Hydrogenation and Dehydrogenation Reactions of C_2H_x Moieties on the Ru(001) Surface

Yuan Ren, Iradwikanari Waluyo, Evan Beale, and Michael Trenary*

*Department of Chemistry, University of Illinois at Chicago, 854 West Taylor Street,
Chicago, IL 60607-7061, USA*

Corresponding Author

*E-mail: mtrenary@uic.edu, Tel: (312) 996-0777

Abstract

Reflection absorption infrared spectroscopy (RAIRS) was used to identify and characterize the surface intermediates formed in the thermal decomposition of ethylene (C_2H_4) on Ru(001). Ethylene is found to adsorb on the surface in a di- σ bonded complex at 95 K and to dehydrogenate to form ethylidyne (CCH_3) at or above 150 K. Upon further annealing to above 320 K, ethylidyne dehydrogenates to ethynyl (CCH). Annealing to higher than 450 K causes ethynyl to decompose to methylidyne (CH). The characterization of surface intermediates formed from the adsorption and decomposition of ethylene provides new insights into the surface chemistry of C_xH_y species on Ru surfaces.

1. Introduction

Ruthenium is an important catalyst for converting syngas (a mixture of CO and H₂) into hydrocarbons (C_xH_y) by the Fischer-Tropsch process [1]. The carbon atoms produced from the dissociation of CO must undergo a series of ill-defined steps involving C–C and C–H bond forming reactions to produce even the simplest hydrocarbons. To gain insights into the elementary steps of these reactions, it is useful to study a simple hydrocarbon that contains both C–C and C–H bonds, such as ethylene, on a well characterized ruthenium single-crystal surface. Despite its relative simplicity, there are numerous pathways that C₂H₄ can follow in the course of its complete decomposition to form adsorbed C and H atoms. These pathways involve several possible C₂H_x intermediates. Whether ethylene undergoes complete dehydrogenation to a C₂ species prior to scission of the C–C bond, or whether the C–C bond breaks within a C₂H_x species to produce, for example, a CH_x species and atomic carbon is an open question. Another important issue is whether the products of dehydrogenation reactions can be hydrogenated back to the starting species or to some other species not formed through ethylene adsorption and decomposition. Although some of these issues have been addressed in earlier experimental work [2-5], more recent theoretical studies [6] and the availability of more sensitive spectroscopic tools provide compelling motivation to revisit this topic.

There have been numerous previous studies of C₂H_x species on transition metal surfaces, and there is a general consensus that ethylidyne (CCH₃) is the most stable [7-9]. On Pt(111), ethylidyne can be produced from the decomposition of ethylene [7] or acetylene [10] at 250-280 K, with a series of intermediates such as ethylidene (CHCH₃),

vinylidene (CCH_2), and vinyl (CHCH_2) proposed. However, the reaction pathway from ethylene to ethylidyne on Pt(111) is still being discussed with the most recent theoretical work [11-13] questioning some of the conclusions reached in earlier experimental studies.

The formation of ethylidyne from the dehydrogenation of ethylene has been studied on Ru(001) with high resolution electron energy loss spectroscopy (HREELS) and reflection absorption infrared spectroscopy (RAIRS) [2-5]. On the basis of their HREEL spectra, Hills et al. [3] proposed that ethylene decomposes to both ethylidyne and ethynyl (CCH) at 280 K with the latter decomposing to methylidyne (CH) at 380 K. However, Parlett and Chesters suggested in their RAIRS study that ethylene dehydrogenates to form only ethylidyne, which decomposes to methylidyne at 380 K without any indication of ethynyl formation [4]. Ande et al. [6] used density-function theory (DFT) calculations to conclude that on Ru(001) the ethylene $\rightarrow$ vinyl $\rightarrow$ vinylidene $\rightarrow$ ethylidyne pathway was most favorable, which was also found to be the case on Pt(111) [11,13] and Pd(111) [13] from DFT and Monte-Carlo simulations. These theoretical results then imply that there are several intermediate species that have yet to be detected spectroscopically. The trend found by Ande et al. [6] that hydrogenation/dehydrogenation reactions are favored over intramolecular 1,2-H shift reactions on Ru(001) is also generally consistent with what was found on Pt, Pd, Rh, and Ni(111) surfaces by Basaran et al [14]. The RAIRS results presented here help to clarify some of the issues that have arisen in these previous studies.

2. Experimental

The experiments were performed in an ultra-high vacuum (UHV) chamber with a base pressure of 1×10^{-10} torr. The chamber is equipped with PHI 15-180 low energy

electron diffraction (LEED) optics, a PHI 10-155 cylindrical mirror analyzer for Auger electron spectroscopy (AES), and a Hiden HAL201/3F quadrupole mass spectrometer for temperature-programmed reaction (TPR). The chamber is coupled to a Bruker IFS-66v/s Fourier-transform infrared (FTIR) spectrometer for RAIRS measurements. The incident and reflected IR beams enter and exit the UHV chamber through differentially-pumped, O-ring sealed KBr windows. RAIR spectra between 800 and 4000 cm^{-1} were obtained using a liquid nitrogen (LN_2)-cooled MCT (HgCdTe) detector and a SiC IR source. An InSb detector with a low wavenumber cutoff of 2100 cm^{-1} and tungsten IR source was used to obtain spectra with better signal-to-noise ratios at higher wavenumbers. Each RAIR spectrum was obtained with 1024 scans and 4 cm^{-1} resolution.

The Ru(001) single crystal was spot-welded to two tantalum wires mounted on a LN_2 -cooled sample holder and was cleaned using a standard procedure that has been described previously [15]. Resistive heating was used for temperatures up to 900 K. For higher-temperature annealing up to 1500 K, a thoriated tungsten filament mounted behind the crystal was used for electron-beam heating with the sample positively biased to 600 V. The crystal was cleaned by argon ion sputtering and annealing to 1500 K, followed by a second round of sputtering and annealing to 850 K. The surface order and cleanness were verified with LEED and AES. Due to the fact that the C KLL Auger peak overlaps with the Ru MNN peak at 273 eV, TPD was also used to check and quantify small amounts of carbon contamination that cannot be detected by AES. The absence of a recombinative CO desorption peak between 500 and 600 K after O_2 exposure indicates the absence of surface carbon.

Research grade ethylene (99.99%) and ultra-high purity (99.999%) hydrogen were purchased from Matheson and Airgas, respectively. Both gases were used without further purification and the purity of both gases was checked periodically by mass spectrometry.

3. Results

3.1. Thermal decomposition of ethylene on Ru(001)

Figure 1 displays a set of RAIR spectra obtained after exposing the Ru(001) surface at 90 K to 5 L (1 L = 1 langmuir = 1×10^{-6} Torr s) of ethylene to form a multilayer followed by heating to 280, 320, 350, 450, 470, and 500 K. The sample was held at the target temperature for 60 s before it was cooled to 90 K, the temperature at which all RAIR spectra were obtained. The peak assignments for molecularly adsorbed ethylene on Ru(001) at 90 K, summarized in Table 1, are inferred from comparisons with the previously reported HREEL and RAIR spectra of di- σ -bonded ethylene on Ru(001) [6-7] together with RAIR spectra of di- σ -bonded ethylene on Pt(111) [3,4,16]. Our spectra confirm that ethylene adsorbs as a di- σ -bonded species at 90 K. As noted by Parlett et al. [4], $\nu(\text{CC})$ at 1040 cm^{-1} , which is identified by Hills et al. [3] with HREELS, might be too weak to observe with RAIRS.

The spectrum in Figure 1 obtained after annealing to 280 K is characteristic of ethylidyne (CCH_3), with peaks due to $\nu_s(\text{CH}_3)$ at 2881 cm^{-1} , $2 \times \delta_{\text{as}}(\text{CH}_3)$ at 2812 cm^{-1} , $\delta_s(\text{CH}_3)$ at 1338 cm^{-1} , and $\nu(\text{CC})$ at 1122 cm^{-1} . The conversion of di- σ -bonded ethylene to ethylidyne begins at 160 K and is complete by about 280 K. Further annealing the surface to 320 K causes a significant decrease in intensity of the peaks associated with ethylidyne and after a 350 K anneal the ethylidyne peaks are absent but a new and

prominent peak appears at 3014 cm^{-1} that is assigned to ethynyl (CCH). With a 450 K anneal, the 3014 cm^{-1} peak grows and a new peak appears at 2912 cm^{-1} , with a weaker peak (unlabeled) seen at 2954 cm^{-1} . The 2912 cm^{-1} peak is assigned to methylidyne (CH), which indicates that CCH_3 is first dehydrogenated to ethynyl and that ethynyl dissociates by breaking the C-C bond. After annealing to 470 K, the relative intensities of the 2912 and 3014 cm^{-1} peaks are reversed, indicating that the species responsible for the former peak is the more stable of the two. Both peaks are still present for the 500 K anneal, but no peaks are detectable for annealing temperatures of 550 K and above. Some C_xH_y must still be present on the surface up to temperatures of 500-700 K as the complementary temperature programmed reaction spectroscopy (TPRS) experiments of Hills et al. [3] reveal that $\text{H}_2(\text{g})$ continues to desorb up to these temperatures.

As a dramatic change is seen in Figure 1 between 320 and 350 K, spectra were also recorded for annealing temperatures of 320, 330, 340, and 350 K starting with 5 L of ethylene in an attempt to identify any additional species that might form in this temperature range. As shown in Figure S1 of the Supporting Information, gradual conversion from ethylidyne to ethynyl was observed. To better illustrate the conversion, the areas of the peaks associated with both species versus annealing temperature are plotted in Figure 2. Although a large drop in the intensity of the ethylidyne peaks between 280 and 320 K is seen in Figure 1 without a concomitant appearance of any decomposition product, Figure 2 implies that in the range of 320 to 350 K, there is a one-to-one conversion of ethylidyne to ethynyl.

More detailed information on the conversion of ethynyl to methylidyne on the surface was obtained by annealing to 450, 460, 470, 480, 490, and 500 K after a 5 L exposure of

ethylene. The spectra are presented in Figure S2 of the Supporting Information whereas Figure 3 shows plots of the peak areas of the C–H stretches of ethynyl (3014 cm^{-1}) and methylidyne (2912 cm^{-1}) versus annealing temperature from 450 to 500 K. From 450 to 480 K, each decrease in intensity of the 3014 cm^{-1} peak is accompanied by an intensity increase for the 2912 cm^{-1} peak. This would suggest that each CCH that decomposes produces a CH. However, the big drop in intensity of the 3014 cm^{-1} peak for the 460 K anneal is accompanied by only a very modest increase of the 2912 cm^{-1} peak. In addition, both peaks decrease at 490 K, but at 500 K a large decrease in the 2912 cm^{-1} peak occurs with little change in the 3014 cm^{-1} peak. Although the results imply that CH is produced from CCH dissociation, it is likely that CCH can also decompose to one or more other species that have no detectable C–H stretch vibrations, such as atomic carbon and hydrogen. It is also noteworthy that although CCH undergoes substantial dissociation at 460 K, its C–H stretch peak remains visible up to 500 K and shows little change in its intensity after the 490 K anneal.

3.2. Hydrogenation of C_2H_x

Further clarification of the identity of the species responsible for the peaks observed here can be obtained from spectra obtained following their reaction with hydrogen. This clarification is desirable as the peaks that we assign to CCH and CH have been assigned differently in previous studies [2-4]. For example Parlett et al. [4] and Hills et al. [3] assigned the peak at 3014 cm^{-1} to methylidyne rather than to ethynyl. Figure 4 shows RAIR spectra after a 5 L ethylene exposure at 90 K, annealing to 470 K, followed by exposure to hydrogen at 90 K and annealing to 280 K. As evident in Figure 4(a), the two species associated with the peaks at 2912 and 3014 cm^{-1} are present on the surface

following the 470 K anneal. As shown in Figure 4(b), after hydrogen co-adsorption at 90 K, the peak at 3014 cm^{-1} decreases in intensity while the one at 2912 cm^{-1} remains unchanged. Meanwhile, a new peak appears at 3030 cm^{-1} , which is assumed to be due to hydrogenation of the species with C–H stretch at 3014 cm^{-1} . According to Figure 4(c), annealing the hydrogen coadsorbed surface to 280 K causes the peak at 3030 cm^{-1} to decrease as ethylidyne forms as revealed by the growth of the 2881 cm^{-1} peak. This clearly implies that the 3030 cm^{-1} peak is due to a species that converts to ethylidyne but is not CCH. In contrast, the species responsible for the 2912 cm^{-1} peak is not hydrogenated to ethylidyne as it remains unchanged. Assigning the 2912 cm^{-1} to CH is consistent with these observations as it would have to undergo C–C coupling followed by hydrogenation to form ethylidyne. This leads us to conclude that the 3030 cm^{-1} peak is due to vinylidene, CCH_2 . This assignment is consistent with the predictions of Ande et al. [6] that ethylidyne forms via a vinylidene intermediate.

4. Discussion

4.1 Ethylene $\rightarrow$ Ethylidyne

The RAIR spectra presented here unambiguously show that adsorbed di- σ -bonded ethylene converts to ethylidyne in the temperature range of 150-280 K. This is in agreement with the previous surface vibrational studies of ethylene on Ru(001) [2-5]. As shown in Table 1, there is generally excellent agreement between the frequencies we observe and earlier values obtained by both RAIRS and HREELS for di- σ -bonded ethylene on Ru(001). Similar values were reported for di- σ -bonded ethylene on Pt(111) [16] but the assignment of the $\omega(\text{CH}_2)$ and $\nu(\text{CC})$ modes is different with the latter assigned to the higher frequency member of the pair of bands on Pt(111). These are

highly mixed modes with both having significant contributions from the $\omega(\text{CH}_2)$ and $\nu(\text{CC})$ motions and determination of which motion is most responsible for which peak is of little importance. However, the recent DFT study by Zhao and Greeley favors the assignment given in Table 1 for di- σ -bonded ethylene on Pt(111) [12]. The HREELS values reported by Hills et al. [3] for ethylidyne are systematically higher than the ones obtained with RAIRS by us and by Parlett and Chesters [4] with, for example, the $\nu_s(\text{CH}_3)$ frequency being 64 cm^{-1} higher than in our spectra. This discrepancy should be considered in attempting to reconcile HREELS and RAIRS results to identify other C_2H_x species, many of which have C–H stretch frequencies that differ by less than the difference between HREELS and RAIRS frequencies for the C–H stretch of ethylidyne.

Neither in our spectra nor in those of the previous vibrational studies were any peaks detected due to intermediates in the conversion of di- σ -bonded ethylene to ethylidyne. Because the reaction involves the loss of two hydrogen atoms from one carbon, the addition of a third hydrogen atom to the second carbon, and a reorientation of the C–C bond from parallel to perpendicular to the surface, it is clear that the reaction must involve several elementary steps. The recent DFT study by Ande et al. [6] shows that the reaction most likely proceeds by an ethylene $\rightarrow$ vinyl $\rightarrow$ vinylidene $\rightarrow$ ethylidyne pathway, suggesting that intermediate vinyl and vinylidene moieties might be detectable spectroscopically. This pathway was also predicted to be the favored one on Pt(111) [11,13]. The lack of spectroscopic evidence for vinyl and vinylidene intermediates in ethylidyne formation from di- σ -bonded ethylene is either because they have no vibrational bands with sufficient intensity to be detectable with either RAIRS or HREELS, or more likely because they react as quickly as they are formed so that their

coverages never rise to a level that makes them detectable. However, when ethylidyne is formed through the hydrogenation of ethynyl, there is evidence for an additional intermediate that may be vinylidene.

4.2 Ethylidyne→Ethynyl→Methylidyne

Our conclusions regarding the ethylidyne decomposition pathway differs from what has have been proposed in the previous surface vibrational studies on Ru(001) [2-5]. With HREELS, Hills et al. [3] found that annealing an ethylene-exposed surface to 280 K yields both ethylidyne and ethynyl. They concluded that the former decomposes to carbon and hydrogen atoms at 350 K, whereas the latter decomposes to methylidyne at 380 K, as indicated by a $\nu(\text{CH})$ peak at 3010 cm^{-1} . Using RAIRS, Parlett and Chesters suggested that ethylidyne decomposes to form only methylidyne, as only a single peak at 3010 cm^{-1} was observed after heating to 380 K [4]. Although these two past studies propose different mechanisms of ethylidyne decomposition, both assign $\nu(\text{CH})$ at 3010 cm^{-1} to methylidyne and conclude that surface C_2H_x species are not stable above 400 K. Of course, given that $\nu_s(\text{CH}_3)$ of ethylidyne in the HREEL spectra of Hills et al. [3] was 64 cm^{-1} higher than as observed here with RAIRS, means that the species responsible for their 3010 cm^{-1} peak might yield a RAIRS peak at about 2950 cm^{-1} . In an ultraviolet photoelectron spectroscopy (UPS) and temperature programmed desorption (TPD) study, Egawa et al. [17] suggested that ethylidyne dehydrogenates to ethynyl at 450 K before ethynyl decomposes to methylidyne at 550 K. Our results support the reaction sequence proposed by Egawa et al. [17], although we find that the transformations take place at somewhat lower temperatures. Our assignment of the peak we observe at 3014 cm^{-1} is compared to previously reported values for $\nu(\text{CH})$ for ethynyl in Table 3, demonstrating

that our observed value is consistent with other assignments to this species. However, we do not observe $\delta(\text{CCH})$ or $\nu(\text{CC})$ of ethynyl, both of which should be surface dipole allowed, although the latter would likely be too weak to observe. Hills et al. [3] reported $\delta(\text{CCH})$ and $\nu(\text{CC})$ of ethynyl at 750 and 1290 cm^{-1} , respectively, but these peaks were correlated with their $\nu(\text{CH})$ peak at 2960 cm^{-1} rather than the one at 3010 cm^{-1} . They associated the latter peak with methylidyne, which was accompanied by a peak at 810 cm^{-1} that they assigned to $\delta(\text{CH})$. As the peaks they observed at 750 and 810 cm^{-1} are below the wavenumber range that we can easily access, the distinction we make between CH and CCH rests mainly on the order in which the two peaks at 2912 and 3014 cm^{-1} evolve with annealing temperature and the assumption that whereas CH can be produced from C–C bond breaking in CCH, carbon-carbon coupling of CH_x species to form CCH is less likely to occur. However, Zhou et al. [18] observed ethylidyne formation following exposure of Ru(0001) to CH_3I , indicating that C–C coupling can occur even under UHV conditions. Although 2912 cm^{-1} is a bit lower than the values of $\nu(\text{CH})$ of CH reported for other surfaces listed in Table 4, it is still within the same general range, particularly since HREELS frequencies are often slightly higher than RAIRS frequencies for C–H stretching vibrations.

The stability and other properties of CH on the Ru(001) surface has been investigated with DFT calculations as it is an important intermediate in Fischer-Tropsch catalysis as well as in methane activation [19-21]. Ciobîcă and coworkers investigated the thermodynamics of methane dissociation on Ru(001) using ab initio periodic slab calculations for CH_x coverages of 25% and 11% [20]. They found that methylidyne is the most stable species, which agrees with previous experimental studies by Wu et al. [22,23]

This is also consistent with our detection of methylidyne at temperatures up to 520 K and our observation that CH does not react with hydrogen to form CH₂ or CH₃. The high stability of CH is in accord with the theoretical calculations of Ge et al. [24] showing that C-C coupling of methylidyne (CH) and methyldiene (CH₂) to form vinyl (CH₂CH) on Ru(001) is endothermic with a reaction barrier at 116.5 kJ/mol, which is also consistent with the lack of experimental evidence for a stable vinyl species on Ru(001). Additional evidence for the exothermic nature of the C+H→CH reaction comes from the work of Barteau et al. who found that C atoms formed from the electron-induced dissociation of CO could be hydrogenated to CH on Ru(001) as indicated by the development of an HREELS peak at 2950 cm⁻¹, unaccompanied by loss features at lower wavenumbers expected for other species, such as CH₂ or CH₃ [2,25].

4.3 Vinylidene

The moiety produced from ethynyl (CCH) hydrogenation that has a $\nu(\text{CH})$ peak at 3030 cm⁻¹ is tentatively identified as vinylidene (CCH₂). This is also consistent with its hydrogenation to ethylidyne after annealing to 280 K. Assignment of the 3030 cm⁻¹ peak to vinylidene is a good match to $\nu_{\text{as}}(\text{CH}_2)$ for CCH₂ in Os₃(CO)₉(μ -H)₂(μ_3 - η_2 -C=CH₂), where $\nu_{\text{s}}(\text{CH}_2)$ and $\nu_{\text{as}}(\text{CH}_2)$ occur at 2986 and 3047 cm⁻¹, respectively [26]. Hills reported that although vinylidene did not form on a clean Ru(001) surface, it could be produced on a (2×2)-O/Ru(001) surface where ethylene first adsorbs as a π -bonded species, converts to ethylidyne after heating to 250 K, with ethylidyne then dehydrogenating to vinylidene by 350 K [27]. Peaks attributed to vinylidene were observed at 895, 956, 1435, 2985, and 3050 cm⁻¹, which were assigned to $\omega(\text{CH}_2)$, $\rho(\text{CH}_2)$, $\delta(\text{CH}_2)/\nu(\text{CC})$, $\nu_{\text{s}}(\text{CH}_2)$ and $\nu_{\text{as}}(\text{CH}_2)$, respectively, with the one at 1436 cm⁻¹

being the most intense [27]. In contrast, Barteau et al. [2] studied ethylene adsorption on the (2×2)-O/Ru(001) surface and although they also found that the molecule initially adsorbed as a π -bonded species, they concluded that upon heating it desorbs molecularly without undergoing any reaction. Wu et al. [23] studied ethylene interaction with a Ru(001) surface in a high pressure microreactor and found with HREELS that it formed methyldiyne and vinylidene, with the latter characterized only by peaks at 1160 and 1395 cm^{-1} , assigned to $\nu(\text{CC})$ and $\delta(\text{CH}_2)$, respectively. There is thus considerable discrepancy among the previous HREELS reports for vinylidene on Ru(001). Although based on frequency alone, the 3030 cm^{-1} peak that we observe matches the expected position of $\nu_{\text{as}}(\text{CH}_2)$ of vinylidene, this mode should be surface dipole forbidden for a μ_3 - $\eta^2\text{-C=CH}_2$ surface structure, whereas the lower frequency $\nu_{\text{s}}(\text{CH}_2)$ mode would be allowed. Also, associating the 3030 cm^{-1} peak with $\nu_{\text{s}}(\text{CH}_2)$ of vinylidene and the 3014 cm^{-1} peak with ethynyl is opposite to the expectation that the C–H stretch of the latter species should be at the higher frequency. Because of these discrepancies along with the absence of other expected vibrational peaks, our identification of a vinylidene moiety on Ru(001) is not definitive. If the experiments had been repeated using C_2D_4 instead of C_2H_4 , these C–H stretch peaks would no doubt have been replaced by the corresponding C–D stretch peaks, but this would not clarify the assignments.

5 Conclusion

Reflection absorption infrared spectroscopy (RAIRS) was used to identify and characterize the surface intermediates formed in the thermal decomposition of ethylene on Ru(001). Ethylene is found to adsorb on the surface in a di- σ bonded complex at 95 K and to dehydrogenate to form ethyldiyne (CCH_3) above 150 K. Upon further annealing

the crystal to above 320 K, ethylidyne dehydrogenates to ethynyl (CCH). Annealing to higher than 450 K causes ethynyl to decompose to methylidyne (CH). When a surface covered with methylidyne and ethynyl is exposed to hydrogen and 90 K and then annealed at 280 K, methylidyne is unaffected, but the ethynyl species, with $\nu(\text{CH})$ at 3014 cm^{-1} , reacts to form a new species with $\nu(\text{CH})$ at 3030 cm^{-1} , and this latter species is further hydrogenated to ethylidyne. Although the surface chemistry implies that this species is vinylidene, the spectroscopic evidence for associating the 3030 cm^{-1} peak with vinylidene is incomplete.

Corresponding Author

*Email: mtrenary@uic.edu

Notes

The authors declare no competing financial interests.

Acknowledgment.

We gratefully acknowledge financial support from the National Science Foundation (CHE-1464816).

Supporting information available: Additional RAIR spectra for annealing experiments at shorter temperature intervals are provided.

References

- [1] G.A. Somorjai, *Introduction to Surface Chemistry and Catalysis*, John Wiley & Sons, Inc., New York, 1994.
- [2] M.A. Barteau, J.Q. Broughton, D. Menzel, *Appl. Surf. Sci.* 19 (1984) 92.
- [3] M.M. Hills, J.E. Parmeter, C.B. Mullins, W.H. Weinberg, *J. Am. Chem. Soc.* 108 (1986) 3554.
- [4] P.M. Parlett, M.A. Chesters, *Surf. Sci.* 357–358 (1996) 791.
- [5] I.A. Ransley, L.M. Ilharco, J.E. Bateman, B.H. Sakakini, J.C. Vickerman, M.A. Chesters, *Surf. Sci.* 298 (1993) 187.
- [6] C.K. Ande, S.D. Elliott, W.M.M. Kessels, *J. Phys. Chem. C* 118 (2014) 26683.
- [7] F. Zaera, T.V.W. Janssens, H. Öfner, *Surf. Sci.* 368 (1996) 371.
- [8] F. Zaera, *Langmuir* 12 (1996) 88.
- [9] F. Zaera, *J. Am. Chem. Soc.* 111 (1989) 4240.
- [10] P.S. Cremer, X. Su, Y.R. Shen, G.A. Somorjai, *J. Phys. Chem. B* 101 (1997) 6474.
- [11] Z.-J. Zhao, L.V. Moskaleva, H.A. Aleksandrov, D. Basaran, N. Rösch, *J. Phys. Chem. C* 114 (2010) 12190.
- [12] Z.-J. Zhao, J.P. Greeley, *Surf. Sci.* 640 (2015) 112.
- [13] H.A. Aleksandrov, L.V. Moskaleva, Z.-J. Zhao, D. Basaran, Z.-X. Chen, D. Mei, N. Rösch, *J. Catal.* 285 (2012) 187.
- [14] D. Basaran, H.A. Aleksandrov, Z.-X. Chen, Z.-J. Zhao, N. Rösch, *J. Mol. Catal. A: Chem.* 344 (2011) 37.
- [15] I. Waluyo, Y. Ren, M. Trenary, *J. Phys. Chem. Lett.* 4 (2013) 3779.
- [16] J. Fan, M. Trenary, *Langmuir* 10 (1994) 3649.
- [17] C. Egawa, S. Naito, K. Tamaru, *J. Chem. Soc., Faraday Trans. 1* 82 (1986) 3197.
- [18] Y. Zhou, M.A. Henderson, W.M. Feng, J.M. White, *Surf. Sci.* 224 (1989) 386.
- [19] I.M. Ciobîcă, F. Frechard, R.A. van Santen, A.W. Kleyn, J. Hafner, *Chem. Phys. Lett.* 311 (1999) 185.
- [20] I.M. Ciobîcă, F. Frechard, R.A. van Santen, A.W. Kleyn, J. Hafner, *J. Phys. Chem. B* 104 (2000) 3364.
- [21] C.-T. Au, C.-F. Ng, M.-S. Liao, *J. Catal.* 185 (1999) 12.
- [22] M.-C. Wu, D.W. Goodman, *Surf. Sci.* 306 (1994) L529.
- [23] M.-C. Wu, D.W. Goodman, *J. Am. Chem. Soc.* 116 (1994) 1364.
- [24] Q. Ge, M. Neurock, H.A. Wright, N. Srinivasan, *J. Phys. Chem. B* 106 (2002) 2826.
- [25] M.A. Barteau, P. Feulner, R. Stengl, J.Q. Broughton, D. Menzel, *J. Catal.* 94 (1985) 51.
- [26] J. Evans, G.S. McNulty, *J. Chem. Soc., Dalton Trans.* (1983) 639.
- [27] M.M. Hills, J.E. Parmeter, W.H. Weinberg, *J. Am. Chem. Soc.* 109 (1987) 597.
- [28] A.M. Baró, H. Ibach, *J. Chem. Phys.* 74 (1981) 4194.
- [29] K.L. Kostov, T.S. Marinova, *Surf. Sci.* 184 (1987) 359.
- [30] L.L. Kesmodel, G.D. Waddill, J.A. Gates, *Surf. Sci.* 138 (1984) 464.
- [31] B.E. Koel, J.E. Crowell, B.E. Bent, C.M. Mate, G.A. Somorjai, *J. Phys. Chem.* 90 (1986) 2949.
- [32] R. Deng, E. Herceg, M. Trenary, *J. Am. Chem. Soc.* 127 (2005) 17628.
- [33] R. Deng, E. Herceg, M. Trenary, *Surf. Sci.* 573 (2004) 310.

Table 1. Comparisons of vibrational frequencies (cm^{-1}) for RAIRS active modes of di- σ bonded ethylene (C_2H_4) on Ru(001) and Pt(111)

Vibrational mode	C_2H_4 / Ru(001) [3] HREELS	C_2H_4 / Ru(001) [4] RAIRS	C_2H_4 / Pt(111) [16] RAIRS	C_2H_4 / Ru(001) RAIRS (this work)
$\nu_s(\text{CH})$	2940	2950	2903	2946
$\delta_s(\text{CH}_2)$	1450	1437	1414	1444
$\omega(\text{CH}_2)$	1145	1130	993	1137
$\nu(\text{CC})$	1040	N/O ¹	1047	N/O

¹ N/O: Not observed

Table 2. Comparisons of vibrational frequencies (cm^{-1}) for RAIRS active modes of ethynidyne (CCH_3) on Ru(001) and Pt(111)

Mode	Pt(111) RAIRS [16]	Ru(001) HREELS [3]	Ru(001) RAIRS [4]	Ru(001) RAIRS (this work)
$\nu_s(\text{CH}_3)$	2885	2945	2875	2881
$\delta_s(\text{CH}_3)$	1340	1370	1338	1338
$2 \times \delta_{\text{as}}(\text{CH}_3)$	2794		2808	2812
$\nu(\text{CC})$	1115	1140	N/O ¹	1122

¹ N/O: Not observed.

Table 3. Comparisons of vibrational frequencies (cm^{-1}) for C-H stretch ($\nu(\text{CH})$) of ethynyl (CCH)

Surfaces	Pt(111)[28] HREELS	Ir(111)[29] HREELS	Pd(111)[30] HREELS	Rh(111)[31] HREELS	Ru(001)[3] HREELS	Ru(001) RAIRS (this work)
Frequencies	3000	3018	3000	3008	2960	3014

Table 4. Comparisons of vibrational frequencies (cm^{-1}) for RAIRS active modes of methyldiyne (CH) on Ru(001) and Pt(111)

Surfaces	Pt(111)[32,33] RAIRS	Rh(111)[31] HREELS	Ru(001)[2,4] RAIRS	Ru(001) HREELS	Ru(001) RAIRS (this work)
Frequencies	2969	2928	3010	2950[25], 3010[3], 3000[18]	2912

Figure 1. Experimental RAIR spectra obtained after exposing Ru(001) to 5 L of ethylene at 90 K, followed by heating to 280, 320, 350, 450, 470, and 500 K. All spectra were measured at 90 K. The low and high frequency regions were acquired using MCT and InSb detectors, respectively.

Figure 2. Plot of the peak area of ethylidyne (2881 cm^{-1}) and ethynyl (3014 cm^{-1}) versus annealing temperature from 320-350 K from spectra in Figure 1 of SI.

Figure 3. Plot of the peak area of ethynyl (3014 cm^{-1}) and methylidyne (2912 cm^{-1}) versus annealing temperature from 450-500 K from spectra in Figure 2 of SI.

Figure 4. Experimental RAIR spectra obtained after (a) exposing Ru(001) to 5 L of ethylene at 90 K followed by heating to 470 K; (b) exposing surface obtained in (a) to 100 L of H_2 at 90 K; (c) heating the surface to 280 K following (b). All spectra were measured at 90 K using an InSb detector.

Figure 5. Proposed reaction scheme for ethylene thermal decomposition on Ru(001)