The Investigation of the Surface Chemistry of Ethylene and Methyl Iodide on Ru(001) using Reflection Absorption Infrared Spectroscopy

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Abstract

Reflection absorption infrared spectroscopy (RAIRS) was used to study the thermal decomposition of ethylene on Ru(001) and surface chemistry of methyl iodide. The RAIR spectrum of ethylene on Ru(001) at 95 K is consistent with a di-σ bonded complex. When the crystal was annealed to above 150 K, ethylene was dehydrogenated to form ethylidyne (CCH_3). Upon further annealing to above 300 K, ethylidyne decomposed to methylidyne (CH). No traces of ethynyl (CCH) were observed in the RAIRS spectrum. Carbon-carbon coupling of methyl groups on Ru(001) was observed but with limited repeatability.

Introduction

The mechanisms of chemical reactions that take place on the surface of transition metals are an important area of research in the field of surface science because they help us to gain a more detailed understanding of the processes that occur in heterogeneous catalysis. Ruthenium is an important catalyst in the Fischer–Tropsch process which deals with the conversion of a mixture of carbon monoxide and hydrogen into liquid hydrocarbons.

$$(2n + 1)\, H_2 + n\, CO \rightarrow C_nH_{(2n+2)} + n\, H_2O \tag{1}$$
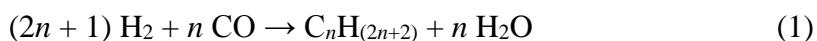
Fischer Tropsch synthesis is used industrially in the production fuels and petrochemical feedstock.[1] The synthetic crude oil obtained as a product of the Fischer Tropsch synthesis can be used directly in refineries through hydrocracking of the hydrocarbons which results in the conversion of synthetic coal to gasoil and kerosene.[1]

One of the most important aspects in the Fischer-Tropsch reaction is the chain growth from a C_1 species to longer chain hydrocarbons. It is, therefore, interesting to study the chemistry of various C_xH_y hydrocarbon fragments on transition metal surfaces as building blocks in the chain growth mechanism. Ethylidyne (CCH_3) is an interesting hydrocarbon fragment that has been studied on many surfaces as the decomposition product of ethylene.[2,3] On Pt(111), the reaction between H_2 and surface C_2 species results in the formation of ethylidyne.[4] In addition, adsorbed methyl groups on Pt(111) can undergo C-C coupling to form ethylidyne.[5]

The formation of ethylidyne on Ru(001) from the dehydrogenation of ethylene has been studied using high resolution electron energy loss spectroscopy (HREELS) and reflection absorption infrared spectroscopy (RAIRS).[2,3,6] However, there is a lack of agreement in the literature about mechanism of ethylene decomposition. An HREELS study by Hills et al. proposed that ethylene decomposed to both ethylidyne and ethynyl (CCH) at 280 K and the latter species decomposed to methylidyne (CH).[2] However, a RAIRS study by Parlett and Chesters

suggested that ethylene is dehydrogenated to form only ethylidyne, which then decomposes to methylidyne.[3]

In this study, we use RAIRS to study the thermal decomposition of ethylene on Ru(001) and the surface chemistry of methyl iodide. With state-of-the-art FTIR spectrometer that can produce spectra with good signal-to-noise ratio, we should be able to detect surface species such as ethynyl that would otherwise give weak signals. In addition, by obtaining high-quality RAIR spectrum of ethylidyne, we can investigate possible C-C coupling of methyl groups on Ru(001).

Experimental Methods

The experiments were performed in an ultrahigh vacuum (UHV) chamber with a base pressure of 2×10^{-10} Torr. The chamber is equipped with a Hiden HAL 201/3F quadrupole mass spectrometer (QMS) for temperature-programmed desorption (TPD), an ion gun for sputtering, a Bruker IFS 66 v/s Fourier transform infrared (FTIR) spectrometer for reflection-absorption infrared spectroscopy (RAIRS), and low energy electron diffraction (LEED) optics. The Ru(001) crystal is spot-welded to two short tantalum wires mounted on a liquid nitrogen (LN_2)-cooled sample holder. The crystal can be resistively heated up to 900 K. A thoriated tungsten filament mounted behind the crystal was used for electron-beam heating up to 1500 K with the crystal positively biased to 600 V.
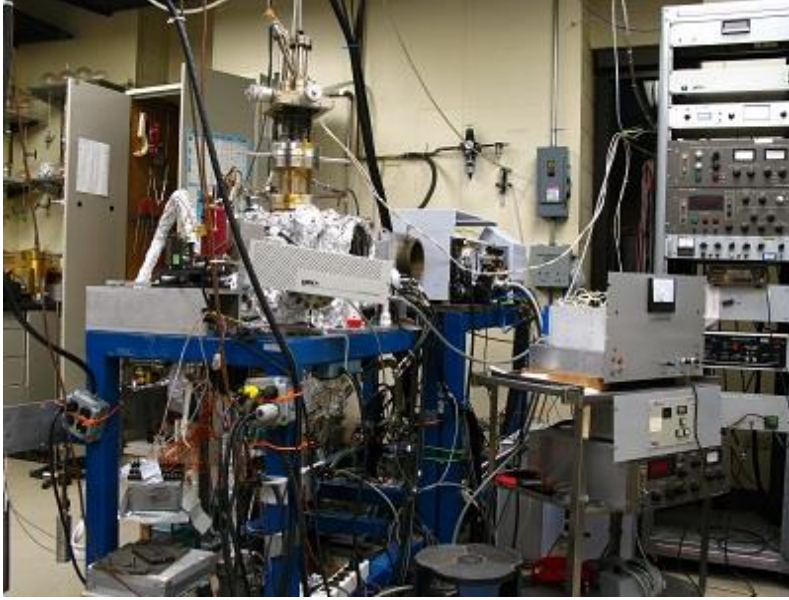
Figure 1. UHV Chamber used for RAIRS studies.

Figure 2. Ruthenium crystal connected to the sample holder by two tantalum wires.

Cleaning the Crystal

Ru(001) crystal was cleaned with two cycles of Ar^+ ion sputtering and annealing. The

pressure of the argon in the chamber during sputtering was 5 x 10^{-5} Torr with a beam voltage of

0.5 kV. The crystal was rotated 5 degrees after the first 3 minutes and then again every 2 minutes

for a total of 17 minutes to ensure uniform sputtering. The first sputtering process was followed

by annealing to 1500 K for 30 seconds while the second was followed by annealing to 850 K for

60 seconds. This method has been proven to yield a clean, ordered surface as evidenced from

LEED, Auger spectra, and CO TPD measurements.

Dosing the Crystal

After cleaning, the sample was cooled down to 150 K using liquid nitrogen. It was

annealed to 550 K to remove any residual CO and was then cooled down to around 95 K. The

crystal was then dosed with 5 L of ethylene (1 L = 1×10^{-6} Torr s) and annealed to various target

temperatures and held at the desired temperature for one minute. For methyl iodide experiments,

the crystal was dosed with 5 L of CH_3I (1 L = 1×10^{-6} Torr s) and annealed to various target

temperatures and held at the desired temperature for one minute. All of the RAIRS

measurements were taken at 95 K. RAIR spectra from 800 to 4000 cm^{-1} were obtained using

either a MCT (HgCdTe) or InSb detector with a SiC mid-IR source. Each spectrum was averaged

from 1024 scans at 2-4 cm^{-1} resolution.

Results and Discussion

After cleaning the crystal with sputtering and annealing, the crystal was then dosed with ethylene. Figure 3 shows the resulting spectra that resulted from annealing the crystal to the target temperatures.
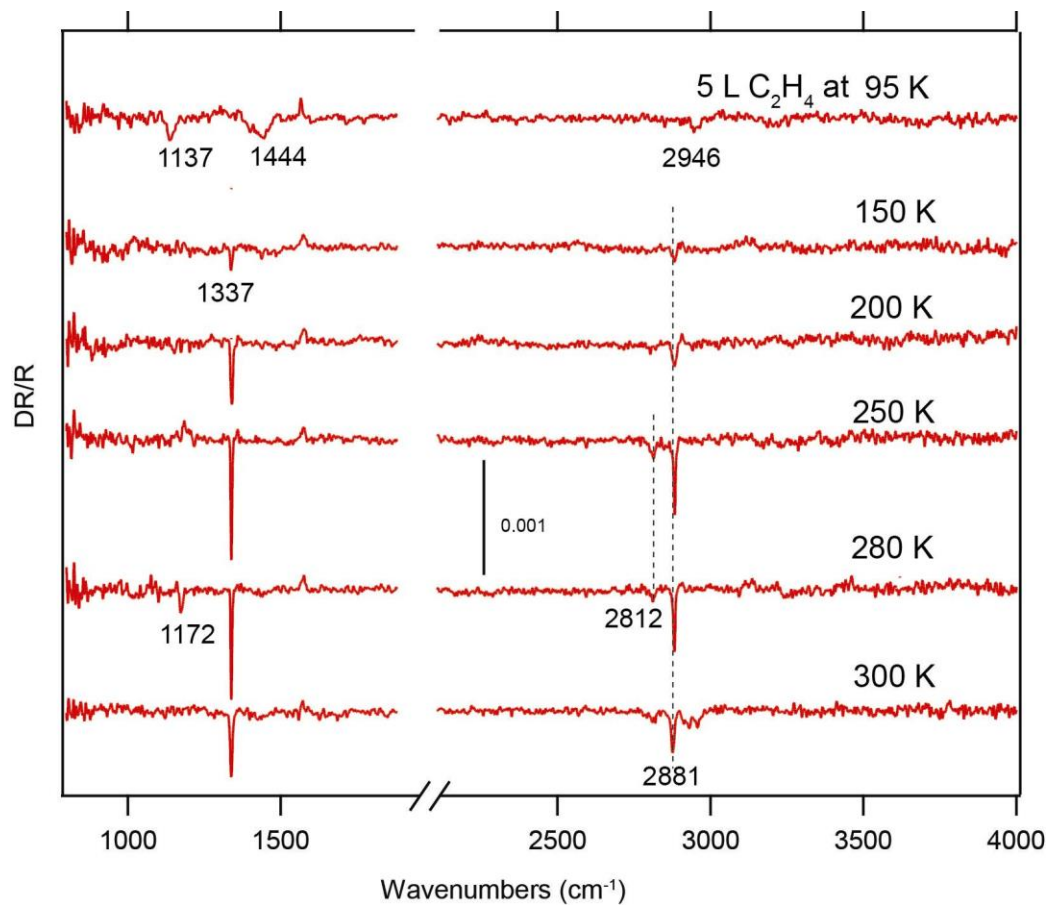
Figure 3. RAIR spectra following 5 L dose of C$_2$H$_4$ on Ru(001) at 95 K and annealing to 150-300 K.

Figure 3 shows the RAIRS spectra after dosing the ruthenium crystal with ethylene at 95 K and annealing to 150-300 K. At 95 K, the peaks at 1137, 1444, and 2946 cm^{-1} show the CH$_2$ wag, CH$_2$ scissors, and CH$_2$ symmetric stretch, respectively. This is a clear indication that only ethylene is present at this temperature, in agreement with the literature.[3] As the crystal is annealed to 150 K, the ethylene peaks begin to disappear and a new set of peaks assigned to

ethylidyne (CCH_3) can be observed, which becomes more intense at 250 K. The peaks at 1337, 2812, and 2881 cm^{-1} are assigned to the CH_3 symmetric deformation, CH_3 asymmetric deformation overtone, and CH_3 symmetric stretch modes, in agreement with the published values in the literature.[3] The small peak at 1172 cm^{-1} may also be an indication of the C-C stretch of ethylidyne. These spectra were obtained using an MCT detector.
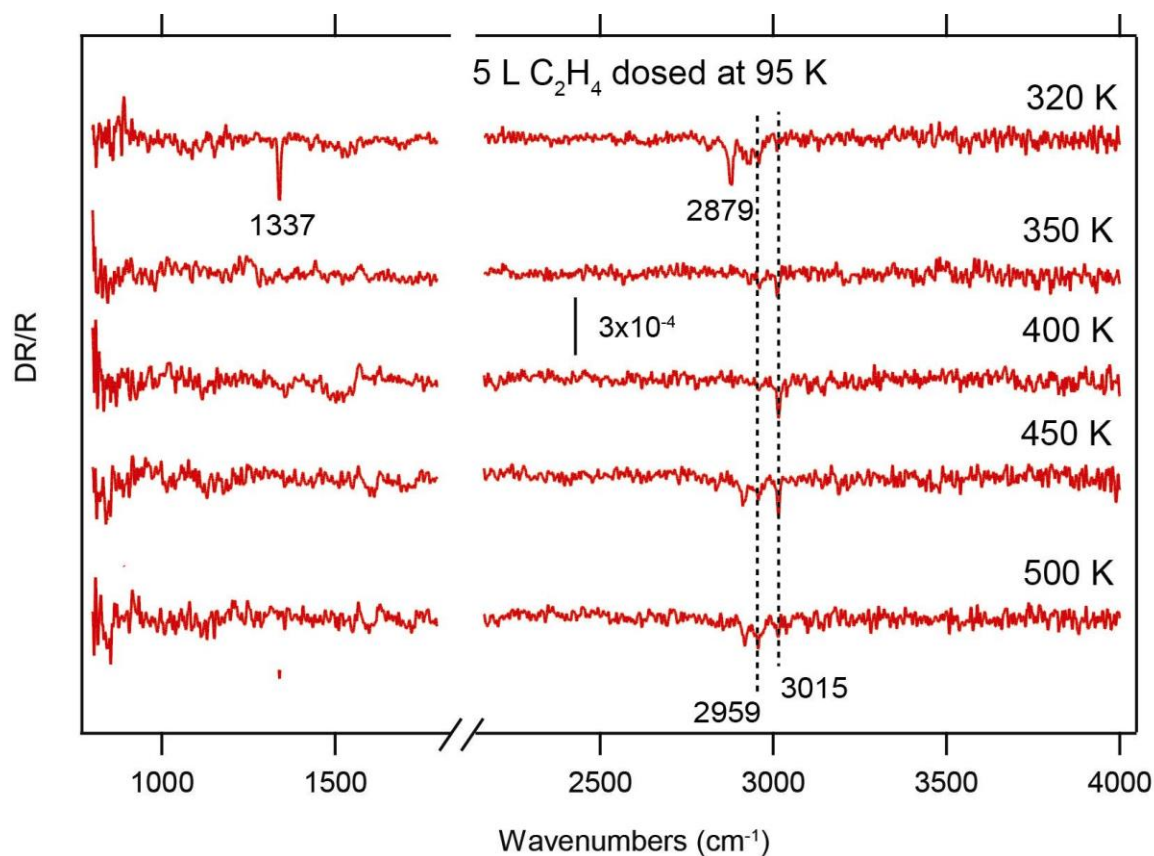
Figure 4. RAIR spectra following 5 L dose of C_2H_4 on Ru(001) at 95 K and annealing to 320-500 K.

Figure 4 shows that the ethylidyne species is no longer present at 350 K and higher temperature as the characteristic peaks at 1337 cm^{-1} and 2879 cm^{-1} go away. At 350 K, methylidyne can be observed to start forming on the surface, noted by the characteristic peak at 3015 cm^{-1} which correlates to the CH stretch of methylidyne from the literature.[3] These spectra

were obtained using an MCT detector, however, the signal-to-noise ratio was too low to study the smaller intensity peaks at higher wavenumbers.
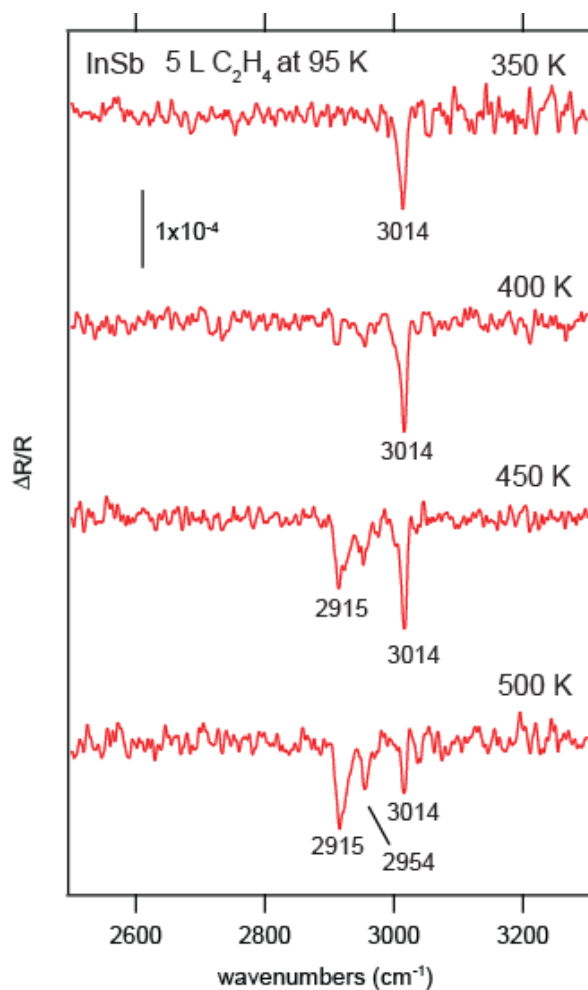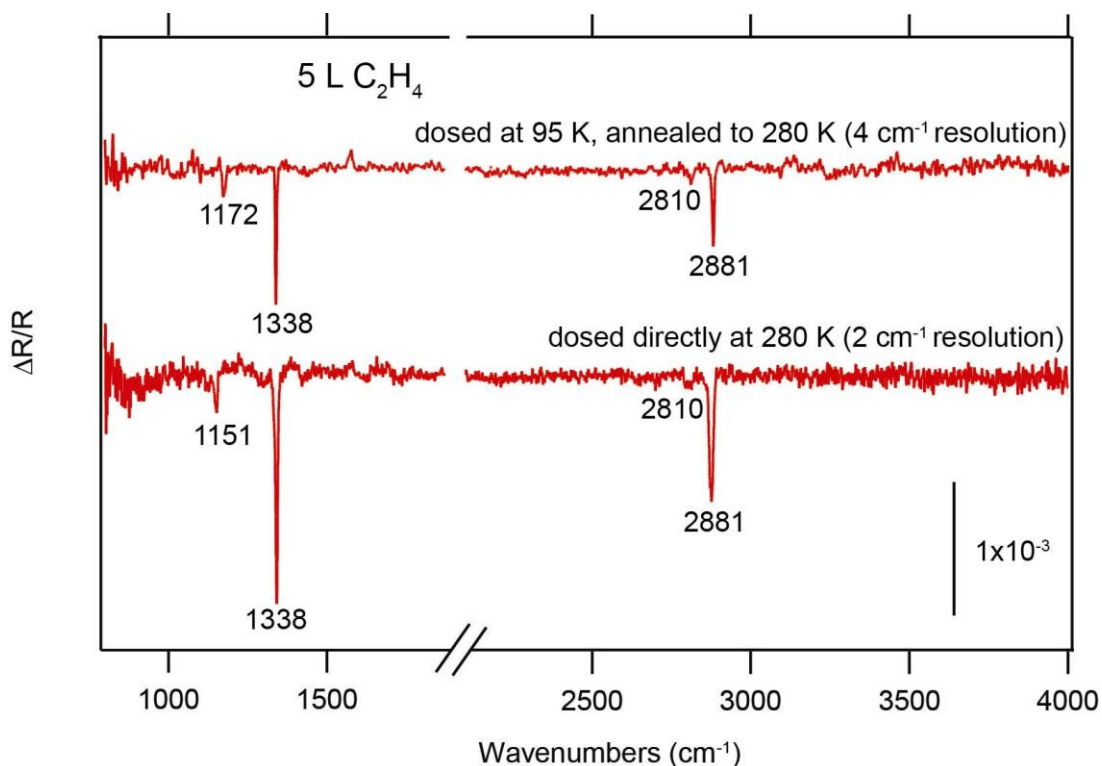

Figure 5. RAIR spectra following 5 L dose of C₂H₄ on Ru(001) at 95 K and annealing to 320-500 K.

Figure 5 shows in greater detail the peaks at the higher wavenumbers. The spectra of the surface species present at annealing temperatures 350-500 K were taken with an InSb detector for better signal-to-noise ratio. The peak at 3014 cm^{-1} agrees with the published value for the CH stretching mode of methylidyne (CH) from RAIRS and HREELS measurements[2,3]. The peaks at 2915 cm^{-1} and 2954 cm^{-1} have still not been assigned to any vibrational stretch as further investigation into the identity of these peaks must be done. Due to the fact that ethylidyne goes

straight to methylidyne with very little amounts of ethynyl observed, it can be concluded that Ru(001) is active toward C-C dissociation.

Figure 6. RAIR spectra following 5 L dose of C_2H_4 on Ru(001) at 95 K and annealing to 280 K in comparison with being dosed directly at 280 K.

Figure 6 shows that the intensity of the characteristic peaks for the ethylidyne species is much greater when the ethylene is directly dosed on the crystal at 280 K instead of dosed at 95 K and then annealed to 280 K. The spectra taken of ethylene directly dosed on the crystal at 280 K was taken with 2 cm^{-1} resolution while the spectra taken after the crystal was dosed with ethylene at 95 k and then annealed to 280 k was taken with 4 cm^{-1} resolution. Figure 6 shows that it is possible to get stronger and more intense peaks by directly dosing the crystal at the target temperature.
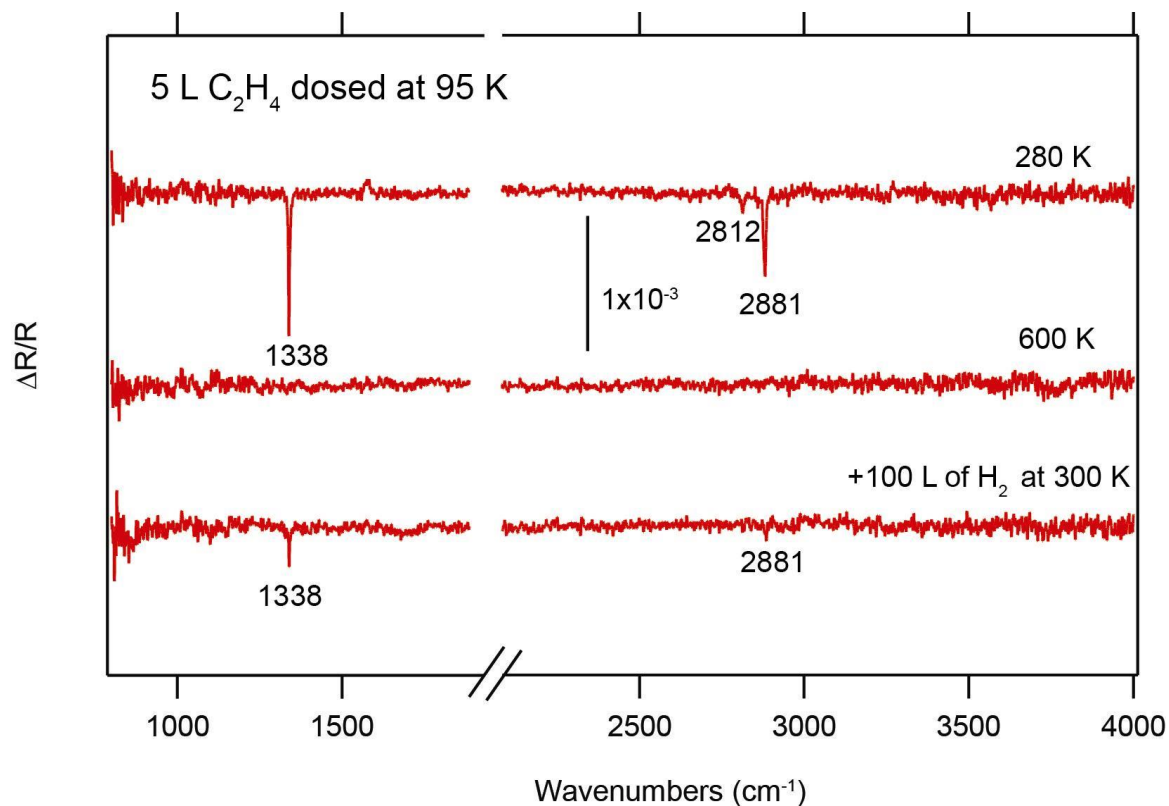
Figure 7. RAIR spectra following 5 L dose of C_2H_4 on Ru(001) at 95 K and annealing to 280 K, 600 K, and then hydrogenated with 100 L of H_2 at 300 K.

Figure 7 shows that after annealing to 600 K, there is no longer any ethylidyne present. However, after re-hydrogenating the surface at 300 K with 100 L of H_2, the ethylidyne is reformed but the peaks are less intense. The peak intensity of reformed ethylidyne is only 9% of the original. This means that some of the carbon species that were adsorbed on the surface of the crystal still retained the C-C bond from the ethylene and ethylidyne because it allowed re-hydrogenation back to ethylidyne. However, most of the carbon-carbon bonds dissociated which is why the peak intensity of the reformed ethylidyne was so small.

| Ethylene	Literature Value (RAIRS)	Literature Value (HREELS) [2]	Experimental Data
CH_2 Sym Stretch	2950 cm^{-1}	2940 cm^{-1}	2946 cm^{-1}
CH_2 Scissoring	1437 cm^{-1}	1450 cm^{-1}	1444 cm^{-1}
CH_2 Wag	1130 cm^{-1}	1145 cm^{-1}	1137 cm^{-1}
Ethylidyne	Literature Value (RAIRS)	Literature Value (HREELS) [2]	Experimental Data
CH_3 Sym Stretch	2875 cm^{-1}	2945 cm^{-1}	2881 cm^{-1}
CH_3 Asym Def Overtone	2808 cm^{-1}	n/o	2812 cm^{-1}
CH_3 Sym Deformation	1338 cm^{-1}	1370 cm^{-1}	1337 cm^{-1}
C-C Stretch	1144 cm^{-1}	1140 cm^{-1}	(1172 cm^{-1}?)
Methylidyne	Literature Value (RAIRS)	Literature Value (HREELS) [2]	Experimental Data
CH Stretch	3010 cm^{-1}	3010 cm^{-1}	3014 cm^{-1}

Table 1. Literature values from RAIRS and HREELS studies in comparison with experimental data for ethylene, ethylidyne, and methylidyne.

Table 1 shows the literature values from RAIRS and HREELS studies next to the experimental data for ethylene, ethylidyne, and methylidyne. The peaks observed from the experimental results match up very well with the literature values from both RAIRS and HREELS studies. The peak at 1172 cm^{-1} is still not confirmed whether or not it is the C-C stretch of ethylidyne because it is farther off from the literature values.

| Methyl iodide Monolayer	Literature Value[7] (HREELS)	Experimental Data
CH$_3$ Sym Stretch	2910 cm^{-1}	2933 cm^{-1}
CH$_3$ Asym Deformation	1320 cm^{-1}	--
CH$_3$ Sym Deformation	1200 cm^{-1}	1221 cm^{-1}
Methyl iodide Multilayer	Literature Value[7] (HREELS)	Experimental Data
CH$_3$ Sym Stretch	3060 cm^{-1}	2952 cm^{-1}
CH$_3$ Asym Deformation	1430 cm^{-1}	1425 cm^{-1}
CH$_3$ Sym Deformation	1250 cm^{-1}	1241 cm^{-1}
CH$_3$ Asym Deformation Splitting	--	1396 cm^{-1}
Unknown	--	1185 cm^{-1}

Table 2. Literature values from HREELS studies in comparison with experimental data for methyl iodide.

Table 1 shows the literature values from HREELS studies next to the experimental data for methyl idodide. The peaks observed from the experimental results matched up with the literature values, however, some of the wavenumbers were a bit off because HREELS is not as accurate as RAIRS. The identity of the peak at 1185 cm^{-1} is still not known, and further investigation into this must be performed.
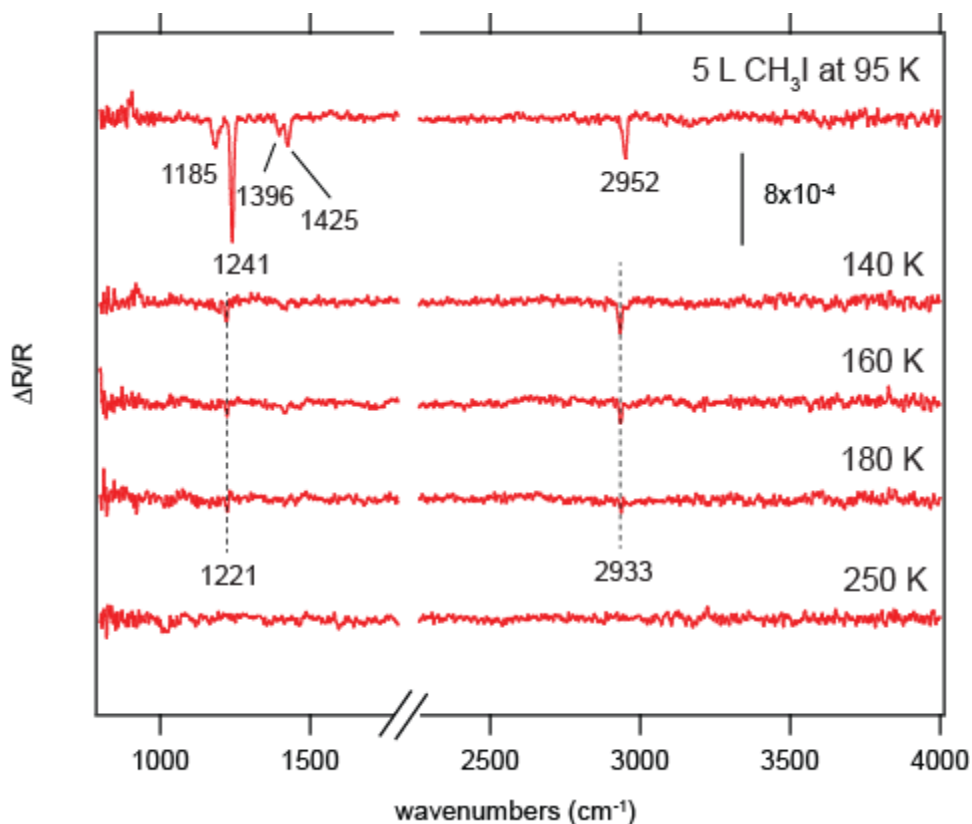
Figure 8. RAIR spectra following 5 L dose of CH₃I on Ru(001) at 95 K and annealing to 140-250 K.

Figure 8 shows the RAIR spectra after dosing the ruthenium crystal with methyl iodide at 95 K and annealing to 140-250 K. At 95 K, the peaks at 1241, 1396, 1425, and 2952 cm^{-1} show the CH_3I multilayer symmetric deformation, CH_3 asymmetric deformation splitting, CH_3 asymmetric deformation, and CH_3 symmetric stretch, respectively. This is a clear indication that CH_3I is present at this temperature, in agreement with literature.[7] The small peak at 1185 cm^{-1} must be further investigated because the identity is still not known. As the crystal is annealed to 140 K, the methyl iodide multilayer peaks begin to disappear and a new set of peaks assigned to the methyl monolayer can be observed. The peaks at 1221 and 2933cm^{-1} are assigned to the CH_3 monolayer symmetric deformation and CH_3 symmetric stretch modes, in agreement with the published values in the literature.[7] At 250 K, the methyl monolayer is completely gone.
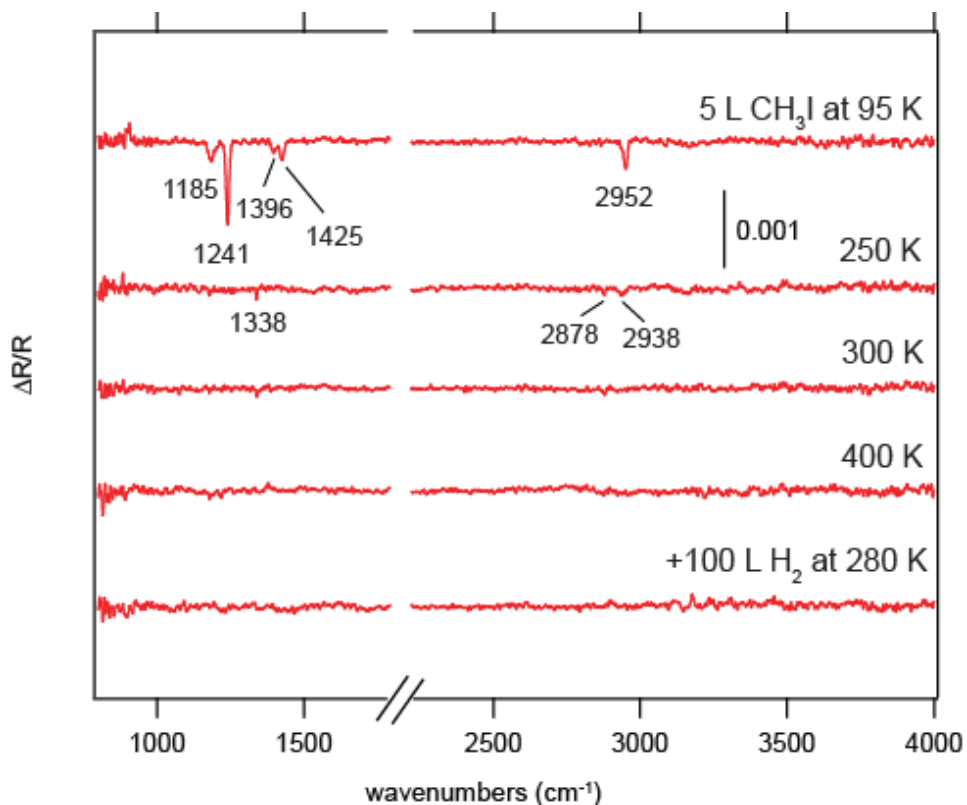
Figure 9. RAIR spectra following 5 L dose of C₂H₄ on Ru(001) at 95 K and annealing to 250-400 K, and then hydrogenated with 100 L of H₂ at 280 K.

Figure 9 shows the RAIRS spectra after dosing the ruthenium crystal with methyl iodide

at 95 K and annealing to 250-400 K, and re-hydrogenating the crystal at 280 K with 100 L of H_2.

As the crystal is annealed to 250 K, the CH_3 peaks begin to disappear and a new set of peaks

assigned to ethylidyne (CCH_3) can be observed. The peaks at 1338 and 2878 cm⁻¹ are assigned to

the CH_3 symmetric deformation and CH_3 symmetric stretch modes, in agreement with the

published values in the literature.[3] The peak at 2938 cm⁻¹ must be further investigated. After

observing ethylidyne being formed at 250 K, the experimental conditions which generated that

result have still not been able to be repeated. Further re-hydrogenation at 280 K did not reform

any hydrocarbons on the crystal. This is an indication that the C_1 species adsorbed on the

ruthenium crystal would not undergo C-C coupling to form ethylidyne or any other higher order

hydrocarbon. Therefore, ruthenium is more selective toward carbon-carbon dissociation instead of carbon-carbon association.

Conclusion:

In conclusion, reflection absorption infrared spectroscopy was successfully used to study the thermal decomposition of ethylene on Ru(001). The experimental results matched up with the literature values. The RAIR spectrum of ethylene on Ru(001) at 95 K is consistent with a di-σ bonded complex. Ethylene was dehydrogenated to form ethylidyne when the crystal was annealed to above 150 K. Ethylidyne decomposed to methylidyne after further annealing to above 300 K. Due to the fact that ethylidyne went straight to methylidyne with very little amounts of ethynyl observed, it can be concluded that Ru(001) is active toward C-C dissociation. Carbon-carbon coupling of methyl groups on Ru(001) was observed but with limited repeatability. Further investigation must be done into determining the situation where ethylidyne was observed on the surface at 250 K with methyl iodide and the unknown peaks observed in the ethylene and methyl iodide experiments must be investigated more in detail.

Acknowledgements

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