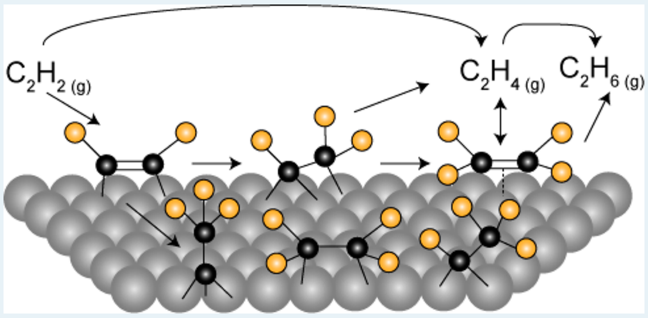
ACS Catalysis
Research Article
pubs.acs.org/acscatalysis

Simultaneous Monitoring of Surface and Gas Phase Species during Hydrogenation of Acetylene over Pt(111) by Polarization-Dependent Infrared Spectroscopy

Joel D. Krooswyk, Iradwikanari Waluyo, and Michael Trenary*

Department of Chemistry, University of Illinois at Chicago, 845 West Taylor Street, Chicago, Illinois 60607, United States



ABSTRACT: Acetylene hydrogenation was monitored at ambient pressure with polarization-dependent reflection absorption infrared spectroscopy (RAIRS), which permitted gas phase and surface species to be simultaneously monitored as C_2H_2(g) was converted first to C_2H_4(g) and then to C_2H_6(g). Experiments in which an acetylene-covered surface was hydrogenated with 1.0×10^{-2} Torr H_2 between 120 and 300 K indicated that vinyl is the intermediate species to ethylene formation and that the addition of one H to acetylene is the rate-limiting step of the reaction. At a C_2H_2(g)/H_2(g) ratio of 1:100, the reaction was monitored from 300 to 370 K and separately in a constant pressure and constant temperature reaction at 370 K. Ethylidyne and di-σ-ethylene were observed on the surface in both reactions and were found to be spectator species in the hydrogenation of ethylene to ethane. A minor hydrogenation pathway involves a third species, which is best assigned to an ethylidene intermediate. A small coverage of π-ethylene was also present during the annealing experiment at 350 K but disappeared at 370 K, indicating that it is also an intermediate in the reaction. In a separate experiment to compare acetylene hydrogenation with ethylene hydrogenation at 370 K, spectra were acquired with a C_2H_4(g)/H_2(g) ratio of 1:10. Ethylene hydrogenation proceeds approximately three times faster when starting with ethylene as compared with hydrogenation of the ethylene produced by acetylene hydrogenation. This indicates that the surface is covered with different intermediates when it is first exposed to acetylene. The results presented here demonstrate a simple way to use polarization-dependent RAIRS to distinguish surface species from gas phase reactants and products. The method should be applicable to a wide range of catalytic reactions over metal surfaces and offers new opportunities for operando studies in catalysis.

KEYWORDS: *acetylene, ethylene, hydrogenation, ambient pressure, polarization modulation, RAIRS*

■ INTRODUCTION

Transition-metal-catalyzed hydrogenations of unsaturated hydrocarbons are among the most important reactions in heterogeneous catalysis. For this reason, numerous fundamental studies of the simplest hydrocarbons containing multiple carbon−carbon bonds, acetylene and ethylene, have been carried out. The goal has been to identify the elementary steps in which H atoms are added or removed from the various possible C_2H_x intermediates that form along the reaction pathway. Much of the experimental work has employed ultrahigh-vacuum techniques because these provide well-defined conditions for the definitive identification of intermediates and their reactions. However, because it is not always clear if the mechanisms deduced from UHV studies are the same ones followed under actual hydrogenation conditions, there is increased interest in operando studies, in which realistic reaction conditions are employed.[1] Here, we have used polarization-dependent reflection absorption infrared spectroscopy (RAIRS) to simultaneously monitor the surface and gas phase species during acetylene hydrogenation over a Pt(111) surface at total gas pressures in the range of 10^{-2} to 4.0 Torr.

There have been numerous experimental studies of the C_2H_x species that form on Pt(111) following exposure of the surface to acetylene.[2−5] At low temperature, C_2H_2 bonds in a di-σ/π configuration in which each C atom forms σ bonds to two Pt atoms at a bridge site and where the CH bonds are bent away from the surface with the HCCH plane tilted from the surface normal such that the remaining CC π bond can also interact with the surface. At temperatures around 350 K, the ethylidyne species, CCH_3, is observed. A variety of other C_2H_x species have been proposed, but their characterization has not been nearly as definitive as for CCH_3. These other species include vinylidene (CCH_2), vinyl ($CHCH_2$), and ethylidene ($CHCH_3$). Ethylidyne could be formed by one elementary step from each of these species: hydrogenation of vinylidene, dehydrogenation of ethylidene, or by a 1,2-H shift in vinyl. Vinylidene, in turn, could be formed from a 1,2-H shift in di-σ/π bonded acetylene. A separate but related issue is the mechanism of hydrogenation of acetylene to ethane. A simple stepwise addition of H atoms

Received: May 5, 2015
Revised: June 12, 2015
Published: June 15, 2015

DOI: 10.1021/acscatal.5b00942
ACS Catal. 2015, 5, 4725−4733

to C_2H_2 would proceed by way of $CHCH_2$ (vinyl), ethylene (C_2H_4), ethylidene ($CHCH_3$), and ethyl (CH_2CH_3) intermediates. Whether one or more of these intermediates can be detected spectroscopically through in situ measurements during the hydrogenation reaction will depend on two main factors: First, there must be sufficient coverage of the intermediate so that the intensity of at least one vibrational mode is high enough to enable detection within the limited sensitivity of the spectroscopic method. Second, the observed vibrational peaks must be uniquely assignable to a specific species. As shown below, this second requirement poses the bigger challenge.

In addition to the growing interest in using in situ spectroscopic methods to investigate surface reactions such as ethylene and acetylene hydrogenation, recent theoretical work using density functional theory (DFT) has provided new opportunities for interpreting experimental work. For example, Zhao et al.[6] investigated the mechanism of ethylidyne formation from ethylene on Pt(111) and reported the adsorption geometries, binding energies, and vibrational frequencies of the various possible C_2H_x species as well as the activation energies for each step of their interconversions. An important conclusion was that simple isomerization reactions involving intramolecular 1,2-H transfers, such as the formation of vinylidene from acetylene, ethylidene from ethylene, or ethylidyne from vinyl, have high barriers and are therefore unlikely to occur. A similar conclusion was reached in a DFT study[7] of ethylidyne formation from acetylene on Pt(111), although in the latter case, no calculated vibrational frequencies were reported. The stabilities and geometric structures of the intermediates are similar to those reported in much earlier work.[8,9] These computational studies have been extended to incorporate kinetic Monte Carlo (kMC) methods by Alexandrov et al.,[10] who concluded that the rate-determining step in ethylidyne formation from ethylene on Pt(111) is the hydrogenation of vinylidene. Podkolzin et al.[11] used DFT methods to determine how reactant coverages affect the mechanism of acetylene hydrogenation over Pt(111). They concluded that both ethylidyne and vinylidene would be present as spectator species and specifically considered the stabilities of other intermediates in the presence of high coverages of these spectator species. Recently, Zhao and Greeley have used DFT to calculate both the intensities and frequencies of the vibrational modes of various C_2H_x intermediates on Pt(111) and to thereby simulate RAIR spectra for direct comparison with the corresponding experimental spectra.[12] They concluded that experimental spectra that had previously been assigned to ethylidene could be better assigned to vinylidene. We consider these reassignments in detail below.

The results reported here clearly show that the surface is covered by ethylidyne as gas phase acetylene is first converted to gas phase ethylene and then the gas phase ethylene is hydrogenated to ethane. The hydrogenation reactions proceed with no significant change in the ethylidyne coverage. The IR spectra of a gas phase mixture that initially consists of $H_2(g)$ and $C_2H_2(g)$ first show a rise in $C_2H_4(g)$ as $C_2H_2(g)$ is consumed, followed by a decrease in $C_2H_4(g)$ as $C_2H_6(g)$ forms. In separate experiments, these results starting from $C_2H_2(g)$ are compared with results obtained when starting with $C_2H_4(g)/H_2(g)$ mixtures. The latter experiments are similar to recent work by Tilekaratne et al.,[13] in which RAIRS was used to probe a Pt(111) surface during ethylene hydrogenation, but in their work, mass spectrometry instead of IR spectroscopy was used to monitor the gas phase species. In both their study and ours, ethylidyne was the only surface species detected during ethylene hydrogenation. However, for acetylene hydrogenation, we find additional weak spectral features with RAIRS, indicating the presence of one or more other surface species.

■ EXPERIMENTAL SECTION

Our implementation of polarization-dependent RAIRS differs somewhat from previous work. According to the IR selection rules, surface species are detected only with p-polarized light, whereas gas phase species are observable with both p- and s-polarizations. In conventional polarization-modulated (PM) RAIRS, which is usually implemented using a photoelastic modulator,[14] spectra of the surface species are given by the expression $(R_p - R_s)/(R_p + R_s)$, and because gas phase species contribute equally to the p- and s-polarized spectra, their difference contains features due only to the surface species. The denominator serves to normalize the spectra against the variation of reflected light intensity versus wavenumber due to variations of the source intensity, optical throughput, and detector response. As implemented in this way, spectra due to surface species can be obtained without the need for a reference spectrum of the clean sample, which is a great advantage for many applications. However, the intensities of p- and s-polarized light reaching the detector are not equal, primarily because of unequal reflectivities of the mirrors in the optical system. Schennach et al.[15] have dealt with this problem by using two polarizers to equalize the detected p- and s-polarized intensities.

We have taken a different approach that relies on the high stability of our system and, hence, the high degree of reproducibility of the spectra. We obtain conventional RAIRS spectra with p-polarized light represented as $\Delta R_p/R_p$, where ΔR_p = p-polarized reflectance of the surface after gas is admitted to the cell minus the reflectance (R_p) of the clean surface before gas is added to the cell. The experiment is repeated with s-polarized light to obtain a $\Delta R_s/R_s$ spectrum. The spectra are then corrected for minor baseline drifts. If exactly the same pressures of the gas-phase species are achieved, then the intensities of the gas phase species in the $\Delta R_p/R_p$ and $\Delta R_s/R_s$ spectra should be exactly equal, such that the difference defined here as $\Delta R/R = (\Delta R_p/R_p) - (\Delta R_s/R_s)$ should yield spectra of surface species free of any gas phase peaks. The results presented here demonstrate that this procedure works quite well. The advantage of using only a single polarizer is that it is simpler and leads to a higher IR signal and, hence, higher signal-to-noise ratios. It has the further advantage of allowing simultaneous detection of gas phase and surface species. As Schennach et al.[15] note, the photoelastic modulator used for conventional PM-RAIRS yields spectra superimposed on a smoothly varying background that makes it difficult to measure spectra over a wide wavenumber range. Neither our method nor that of Schennach et al.[15] suffers from this limitation.

The experiments were performed in an ultrahigh-vacuum (UHV) chamber with an ambient pressure IR cell coupled to a Bruker Vertex 70v FTIR described previously.[16] A rotatable wire-grid polarizer on a ZnSe substrate (Thorlabs) was placed between the Pt(111) crystal and the parabolic mirrors that collimate and focus the IR beam onto the MCT detector. The spectra consist of 1024 scans and were acquired with a resolution of 4 cm^{-1}. The crystal was cleaned using a method previously described,[17] and was cleaned this way between acquisition of the s- and p-polarized spectra.

Atomic absorption grade acetylene (99.6%) was purchased from Airgas and purified by the freeze−pump−thaw method. Research grade ethylene (99.99%) and ultrahigh purity (99.999%) H_2 were purchased from Matheson and Airgas, respectively, and utilized with no further purification. Because acetylene is stabilized with acetone in high-pressure supply cylinders, acetone (parent peak: m/z 43) contamination was checked with mass spectrometry. All other gases were also checked with mass spectrometry; no impurities were detected. Experiments were performed in two ways. For temperatures of 120−300 K, spectra were acquired in the presence of a static pressure of H_2(g) following a fixed C_2H_2(g) exposure in Langmuir units (1 L = 1 × 10^{-6} Torr s). For temperatures between 300 and 370 K, spectra were acquired in the presence of gas phase mixtures of C_2H_2 and H_2 or of C_2H_4 and H_2. For the annealing experiments, the crystal was heated to the target temperature and held there for 30 s and then cooled back to the starting temperature for spectral acquisition.

■ RESULTS

I. Hydrogenation of C_2H_2 between120−300 K under Ambient Pressure H_2. Figure 1 shows RAIR spectra in the C−H stretch region following exposure to acetylene at 120 K, followed by annealing to the indicated temperatures in a background of 1.0 × 10^{-2} Torr of H_2(g). As shown previously,[3] the peak at 2994 cm^{-1} is attributed to acetylene bound to the surface in a di-σ/π structure. This is the only peak of this species that has sufficient intensity to be observed, and for this reason, only spectra in the C−H stretch region were recorded in this experiment. When hydrogen is added and the surface is annealed to 220 K, a separate peak is resolved at 2980 cm^{-1}, which is assigned to the $\nu_s(CH_2)$ mode of vinyl ($CHCH_2$). An unresolved shoulder on the low wavenumber side of the 2994 cm^{-1} peak of acetylene seen in the top spectrum persists and is most likely due to a form of acetylene with a slightly different bonding environment because the intensity of this shoulder relative to the main acetylene peak at 2994 cm^{-1} remains roughly the same for all spectra in Figure 1. A new peak appears at 2918 cm^{-1} after annealing to a slightly higher temperature of 230 K, and its intensity increases by a factor of 2.5 after a 240 K anneal, which also causes a small shift to 2916 cm^{-1}. As further discussed below, this peak can be assigned either to the ν(CH) mode of vinyl or to di-σ-bonded ethylene. As previous studies have shown, the most intense RAIRS peaks for both vinyl[5] and di-σ-bonded ethylene[18−20] occur in the C−H stretch region. By 250 K, the 2994 and 2980 cm^{-1} peaks have disappeared, and the one at 2916 cm^{-1} is greatly diminished. Because previous work has shown that di-σ-bonded ethylene can be hydrogenated to ethane, which would desorb at 252 K,[21] it is assumed that the disappearance of the peaks in Figure 1 is due to the hydrogenation of acetylene to ethane via vinyl and ethylene intermediates.

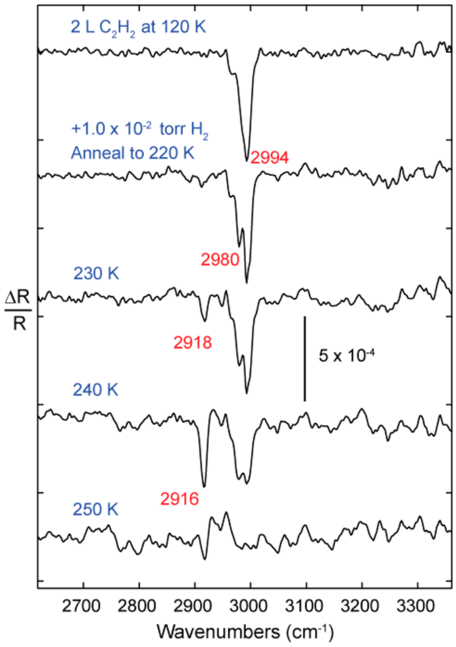


Figure 1. Two langmuirs of C_2H_2 adsorbed on Pt(111) at 120 K. Hydrogen (1.0 × 10^{-2} Torr) was then added, and the crystal was annealed at 220, 230, 240, and 250 K.

Somewhat different results are obtained when starting with a higher acetylene coverage, as shown by the spectra in Figure 2, which were obtained following a 5 langmuir acetylene exposure at 120 K, followed by adding 1.0 × 10^{-2} Torr of H_2(g) to the cell and annealing the surface to the indicated temperatures. As before, a prominent peak at 2994 cm^{-1} due to di-σ/π acetylene is observed, but it is now accompanied by additional peaks, with the most prominent at 3195 cm^{-1}. Following our previous study,[5] this peak as well as the one at 1364 cm^{-1} are assigned to a weakly adsorbed form of acetylene, whereas the just barely observable peak at 3338 cm^{-1} is assigned to multilayer acetylene. No changes are observed upon addition of H_2(g) at 120 K, and only a small decrease in the weakly adsorbed acetylene is observed with the 260 K anneal. In contrast, the form of acetylene with peaks at 3195 and 1364 cm^{-1} desorbs after annealing to 210 K under UHV conditions, indicating that this form of acetylene is stabilized by the presence of H_2(g). After annealing to 300 K, only ethylidyne with peaks at 1129, 1338, 2796, and 2882 cm^{-1}, assigned to ν(CC), $\delta_s(CH_3)$, 2 × $\delta_{as}(CH_3)$, and $\nu_s(CH_3)$, are visible in the spectrum.

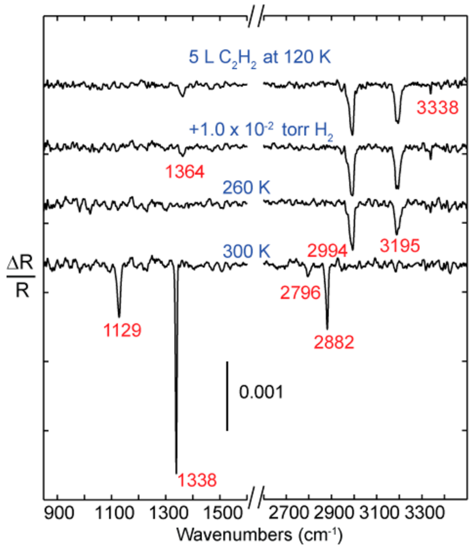


Figure 2. Five langmuirs of C_2H_2 adsorbed onto Pt(111) at 120 K; hydrogen (1.0 × 10^{-2} Torr) was then added, and the crystal was annealed at 260 and 300 K.

II. Hydrogenation of C_2H_2 at Ambient Pressure of C_2H_2 and H_2 at 300−370 K. Figure 3 shows three sets of

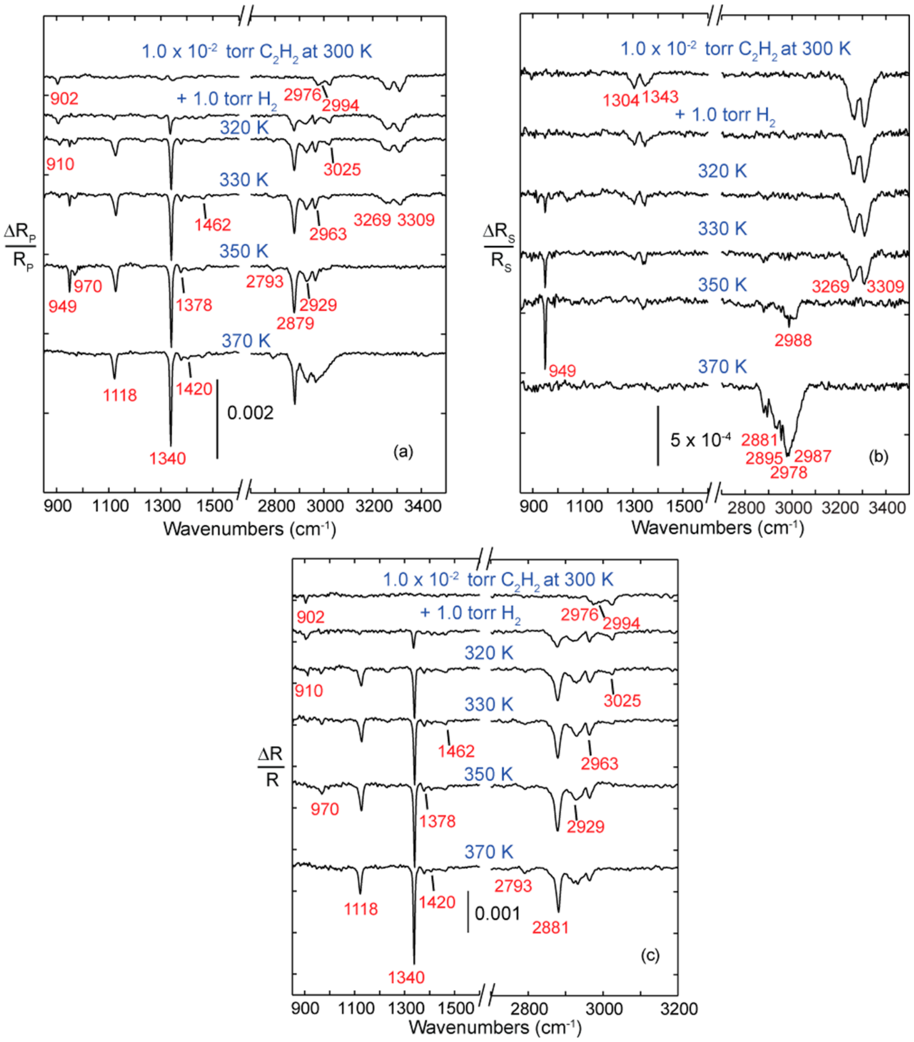


Figure 3. p-Polarized (a), s-polarized (gas phase species) (b), and the s- subtracted from the p-polarized spectra (c) for 1.0×10^{-2} Torr of C_2H_2 leaked into the cell at 300 K. 1.0 Torr of H_2 was then added, and the crystal was annealed at 320, 330, 350, and 370 K.

results for the hydrogenation of acetylene. With the crystal at 300 K, 1.0×10^{-2} Torr of $C_2H_2(g)$ was admitted to the cell, and the topmost spectra were obtained. This was then followed by adding 1.0 Torr of H_2 with the surface still at 300 K. With both gases remaining in the cell, the surface was then annealed to the indicated temperatures. The spectra in Figure 3a were obtained with p-polarized light such that both surface and gas phase peaks are observed, whereas the spectra in Figure 3b were obtained with s-polarized light so that only gas phase peaks appear. The spectra in Figure 3c are the difference between the spectra of panels a and b, showing that all gas phase peaks are subtracted, revealing only peaks due to species on the surface.

Peaks due to three different gas-phase species are evident in Figure 3b. After adding acetylene to the cell, peaks due to $C_2H_2(g)$ appear at 1305 and 1343 cm^{-1} assigned to the P- and R-rotational branches of a combination band of the symmetric and asymmetric bending modes, whereas the peaks at 3269 and 3309 cm^{-1} are the P and R branches of the asymmetric C−H stretch fundamental.[22] The $C_2H_2(g)$ peaks are unaffected by the addition of $H_2(g)$ to the cell at 300 K and are visible up to an annealing temperature of 330 K; however, they disappear after annealing at 350 K, indicating that all the acetylene has been hydrogenated by this temperature. At 320 K, a gas phase peak at 949 cm^{-1} first appears and reaches its maximum intensity for a 350 K anneal, but then is completely absent after annealing at 370 K. This peak is assigned to the $\rho_w(CH_2)$ mode of ethylene, which has B_{1u} symmetry for the D_{2h} point group.[23] The B_{3u} CH stretch of $C_2H_4(g)$ appears at 2988 cm^{-1}. For the 370 K spectrum, no peaks due to $C_2H_2(g)$ or $C_2H_4(g)$ are present, and a series of partially resolved peaks in the C−H stretch region between 2881 and 2987 cm^{-1} are due to gas phase ethane.[23] By detecting only gas phase species, the s-polarized spectra of Figure 3b clearly reveal that acetylene is first hydrogenated to ethylene, and then the ethylene is hydrogenated to ethane. The temperature onset for the appearance of the gas phase hydrogenation products revealed by the spectra of Figure 3b can be correlated with the spectra of the surface species in Figure 3c.

Only weak peaks at 902, 2976, and 3025 are observed after 1.0×10^{-2} Torr of acetylene is added to the IR cell with the surface at 300 K. The presence of some di-σ/π acetylene is evident by the unresolved intensity at 2994 cm^{-1}. When $H_2(g)$ is added to the cell, the intensity at 2994 cm^{-1} disappears and ethylidyne peaks at 1340 and 2879 cm^{-1} first become visible, and then as the temperature increases, the weaker ethylidyne peaks at 1118 and 2793 cm^{-1} are also observable. The intensities of the ethylidyne peaks reach their maximum for the

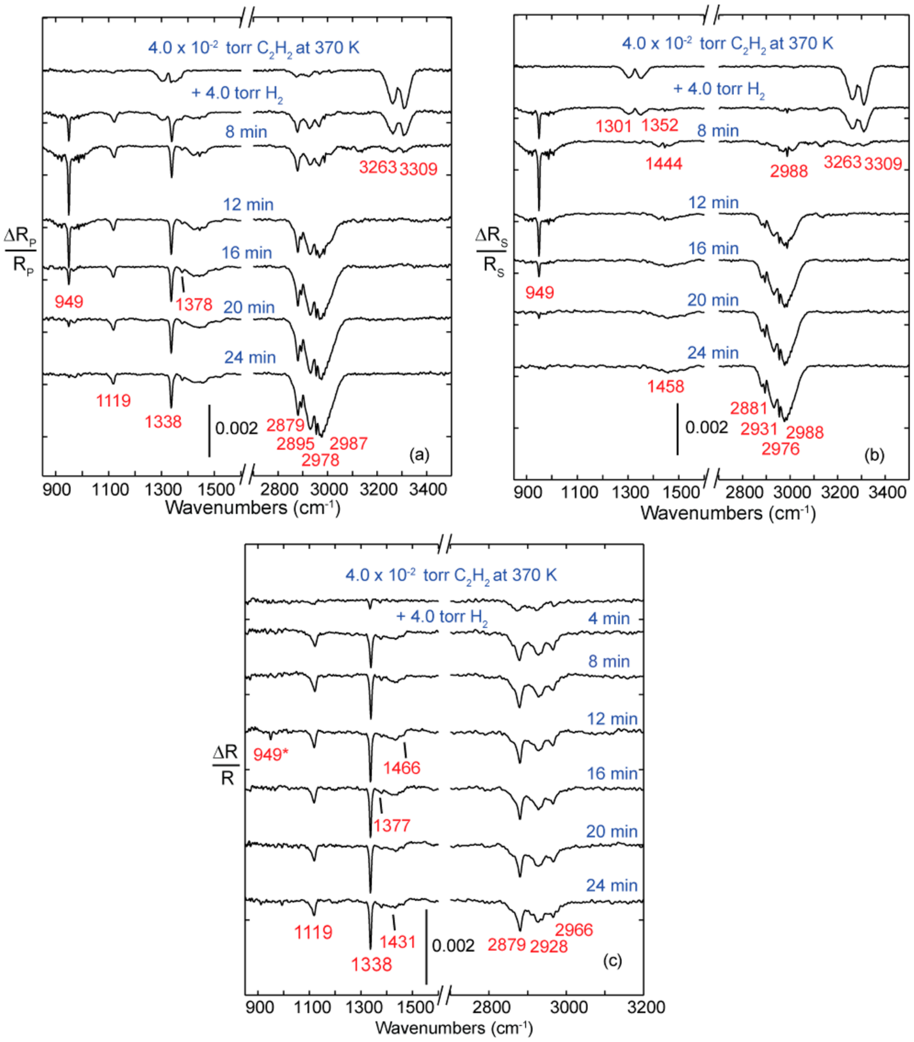


Figure 4. p-Polarized (a), s-polarized (gas phase species) (b), and the s- subtracted from p-polarized spectra (c) for 4.0 × 10^{-2} Torr of C_2H_2 leaked into the cell at 370 K. 4.0 Torr of H_2 was then added, and consecutive scans were acquired (1024 scans/spectrum, ∼4 min/spectrum).

350 K anneal and then decrease somewhat after annealing to 370 K. In addition to the prominent peaks due to ethylidyne, there are a number of very weak peaks that can be due to several possible C_2H_x species, including vinylidene (CCH_2), vinyl ($CHCH_2$), ethyldidene ($CHCH_3$), ethylene (both di-σ- and π-bonded), ethyl (CH_2CH_3), and ethynyl (CCH). The simplest pathway from adsorbed acetylene to gas phase ethane would involve the sequential addition of hydrogen to from vinyl, ethylene, ethylidene, and ethyl intermediates: $C_2H_2 \rightarrow CHCH_2 \rightarrow C_2H_4 \rightarrow CHCH_3 \rightarrow CH_2CH_3$. The spectroscopic and other evidence for and against one or more of these species are discussed below.

The most notable feature of the results in Figure 3 is the strong contrast between the abrupt changes in the gas phase species as the temperature is raised, as seen in Figure 3b, and the very modest changes in the surface species as revealed in Figure 3c. For example, when the surface is heated from 330 to 350 K, all of the $C_2H_2(g)$ disappears and is accompanied by an increase in the amount of $C_2H_4(g)$, and similarly, when the temperature is increased from 350 to 370 K, all of the $C_2H_4(g)$ is hydrogenated to $C_2H_6(g)$. During these hydrogenation reactions, the ethylidyne coverage remains high, reinforcing earlier findings that it is a spectator species in acetylene and ethylene hydrogenation. Although the ethylidyne coverage remains high during the hydrogenation reactions, the weak peaks due to other species remain low for all annealing temperatures. An assumption in annealing experiments is that intermediates present at elevated temperatures where a particular reaction occurs will remain on the surface after the temperature is lowered. An alternative is to obtain spectra as a function of time while holding the temperature constant where a reaction occurs.

The spectra in Figure 4 were obtained after first adding 4.0 × 10^{-2} Torr of $C_2H_2(g)$ to the cell, recording the topmost spectrum, adding 4.0 Torr of $H_2(g)$, and then taking spectra versus time, all with the sample temperature held constant at 370 K. The results from Figure 3 imply that complete hydrogenation of acetylene to ethane can occur at this temperature. As for Figure 3, Figure 4 shows results for p- and s-polarized spectra (a and b) and their difference (c). The spectra of the gas phase species in Figure 4b clearly reveal the stepwise hydrogenation of acetylene to ethylene to ethane. From 8 to 24 min, the spectra indicate that the ethylidyne coverage is roughly constant. At this temperature, peaks due to species other than ethylidyne are larger relative to the ethylidyne peaks, especially in the C−H stretch region, where peaks centered at 2928 and 2966 cm^{-1} are seen. Because the results in Figure 4 were obtained at 370 K, the peaks are all

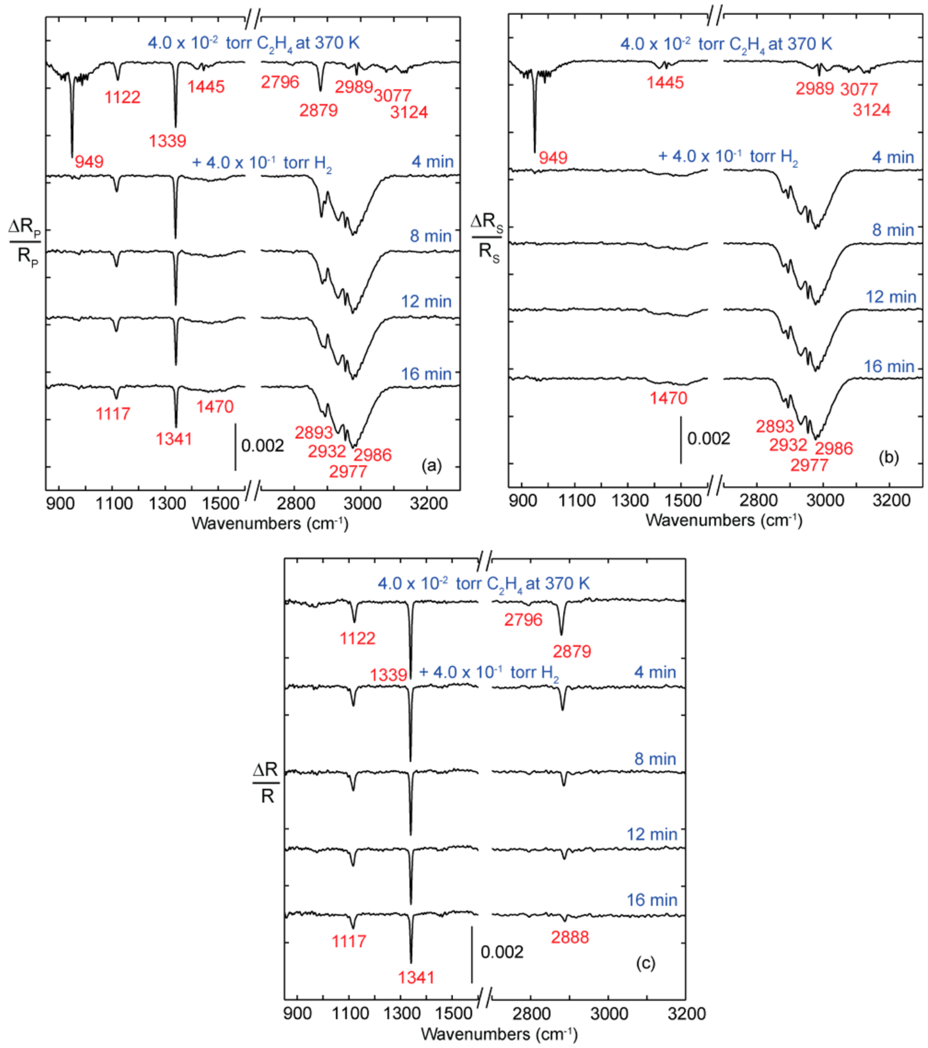


Figure 5. p-Polarized (a), s-polarized (gas phase species) (b), and the s- subtracted from p-polarized spectra (c) for 4.0×10^{-2} Torr of C_2H_4 leaked into the cell at 370 K. 4.0×10^{-1} Torr of H_2 was then added, and consecutive scans were acquired (1024 scans/spectrum, ~4 min/spectrum).

broader than for the annealing experiments of Figure 3 where the spectra were all obtained at 300 K. In the lower wavenumber range, a distinct peak at 1377 cm^{-1} is observable, but only a broad, unresolved structure is seen from about 1400 to 1470 cm^{-1}. The peak at 949 cm^{-1} marked with an asterisk is attributed to gas phase ethylene that was not fully canceled in the subtraction of the s-polarized spectra from the p-polarized spectra.

Because gas phase ethylene is observed in the course of hydrogenation of acetylene, it is useful to compare the acetylene results with those obtained starting with ethylene. Figure 5 shows results analogous to those of Figure 4, which were obtained by adding 4.0×10^{-2} Torr of $C_2H_4(g)$ to the cell, recording the topmost spectrum, and then adding 0.40 Torr of $H_2(g)$ and recording spectra at 4 min intervals with the Pt crystal at 370 K. The gas phase ethylene peaks are labeled at 949, 1445, 2989, 3077, and 3124 cm^{-1}. The first three vibrational modes have symmetries such that the oscillating dipole moment is parallel to the C=C axis, yielding a prominent Q branch in the rotational fine structure, whereas the last two peaks are P and R branches of a vibrational mode with oscillating dipole moment perpendicular to the C=C axis. Upon addition of $H_2(g)$, the gas phase ethylene peaks are replaced by those of ethane, and there is essentially no change with time of the gas phase species.

The spectra of the surface species are again dominated by ethylidyne. The ethylidyne coverage before and 4 min after adding $H_2(g)$ is unchanged, even as all the gas phase ethylene is hydrogenated to ethane. Between 4 and 16 min, the ethylidyne coverage decreases by 30%, indicating a slow hydrogenation pathway. Slight shifts in the ethylidyne peak positions accompany this change in coverage. Separate control experiments verified that there is no decrease in the ethylidyne coverage at 370 K in the absence of $H_2(g)$. The hydrogenation of the surface ethylidyne is not accompanied by any detectable change in the amount of $C_2H_6(g)$, as indicated by the spectra in Figure 5b. Once again, this demonstrates that ethylidyne is mainly a spectator species rather than an intermediate in the hydrogenation reaction.

DISCUSSION

A principal goal of in situ spectroscopic studies of surface-catalyzed reactions is to identify the molecular species present on the surface during the reaction. The presumption is that the detected surface species are reaction intermediates and that their spectroscopic identification will thus establish the reaction mechanism. However, the results presented here are in accord with previous studies with in situ spectroscopy that reveal that the spectra are often dominated by spectator species. This is most clear in our results for ethylene hydrogenation at 370 K, where the conversion of C_2H_4(g) to C_2H_6(g) occurs over an ethylidyne-covered surface with no other surface species detected. This was established earlier by Cremer et al.[24] using sum frequency generation (SFG) and by Ohtani et al.[20] using polarization-dependent RAIRS. These spectroscopic studies confirmed even earlier work showing that ethylidyne was not an intermediate in ethylene hydrogenation over Pt(111).[25] In contrast to our work in which ethylidyne is the only surface species detected under hydrogenation conditions, di-σ- and π-bonded ethylene were also detected by SFG, but at a lower surface temperature of 295 K.[24] Ohtani et al.[20] detected π-bonded ethylene at a surface temperature of 150 K at an ethylene pressure of 0.98 Torr, but only in the absence of H_2(g), and they observed di-σ-ethylene at temperatures up to 320 K in the presence of 0.98 Torr of C_2H_4(g) and 4.9 Torr of H_2(g). Earlier RAIRS results by Kubota et al. had shown that π-bonded ethylene was present on the Pt(111) surface at a temperature of 112 K in an ambient pressure of C_2H_4(g).[26−28] Cremer et al.[24] concluded that π-bonded, rather than di-σ-bonded, ethylene leads to ethane formation by way of an ethyl intermediate. Frei and co-workers also detected an ethyl intermediate in ethylene hydrogenation over a Pt/Al_2O_3 catalyst.[29,30] Our results show that ethylene hydrogenation can take place under conditions where the coverages of these intermediates are too low to be detected even with relatively high sensitivity. Because the higher temperature we used is more representative of the conditions used in practical hydrogenation catalysis, our results reveal some of the subtleties of operando studies with surface vibrational spectroscopy.

In contrast to our spectra of ethylene hydrogenation, for acetylene hydrogenation, we observe other surface species in addition to ethylidyne. The challenge then is to identify these species and to decide if they are merely spectators or intermediates in the formation of ethylidyne or in the hydrogenation of acetylene. As shown in Figure 3, admitting 1.0×10^{-2} Torr of C_2H_2(g) to the cell at 300 K leads to distinct peaks at 3025 and 2976 cm^{-1}, with some intensity at 2994 cm^{-1}. A possible peak a 902 cm^{-1} is also seen. Previous experiments performed by annealing a Pt(111) surface covered with acetylene adsorbed at low temperature to 300 K left some adsorbed acetylene on the surface while also generating a new set of peaks, some of which were attributed to vinyl.[5] This could occur by a simple disproportionation reaction, 2HCCH → $CHCH_2$ + CCH, suggesting that vinyl formation should be accompanied by ethynyl. At the same time, isomerization of HCCH to the more stable vinylidene species, CCH_2, could also occur, as has been found on the Pd(111) surface.[31,32] The formation of multiple C_2H_x species upon annealing an acetylene-covered surface to 300 K is revealed by the multiple peaks observed with surface vibrational spectroscopy and by scanning tunneling microscopy,[33] where individual molecules are resolved and are clearly of several different types. On the basis of this prior work, we assign the peak at 2976 to vinyl, the peak at 3025 to ethynyl, and the peak at 2994 cm^{-1} to di-σ/π-bonded acetylene. The 902 cm^{-1} peak could be due to the CH_2 rocking mode of vinyl or vinylidene, although the calculated values are quite a bit higher but also sensitive to coverage.

When hydrogen is added with the crystal at 300 K, there are no changes to the gas phase spectrum, indicating that no hydrogenation of C_2H_2(g) to C_2H_4(g) occurs, but ethylidyne appears on the surface, as indicated by the peaks at 2881 and 1340 cm^{-1}. Peaks due to one or more other species are observed, as well, at 2963 and 2929 cm^{-1}. The former is most likely due to ethylidene, but the latter is a poor match to di-σ-bonded ethylene, which has been observed at values from 2904 to 2924 cm^{-1} in previous studies.[18,20,26−28] Gas phase ethylene first appears at 320 K and is most abundant at 350 K, but by 370 K, it is completely hydrogenated to C_2H_6(g). The only change in the surface species that correlates with the appearance and disappearance of C_2H_4(g) is the weak peak at 970 cm^{-1}. For π-bonded ethylene, the only peak of sufficient intensity is the CH_2 wagging mode, which has been observed with RAIRS on Pt(111) at 954 cm^{-1} in the presence of 0.98 Torr of ethylene[20] and at 975 cm^{-1} in UHV in the presence of coadsorbed nitrogen atoms.[34] For π-bonded ethylene on Pd(111), the corresponding peak is observed at 1100 cm^{-1} on the clean surface and at 933 cm^{-1} for the hydrogen-covered surface.[35] Although the annealing temperature results of Figure 3 therefore suggest that π-bonded ethylene is the intermediate in the conversion of ethylene to ethane, the coverage of π-bonded ethylene is too low to observe in the time-dependent spectra of Figure 4 obtained at 370 K. The most remarkable finding from Figure 4 is the complete transformation of the gas phase composition from C_2H_2(g) to C_2H_4(g) to C_2H_6(g), with almost no change in the surface composition, which is dominated by ethylidyne, with smaller amounts of two species that we tentatively identify as ethylidene and di-σ-ethylene.

The peak that we observe at 2928 cm^{-1} is only slightly higher in frequency than peaks assigned to di-σ-ethylene observed in the range of 2904−2924 cm^{-1} in previous studies.[18,20,26−28] In a recent DFT study, the $\nu_s(CH_2)$ mode of di-σ-ethylene was calculated to be at 2913 cm^{-1} and to be by far the most intense in the RAIR spectrum of this species. It is therefore reasonable to assign the 2928 cm^{-1} peak observed here to di-σ-ethylene, although more definitive identification of a polyatomic adsorbate is possible when multiple peaks are observed, as in the case of ethylidyne or even for higher coverages of di-σ-ethylene.[18]

There are compelling arguments both for and against assigning the peaks observed here at 1379, 1462, and 2963 cm^{-1} to ethylidene. In the organometallic coordination compound, $(\mu_2\text{-CHCH}_3)Os_2(CO)_8$, 10 peaks were observed and assigned to modes of ethylidene, including ones at 1369, 1447, and 2950 cm^{-1} assigned to $\delta_s(CH_3)$, $\delta_{as}(CH_3)$, and $\nu_{as}(CH_3)$, respectively.[36] Only peaks at 2950 and 1030 cm^{-1} for the complex are listed as having strong intensity.[36] A similar set of three peaks that we observe here and tentatively assign to ethylidene have also been observed on Pt(111) at 1387, 1444, and 2960 cm^{-1} in the course of ethylene conversion to ethylidyne;[37] at 1391, 1444, and 2964 cm^{-1} in the conversion of acetylene to ethylidyne;[5] and most recently at 1393, 1443, and 2958 cm^{-1} in the conversion of vinyl iodide to ethylidyne.[38] The similarity in frequencies and relative intensities of these three peaks indicates that they are due to a common intermediate, and on the basis of their similarity to the organometallic complex, that this species is ethylidene.

Newell et al. presented RAIR spectra for ethyl deposited onto Pt(111) through exposure to supersonic molecular beams of ethane and its subsequent conversion to ethylidyne by way of an intermediate species that yielded clear and distinct peaks at 2980, 2917, 1255, and 1010 cm^{-1}, which they assigned to modes of ethylidene.[39] Of particular note is that the strongest peak shown in their spectra is the one at 1255 cm^{-1}, but there are no features in this region in our spectra.

Other evidence that does not favor our identification of ethylidene comes from the recent work of Zhao and Greeley, who presented simulated spectra for various C_2H_x species based on frequencies and intensities from DFT calculations.[12] For ethylidene, their theoretical RAIRS spectrum is qualitatively different from both our spectra and the spectra of Newell et al.[39] The simulated ethylidene spectrum shows the C−H stretch region dominated by an intense peak at 2864 cm^{-1} due to $\nu_s(CH_3)$, with a much weaker peak at 3046 cm^{-1} due to $\nu_{as}(CH_3)$.[12] Furthermore, they predict three peaks of comparable intensity at 1403, 1245, and 1048 cm^{-1}, with two weaker peaks at 1326 and 935 cm^{-1}. On the basis of this complete mismatch between theory and experiment, they argue that the experimental spectra are better assigned to vinylidene, which has a much simpler simulated spectrum dominated by an intense $\delta(CH_2)$ peak at 1415 cm^{-1}, and weaker peaks at 2960 and 900 cm^{-1}. In contrast to the experimental spectra, the simulated vinylidene spectrum features only a single peak in the region from 1300 to 1450 cm^{-1} and therefore fails to account for our experimental observation of two peaks in this region, assuming the peaks in the experimental spectra are due to a single species. The ability of the calculations to simulate RAIRS spectra accurately is suggested by their results for ethylidyne, for which the frequencies and relative intensities agree quite well with experimental spectra.

A separate argument against ethylidene is that the activation energy for its dehydrogenation to ethylidyne is so low that it is not predicted to be stable enough to be detected spectroscopically.[6] Although a good match between experimental and simulated RAIR spectra would constitute fairly definitive evidence for a particular surface species, this has yet to be achieved for either ethylidene or vinylidene on Pt(111). Therefore, although there is some evidence that favors assigning the peaks that we observe here at 1379, 1462, and 2963 cm^{-1} to ethylidene, this assignment is not supported by DFT calculations[12] or by the experimental results of Newell et al.,[39] possibly indicating that the experimental spectra are due to a mixture of at least two species, one of which may be vinylidene. Table 1 summarizes what we believe to be the most likely assignments of the RAIRS peaks that we observe.

Table 1. Vibrational Mode Assignments and Peak Positions[a] for Species Adsorbed on Pt(111)

vibrational modes	species	peak (cm^{-1})
$\nu(CH)$	acetylene	2994
$\omega(CH_2)$	μ_3-η^2-vinylidene	902, 910
$\nu_{as}(CH_2)$	μ_3-η^2vinylidene	2976
$\nu(CH)$	μ_3-η^2-ethynyl	3025
$\nu(CC)$	ethylidyne	1118
$\delta_s(CH_3)$	ethylidyne	1340
$2 \times \delta_s(CH_3)$	ethylidyne	2798
$\nu_s(CH_3)$	ethylidyne	2879
$\delta_s(CH_2)$	di-σ-ethylene	1420
$\nu_s(CH_2)$	di-σ-ethylene	2929
$\delta_s(CH_3)$	ethylidene	1378
$\delta_{as}(CH_3)$	ethylidene	1462
$\nu_{as}(CH_3)$	ethylidene	2963
$\omega(CH_2)$	π-ethylene	970

[a] Based on Figure 3.

CONCLUSIONS

The results presented here in which surface species are detected during the catalyzed conversion of gas phase acetylene to ethane by way of a gas phase ethylene intermediate indicate that the surface spectra are dominated by spectator species to the hydrogenation reaction. Although previous work had clearly revealed that hydrogenation of ethylene readily proceeds over an ethylidyne-covered surface, the results presented here indicate that di-σ-bonded ethylene and ethylidene are also spectator species for acetylene and ethylene hydrogenation. This implies that although operando spectroscopy of surfaces can readily detect surfaces species during reaction, these species are less likely to be intermediates, which may not build up to detectable coverages during reaction conditions. The determination of intermediates will likely continue to be inferred from indirect observations rather than via direct spectroscopic detection.

AUTHOR INFORMATION

Corresponding Author

*E-mail: mtrenary@uic.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation (CHE-1464816).

REFERENCES

(1) Jones, C. W.; Tao, F.; Garland, M. V. *ACS Catal.* **2012**, *2*, 2444−2445.

(2) Ibach, H.; Lehwald, S. *J. Vac. Sci. Technol.* **1978**, *15*, 407−415.

(3) Avery, N. R. *Langmuir* **1988**, *4*, 445−448.

(4) Cremer, P. S.; Su, X.; Shen, Y. R.; Somorjai, G. A. *J. Phys. Chem. B* **1997**, *101*, 6474−6478.

(5) Deng, R. P.; Jones, J.; Trenary, M. *J. Phys. Chem. C* **2007**, *111*, 1459−1466.

(6) Zhao, Z.-J.; Moskaleva, L. V.; Aleksandrov, H. A.; Basaran, D.; Rösch, N. *J. Phys. Chem. C* **2010**, *114*, 12190−12201.

(7) Lu, X.; Liu, L.; Li, Y.; Guo, W.; Zhao, L.; Shan, H. *Phys. Chem. Chem. Phys.* **2012**, *14*, 5642−5650.

(8) Kua, J.; Goddard, W. A. *J. Phys. Chem. B* **1998**, *102*, 9492−9500.

(9) Jacob, T.; Goddard, W. A. *J. Phys. Chem. B* **2005**, *109*, 297−311.

(10) Aleksandrov, H. A.; Moskaleva, L. V.; Zhao, Z.-J.; Basaran, D.; Chen, Z.-X.; Mei, D.; Rösch, N. *J. Catal.* **2012**, *285*, 187−195.

(11) Podkolzin, S. G.; Alcalá, R.; Dumesic, J. A. *J. Mol. Catal. A: Chem.* **2004**, *218*, 217−227.

(12) Zhao, Z.-J.; Greeley, J. P. *Surf. Sci.* **2015**.

(13) Tilekaratne, A.; Simonovis, J. P.; López Fagúndez, M. F.; Ebrahimi, M.; Zaera, F. *ACS Catal.* **2012**, *2*, 2259−2268.

(14) Rupprechter, G. *Adv. Catal.* **2007**, *51*, 133−263.

(15) Schennach, R.; Hirschmugl, C.; Gilli, E.; Tysoe, W. T. *Appl. Spectrosc.* **2009**, *63*, 369−372.

(16) Krooswyk, J. D.; Yin, J.; Asunskis, A. L.; Hu, X.; Trenary, M. *Chem. Phys. Lett.* **2014**, *593*, 204−208.

(17) Jentz, D.; Celio, H.; Mills, P.; Trenary, M. *Surf. Sci.* **1995**, *341*, 1−8.

(18) Fan, J.; Trenary, M. *Langmuir* **1994**, *10*, 3649−3657.

(19) Ohtani, T.; Kubota, J.; Kondo, J. N.; Hirose, C.; Domen, K. *Surf. Sci.* **1998**, *415*, L983−L987.

(20) Ohtani, T.; Kubota, J.; Kondo, J. N.; Hirose, C.; Domen, K. *J. Phys. Chem. B* **1999**, *103*, 4562−4565.

(21) Godbey, D.; Zaera, F.; Yeates, R.; Somorjai, G. A. *Surf. Sci.* **1986**, *167*, 150−166.

(22) Wiggins, T. A.; Plyler, E. K.; Tidwell, E. D. *J. Opt. Soc. Am.* **1961**, *51*, 1219−1225.

(23) Herzberg, G. *Infrared and Raman Spectra*. Van Nostrand Reinhold Company: New York, 1945.

(24) Cremer, P. S.; Su, X.; Shen, Y. R.; Somorjai, G. A. *J. Am. Chem. Soc.* **1996**, *118*, 2942−2949.

(25) Zaera, F.; Somorjai, G. A. *J. Am. Chem. Soc.* **1984**, *106*, 2288−2293.

(26) Kubota, J.; Ichihara, S.; Kondo, J. N.; Domen, K.; Hirose, C. *Surf. Sci.* **1996**, *357−358*, 634−638.

(27) Kubota, J.; Ichihara, S.; Kondo, J. N.; Domen, K.; Hirose, C. *Langmuir* **1996**, *12*, 1926−1927.

(28) Kubota, J.; Ohtani, T.; Kondo, J. N.; Hirose, C.; Domen, K. *Appl. Surf. Sci.* **1997**, *121−122*, 548−551.

(29) Ko, M. K.; Frei, H. *J. Phys. Chem. B* **2004**, *108*, 1805−1808.

(30) Wasylenko, W.; Frei, H. *J. Phys. Chem. B* **2005**, *109*, 16873−16878.

(31) Ormerod, R. M.; Lambert, R. M.; Hoffmann, H.; Zaera, F.; Wang, L. P.; Bennett, D. W.; Tysoe, W. T. *J. Phys. Chem.* **1994**, *98*, 2134−2138.

(32) Azad, S.; Kaltchev, M.; Stacchiola, D.; Wu, G.; Tysoe, W. T. *J. Phys. Chem. B* **2000**, *104*, 3107−3115.

(33) Okada, T.; Kim, Y.; Trenary, M.; Kawai, M. *J. Phys. Chem. C* **2012**, *116*, 18372−18381.

(34) Yin, J.; Trenary, M.; Meyer, R. *J. Phys. Chem. C* **2010**, *114*, 12230−12233.

(35) Stacchiola, D.; Azad, S.; Burkholder, L.; Tysoe, W. T. *J. Phys. Chem. B* **2001**, *105*, 11233−11239.

(36) Anson, C. E.; Sheppard, N.; Powell, D. B.; Norton, J. R.; Fischer, W.; Keiter, R. L.; Johnson, B. F. G.; Lewis, J.; Bhattacharrya, A. K. *J. Am. Chem. Soc.* **1994**, *116*, 3058−3062.

(37) Deng, R. P.; Herceg, E.; Trenary, M. *Surf. Sci.* **2004**, *560*, L195−L201.

(38) Ren, Y.; Waluyo, I.; Yin, J.; Trenary, M. *Surf. Sci.* **2015**, *637−638*, 29−34.

(39) Newell, H. E.; McCoustra, M. R. S.; Chesters, M. A.; De La Cruz, C. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 3695−3698.