

Formation of Methyne Intermediates by Hydrogenation of Surface Carbon on Ru(001)

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Adsorbed methyne (CH) intermediates were synthesized on the Ru(001) surface by hydrogenation of predeposited carbon under UHV conditions. These species were identified by High-Resolution Electron Energy-Loss Spectroscopy (HREELS) based upon spectra which exhibited an intense CH stretch at 2950 cm^{-1} and no evidence for CH_2 scissor or CH_3 umbrella modes. The adsorbed CH species could be formed by hydrogenation of carbon initially deposited by electron-beam-stimulated dissociation of CO, by thermal decomposition of ethylene, or by ethylene hydrogenolysis. The maximum intensity of the CH stretch was observed for surface temperatures of 370 K; the CH species decomposed completely to H_2 plus adsorbed carbon upon heating the surface to 500 K. These results are consistent with the participation of CH intermediates in the Fischer-Tropsch synthesis via the "active-carbide" mechanism. © 1985 Academic Press, Inc.

I. INTRODUCTION

A number of recent experimental studies (1-5) and reviews (6-9) have suggested that the Fischer-Tropsch synthesis of hydrocarbons on Group VIII transition metals proceeds via the formation and subsequent reaction of "active carbide" species on the surfaces of these catalysts. Biloen and Sachtler (6) have suggested that this active carbide is a heterogeneous mixture of C(ad), CH(ad), and other hydrocarbon intermediates which can undergo both hydrogenation and polymerization to form various hydrocarbon products. Positive spectroscopic identification of these species under reaction conditions is, however, rather difficult to obtain. Although infrared spectra obtained *in situ* show clear evidence of the CH stretch modes of surface hydrocarbon intermediates, it is likely that these are representative of the growing hydrocarbon chains on the surface rather than

the individual carbide species which produce chain growth by insertion. Alternative methods such as the scavenging reactions utilized by Bell and co-workers (8, 10) have provided evidence for surface CH_2 species active for addition to hydrocarbons; however, spectroscopic evidence for such species under reaction conditions is, to date, lacking.

A rather surprising consistency has been observed in the hydrocarbon intermediates formed by hydrocarbon adsorption on transition metal surfaces. High-Resolution Electron Energy-Loss Spectroscopy (HREELS) studies have identified surface ethynyl species ($\text{CH}_3\text{C}\equiv$) following adsorption of ethylene and/or acetylene on single-crystal surfaces of Pt (11, 12), Pd (13), Rh (14), and Ru (15). Further, the dissociation of these species leads to formation of intermediates which have been identified as CH(ad) on most of these metals. However, beyond the ubiquity of these species, which suggests thermodynamic stability, it has not been demonstrated that species such as $\text{CH}_3\text{C}\equiv$ or CH participate directly in hydrocarbon synthesis reactions.

Erley and co-workers (16) have recently

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reported vibrational spectra for surface intermediates remaining on a Fe(110) surface after carrying out Fischer-Tropsch synthesis at 1 atm. The HREELS spectra obtained following reentry of the sample into vacuum were attributed to the presence of CH₂ species, along with possible CH and CCH₂ species. The results of Erley *et al.* (16) appear to provide the strongest spectroscopic evidence to date of the presence of surface species such as CH and CH₂ during Fischer-Tropsch synthesis, although the inadvertent formation of such species by adsorption of residual hydrocarbons cannot be ruled out. If these intermediates arise from hydrogenation of an "active carbide" on the surface during synthesis, then it should also be possible to form them by direct hydrogenation of carbon. As a highly active methanation catalyst, and as a metal on which facile hydrogenation of surface carbon to methane has been demonstrated at atmospheric pressure (4, 17), ruthenium is an attractive candidate with which to test this hypothesis. We report here spectroscopic evidence for the hydrogenation of surface carbon to form CH species on the Ru(001) surface *under vacuum conditions*; the "active-carbide" layers were formed both by hydrocarbon decomposition and by electron-beam-stimulated dissociation of carbon monoxide. These results are clearly indicative of the ease with which carbon species may be hydrogenated on ruthenium, and demonstrate that the intermediate species in methanation and in hydrocarbon synthesis may be isolated for spectroscopic examination.

II. EXPERIMENTAL

Two vacuum chambers were utilized in this research. Both contained four-grid optics for LEED and AES, plus quadrupole mass spectrometers for TPD. The HREELS spectrometer of the Ibach design consisted of two 127° sectors, of which one was used to produce a collimated monochromatic electron beam, and the other for energy analysis of the scattered electrons

(18). An incident-beam energy of 4 to 5 eV was used throughout this work. The highest resolution obtained for the reflected elastic peak was 7 meV (FWHM); typical values during these experiments were approximately 12 meV. The spectra reported here were obtained as single scans of the energy-loss region; no signal averaging was carried out.

Work function change ($\Delta\phi$) measurements were carried out in the second vacuum chamber by the Kelvin method with a probe previously described (19). The noise level in the work function measurements was 0.1 meV_{rms} with a 1-Hz bandwidth. By varying the potential on the shield around the Kelvin probe, extraneous signals not originating from the sample could be screened out. The measured contact potential difference was independent of the distance between the ruthenium sample and the Kelvin probe.

The 5N pure ruthenium single crystals were cut and polished to within 0.5° of the (001) plane. Following installation in one of the vacuum chambers, a sample was cleaned by ion bombardment and by a series of heating cycles between 400 and 1550 K in an atmosphere of 2×10^{-6} Torr O₂. This procedure was sufficient to remove bulk carbon from the sample (25). Carbon deposited in the course of these experiments was removed by a series of oxygen adsorption/desorption cycles, each consisting of an O₂ exposure of ca. 1000 Ex (1 Ex = 1×10^{14} collisions/cm²) followed by heating to 1570 K to desorb CO₂ and O₂. [Note: this temperature was previously reported incorrectly as 1350 K (15).] Three oxygen adsorption/desorption cycles were generally sufficient to remove the carbon deposited by decomposition of the saturation coverage of ethylene and to produce an oxygen desorption signal characteristic of oxygen adsorption on a clean Ru(001) surface.

III. RESULTS

3.1 Deposition and hydrogenation of car-

bon from CO. Surface carbon was deposited by three methods in this study: ethylene thermal decomposition, ethylene hydrogenolysis, and electron-beam-stimulated dissociation of CO. Although these techniques produced adsorbed layers of different coverage and composition, the vibrational spectra observed upon subsequent hydrogenation of these adlayers were essentially indistinguishable.

It is well known that CO does not dissociate upon adsorption on the Ru(001) surface under UHV conditions (20–23). In order to form atomic carbon from CO on the Ru(001) surface, it was necessary to use an electron beam to dissociate the adsorbed molecules. As has been shown by Fuggle *et al.* (22), electron impact on CO/Ru dissociates CO, partly removing the O into the vacuum, partly depositing both C and O atoms on the surface. The latter recombine upon heating around 600 K leading to a “ β -CO” TPD peak; no oxygen detectable by AES remains (22) on the surface following this procedure. Carbon is left behind, its concentration can be increased by repetition of this procedure. The surface in this study was exposed to CO at a pressure of 10^{-6} Torr for 20 min with simultaneous electron bombardment from the glancing incidence gun normally used for AES. The beam voltage and current were 1000 eV and

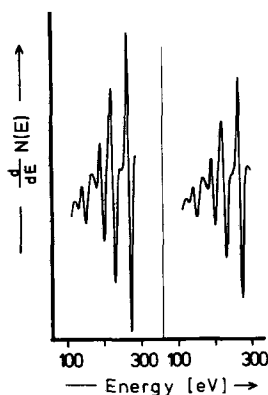


FIG. 1. AES spectra from (left side) the clean sample and (right side) a surface after electron bombardment in CO as indicated in the text.

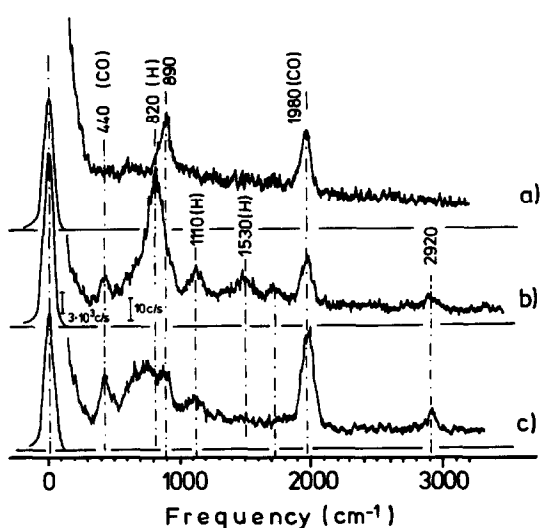


FIG. 2. HREELS spectra of the Ru(001) surface following (a) deposition of carbon by electron-beam dissociation of CO and heating to 800 K, (b) exposure of the surface in (a) to H_2 at 250 K, and (c) heating the surface in (b) to 320 K.

$100 \mu A/cm^2$, respectively. Following this treatment, the chamber was evacuated to 5×10^{-10} Torr, and the Ru sample was heated to 800 K to desorb any molecularly adsorbed CO as well as dissociated β -CO (22). The Auger spectra following this treatment are shown in Fig. 1. Due to the overlap of the carbon KLL (273 eV) and ruthenium MNN (272 eV) lines, it is difficult to obtain a quantitative measure of surface carbon on ruthenium by AES. Figure 1, however, shows clear evidence for the deposition of surface carbon: the Ru (231 eV) peak is attenuated by about 30% from the clean-surface spectrum to that following carbon deposition; likewise, the ratio of the peaks at 273 eV to that at 231 eV increases from 1.54 to 1.62 due to the additional contribution of carbon to the 273-eV signal.

Supporting evidence for the presence of adsorbed carbon was provided by the HREELS spectra following electron-beam dissociation of CO. Figure 2a presents the spectrum for a surface treated as described above. The characteristic spectra for CO(ad) and O(ad) would be expected to ex-

hibit losses at 1960 cm^{-1} ($\text{C}\equiv\text{O}$), 440 cm^{-1} ($\text{M}-\text{CO}$), and 610 cm^{-1} ($\text{M}-\text{O}$) (21). The spectrum for the surface heated to 800 K following CO dissociation shows a loss at 2000 cm^{-1} due to CO from the residual gas (about 10 min elapsed between heating and recording of the spectrum), plus an additional loss at 890 cm^{-1} , which is most likely due to the M-C stretch for adsorbed carbon atoms. No evidence was obtained by either HREELS or AES for adsorbed oxygen atoms following electron-beam-dissociation of CO and desorption of β -CO, in agreement with previous AES and XPS results (22).

Both HREELS and work function measurements provide evidence for the reaction of hydrogen with the carbon adlayer formed above. Also shown in Fig. 2 are the HREELS spectra following exposure of the surface in curve a to a saturation exposure of H_2 at 250 K (curve b) and following subsequent annealing to 320 K (curve c). The adsorption of hydrogen at 250 K produced an additional four losses in the spectrum as compared with that from the carbon-containing surface. Of these losses, those at 820 , 1110 , and 1530 cm^{-1} have previously been observed for hydrogen atoms adsorbed on the clean Ru(001) surface (24, 25), and have been assigned to the symmetric stretch, the asymmetric stretch, and an overtone of the symmetric stretch, respectively, for hydrogen atoms situated in the threefold sites on this surface. The relative intensities of these three modes are strongly dependent upon the incident-beam energy (with an apparent resonance at $E_b \approx 4.5\text{ eV}$). The relative intensities in Fig. 2b are consistent with those observed at the same incident energy following hydrogen adsorption on the clean Ru(001) surface. The fourth loss observed upon exposure of the carbon adlayer to hydrogen is evident at 2920 cm^{-1} , and may be unambiguously assigned to a CH stretch mode of a surface hydrocarbon species. No evidence for formation of OH species, which would be expected in the vicinity of 3300 cm^{-1} , was ob-

served, in agreement with the nonobservation of O atoms before exposure to hydrogen. There is also a weak feature at 1730 cm^{-1} in curve b; this frequency appears to be too great to be attributed to either Ru-H stretch or CH bend modes and is not assigned. Upon heating the surface to 320 K, the hydrogen peaks (and the feature at 1730 cm^{-1}) decreased in intensity while the loss at 2920 cm^{-1} increased in intensity. Hydrogen has been previously observed to desorb from the Ru(001) surface in a pair of broad peaks between 300 and 450 K (26). Thus, as the surface is heated from 250 to 320 K, a portion of the adsorbed hydrogen desorbs from the surface; however, additional CH bond formation must also occur to produce the increase in the C-H stretch intensity. Thus the concentration of surface hydrocarbon intermediates appears to be limited under the conditions of these experiments by the kinetics of C-H bond formation rather than the equilibrium between adsorbed hydrogen and hydrocarbon species.

Evidence for the interaction between hydrogen and adsorbed carbon was also obtained by measurement of the surface work function. Adsorption of hydrogen on the clean Ru(001) surface at temperatures between 95 and 300 K results in minor changes in the work function, $\pm 30\text{ meV}$, depending upon the surface coverage. For hydrogen adsorption in the presence of the carbon adlayer formed as described above, the work function decreases by 150 to 200 meV for surface temperatures between 250 and 300 K. The dependence of the work function change ($\Delta\phi$) on hydrogen exposure of the carbon-containing surface is illustrated in Fig. 3. The observation of work function changes for hydrogen in the presence of surface carbon which exceed by a factor of 7 those possible for hydrogen alone at any coverage is evidence for some interaction between surface carbon and adsorbed hydrogen atoms. In other words, hydrogen is adsorbed on the carbon-covered surface in a fashion not possible on the clean Ru(001) surface. The additional

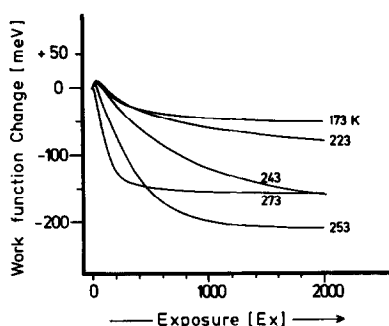


FIG. 3. Work function change by hydrogen adsorption obtained from a carbon-contaminated surface for various sample temperatures.

HREELS results, which show the growth of a loss corresponding to a CH stretch mode over the same temperature range, suggest that the "new form" of hydrogen adsorption on the carbon-covered surface is simply the formation of surface hydrocarbon species. The identification of these species is discussed below.

3.2 Deposition and hydrogenation of carbon from ethylene. Surface carbon was deposited both by thermal decomposition of ethylene and by hydrogenolysis of ethylene in the presence of preadsorbed hydrogen atoms. The carbon layers ultimately deposited by these two techniques were chemically indistinguishable, although the reaction pathways and temperatures at which complete dehydrogenation of the adlayer occurred were quite different. Further, the HREELS spectra for carbon deposited from ethylene by either method exhibited no loss peaks once dehydrogenation was complete, in contrast to the carbon deposited from CO dissociation described above.

As reported previously (15), the dehydrogenation of ethylene to carbon on the Ru(001) surface proceeds through several stable intermediates. Upon adsorption at 170 K, ethylene is rehybridized to form a surface species of the type previously identified as "di- σ -bonded" on several other Group VIII metal surfaces. The significant reduction of the C-C stretch and C-H stretch modes for this species relative to

gas-phase ethylene provide strong evidence for rehybridization. As the surface is heated, this species undergoes dehydrogenation and rearrangement to form an ethylidyne intermediate which is thermally stable between 270 and 350 K. In the course of heating to 460 K, the ethylidyne decomposes to form species which have been previously identified (15) as "inclined CH" intermediates in accord with the assignment of species which give rise to quite similar HREELS spectra on the (111) faces of Pd (13), Ni (27), Pt (28), and Rh (29). On all of these metals this intermediate exhibits a weak C-H stretch in the vicinity of 3000 cm^{-1} with a more intense, dipole-active loss near 800 cm^{-1} , which is typically assigned to the C-H bend of the inclined species. Kesmodel and co-workers (30) have recently revised their earlier assignment of inclined CH species (13) on Pd surfaces to a rehybridized CCH species in which both carbon atoms interact with the surface. This assignment is consistent with the observed stoichiometry on Ru(001) at 460 K and may apply to this surface as well. Upon additional heating the surface hydrocarbon species decompose and H_2 desorbs from the surface. The decomposition of these intermediates is completed below 800 K, the HREELS spectrum following heating of the adlayer to this temperature exhibits no loss features.

The preadsorption of hydrogen or deuterium dramatically altered the chemistry of ethylene on the Ru(001) surface. When a surface containing approximately half the saturation coverage of hydrogen atoms was exposed to ethylene at 170 K, the HREELS spectrum contained only modes attributable to adsorbed hydrogen, plus a weak CH stretch at 2970 cm^{-1} . No evidence for the presence of adsorbed ethylene at 170 K, or of ethylidyne species when the adlayer was heated to 300 K, was observed. Instead, heating of this surface simply resulted in a decrease in the hydrogenic losses and an increase in the intensity of the CH stretch. At 370 K the spectrum contained only weak

hydrogenic losses plus a CH stretch at 2950 cm^{-1} with an intensity five times that at 170 K . Figure 4 illustrates the spectrum obtained by sequential adsorption of $\text{H}_2 + \text{C}_2\text{H}_4$ followed by heating to 370 K . Also shown are the results of the comparable experiment with preadsorbed $\text{D}_2 + \text{C}_2\text{H}_4$. The most prominent feature in that spectrum is a loss at 2180 cm^{-1} corresponding to a C–D stretch. This result clearly demonstrates that the deuterium atoms initially adsorbed on the surface become incorporated into the surface hydrocarbon adlayer.

HREELS spectra identical to those of Figs. 4a and b were produced by hydrogenation of a surface carbon layer. When the surface corresponding to Fig. 4b was heated to 800 K , all deuterium was desorbed from the surface and the loss corresponding to the C–D stretch was elimi-

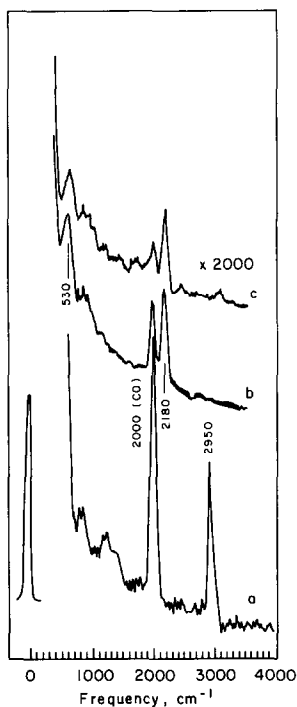


FIG. 4. HREELS spectra of CH (CD) species formed by (a) adsorption of $90\text{ Ex H}_2 + 100\text{ Ex C}_2\text{H}_4$ at 170 K , surface heated to 370 K ; (b) as (a), but initial dose was $90\text{ Ex D}_2 + 100\text{ Ex C}_2\text{H}_4$; and (c) Surface in (b) heated to 800 K , cooled to 200 K , dosed with 90 Ex D_2 , heated to 370 K .

nated. The surface was then cooled to 200 K , exposed to D_2 , and heated to 370 K , and the spectrum in Fig. 4c was obtained. This spectrum clearly shows the reappearance of the C–D stretch mode; further, the spectra in Fig. 4 demonstrate that the same surface hydrocarbon species may be formed at 370 K either by hydrogenolysis of ethylene or by hydrogenation of surface carbon. The ability to switch at will between species exhibiting CH or CD stretches by exposure of the surface carbon layer to H_2 or D_2 clearly demonstrates that surface hydrocarbon species were formed by hydrogenation and not by inadvertent adsorption of background hydrocarbons. These surface hydrocarbon species decompose at relatively low temperature: all traces of the CH stretches in Fig. 4 could be eliminated by heating to 500 K .

The identification of the species formed by ethylene hydrogenolysis/carbon hydrogenation is primarily a matter of elimination. The ability to form this intermediate by hydrogenation of surface carbon suggests that it is unlikely to contain C–C bonds, and therefore that it may be identified as a species containing a single carbon atom. Candidates such as CH_2 or CH_3 should produce strong dipole-active scissor or umbrella modes in the vicinity of $1300\text{--}1500\text{ cm}^{-1}$ which were not observed. Thus it appears most likely that this species is CH(ad) . The intense C–H stretch and unresolved C–H bend modes are consistent with the orientation of the CH bond for this species normal to the surface: the CH stretch mode would be normal to the surface and therefore dipole-active; the CH bend would be parallel to the surface and therefore dipole-inactive. Further, if the CH species is bonded to the surface in a threefold well site in a fashion directly analogous to the ethylidyne, the carbon atom would be sp^3 hybridized, consistent with the observed CH stretch frequency.

While it is difficult to conceive of species other than methyne to which the spectra of Figs. 2 and 4 can be assigned in a fashion

consistent with the dipole selection rules of HREELS, several of the minor features in these spectra are less easily accounted for. Figures 2c and 4a both contain weak loss features near 720 cm^{-1} in addition to the metal-hydrogen symmetric mode at 820 cm^{-1} . The 720-cm^{-1} loss may be assigned to the C-H bend of the methyne species, this mode would be sampled only by impact scattering if the C-H bond is normal to the surface. This assignment is consistent with the spectra for CD species in Figs. 4b and c; the 720-cm^{-1} vibration is absent for the deuterated species, and the loss corresponding to the C-D bend most likely overlaps with the M-D stretch at 540 cm^{-1} . Other features in these spectra, such as the apparent loss at 1730 cm^{-1} in Fig. 2b exhibit quite low intensities, and some care must be taken in assessing the significance of these features since no signal averaging was conducted. Although the possible adsorption of background impurities, or the formation of CH_2 or CH_3 intermediates cannot be ruled out, such species must be present in quite low concentrations, if they are present at all. The interpretation of these spectra based upon assignment of the principal dipole-active modes is thus unchanged: surface carbon may be hydrogenated to form hydrocarbon intermediates on the Ru(001) surface; under the conditions of these experiments the most abundant intermediate is methyne, CH.

IV. DISCUSSION

Given the ease of methanation of surface carbon previously reported for ruthenium catalysts, the hydrogenation of carbon under vacuum conditions to form surface hydrocarbon intermediates, though unprecedented, is not particularly surprising. Indeed, Wise and McCarty (17) have recently determined that the enthalpy of formation of active carbon on ruthenium is positive relative to graphite, and have reported hydrogenation of carbon to methane at temperatures as low as 250 K in 1 atm of hydrogen. Further, although the kinetics of

carbon hydrogenation were not determined in this study, a crude estimate of the activation energy for hydrogenation of surface carbon may be obtained by equating the temperature (370 K) at which the C-H stretch reached maximum intensity with the peak temperature in a desorption experiment. Assuming a normal preexponential factor (10^{13} s^{-1} for a first-order reaction or $10^{-2}\text{ cm}^2\text{ s}^{-1}$ for a second-order reaction), the activation energy obtained is 22 kcal/mol in excellent agreement with the value of 24 kcal/mol for methanation obtained in three previous studies on supported Ru catalysts (31-33). This estimate is not meant to imply that hydrogenation of atomic carbon is the rate-determining step in methanation, but to demonstrate that CH bond formation under the conditions of this study is not inconsistent with the energetics of catalytic methanation. Further, the facile formation of CH bonds under UHV conditions at room temperature *in the presence of a large concentration of adsorbed hydrogen* is in agreement with previous catalytic studies which have demonstrated that hydrogenation of surface carbon proceeds much more rapidly than the methanation reaction (1-4) due to CO inhibition of hydrogen adsorption under methanation conditions.

The relative thermal instability of the CH(ad) species synthesized in this study mitigates against the determination of the hydrogen coverage on the working catalyst by kinetic means. These species were observed to decompose above 400 K on the Ru(001) surface; the hydrogen thus liberated could not be distinguished by TPD from that adsorbed on the bare ruthenium surface. Thus transient response experiments which count all of the hydrogen present on the catalyst may be unable to distinguish between hydrogen adsorbed on the metal surface and that present in CH_x intermediates on the surface. The thermal instability of the CH(ad) species also complicates attempts to characterize the surface species spectroscopically following

rapid evacuation of a working catalyst. The results of this study suggest that quenching of the sample from a typical operating temperature above 500 K may be necessary in order to preserve CH_x intermediates on the surface.

Although the scavenging experiments of Bell and co-workers (8, 10) have provided strong evidence for the presence of $\text{CH}_2(\text{ad})$ species on ruthenium under Fischer-Tropsch conditions, such species were not produced by the reaction of adsorbed carbon and hydrogen under conditions of our experiments. Since hydrogen desorption was observed to occur over a similar temperature range as CH formation and decomposition, the hydrogen coverage during CH formation is considerably smaller than that following the initial adsorption of hydrogen at 170 K. The absence of more highly hydrogenated surface intermediates may simply reflect an unfavorable equilibrium under the UHV conditions of our experiments. Likewise no $\text{CH}_2(\text{ad})$ species were observed in the course of adsorption and thermal decomposition experiments with ethylene (15), in contrast to the previous results of Weinberg *et al.* (34). These workers reported that $\text{CH}_2(\text{ad})$ species were present on the Ru(001) surface at 80 K following small exposure to ethylene or diazomethane. These results in the case of ethylene adsorption are most surprising given the low temperature and the relative strengths of the C=C (146 kcal/mol) and C—H (108 kcal/mol) bonds. In the present study no bond breaking was discernible following ethylene adsorption at 170 K. Upon heating, the first bonds broken were C—H bonds as expected, leading to the ethylidyne species; no C—C bond breaking was observed until this species began to decompose near 350 K, and none may have occurred below 500 K if the high-temperature intermediate on this surface is indeed CCH.

Finally, the nature of adsorbed carbon on ruthenium surfaces is also of interest. Lauderback and Delgass (35) have exam-

ined the surface carbon layers deposited on the Ru(001) surface by ethylene exposure at 323 K by SIMS and TPD. They reported that the surface carbon atoms are immobile below 550 K, with agglomeration of carbon to form graphitic islands above 763 K. The results of the present study did not reveal any change in the reactivity toward hydrogen of surface carbon layers heated to 800 K. The absence of significant agglomeration in the present study may be due to smaller carbon coverages resulting from low-temperature adsorption and thermal decomposition, especially in the case of carbon deposited by ethylene hydrogenolysis. The HREELS results of this study do suggest, however, that different forms of adsorbed carbon may be generated from CO dissociation and ethylene decomposition; both forms may be hydrogenated between 250 and 400 K. Thus in addition to the heterogeneity of the "surface carbide" layer in Fischer-Tropsch synthesis which results from C and CH_x species of various stoichiometries, the species characterized by a single stoichiometry may also be of several types. The determination of which species are active intermediates in this reaction is still not at hand.

V. CONCLUSIONS

Surface carbon deposited on the Ru(001) surface may be hydrogenated under UHV conditions to form methyne, $\text{CH}(\text{ad})$, intermediates. These species are characterized by a strong CH (CD) stretch in HREELS experiments at 2950 cm^{-1} (2180 cm^{-1}), with no evidence for dipole-active CH scissor or bending vibrations expected for more highly hydrogenated intermediates. Although the surface carbon layers deposited by electron-beam-stimulated dissociation of CO and by decomposition or hydrogenolysis of ethylene exhibit different HREELS spectra, the $\text{CH}(\text{ad})$ species formed by hydrogenation of these layers are indistinguishable. These species exist over a relatively narrow range of temperatures, with the most intense CH stretch modes ob-

served between 300 and 400 K. The comparison of the present UHV data with previous catalytic studies on ruthenium suggests that the methyne species formed in this study are active intermediates in the methanation reaction.

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