The Journal of Chemical Physics

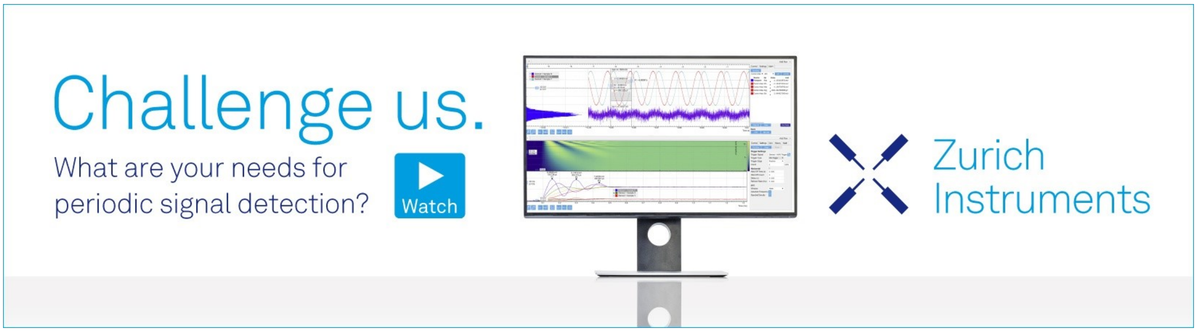
The influence of palladium on the hydrogenation of acetylene on Ag(111)

Cite as: J. Chem. Phys. **154**, 184701 (2021); https://doi.org/10.1063/5.0050587
Submitted: 16 March 2021 . Accepted: 20 April 2021 . Published Online: 10 May 2021

David L. Molina, Mark Muir, Mohammed K. Abdel-Rahman, and Michael Trenary

COLLECTIONS

Paper published as part of the special topic on Heterogeneous Single-Atom Catalysis



AIP Publishing

J. Chem. Phys. **154**, 184701 (2021); https://doi.org/10.1063/5.0050587 **154**, 184701

The Journal of Chemical Physics ARTICLE scitation.org/journal/jcp

The influence of palladium on the hydrogenation of acetylene on Ag(111)

Cite as: J. Chem. Phys. 154, 184701 (2021); doi: 10.1063/5.0050587
Submitted: 16 March 2021 • Accepted: 20 April 2021 •
Published Online: 10 May 2021

David L. Molina, Mark Muir, Mohammed K. Abdel-Rahman, and Michael Trenary[a)]

AFFILIATIONS

Department of Chemistry, University of Illinois at Chicago, 845 W Taylor St., Chicago, Illinois 60607, USA

Note: This paper is part of the JCP Special Topic on Heterogeneous Single-Atom Catalysis.
[a)]**Author to whom correspondence should be addressed:** mtrenary@uic.edu

ABSTRACT

We have used reflection absorption infrared spectroscopy (RAIRS) and temperature programmed reaction (TPR) to study the selective hydrogenation of acetylene on both a clean Ag(111) surface and on a Pd/Ag(111) single-atom-alloy surface. The partial hydrogenation of acetylene to ethylene is an important catalytic process that is often carried out using PdAg alloys. It is challenging to study the reaction with ultrahigh vacuum techniques because H_2 does not dissociate on Ag(111), and while H_2 will dissociate at Pd sites, H-atom spillover from Pd to Ag sites does not generally occur. We bypassed the H_2 dissociation step by exposing the surfaces to atomic hydrogen generated by the hot filament of an ion gauge. We find that hydrogen atoms react with acetylene to produce adsorbed ethylene at 85 K, the lowest temperature studied. This is revealed by the appearance of a RAIRS peak at 950 cm^{-1} due to the out-of-plane wagging mode of adsorbed ethylene when acetylene is exposed to a surface on which H atoms are pre-adsorbed. The formation of both ethylene and ethane are detected with TPR, but no acetylene coupling products, such as benzene, were found. From quantitative analysis of the TPR results, the percent conversion and selectivities to ethylene and ethane were determined. Low coverages of Pd enhance the conversion but do so mainly by increasing ethane formation.

I. INTRODUCTION

The partial hydrogenation of acetylene to ethylene has been a long standing problem in heterogeneous catalysis.[1,2] Its importance stems from the need to remove small amounts of acetylene from the ethylene feedstock used in the production of polyethylene without also hydrogenating ethylene to ethane.[3] While Pd has a high activity for acetylene hydrogenation, it has a low selectivity.[4] To improve the selectivity while retaining high activity, bimetallic alloys of Pd and Ag are often used.[4–7] Studt *et al.* carried out density functional theory (DFT) calculations of the interactions of acetylene and ethylene with Pd-based bimetallic catalysts and noted that the ideal catalysts should bind acetylene strongly enough to achieve high activity but bind ethylene weakly so that once formed, it will desorb without further reaction.[8] Therefore, fundamental studies of the adsorption and hydrogenation of acetylene and ethylene on model PdAg bimetallic catalysts are needed.

A new type of catalyst known as single-atom alloys (SAAs) shows great promise for selective hydrogenation reactions.[9] In a SAA, a low concentration of a catalytically active metal is deposited onto the surface of a relatively inactive host metal. When the thermodynamics are favorable, the dopant metal substitutes into the topmost atomic layer of the host as isolated atoms. In the case of Pd deposited onto a Cu(111) surface, the isolated Pd atoms serve as sites for H_2 dissociation, producing hydrogen atoms that can spillover to Cu sites, where they are weakly bound.[10] These weakly bound H atoms can then participate in selective hydrogenation reactions. Given that PdAg alloys have already proven useful for the selective hydrogenation of acetylene to ethylene, it follows that a SAA consisting of isolated Pd atoms in a Ag(111) surface might provide an effective catalyst for the partial hydrogenation of acetylene while using a minimum amount of Pd.

Recent work has shown that hydrogen atom spillover does not occur on a Pd/Ag(111) SAA surface.[11,12] We used reflection absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD) of CO to probe low coverages of Pd on a Ag(111) surface.[11] We present RAIRS results in the supplementary material showing that when Pd is deposited at 380 K, most of the

Pd atoms are still isolated for coverages less than 2%. TPD experiments for the Pd/Ag(111) SAA after exposure to H_2 indicated that no H-atom spillover from Pd to Ag sites occurred. O'Connor *et al.* used several techniques, including scanning tunneling microscopy (STM), to investigate H_2 interaction with higher coverages of Pd on a Ag(111) surface.[12] By analogy to a Pd/Au(111) SAA where H-atom spillover was not detected,[13] they concluded that H-atom spillover was unlikely to occur for a Pd/Ag(111) SAA. Instead, they found that H-atom spillover from Pd islands to Ag sites could occur and was made thermodynamically favorable by the simultaneous occupancy of Ag and Pd sites.[12] Despite the lack of evidence for H-atom spillover from surface science experiments on the Pd/Ag(111) SAA, a supported PdAg nanoparticle catalyst was found to be effective for the selective hydrogenation of acrolein, and DFT calculations indicated that hydrogen spillover could be involved.[14] In the absence of spillover, the hydrogenation properties of a Pd/Ag(111) SAA can be studied by exposing the surface to atomic hydrogen, which bypasses the need for spillover from Pd to Ag sites. We used this approach in a recent study of acrolein hydrogenation, where we found that the small concentration of surface Pd atoms significantly influenced the reaction.[15] Here, we use a similar approach to compare the reaction of acetylene with hydrogen on Ag(111) and on a Pd/Ag(111) surface.

II. EXPERIMENTAL

The experiments were carried out in an ultrahigh vacuum (UHV) chamber with a base pressure of 1×10^{-10} Torr. The chamber is equipped with a PHI 10-155 cylindrical mirror analyzer (CMA) for Auger electron spectroscopy (AES), PHI 15-120 optics for low-energy electron diffraction (LEED), and a Hiden HAL201/3F quadrupole mass spectrometer for temperature programmed desorption (TPD) and temperature programmed reaction (TPR) studies. The UHV chamber is coupled to a Bruker IFS-66v/s Fourier transform infrared (FTIR) spectrometer. The incident and reflected IR beams enter and exit the UHV chamber through differentially pumped O-ring sealed salt windows. Pressures were measured with a Bayard–Alpert hot filament ion gauge that was also used to dissociate H_2 to provide an effective hydrogen atom source.

The mounting of the Ag(111) crystal and the homemade evaporator used to deposit Pd have been described elsewhere.[11] All deposition was done at a crystal temperature of 380 K. RAIR spectra were acquired with 1024 scans at 4 cm^{-1} resolution, unless otherwise stated. A linear heating rate of 1 K/s was used for TPD and TPR experiments, which were carried out by cooling the crystal to liquid nitrogen temperature and flash annealing at 500 and 300 K for 1 min, for the Ag(111) and Pd/Ag(111) SAA surfaces, respectively. Post-deposition annealing of Pd/Ag(111) was limited to 300 K to avoid Ag diffusion to form Ag-capped Pd islands.[11,12] The surface was cleaned between experiments with Ar^+ bombardment (1 kV, 8 μA) followed by annealing to 800 K for 10 min. CO (99.99%) and hydrogen (99.999%) were purchased from Matheson Tri-Gas and Praxair, respectively, and were used without further purification. Acetylene (AA grade/99.8%) was purchased from Praxair and further purified with freeze–pump–thaw cycles. Ethylene (99.99%) was purchased from Matheson Tri-Gas and further purified with freeze–pump–thaw cycles. The ethane gas (99.999%) was purchased from Matheson Tri-Gas and used without any further purification. The palladium coverage was calculated using AES and CO-TPD peak areas from previously calibrated parameters for our system.[11]

III. RESULTS AND DISCUSSION

A. Acetylene, ethylene, and ethane on Ag(111)

As TPR and RAIRS are used to monitor the hydrogenation of acetylene to ethylene and ethane on both Ag(111) and Pd/Ag(111), it is important to establish with RAIRS and TPD the adsorption properties of each molecule. Figure 1 shows RAIRS and TPD results for

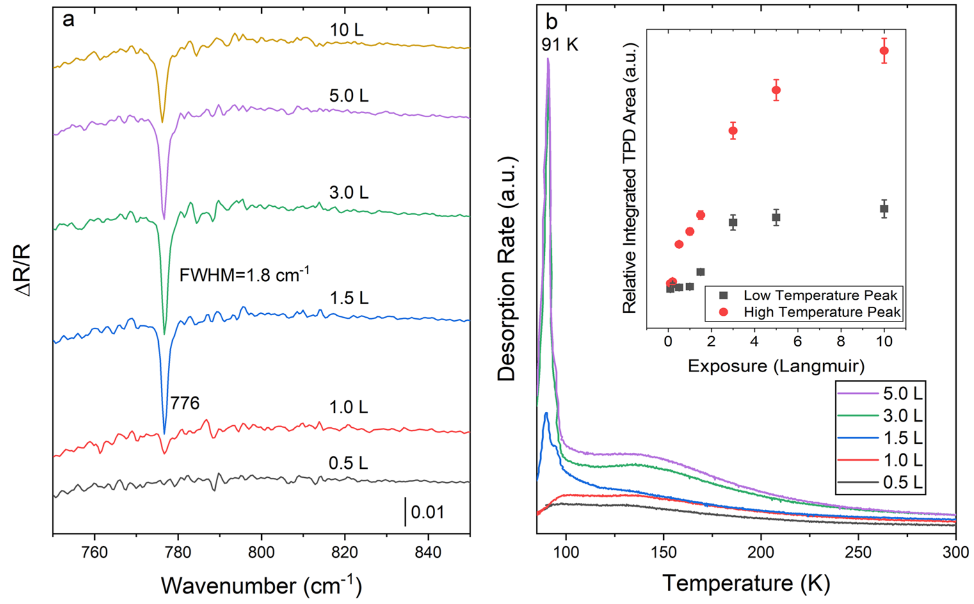


FIG. 1. (a) RAIR spectra with a resolution of 1 cm^{-1} for the indicated exposures of acetylene to Ag(111) at 85 K. The measured full width at half maximum (FWHM) of the bending mode at 776 is 1.8 cm^{-1}. (b) The corresponding TPD results of acetylene (m/z = 26). Mass-to-charge ratios of 25 and 24 were also monitored along with an m/z of 26 and confirm that the m/z = 26 results are entirely due to acetylene.

increasing acetylene exposures to the Ag(111) surface at 85 K. The TPD results reveal broad acetylene desorption over a temperature range from below 100 K to just above 200 K for the lowest exposures. For exposures of 1.5 L and above, a sharp desorption peak develops at 91 K. The inset shows a plot of the areas for the low and high temperature TPD peaks. The low temperature peak saturates after about a 3 L exposure, whereas the high temperature peak continues to grow. Similar behavior is also seen in the TPD results for ethylene and ethane. This is opposite to what is typically observed, where multilayer desorption usually occurs at a lower temperature than monolayer desorption, where the former grows without a limit after the monolayer saturates. These results imply that these molecules interact so weakly with Ag(111) that the interactions between the molecules in the condensed phase are actually stronger than the interactions with the metal surface.

The RAIR spectra in Fig. 1(a) were measured with 1 cm^{-1} resolution and show only one peak at 776 cm^{-1} corresponding to the asymmetric bending mode, which is very close to its value in solid acetylene, indicating that the molecule is not perturbed through interaction with the surface.[16] As the IR signal falls off steeply below 800 cm^{-1}, an extensive baseline correction was needed for these spectra, which caused distortion of the 776 cm^{-1} peak shape in Fig. 1(a) and in the other spectra in this region. Observation of the 776 cm^{-1} peak and the absence of other peaks indicates the acetylene bonds with its molecular axis parallel to the surface. Although the asymmetric C–H stretch should also be allowed by symmetry, it should be quite weak for a parallel orientation and was observed to be much weaker than the asymmetric bend in a HREELS study of acetylene on Ag(110).[17] The 776 cm^{-1} peak is unusually sharp with a measured full width at half maximum (FWHM) of only 1.8 cm^{-1}. A value of 1.5 cm^{-1} for the intrinsic FWHM can be estimated by assuming that the square of the measured FWHM is equal to the sum of the squares of the measured FWHM (1.8 cm^{-1}) and the instrumental resolution of 1 cm^{-1}, although this is only strictly true if the intrinsic and instrumental line shapes are Gaussian. In contrast to the relatively simple exposure dependence of the TPD peak areas, the RAIR spectra show a sudden jump in the intensity of the 776 cm^{-1} peak between 1.0 and 1.5 L, and an even lower intensity for 5.0 and 10 L. Both TPD and RAIRS show that acetylene desorbs molecularly without any coupling reactions, as was observed for acetylene on Ag(110).[17] This contrasts with the Cu(111) surface, where acetylene coupling to form benzene, 1,3-butadiene, and cyclooctatetraene is observed.[18] DFT calculations[19–21] have shown that acetylene chemisorbs to the Ag(111) hollow site, but our experimental results would support physisorption on the surface.

Figure 2 shows RAIRS and TPD results for ethylene on Ag(111). As was the case for acetylene, the TPD results with increasing exposure do not follow the usual pattern of monolayer desorption at a higher temperature followed by a lower temperature multilayer peak that does not saturate with increasing coverage. Instead, the 101 K peak in Fig. 2(b) appears along with the broad higher temperature shoulder for all exposures. In previous TPD studies of ethylene on clean Ag(111), only a single exposure was reported. Kershen *et al.* observed the low temperature peak at 93 K and higher temperature desorption up to 150 K.[22] Stacchiola *et al.* observed the higher temperature desorption in the range of 125–150 K, but did not observe the lower temperature peak.[23] The unusual TPD results in Fig. 2(b) may be related to the ethylene melting point of 104 K. The low temperature peak may correspond to the sublimation from a solid ethylene layer, with the higher temperature desorption from a liquid layer.

The RAIRS results in Fig. 2(a), obtained with 1 cm^{-1} resolution, show a single sharp peak at 949 cm^{-1} assigned to a CH_2 wagging mode. This peak is very narrow with a measured FWHM of 1.4 cm^{-1}. Because this peak is so sharp, we repeated the measurement with 0.5 and 0.25 cm^{-1} resolutions, and the results are presented in the supplementary material. For the 0.25 cm^{-1} resolution

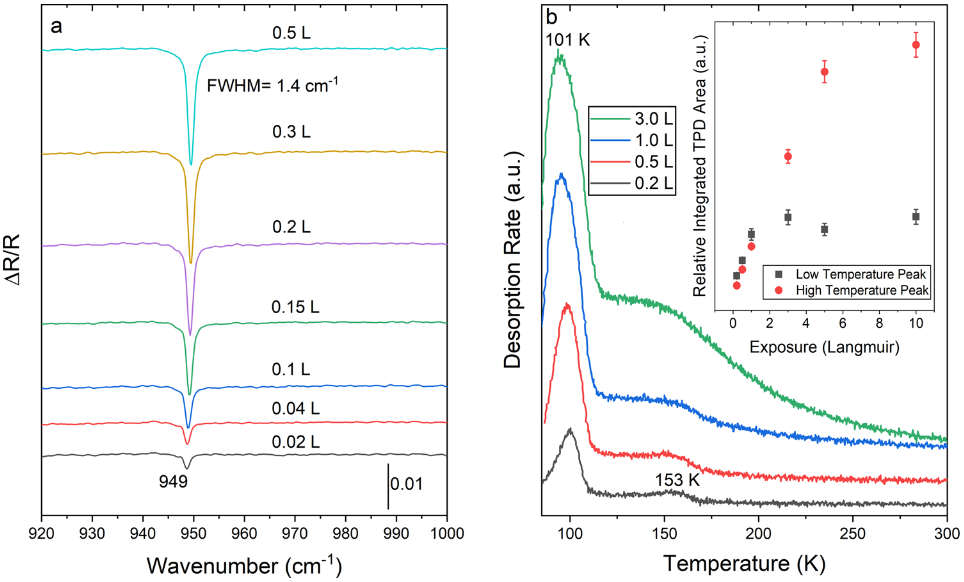


FIG. 2. (a) RAIR spectra with a resolution of 1 cm^{-1} for the indicated exposures of ethylene adsorbed on Ag(111) at 85 K. The measured FWHM for the CH_2 wag at 949 cm^{-1} is 1.4 cm^{-1}. (b) TPD results for ethylene (m/z 28) on Ag(111).

spectrum, the measured FWHM was 0.78 cm^{-1}, implying an intrinsic FWHM of 0.74 cm^{-1}. A similarly sharp wagging mode at 1006 cm^{-1} for 1,3-butadiene on Ag(111) with an intrinsic FWHM of only 0.48 cm^{-1} was reported by Hrbek *et al.*[24] This mode was observed by Osaka *et al.* to be in the range of 1002–1007 cm^{-1} in a RAIR study of 1-3-butadiene on Ag(111), but the spectra were measured with an experimental resolution of 4 cm^{-1}, so the unusual sharpness of the peak was not noted.[25] The 949 cm^{-1} peak seen in Fig. 2(a) is the only one expected for ethylene with the molecular plane parallel to the surface. This is the most intense peak in the IR spectrum of gas phase ethylene, where it is also at 949 cm^{-1}. The absence of a shift from the gas phase position of this mode is further evidence that ethylene has a very weak interaction with the Ag(111) surface. The same RAIRS result was found in the earlier studies of ethylene on Ag(111).[22,23] As was the case for the acetylene results in Fig. 1, the ethylene RAIRS peak does not increase in intensity after 1.0 L, although the ethylene coverage continues to increase with exposure as revealed by the increase in TPD peak area with exposure. Ethylene saturation of the Ag(110) surface was observed with TPD for an adsorption temperature of 105 K.[26]

Fig. 3 shows RAIRS and TPD results for ethane on Ag(111). Ethane desorbs as a sharp peak at 100 K and over the range of 120–200 K. As for acetylene and ethylene, the low temperature peak reaches a constant area, while the higher temperature desorption continues to grow with increasing ethane exposure. The RAIR spectra in Fig. 3(a) for increasing exposures to ethane at 85 K show only the C–H stretch region as no peaks were observed elsewhere. For gas phase ethane, the C–H stretches are by far the most intense in the IR spectrum.[27] The ethane RAIR spectra on Ag(111) at 85 K are similar to what were reported for ethane on Cu films at 50 K,[28] but with a red shift of 20–40 cm^{-1} for the Ag(111) surface. The results indicate weak physisorption of ethane on Ag(111).

B. Hydrogenation of acetylene on Ag(111)

In previous studies, we have shown that the filament of our ion gauge dissociates H_2(g), thus exposing the surface to atomic H.[11] The coverage of atomic hydrogen increases with H_2 exposure with the ion gauge on and reaches a saturation coverage of 0.60 ML,[29] which in our system has been found to be equivalent to a 200 L H_2 exposure with the ion gauge on.[15] This provides a way to study acetylene hydrogenation on Ag(111) by bypassing the dissociative H_2 adsorption step, which has too high a barrier to occur under our conditions. Figure 4 shows RAIR spectra after exposing the surface to H_2 with the ion gauge on followed by a 1.0 L acetylene exposure with the crystal at 85 K. The development of the peak at 950 cm^{-1}, which increases in intensity with increasing H coverage, reveals that acetylene reacts with the adsorbed H atoms to produce adsorbed ethylene at 85 K. This suggests that there is essentially no barrier for the reaction. No peaks were observed outside the spectral range shown. The upward peak at 894 cm^{-1} is likely due to the H–Ag stretch mode as this was observed with HREELS at 856 cm^{-1}.[30] The upward appearance of this peak indicates that some adsorbed H was present in the background scans and was displaced by the acetylene exposures or was consumed in the reaction to form ethylene. Although the ethylene peak also appears for a 0.5 L acetylene exposure, it was absent after exposing the H-covered surface to 3.0 L of acetylene (Fig. S1). A likely explanation for this observation is that for the higher coverage of acetylene, intermolecular repulsions between acetylene and ethylene lower the desorption temperature for ethylene so that it desorbs as soon as it forms at 85 K. Upon annealing to temperatures of 300 K and above and re-cooling to 85 K, no RAIRS peaks are observed suggesting that no other reactions accompany acetylene hydrogenation. Although it appears that the 779 cm^{-1} acetylene peak in Fig. 4 is larger than the 776 cm^{-1} acetylene peak in Fig. 1, even though both were obtained for a 1.0 L C_2H_2 exposure, a direct comparison of peak heights is not valid as the results were obtained for different

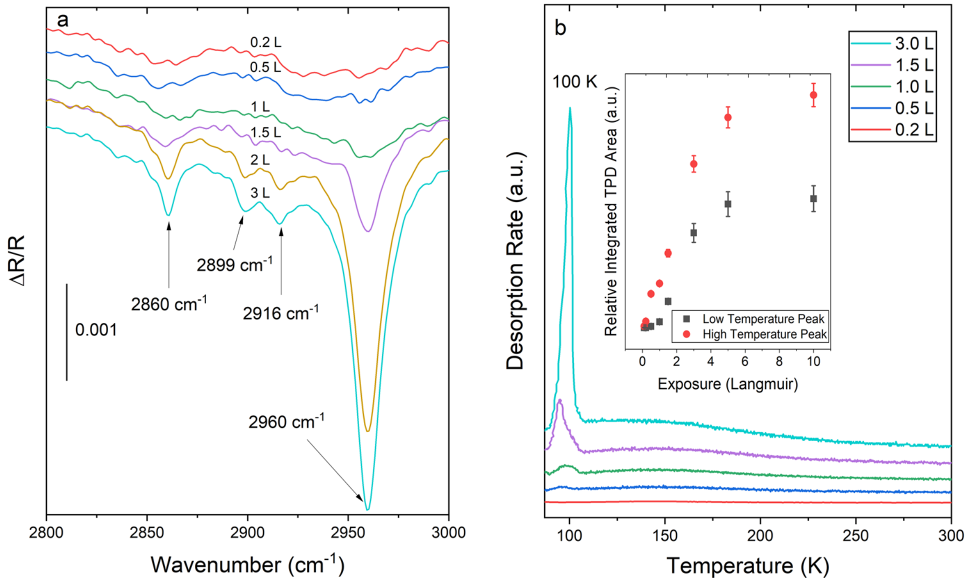


FIG. 3. (a) RAIR spectra for the indicated exposures of ethane to Ag(111) at 85 K. No peaks for ethane were observed outside the C–H stretch region. (b) TPD results for ethane (m/z = 30) on Ag(111).

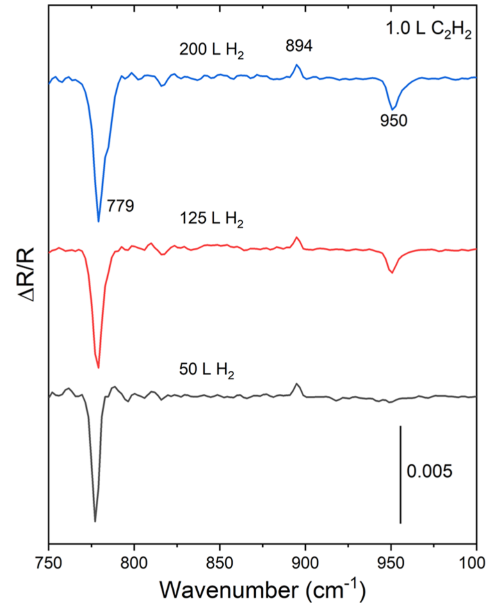


FIG. 4. RAIR spectra obtained at 85 K after exposure of 1.0 L of acetylene to Ag(111) that had previously been exposed to 50, 125, and 200 L of H_2 with the ion gauge on. The 200 L H_2 exposure yields a saturation H-atom coverage of 0.6 ML. The appearance of the peak at 949 cm^{-1} shows that acetylene reacts with the surface H atoms to form ethylene at 85 K.

resolutions (1 cm^{-1} in Fig. 1 and 4 cm^{-1} in Fig. 4). In addition, if the sticking probability is different on the hydrogen-covered and clean surfaces, then an intensity difference may simply reflect different coverages for the same exposure.

The hydrogenation of acetylene to ethylene is also demonstrated by the TPR results shown in Fig. 5, which correspond to the RAIRS results in Fig. 4. These and the other TPR results were deconvoluted with a method described previously,[15] and m/z values were further corrected for ion fragmentation.[31] These procedures are described in the supplementary material. The m/z = 28 results show that the ethylene produced by hydrogenation desorbs at 107 and 161 K. These are similar temperatures to the two ethylene desorption peaks seen in Fig. 2. The integrated area of the ethylene peak in Fig. 5(a) for 1.0 L of acetylene and 200 L of pre-dosed H_2 is only 10% of the integrated area for the 1.0 L ethylene exposure of Fig. 2(b). As the RAIRS results in Fig. 4 show that ethylene is formed upon acetylene exposure to the H-covered surface at 85 K, the TPD results in Fig. 5(a) indicate that ethylene formed by acetylene hydrogenation desorbs through the same channels as when ethylene is adsorbed directly.

As the results in Fig. 5(b) were obtained for 1.0 L of acetylene, the low temperature acetylene desorption peak seen in Fig. 1 for exposures of 1.5 L and above is absent in Fig. 5(b), but the broad acetylene desorption channel is still present. Some ethane is formed as indicated by the m/z = 30 peak at 173 K. Larger hydrocarbons that might result from acetylene coupling reactions do not have m/z = 30 as a major fragment, while it is both the parent peak of ethane and the third most intense one in its spectrum. As 173 K is much higher than the temperature where ethane desorbs, this peak must be surface-reaction kinetics limited. Evidently, the reaction barrier for ethylene hydrogenation to ethane is similar to the barrier for ethylene desorption by the higher temperature channel. The observation in Fig. 6(a) that the m/z = 30 peak shifts to m/z = 32 when $^{13}C_2H_2$ is used instead of $^{12}C_2H_2$ confirms ethane formation. Similarly, the shift of the m/z = 28 peaks in Fig. 5(a) to the m/z = 30 peaks in Fig. 6(a) verifies that these two peaks are due to ethylene formation. To verify that ethylene formed from acetylene hydrogenation can be further hydrogenated to ethane, the results in Fig. 6(b) were obtained following the adsorption of ethylene ($^{12}C_2H_4$) on the H-adsorbed Ag(111) surface. These results show an m/z = 30 peak at 173 K due to ethane. As a control experiment,

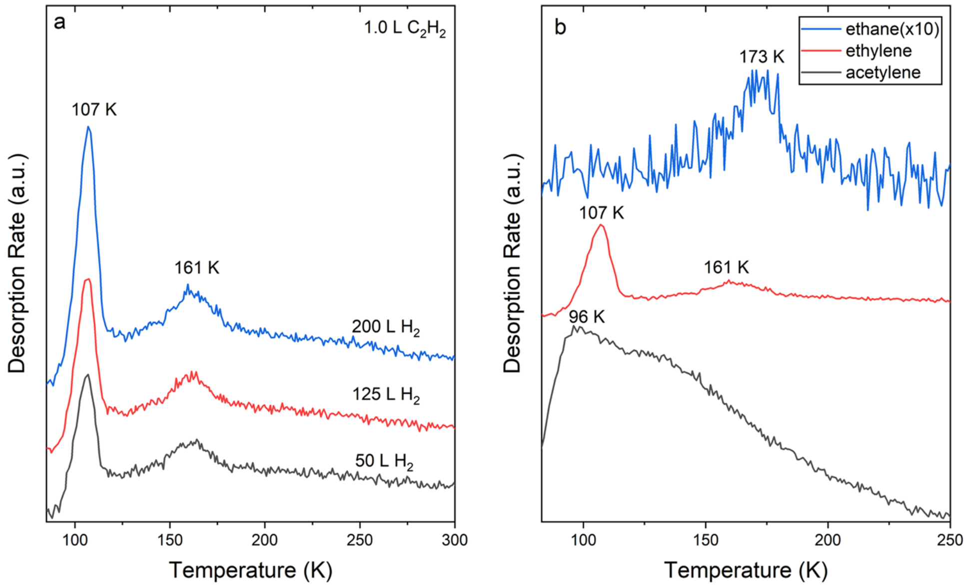


FIG. 5. Deconvoluted and corrected TPR results for acetylene hydrogenation on Ag(111). (a) Desorption of ethylene (m/z = 28) for the indicated H_2 exposures used to pre-adsorb H prior to the 1.0 L acetylene exposure. (b) TPR of acetylene, ethylene, and ethane after 1.0 L of C_2H_2 was exposed to a Ag(111) surface that was first exposed to 200 L of H_2.

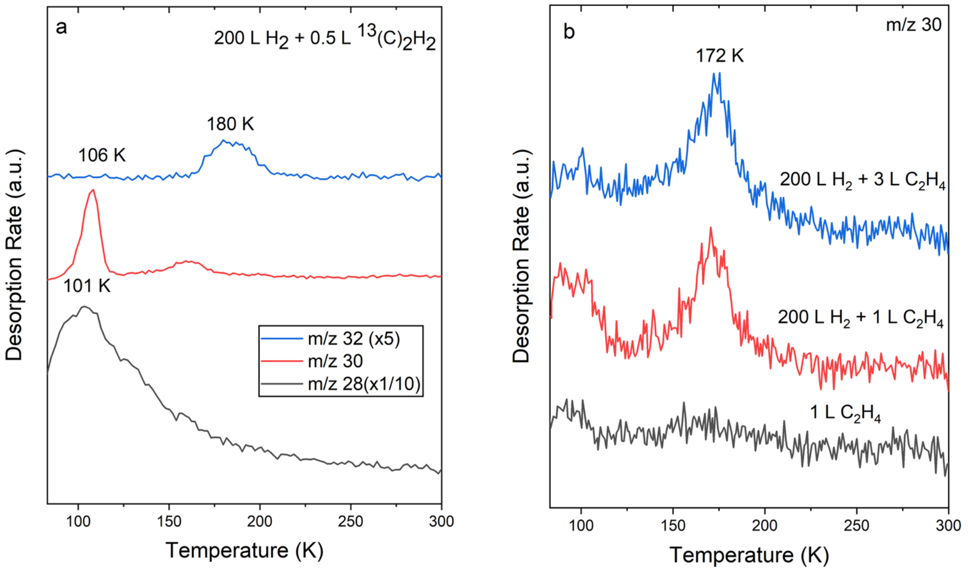


FIG. 6. (a) Uncorrected TPR spectra after exposure to 0.5 L of $^{13}C_2H_2$ to Ag(111) with pre-dosed H. Ethane, ethylene, and acetylene show the same desorption profiles seen in Fig. 5 but with the m/z values shifted by +2 a.m.u. (b) TPR results for ethane formation from ethylene hydrogenation for a 200 L H_2 exposure prior to $^{12}C_2H_4$ exposures of 1.0 and 3.0 L. The result for a 1 L ethylene exposure without pre-adsorbed H is shown for comparison.

no ethane desorption is detected in the absence of pre-adsorbed hydrogen.

C. Hydrogenation of acetylene on Pd/Ag(111)

The presence of a small concentration of Pd on Ag(111) leads to distinct changes in the hydrogenation of acetylene. The Pd was deposited at a surface temperature of 380 K, and coverages were quantified using TPD of adsorbed CO, which allows us to determine the Pd coverages for values below the detection limit of AES. The RAIRS results in Fig. 7 were obtained for a 1.0 L exposure of acetylene to (a) 0.7% Pd/Ag(111) and (b) 1.9% Pd/Ag(111). Both surfaces had been exposed to the indicated amounts of H_2 prior to acetylene exposures. This permits a direct comparison to results in Fig. 4 for the clean surface. For the 200 L H_2 pre-exposure results, the integrated area of the ethylene peak at 950 cm^{-1} for the 0.7% Pd/Ag(111) surface is 77% of the area in Fig. 4, while for the 1.9% Pd/Ag(111), the area is 46% of the area in Fig. 4. These results show that Pd leads to less selectivity toward ethylene formation than for the clean Ag(111) surface.

The ethylene TPR results in Fig. 8 clearly reveal that the presence of Pd affects the hydrogenation reaction. For these results, the surface at 85 K was first exposed to 0.5 L of acetylene followed by 500 L of H_2 with the ion gauge on. Comparison of Fig. 5(a) for the Pd-free Ag(111) surface and the results in Fig. 8(a) indicate that the order of exposure to acetylene and H_2 has little effect on the

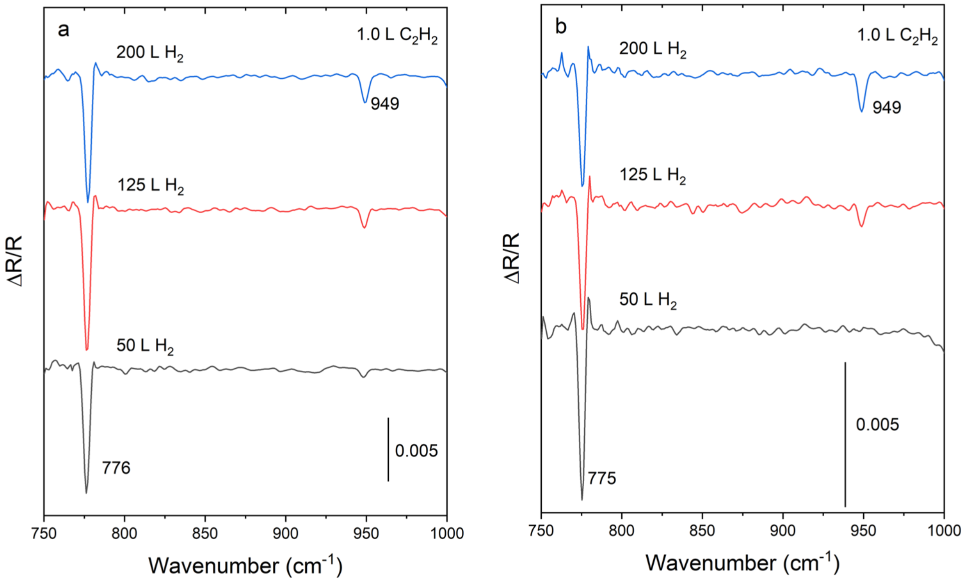


FIG. 7. RAIR spectra of the reaction of 1.0 L acetylene with the indicated amounts of pre-dosed hydrogen (just as in Fig. 4) on (a) a 0.70% Pd/Ag(111) SAA and (b) a 1.9% Pd/Ag(111) SAA at 85 K with the ion gauge on.

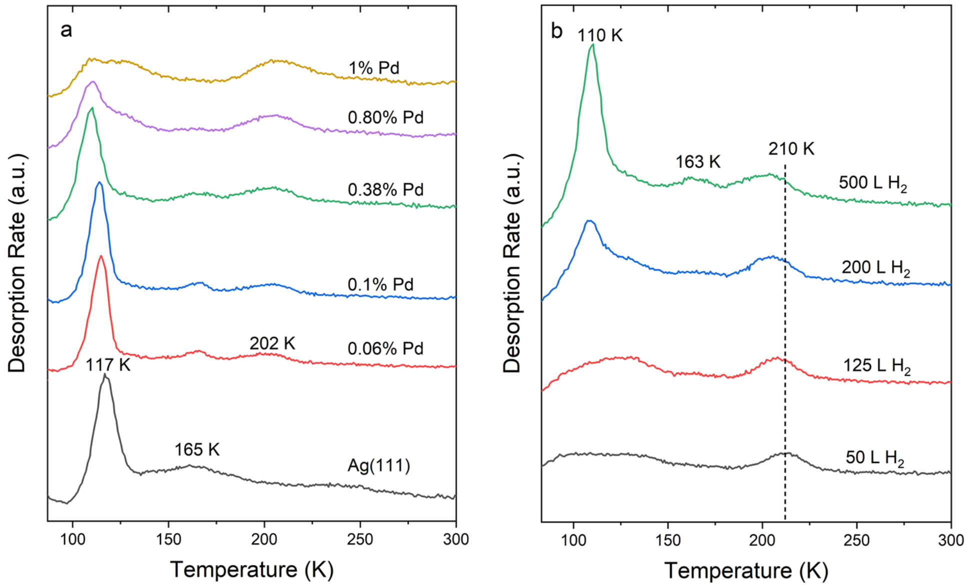


FIG. 8. Deconvoluted and corrected TPR spectra of ethylene (m/z = 28) formed after an acetylene exposure of 0.5 L followed by exposure to hydrogen. (a) After a 500 L H_2 exposure for the indicated Pd coverages. (b) After the indicated hydrogen exposures to a 0.38% Pd/Ag(111) surface.

hydrogenation reaction. Other data presented in the supplementary material further support this conclusion. As the Pd coverage increases, Fig. 8(a) shows that the lower temperature ethylene peak decreases in intensity. The 165 K peak also decreases in intensity, while a new peak at 202 K increases as the Pd coverage increases. The 202 K ethylene peak is likely due to ethylene that forms at a lower temperature on Ag sites and then diffuses to Pd sites where it is more strongly bound before it desorbs. When coadsorbed with hydrogen, ethylene desorbs from Pd(111) at about 200 K,[32] although the desorption of ethylene formed by the hydrogenation of acetylene on Pd(111) is closer to 300 K.[33]

Figure 8(b) shows the effect of increasing hydrogen exposure after 0.5 L of acetylene had been adsorbed on 0.38% Pd/Ag(111). Although the total amount of ethylene formed increases, the area of the 210 K peak remains relatively constant, with most of the increase occurring in the 110 K peak. The results for the 125 L H_2 exposure for the 0.38% Pd/Ag(111) surface in Fig. 8(b) have the same qualitative appearance as the results for a 500 L H_2 exposure to the 1% Pd/Ag(111) surface in Fig. 8(a). This indicates that although ethylene forms on the Ag(111) sites, it migrates to the Pd sites where it either desorbs at 200–210 K or is further hydrogenated to ethane. Once the Pd sites are filled, ethylene desorbs from Ag sites, giving rise to

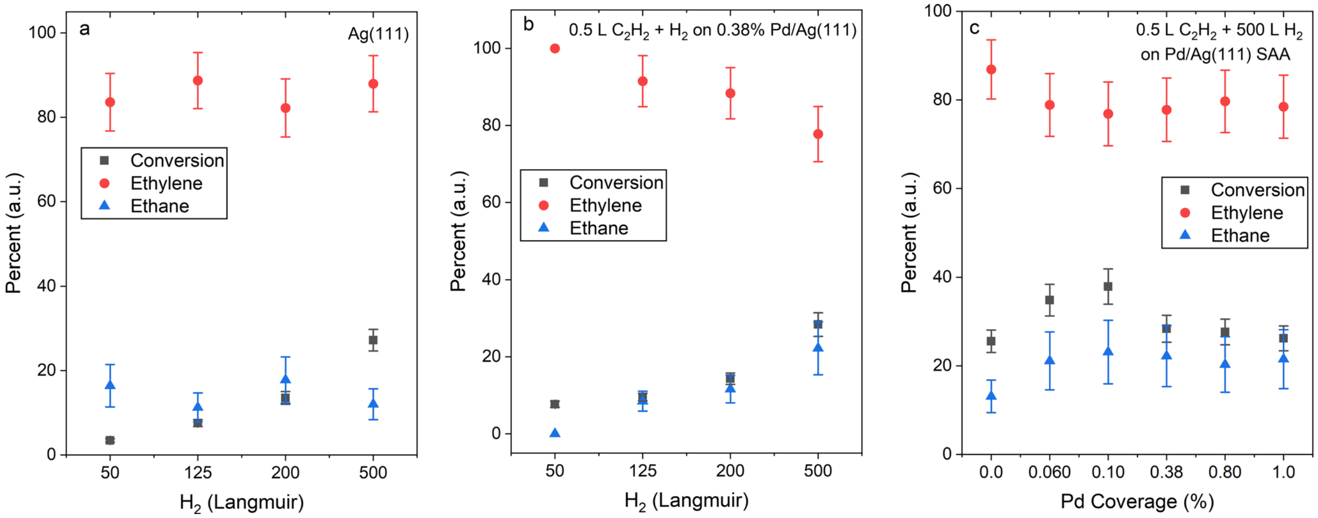


FIG. 9. Conversion and selectivity for the reaction of 0.5 L of C_2H_2 with increasing H_2 exposures for (a) the Ag(111) surface and (b) the 0.38% Pd/Ag(111) SAA surface. (c) For 0.5 L of C_2H_2, followed by 500 L of H_2 to Ag(111) with increasing Pd coverages.

both the 110–117 K and 163–165 K peaks. Ethane formation was also observed with TPR, and the results are given in the supplementary material.

The TPR results can be used to establish the percent of the adsorbed acetylene that is hydrogenated and the selectivity to ethylene, with the assumption that all adsorbed acetylene either desorbs without reaction or is hydrogenated to either ethylene or ethane. Quantitative analysis of TPR data was based on the area of desorption peaks, and relative conversions and selectivities were calculated. The method of relating the amounts of acetylene, ethylene, and ethane that desorb to the TPR peak areas is given in the supplementary material. We define conversion and selectivity to ethylene or ethane as follows:

$$\text{Acetylene conversion} = \frac{C_2H_4 + C_2H_6}{C_2H_2 + C_2H_4 + C_2H_6} * 100\%,$$

$$C_2H_4 \text{ selectivity} = \frac{C_2H_4}{C_2H_4 + C_2H_6} * 100\%,$$

$$C_2H_6 \text{ selectivity} = \left(1 - \frac{C_2H_4}{C_2H_4 + C_2H_6}\right) * 100\%.$$

Figures 9(a) and 9(b) compare the conversion and selectivity vs H_2 exposure to Ag(111) and 0.38% Pd/Ag(111) to which 0.5 L of C_2H_2 had been exposed at a surface temperature of 85 K. On Ag(111), the selectivity is roughly constant at 85% ethylene/15% ethane as the H_2 exposure increases. For the 0.38%Pd/Ag(111) surface, the conversion is similar to the Ag(111) surface, but the selectivity toward ethylene decreases with a concomitant increase in selectivity to ethane. Figure 9(c) shows the conversion and selectivities for increasing Pd coverage for exposures to 0.5 L of acetylene and 500 L of H_2. The conversion initially increases with Pd coverage for the lowest values, but then decreases to a constant value for Pd coverages of 0.38% and higher. Based on the trends for ethane and ethylene selectivities, the maximum in the conversion at a Pd coverage of 0.1% is due to an increased amount of ethane. The maximum in the conversion is near the maximum Pd coverage before the transition from a Pd/Ag(111) SAA to a surface with Pd islands occurs.

IV. CONCLUSIONS

Acetylene is readily hydrogenated by atomic hydrogen at 85 K on Ag(111), with ethylene being the main product with some ethane also produced. The low temperature of the reaction suggests a very low and possibly zero barrier to the reaction. The reaction occurs regardless of the dosing order. However, the acetylene CH bending mode at 776–779 cm^{-1} disappears from the RAIR spectrum when an acetylene covered surface is exposed to atomic H. These results are presented in the supplementary material. In contrast, when hydrogen is dosed first, the formation of ethylene is not accompanied by any significant diminishment in the acetylene RAIR signal. This indicates that exposure to atomic hydrogen leads both to the hydrogenation of adsorbed acetylene and to the displacement of acetylene from the surface. This is consistent with the very weak binding of acetylene to Ag(111). Quantitative measurements of the conversion and selectivity reveal that the presence of low coverages of Pd increases the conversion, mainly by increasing the selectivity toward ethane at the expense of ethylene formation. The increased conversion occurs for Pd coverages that produce the SAA, with a decrease in conversion for coverages where Pd islands form. The results indicate that even if hydrogen spillover occurred, the promotion of ethylene hydrogenation to ethane by the Pd would limit the utility of PdAg SAAs for the selective hydrogenation of acetylene to ethylene.

SUPPLEMENTARY MATERIAL

See the supplementary material for additional results on the hydrogenation reactions under various conditions, ethylene spectra at higher resolution, and information on the TPR deconvolution procedure.

ACKNOWLEDGMENTS

This work was supported by a grant from the National Science Foundation (Grant No. CHE-1800236).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

[1] G. C. Bond, in *Catalysis*, edited by P. H. Emmett (Reinhold Publishing Corporation, New York, 1955), Vol. 3, p. 109.

[2] A. Borodziński and G. C. Bond, Catal. Rev. **48**, 91 (2006).

[3] R. E. Reitmeier and H. W. Fleming, Chem. Eng. Prog. **54**, 48 (1958).

[4] G. C. Bond, D. A. Dowden, and N. Mackenzie, Trans. Faraday Soc. **54**, 1537 (1958).

[5] Q. Zhang, J. Li, X. Liu, and Q. Zhu, Appl. Catal., A **197**, 221 (2000).

[6] R. N. Lamb, B. Ngamsom, D. L. Trimm, B. Gong, P. L. Silveston, and P. Praserthdam, Appl. Catal., A **268**, 43 (2004).

[7] A. Pachulski, R. Schödel, and P. Claus, Appl. Catal., A **400**, 14 (2011).

[8] F. Studt, F. Abild-Pedersen, T. Bligaard, R. Z. Sørensen, C. H. Christensen, and J. K. Nørskov, Angew. Chem., Int. Ed. **47**, 9299 (2008).

[9] R. T. Hannagan, G. Giannakakis, M. Flytzani-Stephanopoulos, and E. C. H. Sykes, Chem. Rev. **120**, 12044 (2020).

[10] G. Kyriakou, M. B. Boucher, A. D. Jewell, E. A. Lewis, T. J. Lawton, A. E. Baber, H. L. Tierney, M. Flytzani-Stephanopoulos, and E. C. H. Sykes, Science **335**, 1209 (2012).

[11] M. Muir and M. Trenary, J. Phys. Chem. C **124**, 14722 (2020).

[12] C. R. O'Connor, K. Duanmu, D. A. Patel, E. Muramoto, M. A. van Spronsen, D. Stacchiola, E. C. H. Sykes, P. Sautet, R. J. Madix, and C. M. Friend, Proc. Natl. Acad. Sci. U. S. A. **117**, 22657 (2020).

[13] F. R. Lucci, M. T. Darby, M. F. G. Mattera, C. J. Ivimey, A. J. Therrien, A. Michaelides, M. Stamatakis, and E. C. H. Sykes, J. Phys. Chem. Lett. **7**, 480 (2016).

[14] P. Aich, H. Wei, B. Basan, A. J. Kropf, N. M. Schweitzer, C. L. Marshall, J. T. Miller, and R. Meyer, J. Phys. Chem. C **119**, 18140 (2015).

[15] M. Muir, D. L. Molina, A. Islam, M. K. Abdel-Rahman, and M. Trenary, J. Phys. Chem. C **124**, 24271 (2020).

[16] D. A. Dows, Spectrochim. Acta **22**, 1479 (1966).

[17] E. M. Stuve, R. J. Madix, and B. A. Sexton, Surf. Sci. **123**, 491 (1982).

[18] G. Kyriakou, J. Kim, M. S. Tikhov, N. Macleod, and R. M. Lambert, J. Phys. Chem. B **109**, 10952 (2005).

[19] P. A. Sheth, M. Neurock, and C. M. Smith, J. Phys. Chem. B **109**, 12449 (2005).

[20] Z. J. Zhao, J. Zhao, X. Chang, S. Zha, L. Zeng, and J. Gong, AIChE J. **65**, 1059 (2019).

[21] E. Vignola, S. N. Steinmann, B. D. Vandegehuchte, D. Curulla, and P. Sautet, J. Phys. Chem. C **120**, 26320 (2016).

[22] K. Kershen, H. Celio, I. Lee, and J. M. White, Langmuir **17**, 323 (2001).

[23] D. Stacchiola, G. Wu, M. Kaltchev, and W. T. Tysoe, Surf. Sci. **486**, 9 (2001).

[24] J. Hrbek, Z. Chang, and F. M. Hoffmann, Surf. Sci. **601**, 1409 (2007).

[25] N. Osaka, M. Akita, and K. Itoh, J. Phys. Chem. B **102**, 6817 (1998).

[26] B. Krüger and G. Benndorf, Surf. Sci. **178**, 704 (1986).

[27] J. D. Krooswyk, I. Waluyo, and M. Trenary, ACS Catal. **5**, 4725 (2015).

[28] A. Priebe, A. Pucci, and A. Otto, J. Phys. Chem. B **110**, 1673 (2006).

[29] G. Lee and E. W. Plummer, Phys. Rev. B **51**, 7250 (1995).

[30] G. Lee, P. T. Sprunger, M. Okada, D. B. Poker, D. M. Zehner, and E. W. Plummer, J. Vac. Sci. Technol. A **12**, 2119 (1994).

[31] E. I. Ko, J. B. Benziger, and R. J. Madix, J. Catal. **62**, 264 (1980).

[32] D. Stacchiola, S. Azad, L. Burkholder, and W. T. Tysoe, J. Phys. Chem. B **105**, 11233 (2001).

[33] R. M. Ormerod, R. M. Lambert, D. W. Bennett, and W. T. Tysoe, Surf. Sci. **330**, 1 (1995).