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Ethanol Dehydrogenation on Pt/Cu(111) Surfaces

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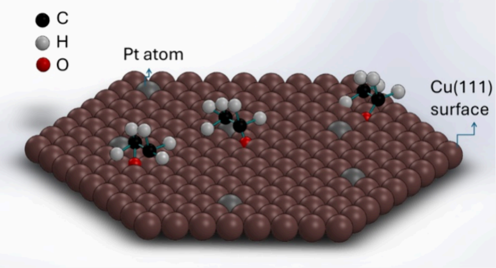
ABSTRACT: Reflection absorption infrared spectroscopy (RAIRS) was used to directly identify an ethoxy intermediate formed by the dry dehydrogenation of ethanol on a Pt/Cu(111) single-atom alloy surface. Temperature-programmed reaction spectroscopy was used to monitor reaction-limited desorption of acetaldehyde that follows from activation of a C−H bond of ethoxy. The RAIRS results for ethoxy formed on the Pt/Cu(111) surface were compared to RAIR spectra of ethoxy at a coverage of 0.5 monolayer formed on oxidized Cu(111). Quantification of the ethoxy coverage from the RAIRS intensities indicated that it was less than the Pt coverage on the Pt/Cu(111) surface. This is contrary to the expectation that one Pt site could form multiple ethoxy molecules on Cu sites through spillover. Possible reasons for not detecting ethoxy spillover in these experiments are discussed.



1. INTRODUCTION

The nonoxidative dehydrogenation of ethanol, a renewable resource, to acetaldehyde and hydrogen is a process with environmental benefits, given that acetaldehyde is a valuable starting material for many other reactions and green hydrogen is desirable for various applications. Acetaldehyde has long been made by the oxidation of ethylene using the Hoechst−Wacker oxidation process, which uses a palladium-based catalyst, although the separation from water by distillation is energy intensive.[1,2] The need to shift from petroleum-derived products to alternative and renewable resources requires different catalysts to drive new promising processes. Despite their overwhelming activity, metals such as Pt, Ru, Rh, and Pd are not very abundant, but in combination with other more plentiful transition metals such as Cu, Ag, and Au, their efficient use can be maximized.

The ability of copper-based catalysts to oxidize alcohols to their respective aldehyde or ketone is well-known and was among the first reactions on metal surfaces to be studied.[3−8] Wachs and Madix[9] used $^{18}O_2$ to oxidize a Cu(110) surface and compared reaction of CH_3CH_2OD on the oxidized and oxygen-free surfaces. They concluded that the oxygen-free Cu(110) surface was active for the nonoxidative dehydrogenation of ethanol, as temperature-programmed reaction spectroscopy (TPRS) showed the desorption of acetaldehyde (CH_3CHO). The data supported formation of an ethoxy intermediate, in both the nonoxidative and oxidative dehydrogenation, consistent with infrared spectroscopy studies by Blyholder and Wyatt on supported catalysts.[10] Complementary studies by Bowker and Madix[11,12] using a combination of X-ray photoelectron spectroscopy, ultraviolet photoelectron spectroscopy, and TPRS of various alcohols including ethanol on both Cu(110) and oxidized Cu(110) showed that the alkoxy species that formed from the alcohols bonded through the oxygen atom. A study of weakly adsorbed molecules, including ethanol, on Cu(100) and Pt(111) by Sexton and Hughes showed that alcohols weakly chemisorb to the metal surfaces through the O 2p or HOMO orbital since this one showed the greatest contribution to the heat of adsorption.[13] A quantitative analysis with reflection absorption infrared spectroscopy (RAIRS) of ethoxy on Cu(111), formed by reacting ethanol with the preoxidized surface, allowed Street and Gellman to show that the C−O bond is tilted approximately 17 ± 2° from the surface normal.[14] Scanning tunneling microscopy (STM) and TPRS studies on sputtered Cu(111) and Cu(110) surfaces have recently shown that the catalytic activity for the nonoxidative dehydrogenation of ethanol comes from kinks and step sites, as these sputtered but unannealed surfaces showed an increased activity versus the annealed surfaces.[15] These studies are in general agreement that the oxygen-free copper surface is selective for the nonoxidative dehydrogenation of alcohols.

Unlike for copper, early studies of alcohols on Pt(111) and oxidized Pt(111) showed that the decomposition did not lead to the respective ketone or aldehyde, but the alcohol was either desorbed molecularly or decomposed to CO, H_2, and surface carbon.[16,17] On Pt(111), ∼90% of the ethanol desorbs molecularly and the remaining 10% undergoes dissociation.[13,17] Using fast XPS, Lee et. al showed that although the ethoxy intermediate on Pt(111) was too short-lived to observe, an acetyl intermediate was stable within a range of temper-

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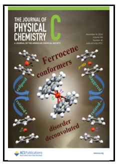

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atures before decomposing further to CO, H_2, and CH_x species.[18]

A Pt/Cu(111) single-atom alloy (SAA), a very dilute heterogeneous bimetallic alloy with single atoms of Pt doped into a Cu(111) surface, has been shown recently through STM and TPRS studies to enhance, compared to the bare Cu(111) surface, the nonoxidative dehydrogenation of ethanol.[15,19] The enhancement was attributed to an entropy-driven spillover of the intermediate species from the Pt single-atom sites to the Cu(111) surface. Specifically, Wang et al. inferred that the intermediate observed with STM was ethoxy.[15,19] They provided RAIR spectra as the Supporting Information to confirm that the intermediate was ethoxy.[15] They estimated that for a 0.01 ML Pt/Cu(111) SAA surface, five ethoxy molecules that formed at Pt sites spilled over to Cu sites to yield an ethoxy coverage of 0.05 ML.

In contrast to STM, vibrational spectroscopy has a high degree of chemical specificity. Here, we use RAIRS to directly detect ethoxy formation on the Pt/Cu(111) SAA surface. Formation of acetaldehyde was also observed with TPRS and was found to desorb at a lower temperature than from clean or oxidized Cu(111) following ethanol adsorption. Attempts to verify the spillover of ethoxy from Pt sites to Cu sites through quantification of the ethoxy coverage relative to the Pt coverage were unsuccessful. We have also investigated coverages of Pt on Cu(111) higher than those of the SAAs and found that in addition to nonoxidative dehydrogenation to form acetaldehyde, the higher Pt coverages lead to decomposition to produce methane and CO, which is characteristic of the surface chemistry of ethanol on Pt surfaces.

2. EXPERIMENTAL SECTION

All experiments were carried out in a stainless-steel ultrahigh vacuum (UHV) chamber with a base pressure of 2×10^{-10} Torr. The chamber is equipped with a PHI 10-115 cylindrical mirror analyzer for Auger electron spectroscopy (AES), PHI 15-120 optics for low-energy electron diffraction (LEED), and a Hiden HAL 201/3F quadrupole mass spectrometer for TPRS. 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 NaCl and KBr windows. Pressures were measured with a Bayard-Alpert hot filament ion gauge.

The copper single crystal from the Surface Preparation Laboratory is circular with a diameter of 15 mm and a thickness of 2.5 mm with a (111) orientation (<0.1° accuracy). It is mounted by passing two tungsten wires through holes (0.75 mm diameter) parallel to the (111) face on opposite edges of the crystal. A K-type thermocouple junction is inserted into a hole in the top edge of the crystal (0.3 mm in diameter with a depth of 0.8 mm). The crystal was cleaned with cycles of Ar sputtering (1 keV, 7−8 μA) and annealing at 900 K for 10 min. The cleanness of the crystal was determined using AES and RAIRS of CO. The absence of a RAIRS peak at room temperature for CO on Pt sites confirmed the absence of platinum. In this way, RAIRS of CO could detect Pt on the Cu(111) surface well below the detection limit of AES.

A commercial electron-beam evaporator (EBE35A ACME) was used to deposit Pt onto the Cu(111) surface while maintaining a background pressure of $\leq 1 \times 10^{-9}$ Torr. The deposition and quantification of Pt have been previously described.[20] The Pt rod (99.99%) was obtained from ESPI Metals. RAIR spectra were collected with 1024 scans, 4 cm^{-1} resolution and are presented after baseline correction. A linear rate of 1 K/s was used to obtain the TPRS traces, all of which were smoothed unless otherwise noted. The CO (99.99%) was obtained from Matheson and used without further purification. 200 proof anhydrous ethanol (≥99.5%), from Sigma-Aldrich, was opened and transferred to a stainless-steel lecture bottle in a glovebox under argon. The ethanol was then purified further through freeze−pump−thaw cycles. The most intense fragments for ethanol, as shown by the mass spectrum, correspond to mass-to-charge ratios (m/z) of 31 and 45.

3. RESULTS

To calibrate results for ethoxy on the Pt/Cu(111) surface, we first obtained RAIRS and TPRS data for high coverages of ethoxy formed on oxidized Cu(111). Figure 1 shows RAIR spectra of ethoxy formed after exposure of 5 L of ethanol to the Cu(111) surface at 250 K, which previously had been exposed to the indicated amounts of O_2 at room temperature. Table 1 shows the vibrational band assignments for the ethoxy spectra in Figure 1, a 0.12 ML Pt/Cu(111) surface, and the values reported by Street and Gellman for ethoxy on Cu(111).[14,21] The band positions vary somewhat with coverage, and the values given in Table 1 are for the maximum ethoxy coverage obtained when 200 L of O_2 was used to oxidize the surface.

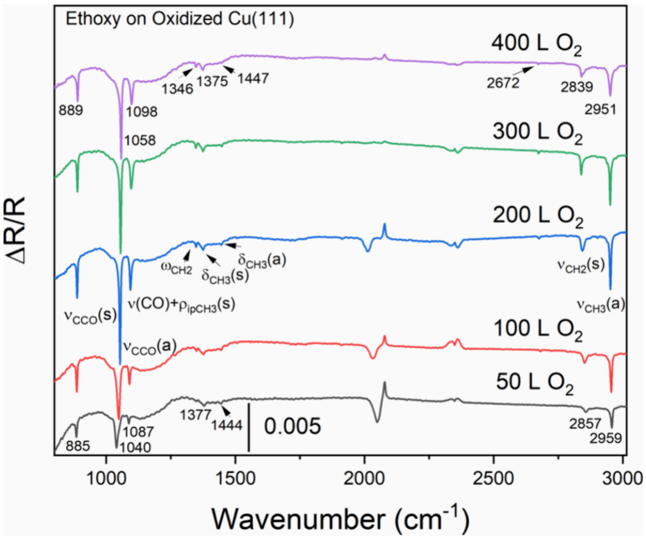

Figure 1. RAIR spectra of ethoxy formed on oxidized Cu(111) after exposing to 5 L of ethanol at 250 K, and then cooling to 90 K where the spectra were obtained. The surface was oxidized using the indicated exposures of O_2 at room temperature.

The intensity of the ethoxy peaks reaches a maximum following a 200 L O_2 exposure. This is consistent with previous studies of ethoxy formation on Cu(111) and Cu(100).[14,21,22] Recent AES results by Zhang et al. showed that a 225 L O_2 exposure to Cu(111) at room temperature led to an O coverage of approximately 0.24 ML.[23] Previous work by Camplin and McCash showed that oxidation of Cu(100) at room temperature with 150 L of O_2 led to the maximum yield of both methoxy and ethoxy upon methanol and ethanol exposures, respectively.[22] This supports our results that a 200 L exposure of O_2 to Cu(111) at room temperature led to the maximum ethoxy coverage. In the net reaction according to

Table 1. Frequency Assignments for Ethoxy On Cu(111) and a 0.12 ML Pt/Cu(111) Alloy and the Assignments of Street and Gellman[21]

vibrational mode	ethoxy on Cu(111)[21]	ethoxy on Cu(111)	ethoxy on 0.12 ML Pt/Cu(111)
ν_{CCO}(s)	886	887	884
ν_{CCO}(a)	1048	1053	1039
$\nu_{CO}+\rho_{ipCH3}$(s)	1093	1094	1087
ω_{CH2}	1354	1348	1349
δ_{CH3}(s)	1380	1375	n.o.
δ_{CH3}(a)	1444	1446	1446
combination	n.o.	2673	n.o.
ν_{CH2}(s)	2857	2844	2862
$2\times\delta_{CH3}$(a)	n.o.	2871	2879
ν_{CH3}(s)	n.o.	2901	n.o.
ν_{CH2}(a)	n.o.	2940	n.o.
ν_{CH3}(a)	2955	2952	2960

Scheme 1, each O atom would react with two ethanol molecules to form two ethoxy adsorbates.

Scheme 1. Oxidative and Nonoxidative Dehydrogenation of Ethanol

$$2CH_3CH_2OH\ (a) + O\ (a) \rightarrow H_2O\ (a) + 2CH_3CH_2O\ (a)$$

$$2CH_3CH_2O\ (a) \rightarrow 2CH_3CHO\ (g) + H_2\ (g)$$

Non-oxidative Dehydrogenation of Ethanol

$$CH_3CH_2OH\ (a) \rightarrow CH_3CH_2O\ (a) + H_a\ (a) \rightarrow CH_3CHO\ (g) + H_2\ (g)$$

We found from the TPRS results described below that upon excess ethanol exposure, all the oxygen reacts, which suggests that approximately 0.5 ML of ethoxy is formed when a 200 L exposure of O_2 is used to oxidize the Cu(111) surface at room temperature. Also present in Figure 1 are the unlabeled peaks around 2350 cm^{-1} due to residual gas-phase CO_2 in the optical path outside the UHV chamber and both negative and positive peaks between 2000 and 2100 cm^{-1} due to CO adsorbed from the UHV background. The positive CO peak is attributed to CO that was present when the background spectrum was obtained, and the negative CO peak at a lower wavenumber is attributed to a red shift of the C−O stretch of CO coadsorbed with ethanol.

Figure 2 shows TPRS results for acetaldehyde formation for the maximum ethoxy coverage corresponding to the RAIR spectra in Figure 1 for an O_2 pre-exposure of 200 L. Mass-to-charge ratios (m/z) of 44 and 29 were monitored corresponding to the parent mass of acetaldehyde and its largest fragment, respectively. The desorption of acetaldehyde at around 370 K has been observed previously where it was attributed to ethoxy decomposition by β-hydride elimination.[24] The measured ratio, based on TPRS areas, for the m/z = 29 and 44 peaks is 2.6, whereas the NIST value is close to 1.2.[25] Although the values differ, m/z = 29 is the most intense fragment expected.

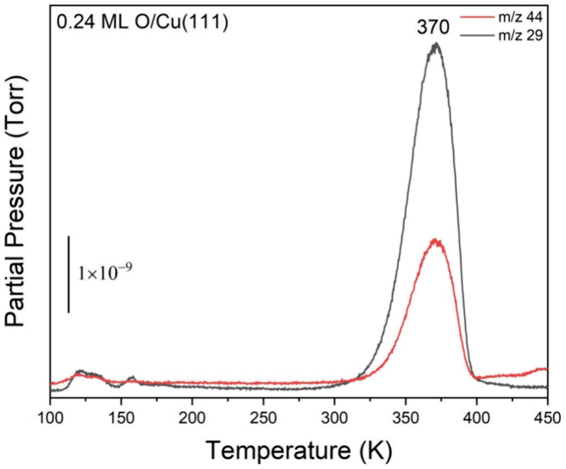

Figure 2. TPRS of acetaldehyde (m/z = 44 and 29) formed from the exposure of 5 L of ethanol at 250 K to a 0.24 ML O/Cu(111) surface formed by exposing the surface at room temperature to 200 L of O_2.

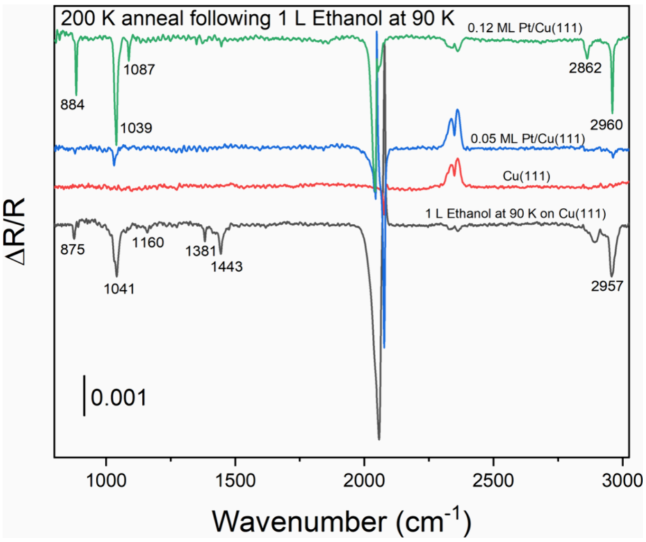

Figure 3. RAIR spectra obtained after a 1 L exposure of ethanol at 90 K to Cu(111), 0.05 ML Pt/Cu(111), and 0.12 ML Pt/Cu(111), annealing to 200 K, and then cooling to 90 K where the spectra were taken. The spectrum (black) obtained after ethanol exposure to Cu(111) before annealing is also shown.

In addition to ethoxy formation through the reaction with adsorbed oxygen, the RAIR spectra in Figure 3 show that it can also be formed by nonoxidative dehydrogenation on a Pt/Cu(111) surface. Spectra are shown for 0.05 and 0.12 ML of Pt deposited onto the Cu(111) surface at room temperature. This was followed by 1 L exposures of ethanol at 90 K, after which the surface was annealed to 200 K. Results are also shown for 1 L of ethanol exposed to the Pt-free Cu(111) surface before and after annealing to 200 K, which shows no evidence for ethoxy formation. Although weak ethoxy peaks are seen for 0.05 ML of Pt, the intensity of the ethoxy peaks is much greater for 0.12 ML of Pt than the 0.12/0.05 Pt coverage ratio would imply, indicating that the ethoxy coverage is not simply proportional to the Pt coverage. As in Figure 1, peaks due to gas-phase CO_2 and adsorbed CO are also observed in Figure 3. The much higher intensity of the adsorbed CO peaks in Figure 3 compared to Figure 1 is due to obtaining the background and sample spectra in Figure 3 at 90 K, well below the highest CO desorption temperature of 190 K from Cu(111),[26] whereas in Figure 1, the ethanol exposures were performed at 250 K. As ethoxy and ethanol are structurally similar, their vibrational spectra are also quite similar except that ethoxy lacks an O−H stretch. To more clearly detect the transformation from ethanol to ethoxy, Figure 4 shows RAIR spectra in the C−H and O−H stretching regions after adsorbing 1 L of ethanol on the 0.12 ML Pt/Cu(111) surface

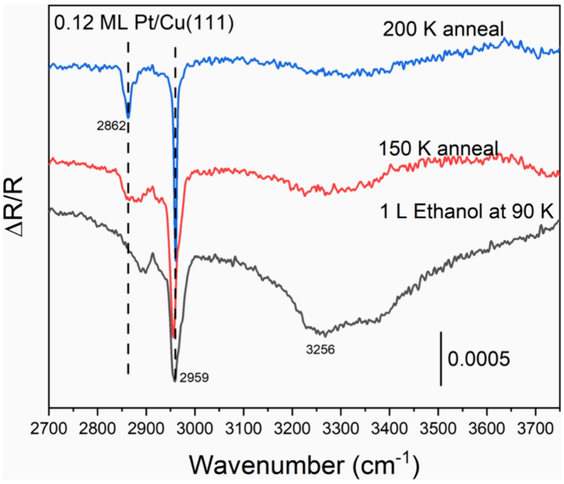

Figure 4. RAIR spectra in the C−H and O−H stretch regions for 1 L of ethanol on the 0.12 ML Pt/Cu(111) surface after ethanol exposure at 90 K (black) and after annealing to 150 (red) and 200 K (blue).

at 90 K and after annealing to 150 and 200 K. The formation of ethoxy is revealed by the sharpening of the peaks and the loss of the broad O−H stretch peak.

Figure 5 shows TPRS results for acetaldehyde produced from the decomposition of ethoxy formed on the 0.12 ML Pt/Cu(111) surface. The minor peaks seen in Figure 2 at 148 and 178 K for ethanol exposure to the O-covered Cu(111) surface are also observed in Figure 5 and are attributed to fragments of ethanol, which desorbs at these temperatures. As no ethanol desorption is expected above 250 K, the 282 K peaks in Figure 5 are attributed to acetaldehyde desorption. If we assume that all ethoxy decomposes to desorb acetaldehyde, comparison of the acetaldehyde TPRS peak areas in Figures 2 and 5 and assuming that the coverage of ethoxy formed on the 0.24 ML O/Cu(111) surface is approximately 0.5 ML, we conclude that 0.02 ML of ethoxy forms on the 0.12 ML Pt/Cu(111) surface.

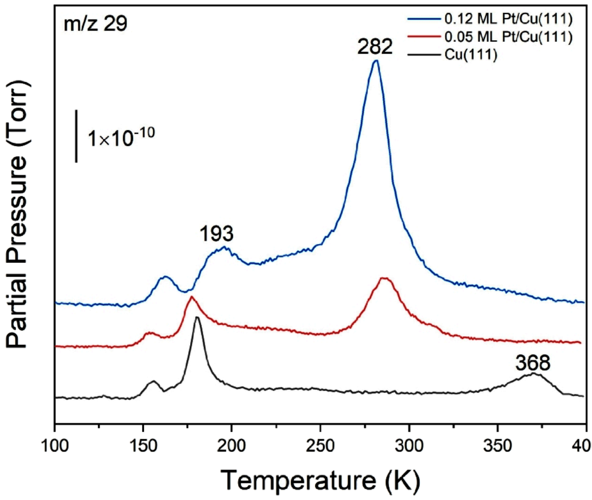

Figure 5. TPRS results (not smoothed) for acetaldehyde, m/z = 29, from Cu(111), 0.05 ML Pt/Cu(111), and 0.12 ML Pt/Cu(111) following a 1 L exposure of ethanol at 90 K, annealing to 200 K to convert ethanol to ethoxy and desorb excess ethanol, and then cooling back to 90 K before initiating the temperature ramp.

Results obtained for higher Pt coverages and for Pt deposited on the Cu(111) surface at higher temperatures are presented in the Supporting Information. Figures S1−S4 show RAIRS and TPRS results for 0.23 and 0.45 ML of Pt deposited at room temperature. Our previous work has shown that under these conditions, Pt islands and other aggregates are formed but with bare patches of Cu(111) still present.[20] Therefore, the interaction of ethanol with such a surface can be expected to display reactions characteristic of both Pt(111) and Cu(111). Ethanol, like other alcohols, has been shown to decompose on Pt(111), leading to the formation of CO, H_2, and CH_x fragments.[16−18] As shown in Figures S1 and S3, at these higher Pt coverages, we observe ethoxy with RAIRS, but the intensities are less than in spectra for the 0.12 ML Pt/Cu(111) surface in Figure 1. Although Lee et al. concluded in their fast XPS study of the decomposition of ethanol on Pt(111) that ethoxy is an intermediate, they found that it is not stable and was not directly detected in their experiments.[18] They did find evidence, however, for acetyl (CH_3CO) and CH_x species. The TPRS results in Figures S2 and S4 for the higher Pt coverages showed methane desorption (m/z = 16) that was not simply a fragment of acetaldehyde, consistent with the work by Lee et al.[18] In contrast, Sexton et al. using conventional XPS and TPRS concluded that ethanol would either desorb molecularly on Pt(111) or completely dissociate to desorb as CO and H_2.[17] We did not detect any vibrational features of acetyl or CH_x. We concluded that the ethoxy that we observed for Pt coverages of 0.23 and 0.45 ML was formed on the exposed Cu(111) areas of the surface, with no species detected on the Pt-covered areas.

The Pt deposition temperature determines how well dispersed the Pt atoms are on the Cu(111) surface and the extent of Pt diffusion into the subsurface. Figure S5 shows RAIR spectra for Cu(111) and low coverages of Pt deposited at 298, 380, and 450 K after dosing 1 L of ethanol at 90 K and then annealing to 200 K to desorb the excess ethanol and form ethoxy. The ethoxy peaks at 879, 1031, and 2962 cm^{-1} are most apparent for Pt deposited at 298 K, weaker for the 380 K deposition, and not detectable for the 450 K deposition. The TPRS results in Figure S6, corresponding to the RAIRS results in Figure S5, show that the temperature of the acetaldehyde desorption increases and the amount decreases somewhat with higher Pt deposition temperature. The peak acetaldehyde desorption temperature of 355 K in Figure S6 is slightly lower than the temperature of 370 K for acetaldehyde desorption from oxidized Cu(111) in Figure 2. As acetaldehyde desorption is ethoxy decomposition rate limited, the higher desorption temperatures in Figure S6 indicates that although ethoxy formation requires the presence of Pt, its decomposition for well-dispersed Pt is mainly associated with Cu sites. This would be consistent will spillover of ethoxy from Pt to Cu sites.

4. DISCUSSION

The formation of ethoxy was directly detected with RAIRS on the Pt/Cu(111) surfaces but not on the Pt-free Cu(111) surface. The spectroscopic features of ethoxy on Pt/Cu(111) are the same as those of ethoxy formed through the reaction of ethanol with an oxygen-covered Cu(111) surface. The results thus confirm that the Pt/Cu(111) SAA surface is effective for the nonoxidative dehydrogenation of ethanol. Other work has indicated that this reaction can occur at defect sites on Cu(111) even in the absence of surface Pt or O. To investigate this possibility, we obtained the RAIRS and TPRS results shown in Figures S7 and S8 to examine the reaction of ethanol with a sputtered and unannealed Cu(111) surface. A weak peak at 1038 due to the C−O stretch is observed in Figure S7 that persists after annealing to 250 K revealing ethoxy formation. Figure S8 shows that acetaldehyde desorbs at around 315 K. These TPRS results reproduce those of Wang et al.[15,19]

Although ethoxy is detected with RAIRS on the Pt/Cu(111) surface, but not on the flat Cu(111) surface, the extent of the spillover from the Pt sites to the Cu sites is not clear. Wang et al. concluded that for a 0.01 ML Pt coverage, the ethoxy coverage was 0.05 ML, based on the observation that the amount of acetaldehyde detected with TPRS from the 0.01 ML Pt/Cu(111) SAA was five times the amount formed on the flat Cu(111) surface.[19] It was further assumed that the acetaldehyde only formed at the step sites of the Pt-free Cu(111) surface and that these constituted 2% of the total sites, but only half of these sites were effective for ethanol dehydrogenation. In the Supporting Information of their study of ethanol dehydrogenation on flat and roughened Cu(111), they concluded that the active sites on the flat Cu(111) surface were present at 0.01 ML.[15] This estimate was based on TPRS data revealing separate peaks for ethanol desorption from terrace and step sites. The TPRS peak areas were then used to quantify the step site density based on the assumption that the total ethanol saturation coverage was 1 ML, i.e., 1 ethanol per Cu atom. If the absolute coverage of the saturation coverage of ethanol is less than 1 ML, the estimate of the number of ethoxy molecules produced per Pt atom would be less. However, if five ethoxy molecules formed per Pt atom for our 0.05 ML Pt/Cu(111) SAA, then we would expect an ethoxy coverage of 0.25 ML, i.e., half of the presumed saturation coverage, implying that the ethoxy RAIRS peak at 1040 cm^{-1} in Figure 3 should be about half as intense as the most intense 1053 cm^{-1} peak seen in Figure 1. In contrast, the weak intensity of the 1031 cm^{-1} peak for 0.05 ML Pt in Figure 3 implies an ethoxy coverage of only 0.005 ML, assuming that peak intensities are proportional to coverage. It might be that the ethoxy/Pt ratio would be highest for the lowest Pt coverages, but we were unable to detect ethoxy with RAIRS for Pt coverages less than 0.05 ML. Even if only one ethoxy formed per Pt atom, an ethoxy coverage of 0.01 ML should have produced a peak about twice as intense as the one observed in Figure 3 for 0.05 ML of Pt. A more intense ethoxy peak was observed for 0.12 ML of Pt, but it would correspond to an ethoxy coverage of only 0.02 ML. Despite the difficulty in quantifying the extent of the ethoxy spillover from RAIRS intensities, the nearly identical peak frequencies for ethoxy formed on oxidized Cu(111) and on Pt/Cu(111) suggests that in both cases, the ethoxy is bonded only to Cu sites.

A difficult-to-control variable that could affect the extent of ethoxy spillover is the CO coverage. As CO is always present as a background gas in even the cleanest UHV chambers, some CO adsorption inevitably occurs. The presence of adsorbed CO is readily detected with RAIRS, as seen for example in Figure 3 for the Pt/Cu(111) surfaces. As CO does not desorb from the Pt sites of Pt/Cu(111) below room temperature, at least some of the Pt sites must be occupied by CO during the conversion of ethanol to ethoxy on the Pt/Cu(111) surface. Marcinkowski et al. showed that CO can act as a "molecular cork" to block the dissociation of H_2 on a Pd/Cu(111) SAA surface, thus limiting the number of H atoms that can spill over to Cu sites.[27] A similar effect may occur here, with CO on Pt sites inhibiting the activation of the O−H bond of ethanol. We previously showed that CO desorption from isolated Pt atoms of a Pt/Cu(111) SAA occurs at ∼340 K,[20] whereas CO desorbs from the Pd atoms of a Pd/Cu(111) SAA at ∼270 K.[27] This suggests a stronger molecular cork effect for CO on Pt/Cu(111). As the conversion of ethanol to ethoxy occurs below 160 K, occupation of Pt sites by CO would be expected to suppress ethoxy formation. Furthermore, a greater fraction of the Pt atoms would be expected to be occupied by CO adsorbed from the background at lower Pt coverages. This would explain why the ethoxy signal in the RAIRS results for a Pt coverage of 0.05 ML was disproportionately lower than for a Pt coverage of 0.12 ML, and why it proved impossible to detect ethoxy for Pt coverages even lower than 0.05 ML. As the amount of background CO will vary from one laboratory to the next, it may be difficult to quantitatively reproduce the extent of spillover from different laboratories.

The acetaldehyde desorption temperature difference observed between the preoxidized Cu(111) surface and the Pt/Cu(111) alloys can be explained by the difference in binding site for ethoxy. On the oxidized Cu(111) surface, ethoxy is expected to bind to terrace Cu atoms after transfer of the hydroxyl H from ethanol to O to form OH. Ethoxy on the Pt/Cu(111) alloys will form near step edges, as that is where Pt dosed near 300 K resides.[28] The Pt atoms will activate the O−H bond, stabilizing the H_a in the nearest hollow site, and ethoxy will bind to a Cu site near the step edge. Since kink and step sites are known to be more reactive, it is reasonable that these sites will offer a lower activation energy for C−H bond scission in ethoxy. For the Pt/Cu(111) alloys, the Pt atoms appear to promote C−H activation since acetaldehyde desorbs at lower temperatures as the Pt coverage increases as observed in Figure 5 and Figures S2 and S4, where acetaldehyde is seen to desorb as low as 250 K from a 0.45 Pt/Cu(111) surface and at 275 K from 0.23 ML Pt/Cu(111). The decreasing desorption temperature with increasing Pt coverage coincides with the presumed C−H activation of ethoxy near 200 K on Pt(111).[18] This agrees with Wang et al., where the acetaldehyde desorbed ∼10 K lower from a Pt/Cu(111) SAA than from a sputtered Cu(111) surface.[15,19] On the other hand, the desorption temperature increases for Pt deposition at higher temperatures as shown in Figure S6 because the Pt is more widely distributed on the Cu(111) terraces. Thus, ethoxy forms near the terrace Pt atoms then spills over to adjacent Cu(111) sites where the C−H activation energy is higher than at either Cu(111) step sites or Pt sites. As the Pt deposition temperature was increased from room temperature to 450 K, the acetaldehyde desorption temperature approaches 370 K as seen for the oxidized Cu(111) surface in Figure 2. The larger distance between Pt atoms for higher deposition temperatures makes it more likely for C−H bond activation to occur at Cu rather than Pt sites. In addition, as the Pt atoms become more dilute, their electronic properties will be moderated from those of Pt atoms present in higher concentration or even present as Pt clusters.[29] Because the coverage of acetaldehyde formed is lower than the Pt coverage for the surfaces studied here, our results imply that spillover from Pt atoms to the Cu(111) surface does not go beyond the neighboring Cu atoms. If the ethoxy intermediate could diffuse to more stable sites, such as the step edges or kinks, the acetaldehyde desorption would not be higher than ∼315 K seen in Figure S8, where the ethoxy C−H bond is activated at defect sites.

5. SUMMARY

The formation of ethoxy from the nonoxidative dehydrogenation of ethanol on Pt/Cu(111) surfaces was directly detected with RAIRS. No ethoxy was detected on flat, clean Cu(111). Comparison of the RAIRS peak intensities for ethoxy formed on Pt/Cu(111) and on an oxidized Cu(111) surface indicates that the ethoxy coverage was less than the Pt coverage, contrary to what would be expected for the spillover effect. Ethoxy formation was also observed with RAIRS from a sputtered but unannealed Cu(111) surface, indicating that it can form at Cu defect sites even in the absence of Pt or O on the surface. For all surfaces on which ethoxy was detected with RAIRS, acetaldehyde was detected with TPRS. In addition, a small amount of acetaldehyde desorption was observed from the clean, flat Cu(111) surface, which was attributed to ethoxy formation at the step sites of the surface, which were present at too low a concentration to be detected with RAIRS.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.4c05508.

RAIRS and TPRS results following ethanol exposures at Pt coverages of 0.23 and 0.45 ML, after Pt deposition at 380 and 450 K, and after sputtering but not annealing the Cu(111) surface (PDF)

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https://pubs.acs.org/10.1021/acs.jpcc.4c05508

Notes

The authors declare no competing financial interest.

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