Ethanol Decomposition on Pd–Au Alloy Catalysts

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1. INTRODUCTION

Alloy catalysts are important because of their capacity for tuning adsorbate binding energies and catalytic activity. Many alloy catalysts have shown promising activity and/or selectivity for industrially significant heterogeneous catalysis, such as oxygen reduction, hydrogen evolution, CO oxidation, hydrogenation, and dehydrogenation. Understanding catalytic mechanisms on alloy surfaces can be difficult for two reasons: (i) there are several effects, including strain, electronic, and atomic ensembles, that affect activity; (ii) experimental determination of short-lived intermediates or transition states is difficult. Therefore, the rational design and tailoring of alloyed catalytic surfaces for specific reactions is particularly challenging but also very important.

Ethanol (EtOH) decomposition is a key step in industrially relevant reactions such as EtOH steam reforming and EtOH partial oxidation, whether as an unwanted side reaction or a step in the desired reaction. Compared to simpler reactions, EtOH decomposition is less well understood due to the numerous possible dehydrogenation steps as well as the possible order of C–C bond cleavage on various surfaces. To understand the EtOH decomposition mechanism, density functional theory (DFT) has proven to be a powerful method for monometallic surface studies including Pd, Pt, and Rh. Using DFT and Brønsted–Evans–Polanyi (BEP) relationships, Dumesic et al. developed a model for specific C–C bond cleavage for EtOH species on Pt, with good agreement with experiments. Mavrikakis et al. further generalized this method with scaling relationships that allowed for modeling EtOH decomposition on the close-packed surfaces of Cu, Pt, Pd, Ni, Ir, Rh, Co, Os, Ru, and Re. Their combined modeling and experimental study showed that most of these transition metals favor C–C bond cleavage of the CHCO species, leading to the selective formation of CH4. Weststrate et al. then experimentally found that C–O cleavage is also feasible on Co, suggesting that there are still mysteries related to EtOH decomposition on close-packed Pd–Au catalytic surfaces using density functional theory (DFT) calculations and derived Brønsted–Evans–Polanyi (BEP) relationships. Three characteristic Pd–Au surfaces are considered, Pd1Au2(111), Pd2Au1(111), and a Pd monolayer (ML), PdML(111), on a Au substrate. We show that, on close-packed Pd–Au surfaces, the C–C bond is easier to cleave than C–O, indicating that the formation of CH4 and CO is favored as the products of EtOH decomposition. Interestingly, we find that, though the C–C and C–O activation barriers on PdML(111) are generally lower than those on the other two surfaces, it is less active for EtOH decomposition due to a slow release of H2 and possible carbon coking. Pd1Au2(111), on the other hand, has a higher theoretical reaction rate due to facile H2 evolution from the surface and less carbon coking. A comparison of the surface d-band with the activation energy barriers shows that there is a trade-off between the barriers for C–C bond cleavage and H2 association, with Pd1Au2(111) having the best performance. Temperature-programmed desorption experiments of EtOH on Pd/Au surfaces show significant C–C bond cleavage and both CH4 and CO production on surfaces with Pd–Au interface sites. Furthermore, neither Auger electron spectroscopy nor EtOH reflection–desorption infrared spectroscopy provide evidence of C–O bond cleavage. Finally, the experimental reaction rate for methane production from C–C bond cleavage was higher on surfaces with more Au present due to minimal carbon contamination and the promotion of product desorption. This combined theoretical and experimental study shows that, though Au is catalytically inactive for EtOH decomposition, it can dramatically promote the surface activity for EtOH steam reforming due to the existence of active Pd–Au surface ensemble sites.
decomposition on catalysts. Xu et al.24,25 also systematically studied the Pt3M (M = Pt, Ru, Sn, Re, Rh, and Pd) catalysts for EtOH partial oxidation with DFT calculations. Very recently, we found that different surface structures of PdAu(111) and RhAu(111) lead to a variety of EtOH dehydrogenation activities and selectivities.16,12 Specifically, it was shown that tailoring the specific alloy ensembles could selectively target specific initial dehydrogenation of O−H, α-C−H, or β-C−H.4,16 Experimentally, Kumar et al.26 found that, similar to Ni, EtOH decomposition on CuNi bimetallic alloys leads to C−C bond cleavage, while pure Cu leads to only acetaldehyde at low temperature. Skoplyak et al.27 found that M/Pt(111) (M = Ni, Fe, and Ti) bimetallic surfaces yield high H2 production during EtOH reforming, with trends that correlate well with the calculated d-band center. However, due to the variety of dehydrogenated EtOH species and computational cost of many activation energy calculations, to the best of our knowledge, a kinetic and thermodynamic understanding of EtOH decomposition on an alloyed surface is not yet established.

As a miscible bimetallic, PdAu alloy is widely studied as a catalyst because it is relatively easy to prepare, it has good tunability of adsorbate binding, and it shows versatile catalytic performance.1,11,12,28–30 Our previous studies have found that, though Au is catalytically inactive for hydrogenation/dehydrogenation, the addition of Pd onto Au surfaces can result in enhanced alkane and allyl alcohol hydrogenation as compared to monometallic Pd.1,9 Our recent study on PdAu close-packed surfaces shows that a very small amount of Pd alloyed on Au(111) leads to the selective formation of H2 and acetaldehyde, while, when the surface contains predominately Pd−Au interface sites, there is a high production of H2 and CO.12 Motivated by this result and the recognition that the mechanism of EtOH decomposition can affect the products of EtOH reactions, we selected a PdAu(111) alloy catalyst as a case study for modeling EtOH decomposition. Using DFT calculations, we found that, on PdAu(111) surfaces, C−C bond cleavage is favorable, leading to selective CH4 and CO formation. Our model shows that Pd(111)-like sites are favorable for C−C bond cleavage but can also result in coking, while Pd−Au interface sites are more favorable for H2 desorption and resist coking. To support our model, ultrahigh vacuum (UHV) experiments were performed on two Pd−Au catalysts with different surface site compositions, to show the production of CH4, CO, and carbon poisoning, in good agreement with our theoretical predictions.

2. METHODS

2.1. Computational and Modeling Methods. All DFT calculations were performed using the Vienna ab initio simulation package (VASP). A projector augmented-wave method was used to describe the core electrons.31 The generalized gradient approximation with the Perdew–Burke–Ernzerhof (PBE) functional was employed to describe the electronic exchange and electronic correlation.32 For the valence electrons, Kohn–Sham wave functions were expanded in a plane wave basis.33 The energy cutoff of all calculations was set at 300 eV. Soft potentials were used to describe the electrons of oxygen and carbon. The Brillouin zone was sampled with a 3 × 3 × 1 Monkhorst–Pack k-point mesh. Geometries were optimized when the force per atom was lower than 0.05 eV Å−1. All transition states and energy barriers were calculated using the climbing image nudged elastic band (CINEB) method,34 where more than five intermediate images were generated between the initial and final states. Convergence tests were performed by increasing the cutoff, force criterion, and number of layers in the slab model, with standard PAW potentials (Tables S1 and S2); no significant changes in the binding energies, energy barriers, or the optimized structures were found. Spin-polarization was tested and found to have a negligible influence on the thermodynamic and kinetic results. Therefore, spin polarization was not included in the calculated results of this paper.

In regard to influencing the selectivity and activity for hydrogenation, dehydrogenation, and oxygen reduction reaction on alloy surfaces, our previous studies show that atomic ensemble effects are generally more significant as compared to electronic (ligand) and strain effects when considering the adsorption of hydrogen, oxygen, hydroxyl, and other EtOH-related species.35−10,12,28 This observation is consistent with our current results showing similar binding energies on Pd monolayers (MLs) on different subsurface alloys, while the bonding energies on three surfaces with different surface compositions, shown in Figure 1, are significantly different (Table S3). This shows that the contributions from subsurface alloying and surface strain to the binding energy of adsorbates are less important than the ensemble effect for our random alloys. Therefore, we do not consider the sublayer composition in our study. On the PdAu(111) alloy surfaces, the triatomic ensembles (Au3, Pd3Au, and Pd3) are the smallest unit that determine adsorbate binding of H2, O, OH, and CO.1,9,13,28 In light of this result, all calculations were performed on the three PdAu surfaces: Pd3Au, Pd3, and Pd3 shown in Figure 1; these surfaces present the Pd3Au, Pd3, and Pd3 triatomic ensembles, respectively. Previous theoretical studies show that these three alloy surfaces are representative models for the evaluation of ensemble effects on close-packed surfaces.29,35 All three surfaces were modeled as a four-layer slab with (3 × 3) unit cells, with a vacuum layer of 12 Å separating periodic images of the slab. For each slab, the bottom two atomic layers were kept fixed in bulk positions, while the topmost two layers were allowed to relax freely. The lattice constant C used for this study was calculated according to the composition of Pd−Au in the model

\[
C = C_{Pd} \cdot Pd\% + C_{Au} \cdot Au\%
\]

(1)

where \(C_{Pd}\) and \(C_{Au}\) represent the lattice constants of Pd and Au, respectively, and \(Pd\%\) and \(Au\%\) represent the composition of Pd and Au, respectively. In this study, \(C_{Pd} = 3.89 Å\) and \(C_{Au} = 4.08 Å\). Therefore, the lattice constants of Pd3Au(111), Pd3Au(111), and Pd3(111) are 4.06, 4.05, and 4.03 Å, respectively. All of the binding energies \(E_b\) were calculated using eq 2.

Figure 1. Three types of PdAu(111) surfaces considered in our DFT calculations, consisting of the triatomic ensembles of Pd3Au, Pd3, and Pd3. Blue and golden spheres represent Pd and Au atoms, respectively.

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where \( E_{\text{ads}} \) is the energy of the surface with adsorbate, \( E_{\text{ss}} \) is the energy of the bare surface, and \( E_{\text{ads}} \) is the energy of the adsorbate in a vacuum.

2.2. Experimental Methods. In this study, experiments were performed in a molecular beam scattering UHV apparatus with a base pressure of \( 1 \times 10^{-10} \) Torr that has been described previously.\(^{36,56,57}\) The apparatus is equipped with a quadrupole mass spectrometer (QMS) for detection of gaseous reactants and products, Auger electron spectroscopy (AES) with an electron beam energy of 3 keV and emission current of 1.5 mA to verify Pd deposition and cleanliness of the Au(111) substrate, and reflection–adsorption infrared spectroscopy with all spectra reported being an average of 512 scans at a resolution of 4 cm\(^{-1}\).

The Pd–Au model catalysts were prepared by depositing Pd via a thermal evaporator onto a 11 mm diameter Au(111) single crystal surface at 77 K, followed by annealing at 500 K for 10 min. A quartz crystal microbalance controller was used to calibrate the Pd deposition rate with the assumption that the thickness of 1 Pd monolayer (ML) is equivalent to the diameter of a Pd atom (0.274 nm). Before Pd deposition, the Au(111) substrate was cleaned by argon ion bombardment (2 keV), followed by annealing to 800 K for 15 min. EtOH was exposed to our catalysts via a molecular beam that is directed by a series of aligned apertures. After exposure, temperature-programmed desorption (TPD) measurements were conducted by heating the Pd–Au catalysts at a rate of 1 K/s. Reactants and various potential products were monitored using their corresponding QMS signals.

3. RESULTS AND DISCUSSION

3.1. C–C and C–O Cleavage. With the CINEB method, we calculated the activation energies of C–C and C–O bond cleavage of EtOH and dehydrogenated EtOH species. In total, we calculated 34, 38, and 33 activation energies on the Pd\(_2\)Au\(_1\)(111), Pd\(_3\)Au\(_4\)(111), and Pd\(_{\text{ML}}\)(111) surfaces, respectively. To estimate the remaining possible activation energy barriers, given all possible surface sites and bonds to cleave, a BEP relationship for each surface was acquired (Figure 2) using the transition state and final state energies \( E_{\text{TS}} \) and \( E_{\text{FS}} \). It can be seen that the \( R^2 \) values of the three BEP relationships are high (0.94, 0.91, and 0.87, respectively), which justifies our use of linear scaling relationships. The slopes and intercepts of the three regression lines are similar. Reassuringly, these regression lines are also similar to a previous study on Pt(111) and Ru(0001),\(^{38}\) which indicates that the BEP relationships of EtOH decomposition are fairly general on different close-packed surfaces.

Figure 2. BEP correlation between the transition state (TS) energy and the final state (FS) energy for C–C and C–O bond cleavage on Pd\(_2\)Au\(_1\)(111) (red), Pd\(_3\)Au\(_4\)(111) (green), and Pd\(_{\text{ML}}\)(111) (blue). The values of \( E_{\text{TS}} \) and \( E_{\text{FS}} \) are relative to the bare slab, EtOH (in gas phase) and H\(_2\) (in gas phase).

Though activation energies can be acquired from the CINEB method with DFT, there are still 39 missing activation energies due to the combinatorial complexity of the potential energy surfaces. Here, following a method similar to previous studies,\(^{16,17}\) we use the BEP relationships acquired from Figure 2 to predict the activation energies of the remaining 39 C–C/C–O bond cleavage steps. To reduce the uncertainty in the model, we calculated all of the final state energies, \( E_{\text{FS}} \) with DFT. All of the activation energy barriers (both calculated and BEP-predicted) are shown in Figure 3. It can be seen that, with a higher surface Pd composition, the energy barrier for both C–C and C–O bond cleavage generally decreases, in good agreement with our previous experimental and theoretical work.\(^{10,12}\) This also shows that less dehydrogenated EtOH species tend to have a lower C–O bond cleavage barrier, while higher dehydrogenated EtOH species generally tend to have a lower C–C bond cleavage barrier.

To better understand C–C and C–O bond cleavage trends on the three surfaces, the projected density of states (PDOS) of the surface d-band were calculated and shown in Figure 4. It can be seen that, with increased Pd alloyed on the (111) surface, the PDOS is more contracted. Also, the d-band is closer to the Fermi level with more surface Pd, indicating more facile O–H, C–H, C–C, and C–O bond activation.\(^{38}\) However, this upward shift of the d-band also leads to stronger binding of H and a possible bottleneck of H\(_2\) evolution from the surface for EtOH decomposition. We will discuss these two effects in the following sections.

3.2. Calculations of the Catalytic Activity for EtOH Decomposition. The H\(_2\) association barriers and cleavage of the C–O and C–C bonds, as presented in Table 1, show that the H\(_2\) association energy generally increases with an increase of Pd composition, as we have seen previously.\(^{12}\) In terms of the C–C and C–O bond cleavage, all steps are endothermic on Pd\(_2\)Au\(_1\)(111), indicating a low EtOH decomposition activity, which is consistent with our previous experimental results: when the PdAu(111) surface contained a small amount of Pd, only acetaldehyde was detected during EtOH reforming and no subsequent products were detected.\(^{12}\) On Pd\(_2\)Au\(_1\)(111), all C–O bond cleavage steps are endothermic and only the C–C bond cleavage on CHCO is significantly exothermic (–0.48 eV). On Pd\(_{\text{ML}}\)(111), CH\(_2\)CH\(_2\)O has the only significant exothermic step for C–O bond breaking (–0.14 eV), while CHCO has the most exothermic C–C bond cleavage step (–0.89 eV). However, on Pd\(_{\text{ML}}\)(111), C–O bond cleavage has a higher energy barrier (0.89 eV) than C–C bond cleavage (0.42 eV), indicating that C–C bond cleavage is the favorable step on Pd\(_{\text{ML}}\)(111). Both for this reason and considering our subsequent experimental observation that no C\(_2\) products were detected, we do not consider C–O bond cleavage in our kinetic model; additionally, our experiments, discussed later, justify this exclusion. The complete thermodynamic and kinetic data can be found in Tables S4 and S5.
there are also several intermediate species with exothermic steps found on Pd2Au1(111) and PdML(111), CHCO still has the most significantly exothermic energy for C–C cleavage. Details of the reaction pathways at CHCO* can be found in Figure S1.

To model the reaction rates of C–C and C–O cleavage on PdAu(111), we used the simplified EtOH decomposition.
PdML(111) can be calculated as a function of temperature assumption that, compared to C

\[ Pd_{2}Au_{1}(111) \text{ has a higher H}_2 \text{ desorption energy (1.21 eV) than } \]

PdML(111) has a higher H\textsubscript{2} desorption energy (1.21 eV) than Pd\textsubscript{2}Au\textsubscript{1}(111) (0.68 eV), which leads to slower H\textsubscript{2} release from the Pd\textsubscript{ML}(111) surface, hindering subsequent C–C bond cleavage. The energy profile of H\textsubscript{2} desorption can be found in Figure S2. It should be noted that, in our experiments, if the PdAu alloy is randomly distributed, there will be a distribution of PdAu ensembles. With the previous conclusions that on close-packed PdAu surfaces all PdAu ensembles can be classified as three different 3-fold triatomic ensembles (Au\textsubscript{1}Pd\textsubscript{2}, Au\textsubscript{2}Pd\textsubscript{1}, and Pd\textsubscript{3}), we consider only the three surfaces shown in Figure 1 as models in this study. Since the Pd\textsubscript{ML}(111) model has a log(r\textsubscript{C–C}) value lower than 0 when the temperature is lower than 800 K, it is expected that a pure Pd ML surface should be less catalytically active experimentally. Therefore, our theoretical modeling predicts that a PdAu surface containing Pd–Au interface sites should facilitate significant CO and CH\textsubscript{4} production, while surfaces containing only Pd(111)-like sites should be significantly less active for EtOH decomposition below 500 K. It should be noted that this kinetic model is not expected to be quantitatively accurate and only qualitative trends should be compared to experiments. Therefore, in the UHV experiments discussed in the following section, we focus on mechanistic differences between the Pd–Au interface and Pd(111)-like sites under the same experimental conditions. To better understand the activity differences of the three surfaces, a d-band center model clearly shows that there is a trade-off between C–C bond cleavage and H\textsubscript{2} association: shifting the d-band toward the Fermi level leads to a lower C–C cleavage barrier but also a higher H\textsubscript{2} association barrier (Figure 5b). Thus, from a catalyst design perspective, there is no way to lower both of these barriers. This could, however, explain why Pd\textsubscript{2}Au\textsubscript{1}(111) theoretically performs better than Pd\textsubscript{Au}(111) and Pd\textsubscript{ML}(111): a careful tuning of the d-band center would maintain both C–C bond cleavage activity as well as H\textsubscript{2} desorption.

In addition to the kinetics and thermodynamics of the reactions, carbon coking is another important issue that should be considered. With the assumption that carbon coking correlates with the carbon binding energy through a scaling relationship, we calculated the carbon binding energy on the three modeled surfaces (Figure 6). It can be clearly seen that, with the increase of surface Pd, the carbon binding energy increases linearly, indicating that larger Pd ensembles should lead to more coking, in agreement with the d-band theory (Figure 6, inset). This is consistent with our previous studies.

\[ \text{CH}_3\text{CH}_2\text{OH}(g) + * \rightarrow \text{[CH}_3\text{CH}_2\text{OH}^*]^e + (6 - x - y - z)/2\text{H}_2(g) \]

\[ \text{(3)} \]

where x, y, and z represent the number of H atoms in their corresponding functional groups after EtOH dehydrogenation. From Table 1, we can see that the most favorable species for C–C bond cleavage on metallic surfaces can be derived from transition state theory (see the Supporting Information) and the theoretical activity of the C–C bond cleavage reaction rate log(r\textsubscript{C–C}) on Pd\textsubscript{Au}(111) and Pd\textsubscript{ML}(111) can be calculated as a function of temperature (Figure 5). Although the C–C bond cleavage step on

Figure 5. (a) Modeled reaction rates of EtOH C–C bond cleavage (log(r\textsubscript{C–C})), unit: log(s\textsuperscript{−1})) on Pd\textsubscript{Au}(111) and Pd\textsubscript{ML}(111). The catalytic modeling details can be found in the Supporting Information. (b) Calculated d-band center versus activation energies for H\textsubscript{2} association and C–C bond cleavage at CHCO.

Pd\textsubscript{2}Au\textsubscript{1}(111) has a higher energy barrier than that on Pd\textsubscript{ML}(111) (Table 1), its theoretical reaction rate is significantly higher than that of Pd\textsubscript{ML}(111). This is because Pd\textsubscript{ML}(111) has a higher H\textsubscript{2} desorption energy (1.21 eV) than Pd\textsubscript{2}Au\textsubscript{1}(111) (0.68 eV), which leads to slower H\textsubscript{2} release from the Pd\textsubscript{ML}(111) surface, hindering subsequent C–C bond
of sulfur poisoning on PdAu, where larger Pd ensembles increase sulfur poisoning on PdAu(111) and significantly decrease the nitrite reduction activity of pure Pd nanoparticles to almost zero.\textsuperscript{38} With the calculated surface d-band, we expect the binding of other carbon species would also be strengthened when the surface Pd composition is increased, leading to significant coking. Therefore, it is expected that on the Pd\textsubscript{44}Au\textsubscript{56}(111) surface there should be less activity than Pd\textsubscript{2}Au\textsubscript{1}(111) because of the slow H\textsubscript{2} evolution kinetics as well as additional carbon coking.

3.3. UHV Experiments. To provide experimental evidence for the theoretical calculations presented above, we conducted UHV experiments on Pd–Au model catalysts. In this study, we studied two Pd–Au model catalysts: Au(111) with 2 and 4 ML Pd as measured by the initial coverage. After annealing at 500 K for 10 min, the 2 ML Pd–Au coverage formed a surface containing a 74.9% Pd–Au interface and 25.1% Pd(111)-like sites, whereas the 4 ML Pd–Au coverage formed a surface containing only Pd(111)-like sites. The site composition was quantified by H\textsubscript{2} temperature-programmed desorption (TPD). Determination of the surface composition is supported by our previous studies using H\textsubscript{2}, O\textsubscript{2}, and CO TPD and reflection-absorption infrared spectroscopy (RAIRS) experiments for similar Pd deposition and annealing conditions.\textsuperscript{11,12,40−44} In our previous work, we showed that the 2 ML Pd–Au catalyst showed the highest activity for H\textsubscript{2} production from EtOH at 500 K.\textsuperscript{12} To investigate the EtOH decomposition products on the surface, we impinged 1.0 ML of EtOH (or CD\textsubscript{3}CH\textsubscript{2}OH) on 2 ML Pd–Au via a molecular beam and conducted TPD experiments, as shown in Figure 7a. Here, we see the production of CO (m/z = 28) at 455 K, CH\textsubscript{4} (m/z = 16) at 300 K, and HD (m/z = 3) at 350 K. The production of CO and CH\textsubscript{4} is indicative of C–C bond breakage, which is consistent with previous studies on a Pd(111) surface and the theoretical work described above.\textsuperscript{17,45} Furthermore, the HD production suggests dehydrogenation of the methyl group, making C–C bond breakage more favorable per the theoretical results shown in Figure 3. CO, CH\textsubscript{4}, and H\textsubscript{2} were also produced on the 4 ML Pd–Au catalyst (not shown) at similar product yields as the 2 ML Pd–Au catalyst. This is not surprising considering that EtOH decomposition has previously been shown on Pd(111) model catalysts.\textsuperscript{46} It is worth noting that, due to a signal contribution of background H\textsubscript{2}, it was difficult to distinguish between H\textsubscript{2} that adsorbed on the surface and H\textsubscript{2} that was produced from EtOH. Therefore, we used CD\textsubscript{3}CH\textsubscript{2}OH to highlight the decomposition of the EtOH’s methyl group on the surface.

We also conducted Auger electron spectroscopy (AES) on the 2 and 4 ML Pd–Au surfaces before and after EtOH exposure (Figure 7b). There was no observation of an oxygen feature (503 eV), which we would expect if there was significant C–O cleavage of EtOH. However, we do suspect a carbon contribution to the Auger spectra on the 2 ML Pd–Au surface after EtOH desorption. Pd has three prominent features at 243, 279, and 330 eV. The 279 eV feature dwarfs the 272 eV carbon feature, making it difficult to confirm the presence of carbon on Pd surfaces. However, we see two telltale changes in the second Pd feature after EtOH desorption. First, the bottom peak shifted to a lower kinetic energy by 4 to 274 eV, which suggests a convolution of the 272 eV carbon feature with the 279 eV Pd feature. Second, the peak-to-peak intensity of this feature is larger relative to the other two Pd features when compared to the clean 2 ML Pd–Au catalyst. This is indicative of contribution from another element, which would be carbon. Additionally, the HD production from CD\textsubscript{3}CH\textsubscript{2}OH decomposition, shown in Figure 7a, supports the production of carbon. Dehydrogenation of the methyl group can result in surface carbon that may be observed in AES (Figure 7b). For the 4 ML Pd–Au catalyst, the 279 eV Pd feature is too large to see the presence of carbon. There is no shift in the peak nor is there a change in the relative size of this second feature. However, we suspect that there is still carbon contamination that is occurring on our catalysts, as seen on Pd(111).\textsuperscript{46} More importantly, there was no presence of oxygen, indicating no C–O dissociation on the 4 ML Pd–Au surface. From AES, we see changes in the spectra indicative of carbon contamination from EtOH decomposition, but the absence of an oxygen feature suggests there is minimal C–O cleavage of the EtOH molecule, in agreement with the theoretical results.

Additionally, we conducted ethanol reflection–absorption infrared spectroscopy (EtOH-RAIRS) on the 2 ML Pd–Au surface to obtain insight into EtOH decomposition on the catalytic surface. In Figure 8, we have EtOH-RAIRS spectra of the 2 ML Pd–Au surface with EtOH coverages from 1 to 4 ML with the assignment of the peaks to their vibrational modes in Table 2. Assignments were made by comparison with high resolution electron energy loss (HREEL) spectroscopy of EtOH on Pd(111) and EtOH in an argon matrix.\textsuperscript{45} At 1 ML EtOH, we see the O–H, CH\textsubscript{3}, and asymmetric C–C–O stretches. Even at low coverage, the asymmetric C–C–O stretch has a relatively large intensity which is indicative of being a prominent species on the surface and is predominantly...
In our previous work, we impinged EtOH on Au(111), 2 ML Pd–Au, and 4 ML Pd–Au at 350 K. Pd–ML(111) models and the 4 ML Pd–Au catalyst is analogous to PdML(111). From impinging EtOH on our catalytic surfaces at elevated temperatures and detecting CH4, we can provide experimental support to the theoretical reaction rates shown in Figures 5 and 6. In our previous work, we impinged EtOH on Pd–Au surfaces at 500 K, observing H2 and CO evolution, but we were unable to observe a measurable amount of CH4. TPD of EtOH on 2 ML Pd–Au shows us that decomposition of the methyl group occurs at 350 K, as shown in Figure 7a. Therefore, impinging EtOH on the catalytic surface above 350 K results in methyl decomposition instead of methane evolution that is observable via the QMS. Lowering the temperature enables the recombination of methyl groups with H atoms to produce methane. In Figure 9, we show methane (m/z = 15 and 16) spectra from a modified King and Wells experiment impinging EtOH on an inert Au(111), 2 ML Pd–Au, or 4 ML Pd–Au at 350 K for 30 s each. EtOH is nonreactive on Au(111) at 350 K, so it can serve as a baseline for methane production compared to the other two Pd–Au surfaces. From 85 to 115 s, we see production of methane on the 2 ML Pd–Au surface, but the 4 ML Pd–Au surface resembles that of the inert Au(111) sample, which is consistent with the higher theoretical reaction rates of C–C bond breakage for the PdAu(111) surface. With the surface largely covered by Pd on the 4 ML Pd–Au catalyst, the surface remains reactive but may result in more carbon contamination instead of methane evolution. With the presence of more Au on the surface, CH4 more readily desorbs, as shown by the 2 ML Pd–Au catalyst. It is worth noting that m/z = 15 is also a mass fragment of EtOH, which is why there is an increase in that signal upon impinging EtOH on the inert flag. With the modified King and Wells experiment, we can further confirm C–C bond cleavage on the Pd–Au catalysts and observe better product evolution from the surface with predominately Pd–Au interface sites. These results are in good agreement with our calculations. However, given the intrinsic differences between the theoretical model and the experiments, we have not compared the precise reaction temperature between theory and experiment. We also expect that a full kinetic model with more calculations of EtOH dehydrogenation mechanisms would provide a more quantitative comparison with experiment but not alter the qualitative trends derived from our present model.

### 4. Conclusion

In this paper, we have conducted a combined theoretical and experimental study to understand EtOH decomposition on Pd–Au alloy catalysts. Using DFT calculations and the BEP relationships, we constructed an activation energy database for possible EtOH C–C and C–O bond cleavage mechanisms on three characteristic Pd–Au close-packed surfaces: Pd3Au1(111), Pd2Au2(111), and PdML(111). Both the calculated kinetic and thermodynamic results show that, on PdAu(111), C–C bond cleavage is more favorable than C–O bond cleavage. Using the computational method developed from previous studies, we estimated the theoretical catalytic activities of C–C bond cleavage as a function of reaction temperature. Our results show that a PdAu(111) surface should have a high EtOH decomposition activity, while Pd3Au1(111) and PdML(111) are less active. These results can be explained by the trade-off between C–C cleavage and H2 association as a function of the surface d-band. Using UHV...
ETOH decomposition experiments, we have been able to provide experimental support to the theoretical calculations. TPD of ETOH on Pd–Au shows the production of CH2, CO, and H2, indicating that C–C bond cleavage is favorable. The absence of oxygen in AES after ETOH decomposition and the intense peak for C–O vibration in ETOH-RAIRS suggest that C–O bond cleavage is not prominent on the Pd–Au surface. Finally, we see a similar trend in the C–C bond cleavage reaction rate where a surface containing predominantly Pd–Au interface ensembles has a higher ETOH decomposition catalytic activity than surfaces with Pd(111)-like and pure Au(111) sites. These experimental results are qualitatively consistent with the theoretical model. We expect that both the theory and experiments in this study will help to understand the activity and selectivity of ETOH decomposition on the alloyed catalytic surface and more generally for tailoring alloyed systems for industrial catalyst design.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.8b08150.

Modeling details, convergence tests, calculated thermodynamic and kinetic data, C–O and C–C cleavage mechanisms of CHCO, and the most significant geometric coordinates of our models (PDF)

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**REFERENCES**


(22) Gursahani, K. I.; Alcalá, R.; Cortright, R. D.; Dumesic, J. A. Reaction Kinetics Measurements and Analysis of Reaction Pathways


