JOURNAL OF CATALYSIS 62, 19–25 (1980)

Evidence for Intermediates Involved in Fischer–Tropsch Synthesis over Ru

JOHN G. EKERDT[1] AND ALEXIS T. BELL

Materials and Molecular Research Division, Lawrence Berkeley Laboratory, and Department of Chemical Engineering, University of California, Berkeley, California 94720

Received February 19, 1979; revised June 15, 1979

Recent studies of Fischer–Tropsch synthesis over Ru catalysts have suggested that the growth of hydrocarbon chains may involve the addition of methylene groups to either alkylidene or alkyl species present on the catalyst surface. In the present investigation an attempt was made to detect the growing chains by their reaction with an olefin, an approach suggested by recent experiments with metal complexes containing alkylidene or alkyl ligands. The addition of ethylene to the feed of CO and H_2 enhanced the formation of propylene, while the addition of cyclohexene led to the formation of methyl- and ethylcyclohexane and ethyl-, propyl-, and butylcyclohexane. While the observed reaction products did not permit an unambiguous distinction between the two possible surface species, the distribution of products obtained from cyclohexene addition and the influence of cyclohexene on the production of normal alkanes, suggests that the olefin reacts with species involved in chain propagation.

INTRODUCTION

Several recent studies dealing with Fischer–Tropsch synthesis over Ru (*1–4*) have shown that chemisorbed carbon, formed by the dissociation of absorbed 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, one may envision that methylene groups, formed by the partial hydrogenation of chemisorbed carbon, act as the principal monomer units and that chain growth occurs by the addition of methylene units to adsorbed alkylidene species (*4*) or by the insertion of methylene units into the metal–carbon bond of adsorbed alkyl species. Both of these schemes represent a modification of the carbide mechanism originally proposed by Fischer (*5*) and later elaborated by Craxford and Rideal (*6*).

The present studies were undertaken to find evidence for either alkylidene or alkyl species during Fischer–Tropsch synthesis over Ru. Since previous investigations (*4, 7, 8*) had shown that reaction intermediates could not be observed by infrared spectroscopy, an effort was made to detect adsorbed alkylidene and alkyl species by their reaction with an olefin. This approach was motivated by the known reactivity of gas-phase alkylidenes with olefins (*9–10*) and recent reports that both alkylidene (*11–13*) and alkyl (*14*) 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

---

[1] Present address: Department of Chemical Engineering, University of Texas, Austin, Tex. 78712.

0021-9517/80/030019-07$02.00/0

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 gas chromatograph–mass spectrometer, fitted with a glass capillary column, coated with SP2100.

A 5% Ru/SiO_2 catalyst was prepared by impregnation of Cab-O-Sil HS 5 with an aqueous solution of $RuCl_3 \cdot 3H_2O$. 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 hr.

The gases H_2 (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 H_2/CO ratio equal to 2. After initiating the synthesis with H_2 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.

TABLE 1

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

Experimental sequence	Component	Feed composition (mole%)	Product composition (mole%)
0–38 min	CH_4	0	2.4×10^{-3}
Feed I	C_2H_4	0	$<5 \times 10^{-4}$[b]
(sample taken	C_2H_6	0	8.5×10^{-4}
at 10 min)	C_3H_6	0	3.5×10^{-3}
	C_3H_8	0	0
38–80 min	CH_4	2.1×10^{-2}	3.2×10^{-2}
Feed II	C_2H_4	1.8	1.5
(sample taken	C_2H_6	5.5×10^{-2}	2.6×10^{-1}
at 50 min)	C_3H_6	7.1×10^{-3}	2.0×10^{-2}
	C_3H_8	0	1.0×10^{-3}
80–120 min	CH_4	0	1.6×10^{-3}
Feed I	C_2H_4	0	$<5 \times 10^{-4}$[b]
(sample taken	C_2H_6	0	$<5 \times 10^{-4}$[b]
at 120 min)	C_3H_6	0	2.9×10^{-3}
	C_3H_8	0	0

[a] Feed I: H_2/He at mole% 46.2/23.2/balance; Feed II: $H_2/CO/C_2H_4/{}^4He$ at mole% 45.8/22.9/1.8/balance

[b] Lower detectable limit.

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

TABLE 2

Product Composition Resulting from the Hydrogenation and Hydrogenolysis of Ethylene[a]

Component	Feed composition (mole%)	Product composition (mole%)
CH_4	3.5×10^{-2}	4.0×10^{-1}
C_2H_4	1.6	1.6×10^{-1}
C_2H_6	5.2×10^{-2}	1.6
C_3H_6	6.4×10^{-3}	0
C_3H_8	0	2.8×10^{-3}

[a] Feed: $H_2/C_2H_4/He$ at mole% 57.6/1.6/balance.

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 C_2 and C_3 hydrocarbons. Based upon previous studies (*4*), a temperature of 225°C, a CO partial pressure of 177 Torr, and a H_2/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 mmole 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 and 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

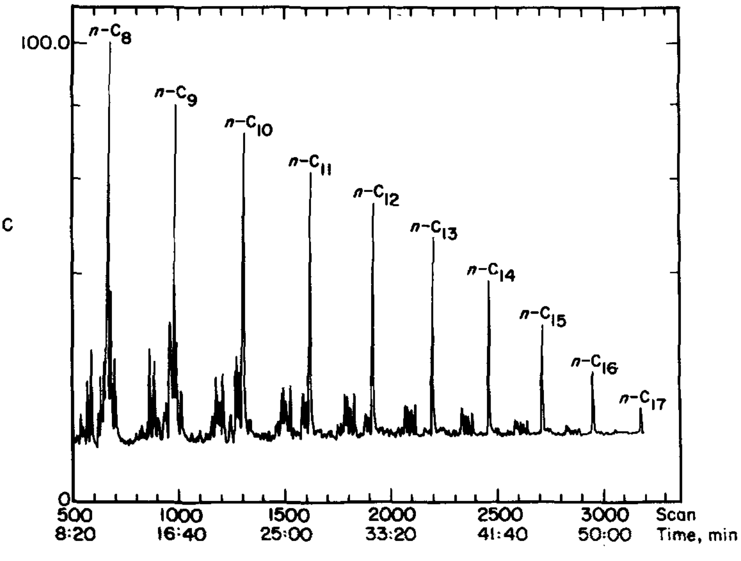

FIG. 1. Chromatogram of the synthesis products (scans 500 to 3200).

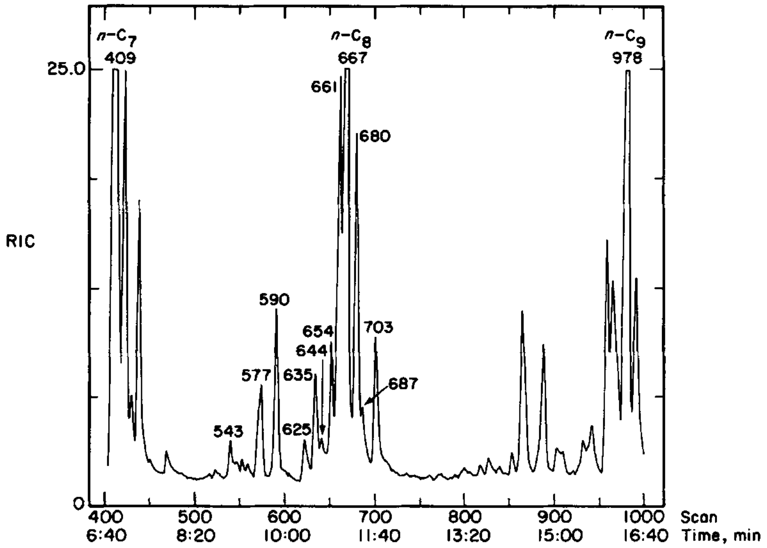

FIG. 2. Chromatogram of the synthesis products (scans 400 to 1000).

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 identities 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

TABLE 3

Identification of Chromatographic Peaks

Compound	Location (scan No.)	
	Fig. 2	Fig. 4
2,3-Dimethyl-2-hexene	543	543
2-Methylheptane	577	582
3-Methylheptane	590	593
Octene (4- or 2-)[a]	625	627
1-Octene	635	636
2-Methyl-3-heptane	644	646
Octene (4- or 2-)[a]	654	656
3-Octene	661	663
Octane	667	671
Octene (2-, 4-, or 1-)[a]	680	681
3-Methylene heptane	689	692
Octene (4- or 2-)[a]	703	703

[a] Clear distinction between the indicated isomers is not possible.

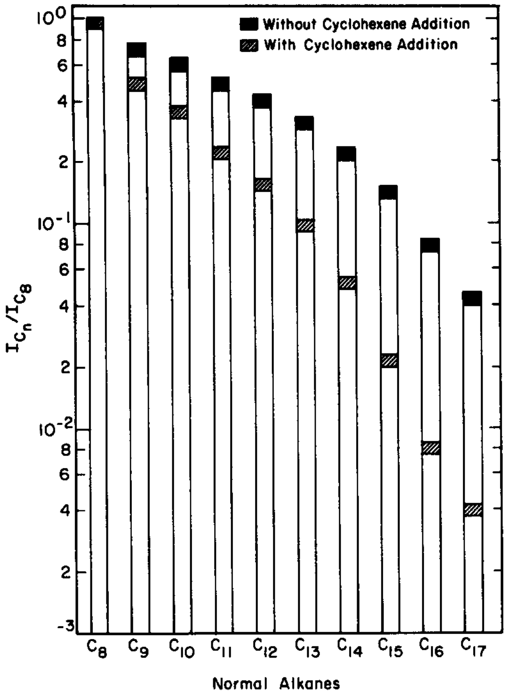

FIG. 3. Normal alkane product intensities versus carbon number.

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 GC-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

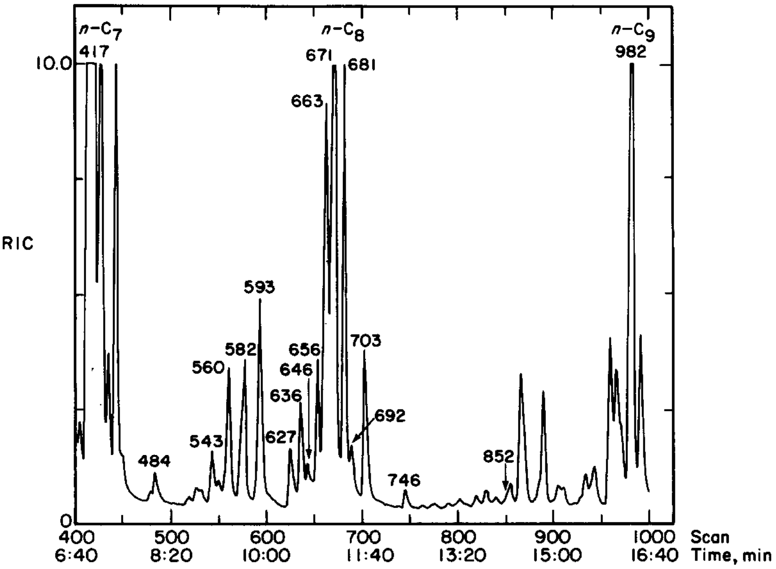

FIG. 4. Chromatogram of synthesis products when cyclohexene is present (scans 400 to 1000).

TABLE 4

Products of Reaction with Cyclohexene

Compound	Peak intensities (ion count)
1-Methylcyclohexene	4.8×10^4
3-Methylcyclohexene	1.5×10^4
1-Ethylcyclohexene[a]	9.1×10^3
Ethylcyclohexane	5.9×10^3
Propylcyclohexane	1.9×10^3
Butylcyclohexane	6.8×10^2

[a] Present as a shoulder on the leading edge of a larger peak.

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 questions is whether it is possible to identify the reacting species from the observed products. To address this question it is useful to review what is known about the reaction of olefin with alkylidene and alkyl species. Several recent studies have shown that olefins will eliminate alkylidenes present as ligands in metal complexes. For example, Fellman *et al.* (*11*) have observed that ethylene will react with Te and Nb-bisneopentylidene to produce 4,4-dimethyl-1-pentene, and Stevens and Beauchamp (*12*) have noted the elimination of methylene groups, presumably as norcarane, when $CpFe(CO)_2(CH_2)^+$ reacts with cyclohexene. The elimination of a methylene group from Ni complexes has also been reported by Grubbs and Miyashita (*13*). In the literature pertaining to homogeneous catalysis, it has also been suggested that olefins will react with alkyl ligands. Thus, it has been proposed that the dimerization, oligomerization, and polymerization of ethylene proceed by insertion of the olefin into the metal–carbon band of a metal alkyl (*15, 16*). Stable olefinic products are then formed by β-elimination of hydrogen. It should be noted, however, that the validity of this mechanism had been questioned due to the lack of unambiguous experimental evidence (*17*). Confirmation of the proposed scheme has only recently been provided by Evitt and Bergman (*14*). Their studies showed that $CpPh_3PCo(CH_3)_2$ would react with ethylene to produce methane and propylene. If the methylene groups were perdeuterated, only CD_3H was produced, indicating that the reaction proceeded by ethylene insertion and subsequent β-elimination of hydrogen.

The foregoing discussion indicates that olefins will react with both alkylidene and alkyl groups to produce similar products. Since the literature pertaining to this subject is as yet limited, it is not possible to clearly establish which group would react preferentially if both were present simultaneously. Given this perspective, we must conclude that in the present studies the additional propylene formed when ethylene is added to the synthesis gas feed might arise from either methylene or methyl groups. Likewise, the alkyl cyclohexenes detected when the cyclohexene is added to the feed could result from reactions with either alkylidene or alkyl groups. The presence of saturated products together with the olefins (i.e., propane and alkyl cyclohexanes) most likely results from a partial hydrogenation of the olefins. The decline in concentration of the alkyl cyclohexene and cyclohexane products with increasing length of the alkyl group does suggest, however, that the cyclohexene is scavenging intermediates in the chain growth process.

The influence of cyclohexene on the distribution of normal alkane products provides the only evidence on which to contend that methylene groups may be present on the catalyst surface. The arguments for this interpretation are as follows. If it is assumed that chain propagation occurs via the addition of methylene groups, and that the propagation step is at equilibrium with respect to all surface species involved, then it follows that the rate of formation of a hydrocarbon containing n carbon atoms will be proportional to the nth power of the methylene surface concentration. A reduction in the surface concentration of these groups by reaction with cyclohexene would be expected to produce a suppression in the rate of hydrocarbon formation. Furthermore, the degree of suppression should be greater, the higher the carbon number. This is exactly the effect observed in Fig. 3. It should be noted, however, that while the data presented in Fig. 3 are suggestive of the participation of methylene groups in the chain growth process, they do not constitute proof for the presence of such groups.

In summary, the present study has provided evidence that alkylidene and alkyl groups present on the surface of a Ru catalyst during Fischer–Tropsch synthesis can be detected by their reaction with olefins. The polymerization of methylene groups to form higher molecular weight alkylidenes is also suggested by these results.

ACKNOWLEDGMENT

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 W-7405-Eng-48.

REFERENCES

1. Rabo, J. A., Risch, A. P., and Poutsma, J. L., *J. Catal.* **53**, 295 (1978).
2. Low, G. G., and Bell, A. T., *J. Catal.* **57**, 397 (1979).
3. McCarty, J. Wentrcek, P., and Wise, J., SRI-International, Menlo Park, Calif., personal communication.
4. Ekerdt, J. G., and Bell, A. T., *J. Catal.* **58**, 170 (1979).
5. Storch, H., Golumbic, N., and Anderson, R., "The Fischer–Tropsch and Related Synthesis." Wiley, New York, 1951.
6. Craxford, S. R., and Rideal, E. K., *J. Chem. Soc.* 1604 (1939).
7. Dalla Betta, R. A., and Shelef, M., *J. Catal.* **48**, 111 (1977).
8. King, D. L., *Prepr. Amer. Chem. Soc. Div. Petrol. Chem.* **23**, 482 (1978).
9. Kirmse, W., "Carbene Chemistry," 2nd ed. Academic Press, New York, 1971.
10. DeMore, W. B., and Benson, S. W., "Advances in Photo-Chemistry" (W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr. Eds.), Vol. 2. Interscience, New York, 1964.
11. Fellman, J. D., Rupprecht, G. A., Wood, C. D., and Schrock, R. R., *J. Amer. Chem. Soc.* **100**, 5962 (1978).
12. Stevens, A. E., and Beauchamp, J. L., *J. Amer. Chem. Soc.* **100**, 2584 (1978).
13. Grubbs, R. H., and Miyashita, A., *J. Amer. Chem. Soc.* **100**, 7418 (1978).
14. Evitt, E. R., and Bergman, R. G., *J. Amer. Chem. Soc.* **101**, 3973 (1979).
15. Reich, L. S., and Schindler, A., "Polymerizations by Organometallic Compounds." Wiley-Interscience, New York, 1966.
16. Taqui Khan, M. M., and Martell, A. E., "Homogeneous Catalysis by Metal Complexes," Vol. II. Academic Press, New York, 1974.
17. Ivin, K. J., Rooney, J. J., Stewart, C. D., Green, M. L. H., and Mahtab, R., *J. Chem. Soc. Commun.*, 604 (1978).