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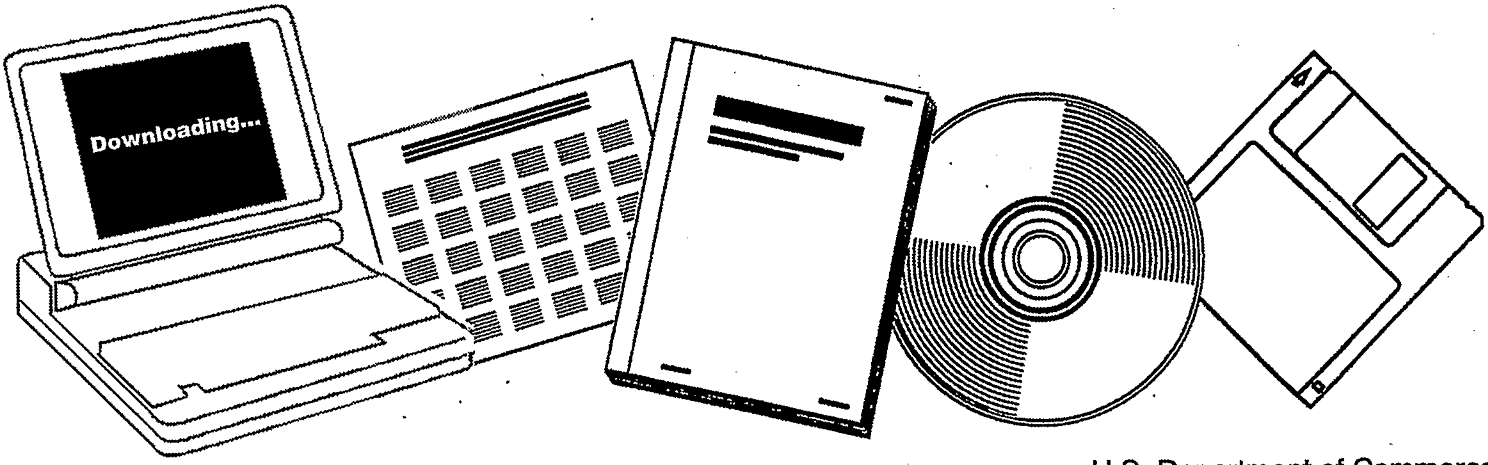

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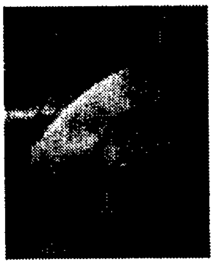

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DOE/PC/80526-T4

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DE86 011591

CHEMICAL TRAPPING OF CO/H_2 SURFACE SPECIES

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FG22-85PC80526

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Received by OSTI

JUN 16 1986

Introduction

CO hydrogenation reactions over supported metal catalysts can produce a wide spectrum of hydrocarbon and oxygenated compounds depending to a large extent on the type of metal used. Elucidating the nature of the intermediate species formed on metal surfaces may provide the key to understanding the pathways through which these reactions proceed on different metals. The number of different techniques which have been employed in search of this understanding attests not only to the importance of but also to the difficulties inherent in the identification of reactive surface species.

One common method of obtaining evidence of the participation of a postulated reaction intermediate is the use of labelled molecules during reaction (1,2). Other kinds of experiments have involved generating certain labelled or unlabelled species on the catalyst surface and then reacting them to prove their participation in CO hydrogenation reactions (3). Another elegant kind of tracer experiment is carried out by instantaneously switching a CO/H_2 reaction mixture to a stream in which an isotopic analog of one of the reactive components is present (4) and then monitoring the reaction kinetics during the transient period that follows. Other creative experiments have used reactive molecules not part of the reaction scheme to scavenge surface intermediates (5).

Each of these experiments has added greatly to our knowledge of the chemistry of the catalyst surface under reaction conditions. The unanswered questions that remain, however, have emphasized the need for unequivocal surface species identification. This in turn has led us to investigate a novel technique which has recently been developed (6) for chemically trapping adsorbed species. This trapping technique involves introducing an alkylating reagent onto the catalyst surface after it has been contacted with the CO/H_2 reactants. It is postulated that the reagent reacts with the surface intermediate species by alkylating it at each point of former attachment to the catalyst surface. Identification of the products of this alkylation reaction may then lead to back-deduction of the identity of the surface species itself. The schematic in Figure 1 portrays the reaction of alkylating reagents such as CH_3I and $(C_2H_5)_2SO_4$ with some postulated intermediate species. The ideas behind the development of this technique draw upon methods used in the determination of mechanisms of organic reactions (7).

Chemical trapping experiments to date have been of limited use in elucidating catalytic reaction mechanisms because they have not been carried out under reaction conditions. Moreover, questions have been raised about whether the trapping reagents actually react quantitatively with surface species in the manner postulated. The purpose of our investigation is to delineate how the trapping reagent reacts with the catalyst surface and to employ the technique to probe the nature of reactive surface intermediates on supported metal catalysts during CO hydrogenation reactions.

Discussion of Experiments

Preliminary chemical trapping experiments were carried out in-situ under CO hydrogenation conditions on a 3% RuKY zeolite catalyst. The addition of CH_3I to a CO/H_2 reaction stream resulted in a profound alteration of the typical ASF product distribution for this catalyst. A dramatic decrease in C_1-C_3 hydrocarbons was observed concomitant with a similarly sharp increase in C_4-C_6 hydrocarbons. The distribution of C_4 products was also significantly altered as shown in Figure 2. These results indicate that addition of the trapping reagent causes perturbations in the observed CO/H_2 products which may be caused by alkylation of surface species by the reagent. However, the complexity of the results make it difficult to clearly identify surface species or to understand the action of the trapping reagent on these surface species.

The complex action of the trapping reagent on metal-adsorbate bonds might be made more clear with the substitution of model organometallic complexes for the catalyst-adsorbate systems under study. These model complexes simulate organic species adsorbed on metal surfaces. The interaction of the organic ligands with chemical trapping reagents may provide important clues about how these reagents interact with species adsorbed on the surface of a metal catalyst. Figure 3 shows the structure of two organometallic complexes now under study using the chemical trapping technique.

The investigations involving model complexes are being coupled with further in-situ trapping experiments on supported Ni and Pd catalysts during CO/H_2 reactions. These two metals yield very different product distributions, but both are generally less complex than those obtained from Ru. Coupled with investigations on model organometallic systems, these trapping studies promise to provide a framework for understanding differences in CO hydrogenation reaction pathways over different metals.

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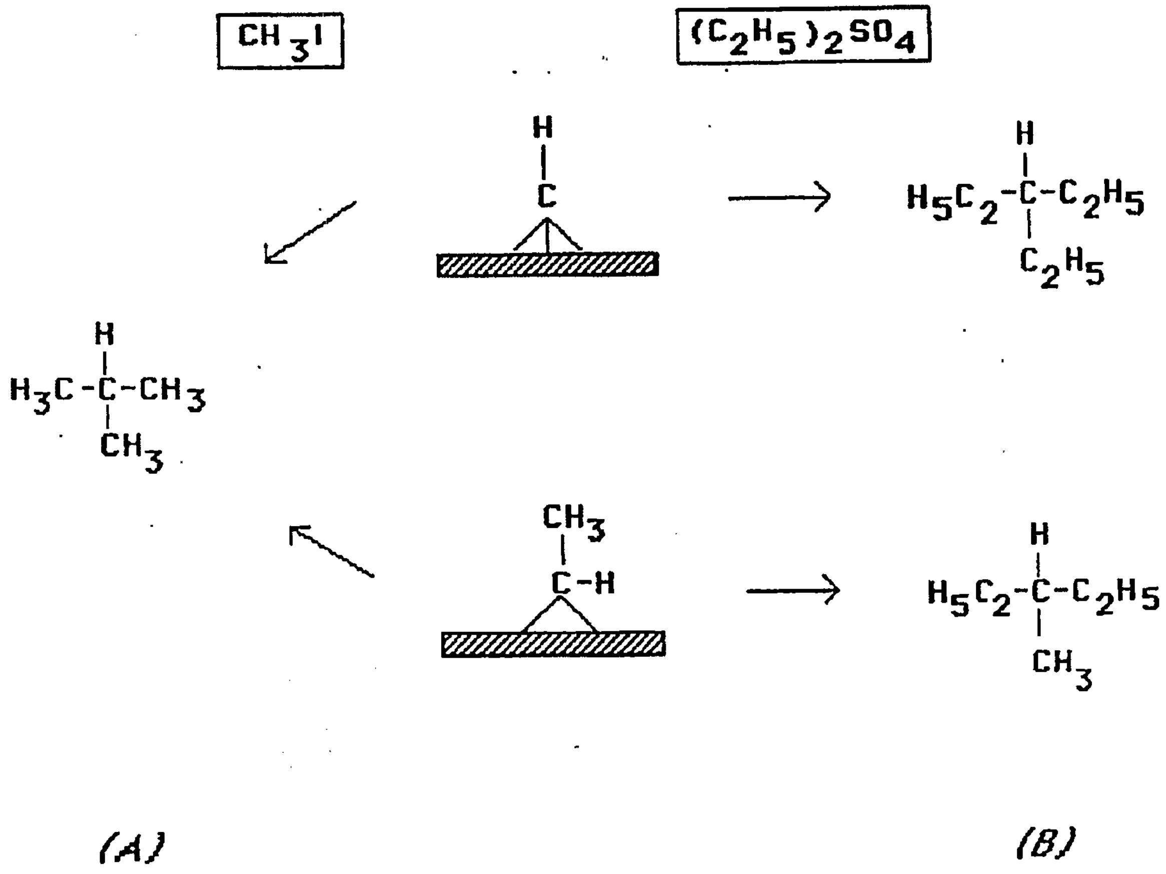


FIGURE 1. Schematic of the reaction of alkylating reagents with some postulated surface intermediate species

(A) products derived from a C_1 *alkylating reagent*

(B) products derived from a C_2 *alkylating reagent*

Figure 2A. Total Product Distribution

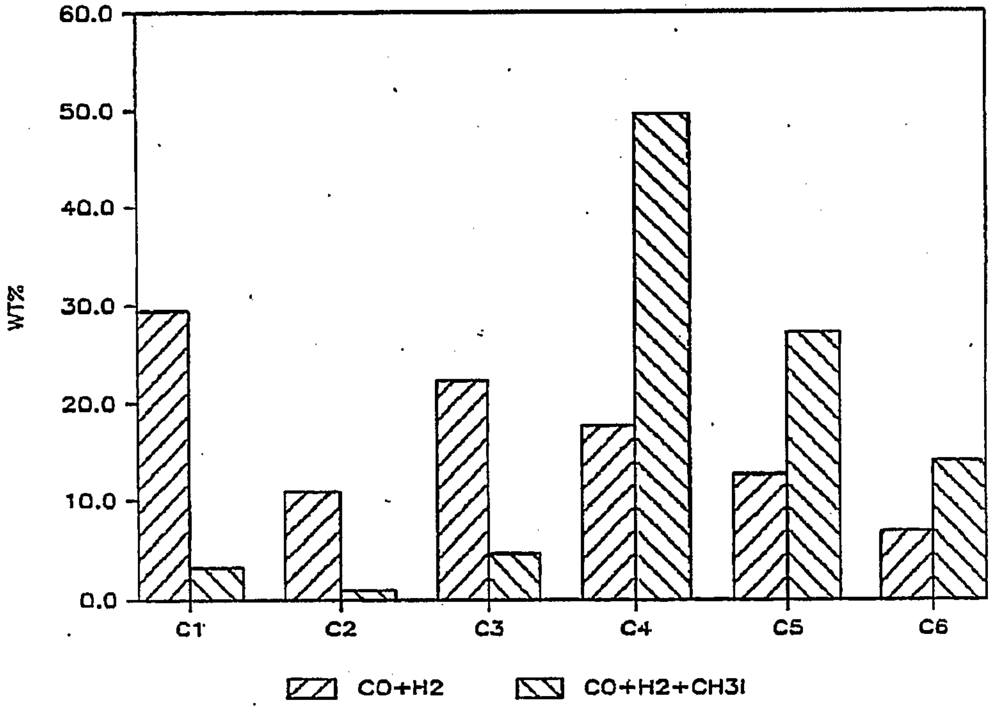
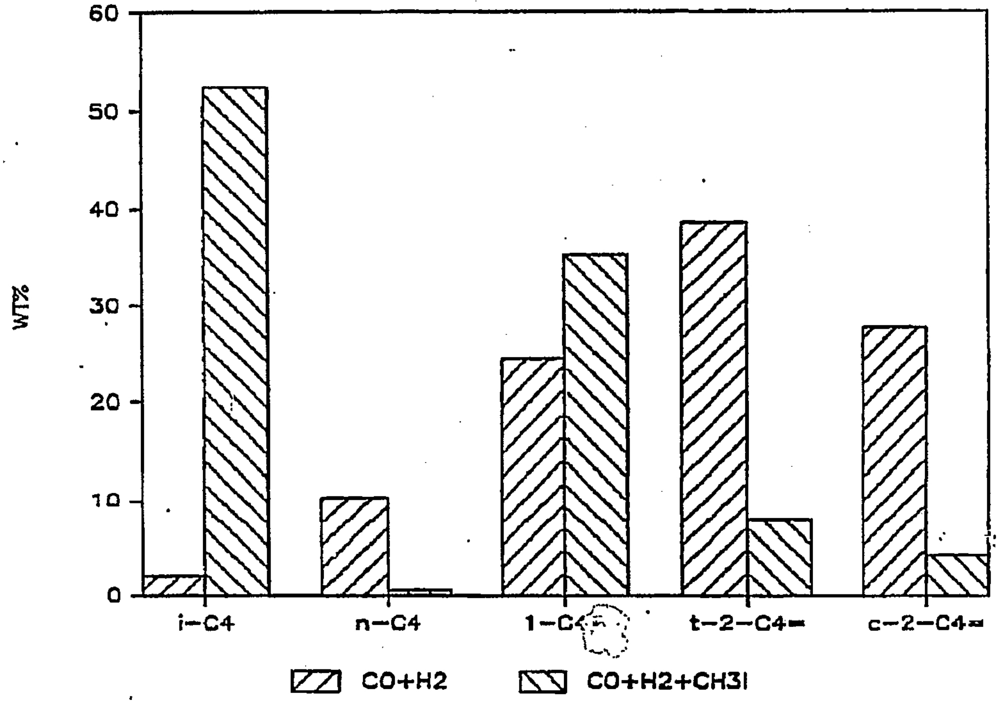
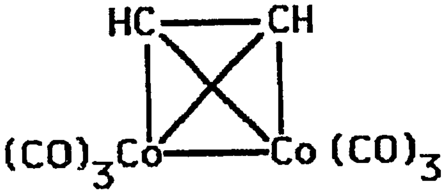


Figure 2B. Composition of C4 Products



(A)



(B)

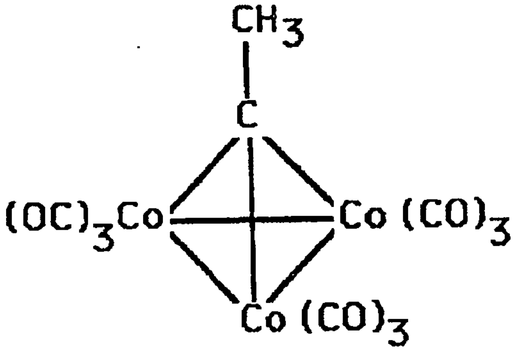


FIGURE 3. Organometallic complexes under study as model metal-adsorbate systems for chemical trapping

(A) acetylene dicobalt hexacarbonyl

(B) ethyl tricobalt enneacarbonyl

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