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Evidence for Alkylidene Intermediates in Fischer-Tropsch Synthesis Over Ru

by

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ABSTRACT

Recent studies have shown that carbenes can be eliminated from transition metal complexes by reaction with an olefin. This approach was used to search for the presence of alkylidenes, anticipated as intermediates in Fischer-Tropsch synthesis over a Ru catalyst. Addition of ethylene to the synthesis gas enhanced the formation of propylene, and the addition of cyclohexene led to the formation of methyl- and ethylcyclohexene and ethyl-, propyl-, and butylcyclohexane. These observations support the hypothesis of alkylidene intermediates.

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INTRODUCTION

Several recent studies dealing with Fischer-Tropsch synthesis over Ru (1-4) have shown that chemisorbed carbon, formed by the dissociation of adsorbed CO, will readily hydrogenate to form methane and higher molecular weight hydrocarbons. In a previous publication by the present authors (4) it was further established that the synthesis of ethane and propane could be achieved in the absence of chemisorbed CO, suggesting that this species does not participate in chain propagation over Ru. As an alternative it was proposed that methylene groups, formed by the partial hydrogenation of chemisorbed carbon, polymerize to produce surface alkylidenes, which, in turn, undergo rearrangement to form olefins or hydrogenation to form alkanes. A mechanism of this type represents a modification of the carbide mechanism originally proposed by Fischer (5) and later elaborated by Craxford and Rideal (6).

While chain propagation via methylene polymerization has not been established there is growing evidence for the bonding of alkylidenes to group VIII metals. For example, methylene and ethylidene have been reported as ligands in Ru (7) and Os (8,9) cluster complexes and in mononuclear Fe complexes (10,11). Ethylidene groups have also been observed on a Pt (111) surface (12).

This investigation was undertaken in an effort to find evidence for alkylidene species during Fischer-Tropsch synthesis over Ru. Since previous studies (4,13,14) had
shown that reaction intermediates could not be observed by infrared spectroscopy, an effort was made to detect alkylidenes by their reaction with an olefin, added to the synthesis gas mixture. This approach was motivated by the known reactivity of gas phase alkylidenes towards olefins (15,16) and recent reports (11,17) that alkylidene ligands can be eliminated from metal complexes by reaction with olefins. The olefins used in this work were ethylene and cyclohexene.

EXPERIMENTAL METHODS

The apparatus used for these studies has been described previously (4). In short, it consists of a reactor and a gas handling system. The reactor is connected to a gas recycle loop. A flow of reactants is continually fed to the recirculating gas and a flow of products is continuously removed for analysis. For the experiments in which ethylene was added to the feed, the products were passed through a dry ice trap to remove water and then analyzed by a gas chromatograph, containing a column packed with Porapak Q. When cyclohexene was added to the feed the products were frozen in a liquid nitrogen trap. Prior to analysis the frozen products were thawed and the hydrocarbons disengaged from water by extraction with diethyl ether. The ether solution was then analyzed on a Finnigan 4023 GC-MS, filled with a glass capillary column, coated with SP2100.

A 5% Ru/SiO₂ catalyst was prepared by impregnation of Cab-O-Sil HS 5 with an aqueous solution of RuCl₃·3H₂O₂. The resulting slurry was reduced in hydrogen at 400°C. A small
portion of the catalyst (180 mg) was then placed in the reactor and further reduced at 275°C for 48 hours.

The gases H₂ (99.999%) and He (99.998%) were used without further purification. Carbon monoxide was purified by passage through a dry ice trap. Ethylene (99.5%) and reagent grade cyclohexene were used without purification.

RESULTS

Ethylene Addition

The addition of ethylene was carried out at 191°C using a CO partial pressure of 180 torr and a H₂/CO ratio equal to 2. After initiating the synthesis with H₂ and CO, 15 torr of ethylene was added to the feed. The flow of ethylene was terminated after 42 min and the synthesis was continued for an additional 40 min. Product compositions during the three phases of this experiment are given in Table 1.

Prior to the introduction of ethylene, the products are mainly methane and propylene. A smaller amount of ethane is evident and a trace of ethylene is observed. When ethylene is added to the feed the distribution of hydrocarbon products is altered. It should be noted that only 17% of the ethylene fed is converted. Upon elimination of ethylene from the feed gas, the product concentrations return approximately to their original levels. The decrease in product concentrations relative to those observed prior to the addition of ethylene can be ascribed to a slow deactivation of the catalyst (4).
The change in product composition upon introduction of ethylene must be examined carefully in view of the hydrocarbon impurities present in the ethylene. It is apparent from Table 1 that about 12% of the ethylene is hydrogenated to ethane. The high activity of Ru for this reaction is substantiated by the results shown in Table 2, which indicate that in the absence of CO 95% of the ethylene is converted to ethane. The increase in methane concentration above the impurity level present in the ethylene can be ascribed to a partial hydrogenolysis of the ethane formed from ethylene. This interpretation is supported by the data in Table 2.

The concentration of propylene in the products during the addition of ethylene is significantly larger than that observed prior to ethylene addition or as an impurity in the ethylene itself. If it is assumed that most of the propylene which enters as an impurity is unreacted, then the increase in propylene production due to the presence of ethylene is a factor of 3.6. The appearance of some propane during the period of enhanced propylene production is probably the result of a partial hydrogenation of the propylene. Notice that in the absence of CO in the feed (Table 2) about 44% of the impurity propylene is converted to propane, the balance presumably undergoing hydrogenolysis to form methane and ethane.

Cyclohexene Addition

The synthesis conditions used for the experiments in which cyclohexene was added were chosen to maximize the rates of formation of C₂ and C₃ hydrocarbons. Based upon previous
studies (4), a temperature of 225°C, a CO partial pressure of 177 torr, and a H₂/CO ratio of 3 were selected. After initiating the synthesis reaction, pulses of He saturated with cyclohexene at 25°C were injected into the feed stream to the reactor. Five pulses, each containing 0.5 mmol of cyclohexene, were introduced at 30 min intervals. Following each injection, the reaction products were collected in a liquid nitrogen trap for a period of 10 min. During the remaining 20 min between injections the trap was bypassed. Use of this procedure maximized the concentration of trapped products, formed by reaction with cyclohexene.

A chromatogram of the synthesis products obtained prior to the injection of cyclohexene is shown in Fig. 1. The reconstructed ion count (RIC), displayed on the ordinate, represents the sum of all ion counts between 35 to 350 AMU for each scan, one scan being taken each second. Only the portion of the chromatogram appearing between scans 500 and 3200 is shown, to enhance the visibility of the smaller peaks. The regular sequence of large peaks appearing in Fig. 1 are identified, on the basis of mass fracturing patterns, as normal alkanes, ranging from n-heptane at scan 417 to n-heptadecane at scan 3185. The smaller peaks observed near each of the large peaks are due to a variety of branched alkanes and both normal and branched olefins. Figure 2 illustrates these peaks more clearly for the portion of the chromatogram between scans 400 and 1000. The identity of the peaks present in the region near n-octane are listed in Table 3.
The chromatogram of products obtained when cyclohexene is added to the feed stream is very similar to that obtained during synthesis in the absence of cyclohexene. Both cyclohexene and cyclohexane are observed in the portion of the chromatogram below scan 500, and it is estimated that about 13% of the injected cyclohexene is converted to cyclohexane. The principal difference in the chromatograms obtained with and without cyclohexene injection is that the intensities of the normal alkane peaks fall off more rapidly when cyclohexene is present. This point is brought out in Fig. 3 which shows a bar graph of peak intensities versus carbon number. Notice that with increasing carbon number the difference in peak intensities increases.

Figure 4 illustrates the portion of the chromatogram between scans 400 and 1000, for an experiment in which cyclohexene is present. Comparison of Figs. 2 and 4 clearly demonstrates that cyclohexene addition does not perturb significantly the nature or distribution of minor synthesis products.

Further examination of Fig. 4 reveals three peaks not present in Fig. 2. These features are located at scans 484, 560, and 746. A partially resolved peak is also seen at scan 852. An identification of these peaks was carried out by comparing the associated mass spectra with mass spectra of known compounds contained in the library of the GS-MS. By this means the peaks at scans 484, 560, and 746 were positively identified as 3-methylcyclohexene, 1-methylcyclohexene, and ethylcyclohexane, respectively. The small peak at scan 852 was identified as 1-ethylcyclohexene, but the quality of this
identification is not as high as that of the fully resolved peaks. Examination of the chromatogram in the region between scans 1000 to 1400 revealed small peaks at scans 1055 and 1385 which could be identified as propyl- and butylcyclohexane, respectively. The intensities of the alkyl-cyclohexene and alkyl-cyclohexane products are listed in Table 4. It is significant to note that none of the products listed in Table 4 were observed as impurities in the cyclohexene or in the synthesis products collected when cyclohexene was absent from the feed.

A careful examination of the chromatogram was made to determine whether other products such as norcarane, methylcyclohexane, propylcyclohexene, and butylcyclohexene, could be identified. No definitive conclusions could be reached since each of these compounds was estimated to elute at the same time as one of the synthesis products.

DISCUSSION

The present experiments demonstrate that ethylene and cyclohexene will react with carbon containing species present on a Ru catalyst during Fischer-Tropsch synthesis. The important question is whether the products of such reactions can be interpreted as evidence for surface alkylidene groups. To initiate this discussion, it is useful to review what is known about the reactions of alkylidenes with ethylene and cyclohexene. Several studies (15,16) have shown that the reaction of gas phase methylene groups with ethylene produces cyclopropane and to a lesser extent propylene. In a similar fashion the reaction of methylene groups
with cyclohexene produces norcarane and smaller quantities of 1-, 3-, and 4-methylcyclohexene. There have been studies of the reactions of olefins with alkylidenes complexes to metals, but what information is available suggests that the products obtained are very similar to those produced in reactions with free alkylidenes groups. For example, Fellmann et al. (17) have shown that ethylene will react with Ta and Nb-bisneo-pentylidene to product 4,4-dimethyl-1-pentene, and Stevens and Beauchamp (11) have noted the formation of norcarane when $\text{CpFe(CO)}_2(\text{CH}_2)$ reacts with cyclohexene.

Based on the available evidence, one is led to conclude that cyclopropane and norcarane should be the characteristic products formed by reaction of an adsorbed methylene group with ethylene and cyclohexene respectively. Alternately, one might expect to detect propylene and methyl cyclohexene, which are the thermodynamically more stable isomers of cyclopropane and norcarane. Given this perspective, it seems reasonable to propose that the nearly four-fold increase in propylene production observed during ethylene addition to the feed can be explained by a reaction involving adsorbed methylene groups. This interpretation is further supported by the detection of methylcyclohexene when cyclohexene is added to the feed.

The observation of ethylcyclohexene and ethyl-, propyl-, and butylcyclohexane may be viewed as further evidence for the pressure of adsorbed alkylidenes. The formation of alkyl-cyclohexanes most likely proceeds by initial reaction of an alkylidene with cyclohexene and subsequent hydrogenation of the reaction.
intermediate. It is interesting to observe that the intensities for the alkyl-cyclohexane peaks listed in Table 4 decrease as one proceeds from ethyl- to butylcyclohexane. This pattern parallels the rates of formation of C\textsubscript{2} through C\textsubscript{4} products (18) and is suggestive of a chain growth process involving the polymerization of adsorbed methylene groups.

The participation of adsorbed methylene groups in the mechanism of chain growth on Ru is further supported by the influence of cyclohexene on the distribution of C\textsubscript{8} through C\textsubscript{17} normal alkanes, presented in Fig. 3. If methylene groups are involved in chain propagation, then a reduction in the surface concentration of these groups would be expected to suppress the formation of higher molecular weight products. Furthermore, the degree of suppression should be greater, the higher the carbon number. These are exactly the effects produced by the addition of cyclohexene to the synthesis feed.

In summary, the present study has provided evidence that alkylidene groups may be present on the surface of a Ru catalyst during Fischer-Tropsch synthesis. The polymerization of methylene groups to form higher molecular weight alkylidenes is also indicated by these results.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the aid of Dr. Amos Newton who performed the GC-MS analyses reported here. This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under contract No. W-7405-Eng-48.
REFERENCE


Table 1

Changes in Product Composition upon Addition of Ethylene to the Synthesis Feed Gas

<table>
<thead>
<tr>
<th>Experimental Sequence</th>
<th>Component</th>
<th>Feed Composition (Mole %)</th>
<th>Product Composition (Mole %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-38 min Feed I</td>
<td>CH$_4$</td>
<td>0</td>
<td>2.4 x 10^{-3}</td>
</tr>
<tr>
<td>(sample taken at 10 min)</td>
<td>C$_2$H$_4$</td>
<td>0</td>
<td>&lt; 5 x 10^{-4}(a)</td>
</tr>
<tr>
<td></td>
<td>C$_2$H$_6$</td>
<td>0</td>
<td>8.5 x 10^{-4}</td>
</tr>
<tr>
<td></td>
<td>C$_3$H$_6$</td>
<td>0</td>
<td>3.5 x 10^{-3}</td>
</tr>
<tr>
<td></td>
<td>C$_3$H$_8$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>38-80 min Feed II</td>
<td>CH$_4$</td>
<td>2.1 x 10^{-2}</td>
<td>3.2 x 10^{-2}</td>
</tr>
<tr>
<td>(sample taken at 50 min)</td>
<td>C$_2$H$_4$</td>
<td>1.8</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>C$_2$H$_6$</td>
<td>5.5 x 10^{-2}</td>
<td>2.6 x 10^{-1}</td>
</tr>
<tr>
<td></td>
<td>C$_3$H$_6$</td>
<td>7.1 x 10^{-3}</td>
<td>2.0 x 10^{-2}</td>
</tr>
<tr>
<td></td>
<td>C$_3$H$_8$</td>
<td>0</td>
<td>1.0 x 10^{-3}</td>
</tr>
<tr>
<td>80-120 min Feed I</td>
<td>CH$_4$</td>
<td>0</td>
<td>1.6 x 10^{-3}</td>
</tr>
<tr>
<td>(sample taken at 120 min)</td>
<td>C$_2$H$_4$</td>
<td>0</td>
<td>&lt; 5 x 10^{-4}(a)</td>
</tr>
<tr>
<td></td>
<td>C$_2$H$_6$</td>
<td>0</td>
<td>&lt; 5 x 10^{-4}(a)</td>
</tr>
<tr>
<td></td>
<td>C$_3$H$_6$</td>
<td>0</td>
<td>2.9 x 10^{-3}</td>
</tr>
<tr>
<td></td>
<td>C$_3$H$_8$</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Feed I: H$_2$/CO/He @ mole% 46.2/23.2/balance

Feed II: H$_2$/CO/C$_2$H$_4$/He @ mole% 45.8/22.9/1.8/balance

(a) Lower detectable limit
Table 2

Product Composition Resulting from the Hydrogenation and Hydrogenolysis of Ethylene

<table>
<thead>
<tr>
<th>Component</th>
<th>Feed Composition (Mole %)</th>
<th>Product Composition (Mole %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>$3.5 \times 10^{-2}$</td>
<td>$4.0 \times 10^{-1}$</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>1.6</td>
<td>$1.6 \times 10^{-1}$</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>$5.2 \times 10^{-2}$</td>
<td>1.6</td>
</tr>
<tr>
<td>C$_3$H$_6$</td>
<td>$6.4 \times 10^{-3}$</td>
<td>0</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>0</td>
<td>$2.8 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

Feed $H_2/C_2H_4/He$ @ mole% 57.6/1.6/balance
<table>
<thead>
<tr>
<th>Compound</th>
<th>Location (Scan no.)</th>
<th>Fig. 2</th>
<th>Fig. 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,3-dimethyl-2-hexene</td>
<td>543</td>
<td>543</td>
<td></td>
</tr>
<tr>
<td>2-methylheptane</td>
<td>577</td>
<td>582</td>
<td></td>
</tr>
<tr>
<td>3-methylheptane</td>
<td>590</td>
<td>593</td>
<td></td>
</tr>
<tr>
<td>octene (4- or 2) (a)</td>
<td>625</td>
<td>627</td>
<td></td>
</tr>
<tr>
<td>1-octene</td>
<td>635</td>
<td>636</td>
<td></td>
</tr>
<tr>
<td>2-methyl-3-heptene</td>
<td>644</td>
<td>646</td>
<td></td>
</tr>
<tr>
<td>octene (4- or 2-)</td>
<td>654</td>
<td>656</td>
<td></td>
</tr>
<tr>
<td>3-octene</td>
<td>661</td>
<td>663</td>
<td></td>
</tr>
<tr>
<td>octane</td>
<td>667</td>
<td>671</td>
<td></td>
</tr>
<tr>
<td>octene (2-, 4-, or 1-) (a)</td>
<td>680</td>
<td>681</td>
<td></td>
</tr>
<tr>
<td>3-methylene heptane</td>
<td>689</td>
<td>692</td>
<td></td>
</tr>
<tr>
<td>octene (4- or 2-) (a)</td>
<td>703</td>
<td>703</td>
<td></td>
</tr>
</tbody>
</table>

(a) Clear distinction between the indicated isomers is not possible
Table 4

Products of Reaction with Cyclohexene

<table>
<thead>
<tr>
<th>Compound</th>
<th>Peak Intensities (Ion counts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-methylcyclohexene</td>
<td>$4.8 \times 10^4$</td>
</tr>
<tr>
<td>3-methylcyclohexene</td>
<td>$1.5 \times 10^4$</td>
</tr>
<tr>
<td>1-ethylcyclohexene(a)</td>
<td>$9.1 \times 10^3$</td>
</tr>
<tr>
<td>ethylcyclohexane</td>
<td>$5.9 \times 10^3$</td>
</tr>
<tr>
<td>propylcyclohexane</td>
<td>$1.9 \times 10^3$</td>
</tr>
<tr>
<td>butylcyclohexane</td>
<td>$6.8 \times 10^2$</td>
</tr>
</tbody>
</table>

(a) Present as a shoulder on the leading edge of a larger peak
Figure Captions

Fig. 1 Chromatogram of the synthesis products (scans 500 to 3200)

Fig. 2 Chromatogram of the synthesis products (scans 400 to 1000)

Fig. 3 Normal alkane product intensities versus carbon number

Fig. 4 Chromatogram of synthesis products when cyclohexene is present (scans 400 to 1000)
Without Cyclohexene Addition
With Cyclohexene Addition

$\frac{I_{C_n}}{I_{C_8}}$

Normal Alkanes

Fig. 3
Fig. 4
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