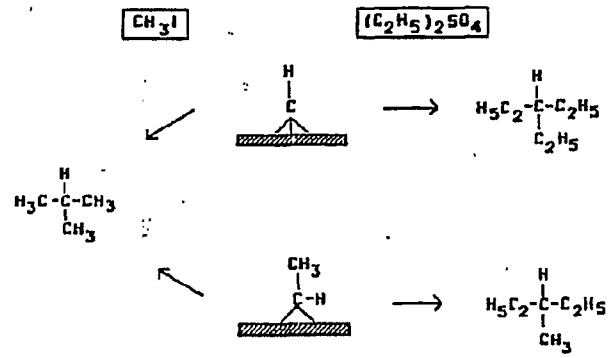
Prepared for the U.S. Department of Energy
under Grant No. DE-FG22-85PC80526

I. INTRODUCTION

Understanding the nature of active intermediate species present on the surface of supported metal catalysts has long been a goal of catalytic scientists. Although many different techniques have been used to probe the surface chemistry of catalysts in-situ during reactions such as CO hydrogenation, much remains to be learned about the nature of the surface species and the mechanisms by which they participate in catalytic reactions. This project proposed to develop and use a novel technique for identifying surface species by chemically trapping them during CO hydrogenation reactions. This chemical trapping technique was first introduced by Deluzarche and coworkers (1) in Strasbourg, France. These researchers have reported a wealth of experimental evidence attempting to show that surface intermediate species can be identified by chemically trapping them with reagents such as CH_3I and $(CH_3)_2SO_4$. The principal of chemical trapping for surface species identification is shown in the figure below.

CHEMICAL TRAPPING OF REACTION INTERMEDIATES

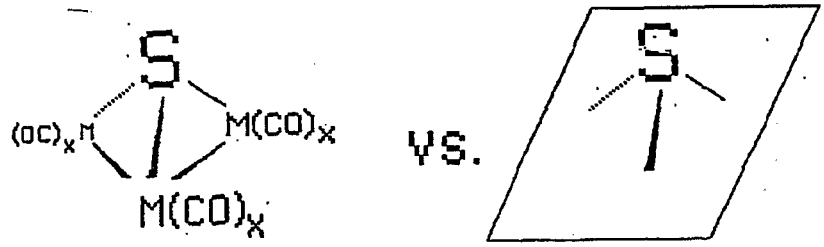


These experiments have not been, however, sufficient to answer all of the questions which arise concerning the technique itself. In essence, the chemical trapping reaction is far from being a simple method of probing the surface. The trapping reaction itself causes significant perturbations of the surface chemistry which are not yet well understood. Our first goal in this project is to develop an understanding of the mechanism of the trapping reaction. This understanding will hopefully lead us to the application of chemical trapping as a method of identifying species on catalyst surfaces during catalytic reactions.

II. METHOD

The method we have chosen to investigate the reactions between trapping reagents and metal-hydrocarbon bonds involves the use of model organometallic complexes. The schematic below illustrates the analogy between an organometallic complex and a catalyst surface.

METAL CLUSTERS AS MODELS OF
SUPPORTED METAL SURFACE SPECIES



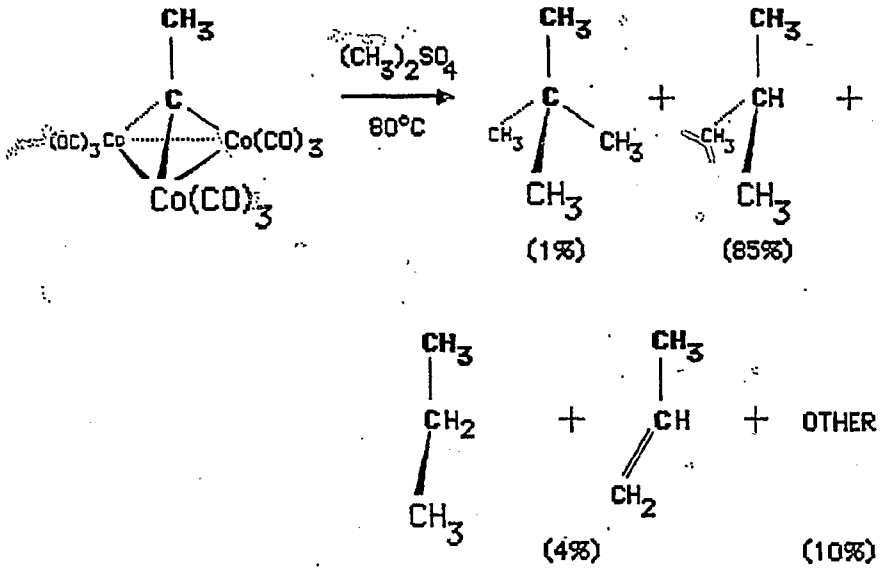
The organometallic complex represents a system in which the species bound to the metal atoms is well-characterized; if we can follow the action of a trapping reagent on this known "surface" complex, perhaps we may obtain information about the mechanism of the reaction that will enable us to extend its use to catalytic surfaces where the adsorbed species is unknown.

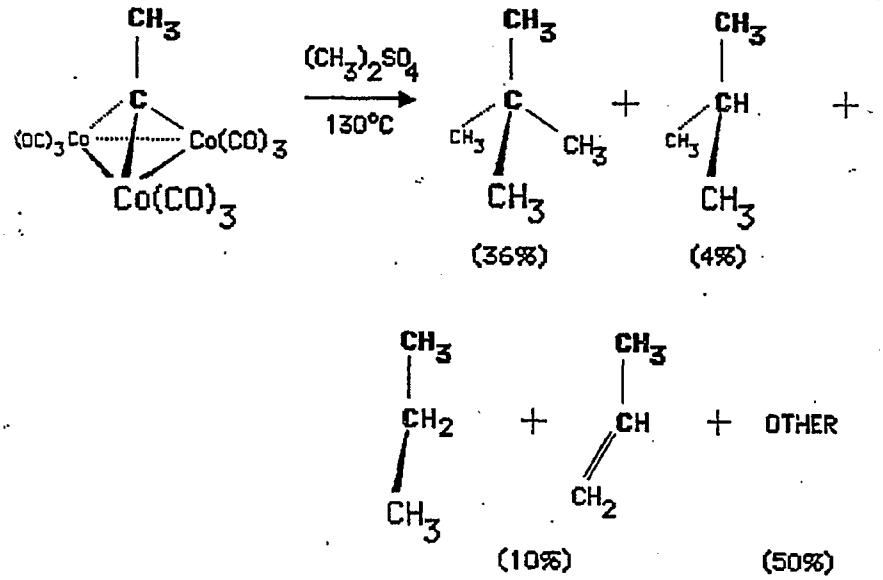
III. EXPERIMENTAL RESULTS

Experiments have been performed with ethylidyne tricobalt enneacarbonyl as a model organometallic complex. The chemical trapping reagents which have been employed include CH_3I and $(CH_3)_2SO_4$. The complex and trapping reagent are mixed with a solvent such as dodecane. Reactions have been monitored between 80 °C and 130 °C. The lower temperature limit represents the point at which the complex begins to react with the reagent, while the upper limit is near the temperature at which the complex begins to decompose.

The results of the highest and lowest temperature experiments are shown on the following page. At low temperature, the predominant product indicates that two of the three Cθ-C bonds have been alkylated by the reagent while the third was hydrogenated. The high temperature reaction showed significantly more neopentane, which is the expected product if the trapping reagent is 100% efficient. In addition, at high temperature there is a significant amount of C_2 and C_1 products which are listed as "other." A blank run with the trapping reagent alone in the solvent showed that most of these products come from decomposition of the trapping reagent itself. Hence, the high

REACTION OF A MODEL COMPLEX WITH A TRAPPING AGENT





temperature results indicate an even higher fraction of the expected product, neopentane, than is noted in the figure.

IV. FUTURE WORK

The positive results achieved to date using organometallic complexes as models of the catalyst surface have led us to expand this part of the project. Plans for future work include:

1. further investigation of the temperature behavior of the trapping reagent/model complex reaction; determination of activation energies for the reactions; comparison with E_a for catalytic reactions of hydrocarbons.
2. use of deuterated trapping reagents coupled with GC-MS analysis to determine precisely how the reagent interacts with the metal-carbon bonds
3. investigations of other model complexes, beginning with a second cobalt complex, acetylene dicobalt hexacarbonyl.

V. REFERENCES

1. Deluzarche, A., Hindermann, J.P., Kiennemann, A., and Kieffer, R., J. Mol. Catal., 31, 225 (1985).

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