

Evidence for CH_x Surface Species after the Hydrogenation of CO over an Fe(110) Single Crystal Surface

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A combined apparatus which enables the transfer of a catalyst sample from a high pressure reaction cell (~1 atm) into an ultrahigh vacuum chamber (<10⁻¹⁰ Torr) is described. High resolution electron energy loss spectroscopy (EELS) is used for a post reaction study of the catalyst surface. An Fe(110) surface was used as a model catalyst. Fischer-Tropsch synthesis (FTS) reactions were performed in the reaction chamber, with the iron surface at 300°C, using a total pressure of 1 atm at a fixed H₂/CO ratio. After the reaction the iron sample was transferred into the UHV chamber and subsequently analyzed by EELS. Among the observed vibrational losses those at 870 and 3100 cm⁻¹ are characteristic for surface CH and those at 1420 and 3010 cm⁻¹ for CH₂ groups. An additional loss at 1200 cm⁻¹ is possibly due to a C₂ species on the active surface. Experiments using a carbon pre-covered iron surface in a pure hydrogen atmosphere (1 atm 300°C) produced similar EELS spectra. The present results add to the body of work which indicates that the methanation reaction and the FTS proceed through the hydrogenation of surface carbon. Further, the EELS spectra provide direct evidence for the presence of partially hydrogenated carbon on the active Fe(110) surface. These hydrocarbon species are CH₂ and probably a mixture of CH and CCH₂. It is possible that some or all of these species are reaction intermediates under synthesis conditions.

INTRODUCTION

The work of Wentrcek, Wood, and Wise (1) and Araki and Ponc (2) established that surface carbon, formed by CO dissociation at low temperatures, is the initial intermediate in the methanation reaction. CH_x surface species formed by successive hydrogenation of active carbon are assumed to be further intermediates in methane production (3-5). Moreover, there is clear experimental evidence (6, 7) that the chain growth of higher hydrocarbons during Fischer-Tropsch synthesis (FTS) is propagated by the insertion of CH_x units rather than by the insertion of CO.

Infrared spectroscopy has been used for the *in situ* observation of surface species under reaction conditions (8-13), e.g., at pressures up to 1 atm and higher. Most of these ir studies indicate the presence of hydrocarbon species on the catalyst surfaces, as indicated by bands in the range 2800-

3000 cm⁻¹, but it is not clear whether the bands arise from FTS reaction intermediates. The difficulty in interpreting (4) the ir results arises in part from the complex structure of supported catalysts. The latter problem could possibly be overcome by using single crystal surfaces as model catalysts which have a well defined surface structure and composition. However, such low area catalysts have a considerably reduced number of scattering centers if compared with large area supported catalysts. Hence the sensitivity of infrared spectroscopy is too low for detecting hydrocarbons adsorbed on single crystal surfaces.

High resolution electron energy loss spectroscopy (EELS) has been demonstrated to be a technique sensitive enough to detect hydrocarbon species adsorbed on single crystal surfaces (14). The main disadvantage is that *in situ* observations during reaction conditions are not possible. The catalyst surface can only be inspected

after a transfer from the high pressure reaction chamber into an ultrahigh vacuum (UHV) system. Combined apparatus allowing an analysis of the surface of the catalyst has been used in the past by several authors (15–17). In the present study the combined apparatus was equipped with an EELS spectrometer which enabled the direct observation of hydrocarbon surface species after the hydrogenation of carbon monoxide over an Fe(110) single crystal.

EXPERIMENTAL

The apparatus used in the present study is schematically shown in Fig. 1. It consists of an ion-pumped stainless steel UHV chamber and an attached reaction cell which can be isolated from the UHV chamber by a gate valve.

The sample is mounted on the end of a rigid rod which travels vertically over a distance of 800 mm to the various positions and is rotated 360° about its axis. Both lin-

ear motion and rotation of the sample rod are carried out and controlled by dc step motors. Programmed power supplies allow one to dial any angular and translational position along the system axis.

The sealing of the sample rod between atmospheric pressure and UHV is achieved by two O-ring-sealed differential pumping sections (rough pump and turbomolecular pump) and by an additional gap seal between reaction cell and UHV chamber. Base pressures in the 10^{-11} Torr range are routinely obtained in the UHV chamber.

Inside the sample rod there are electric feedthroughs for thermocouple wires and high voltage supply and a coaxial stainless steel tube for liquid nitrogen cooling. The sample temperature is monitored by a Chromel–Alumel thermocouple spot-welded to the upper edge of the sample. The lowest achievable temperature is 110 K.

As indicated in Fig. 1 there are three

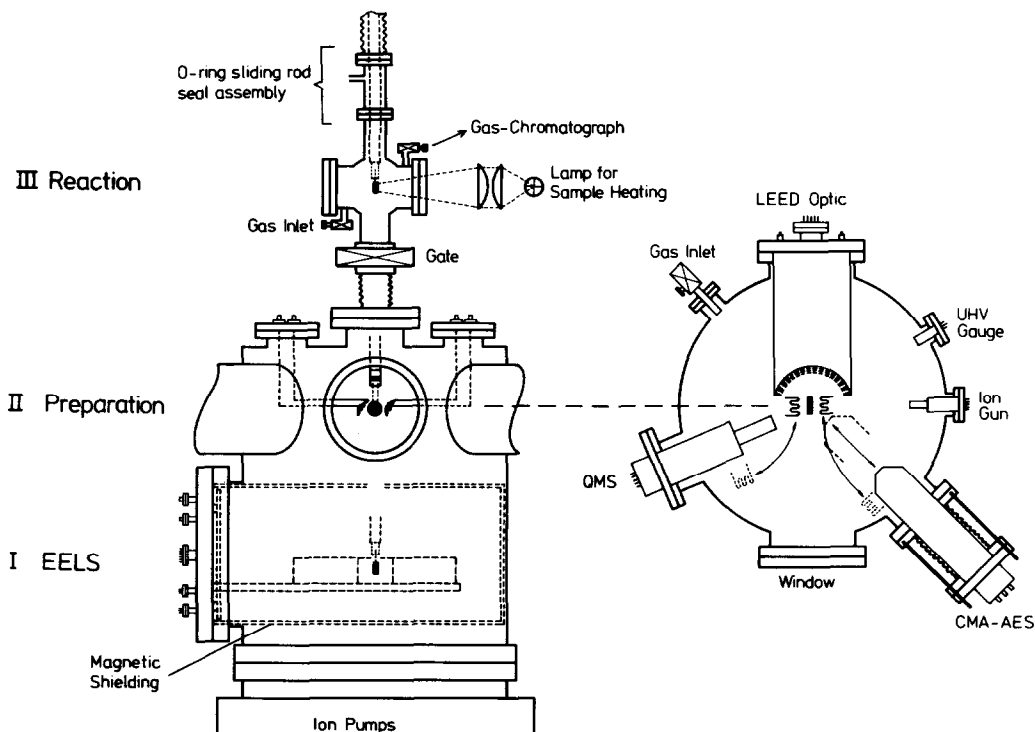


FIG. 1. Apparatus featuring a reaction chamber, a preparation stage, and an electron loss spectrometer.

different operating levels (I, II, and III). In the lowest position (I) adsorbates on the sample surface may be analyzed using an EELS spectrometer. The spectrometer is a single pass type using cylindrical condensers as energy dispersing elements. Spectra are taken at an angle of reflection of 70° from the sample normal. The spectrometer resolution was typically between 50 and 70 cm⁻¹ and the incident beam energy was 2.5 eV. As the sample cannot be moved horizontally, the complete spectrometer is mounted onto a movable plate which is manipulated from outside to perform shifts up to 10 mm along the *x* and *y* directions. This is necessary for a proper adjustment of the sample spectrometer geometry if the spectrometer is used in the reflection mode.

In the middle position (II) the sample can be prepared and analyzed by a variety of techniques: the equipment consists of a cylindrical mirror analyzer (CMA) for Auger electron spectroscopy (AES), a four-grid optics for low energy electron diffraction (LEED), a quadrupole mass spectrometer (QMS), and an ion sputter gun. All components are aimed at the center of the cylindrical chamber. Research grade gases are introduced via adjustable leak valves. In this position the sample is heated either by radiation or electron bombardment from a tungsten filament which can be turned close to the rear of the sample.

In the upper position (III) the sample is located in a reaction cell. The cell is isolated from the UHV chamber by a gate valve which enables operation near atmospheric pressures while UHV is maintained in the main chamber.

The reaction cell operates as a flow reactor. However, because of the relatively large volume (~660 cm³) a partial accumulation of reaction products occurs which also facilitates their detection. During a reaction run the sample is heated via optical windows by the focussed radiation of two projector lamps. Temperatures up to 500°C are obtained by this method. To avoid side

reactions on the walls the inside of the cell has been plated with gold.

Reaction products are analyzed with gas chromatography (Hewlett-Packard 5840A) using flame-ionization detection. For the separation of products a Poropak Q column has been used. After the termination of the reaction the cell was pumped down rapidly to the 10⁻⁸ Torr range using a 120 liters/min turbomolecular pump. An additional gap seal for the sample rod located between reaction cell and UHV chamber ensures that the pressure in the UHV chamber never exceeded 5 × 10⁻¹⁰ Torr during sample transfer. The total time needed to bring the sample from atmospheric pressure into an UHV of 5 × 10⁻¹⁰ Torr was less than 4 min.

An iron single crystal 2 mm thick and 6 mm in diameter, which was polished on both sides to expose (110) planes, served as a model catalyst. The sample was cleaned by argon ion sputtering at elevated temperatures. The cleaning procedure has been described in detail elsewhere (18). For some experiments the Fe(110) surface was deliberately covered with a carbon layer by exposing the sample to acetylene at 800 K. After the transfer of the sample into the reaction position and closure of the gate valve, the reaction cell was pressurized with a H₂/CO mixture, or with pure hydrogen in the case where the sample surface had been covered with carbon. Both CO and H₂ were passed over chromium oxide adsorption cells (Messer-Griesheim "Oxisorb") for further purification. In addition the CO was passed through a copper coil heated to 200°C to remove carbonyls. The flow rates of both the CO and H₂ were adjusted before entering the reaction cell and were maintained constant using flow meters and servo-valves. The pressure in the reaction cell was always slightly above atmospheric pressure as measured by a Baratron pressure gauge.

RESULTS AND DISCUSSION

Figure 2 shows a typical gas chromatogram taken during a Fischer-Tropsch reac-

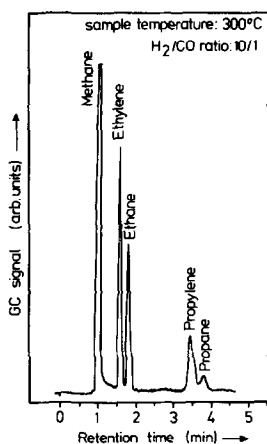


Fig. 2. Typical gas chromatogram obtained at high methanation rate. Only products up to C_3 are shown.

tion over an Fe(110) single crystal. During the reaction the CO/H_2 ratio was held constantly at 1:10 and the sample was heated to $300^\circ C$. As seen from Fig. 2 the main product is methane. In addition to methane higher hydrocarbons, up to C_5 , were observed. The chromatogram is truncated at C_3 because C_4 and C_5 products were near the detection limit. The ratio of ethylene to ethane (and propylene to propane) produced depended on the H_2/CO ratio and the alkane fraction became dominant for highly hydrogen-rich feed-gas mixtures. The product distribution is typical for low conversion conditions and is very similar to that found for polycrystalline iron surfaces (16) and for a Fe(100) single crystal (19).

After the FTS reaction was interrupted at high methane production rate by turning off the sample heating, the reaction cell was pumped off and the iron sample was transferred into the EELS spectrometer position. The EELS spectrum shown in Fig. 3c is the vibrational spectrum of the catalytically active surface. The intensity of the elastic reflected electrons along the specular direction is drastically reduced as compared to the reflected intensity of a clean iron surface shown in the lower part of Fig. 3a. This is obviously caused by the rela-

tively strong carbon contamination as indicated by AES. In the high frequency loss regime two well resolved losses at 3010 and 3100 cm^{-1} are observed, and are in the range for CH stretching vibrations of adsorbed hydrocarbons. A further relatively intense loss at 1420 cm^{-1} is observed and is attributed to a bending mode of an adsorbed hydrocarbon species. The existence of surface species such as chemisorbed acetylene or ethylene are excluded as the corresponding spectra (20) differ significantly from the spectrum shown in Fig. 3c. Similarly OH containing surface species may be excluded as OH stretching vibrations near 3600 cm^{-1} were not observed (21). In the low frequency regime a number of relatively weak losses on a high background are observed which are probably due to carbon-iron stretching vibrations. A recent work (22) reports an EELS spectrum of isolated CH_2 species adsorbed on a Fe(110) single crystal surface. The CH_2 species were produced by the decomposition of ketene and are characterized by a scissors vibration at 1420 cm^{-1} and a CH stretching vibration at 2980 cm^{-1} . Consequently we attribute the two vibrational losses observed at 1420 and 3010 cm^{-1} , after interrupting the FTS reaction, to the scissoring and stretching vibrations of adsorbed CH_2 fragments, respectively. The small difference in frequencies of the CH stretching vibrations (30 cm^{-1}) may be explained by the strong carbon contamination of the iron sample during the FTS reaction.

The relatively high frequency at 3100 cm^{-1} shown in the spectrum of Fig. 3c may be attributed to the CH stretching vibration of an adsorbed CH species. Isolated CH surface species have been obtained after the thermal decomposition of acetylene on a Fe(110) surface (20) which are characterized by a CH stretching vibration at 3050 cm^{-1} and a CH bending mode at 880 cm^{-1} . Similar frequencies at 2980 and 790 cm^{-1} , respectively, have been observed by Demuth and Ibach (23) for adsorbed CH species on a Ni(111) surface after the thermal

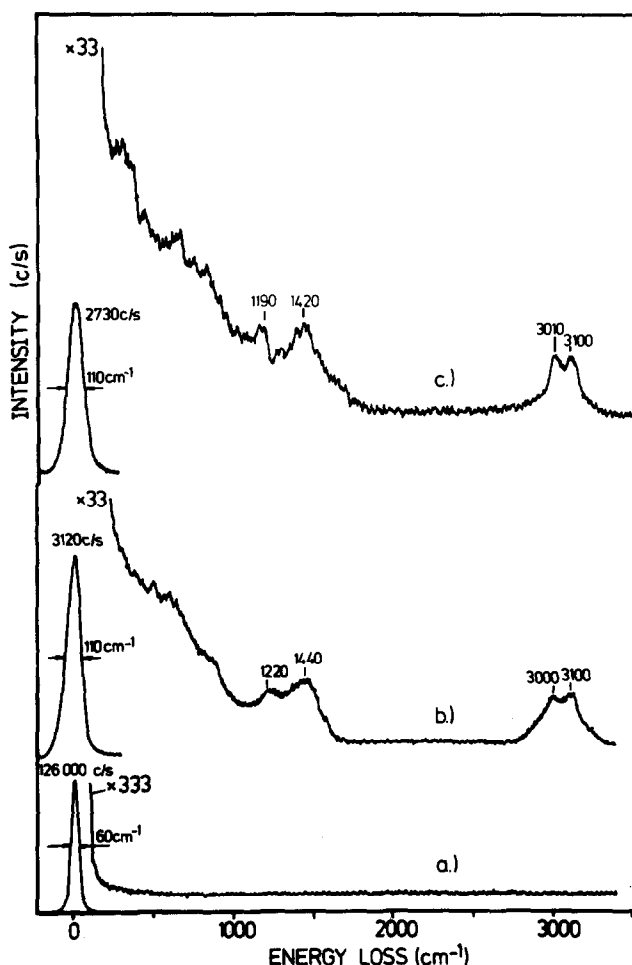


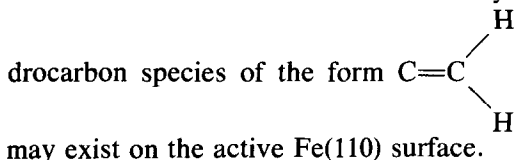
FIG. 3. EELS spectrum of (a) the clean Fe(110) surface, (b) after hydrogenation of the carbon pre-covered Fe(110) surface, and (c) after interrupting the FTS reaction (CO/H₂ ratio 10:1).

decomposition of acetylene. In both cases the frequency of the adsorbed CH stretching vibration of the adsorbed CH species is shifted upward, compared to the corresponding frequency for acetylene. In consequence the high frequency loss at 3100 cm⁻¹ observed in the spectrum shown in Fig. 3c is at least partially attributed to the CH stretching vibration of an adsorbed CH fragment. Again, the somewhat higher frequency may be caused by the relatively strong carbon contamination produced during the FTS reaction. Further support of a CH surface species comes from the observation of a loss at 870 cm⁻¹ which may be attributed to the CH bending mode. Hence

the spectrum shown in Fig. 3c gives evidence for adsorbed CH in addition to adsorbed CH₂. In a recent microreactor-XPS/AES study of the FTS reaction on Fe(110) Bonzel and Krebs (24) also found evidence for adsorbed CH_x species.

A loss observed at 1190 cm⁻¹ indicates the possible existence of C₂ surface species as this frequency value is typical for CC bonds in adsorbed acetylene and ethylene (20). From studies using different CO/H₂ ratios some correlation between the peak at 1190 cm⁻¹ and the one at 3100 cm⁻¹ was observed, indicating that they may arise from the same surface species. Similar losses at 1230 and 3050 cm⁻¹ have been re-

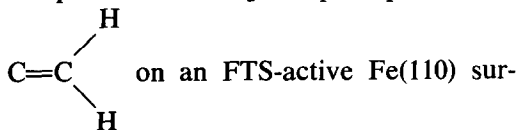
ported in the recent work of McBreen *et al.* (22) for CH₂ species bonded to surface carbon. Hence it is concluded that further hydrocarbon species of the form



may exist on the active Fe(110) surface.

It is noted that a nearly identical EELS spectrum (Fig. 3b) is obtained if a carbon pre-covered Fe(110) surface is reacted at 300°C in an atmosphere of pure hydrogen (~1 atm). This result supports the carbide theory first proposed by Fischer and Tropsch (25) which assumes a direct hydrogenation of surface carbon. Moreover, the presence of olefins and alkenes up to C₅ in the product distribution formed during the hydrogenation of surface carbon in the absence of CO suggests, in agreement with the results of other workers (6, 7), that the insertion of CO molecules into the surface complex is not a necessary prerequisite for the chain growth of higher hydrocarbons. Similar conclusions have been drawn recently in a paper by Biloen *et al.* (7) who investigated the FTS reaction over supported catalysts of Ni, Co, and Ru using isotopically labeled ¹²CO and ¹³CO.

The EELS spectra obtained in the present study provide direct evidence for the presence of CH₂ and perhaps CH and



Although the EELS spectra were obtained under UHV conditions it is likely that the observed surface species are also present under synthesis conditions. Indeed experiments using scavengers (5) and relaxation experiments (26) have provided indirect evidence that surface methylene is a reaction intermediate under synthesis conditions. The present results show that CH₂ is stable on a FTS active Fe(110) surface, and the intense losses associated with it indicate that the surface concentration of CH₂(ads) is high.

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