Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Mechanistic Insights on Ethanol Dehydrogenation on Pd-Au Model Catalysts: A Combined Experimental and DFT Study

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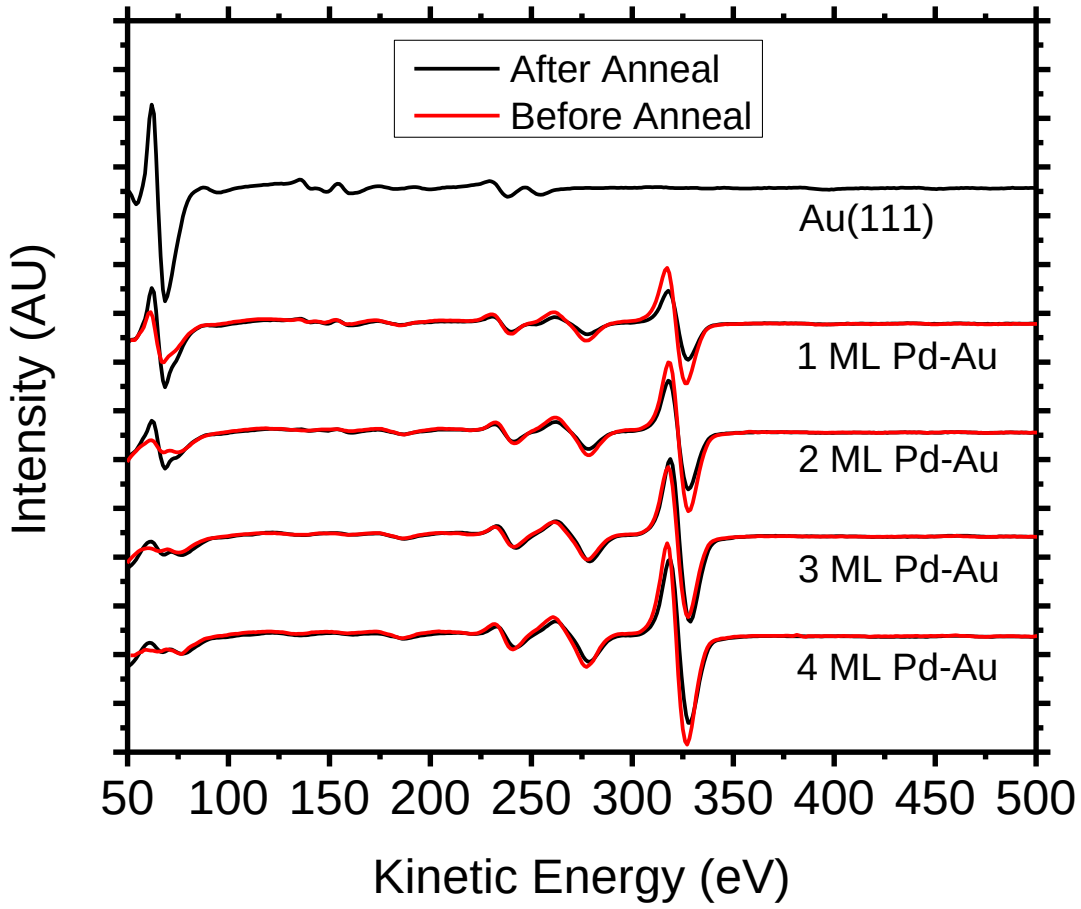

Figure S1. Auger Electron Spectroscopy (AES) spectra of Au(111) with Pd coverages of 1 ML, 2 ML, 3 ML, and 4 ML before and after annealing at 500K for 10 minutes.

Table S1: Pd(328eV)/Au(69eV) peak to peak ratios from AES spectra of Au(111) with Pd coverages of 1 ML, 2 ML, 3 ML, and 4 ML Pd before and after annealing at 500K for 10 minutes

Pd(328eV)/Au(69eV) Ratios		
	Before Anneal	After Anneal
1 ML Pd-Au	2.31	0.69
2 ML Pd-Au	12.18	2.28
3 ML Pd-Au	50.37	12.45
4 ML Pd-Au	108.92	18.02

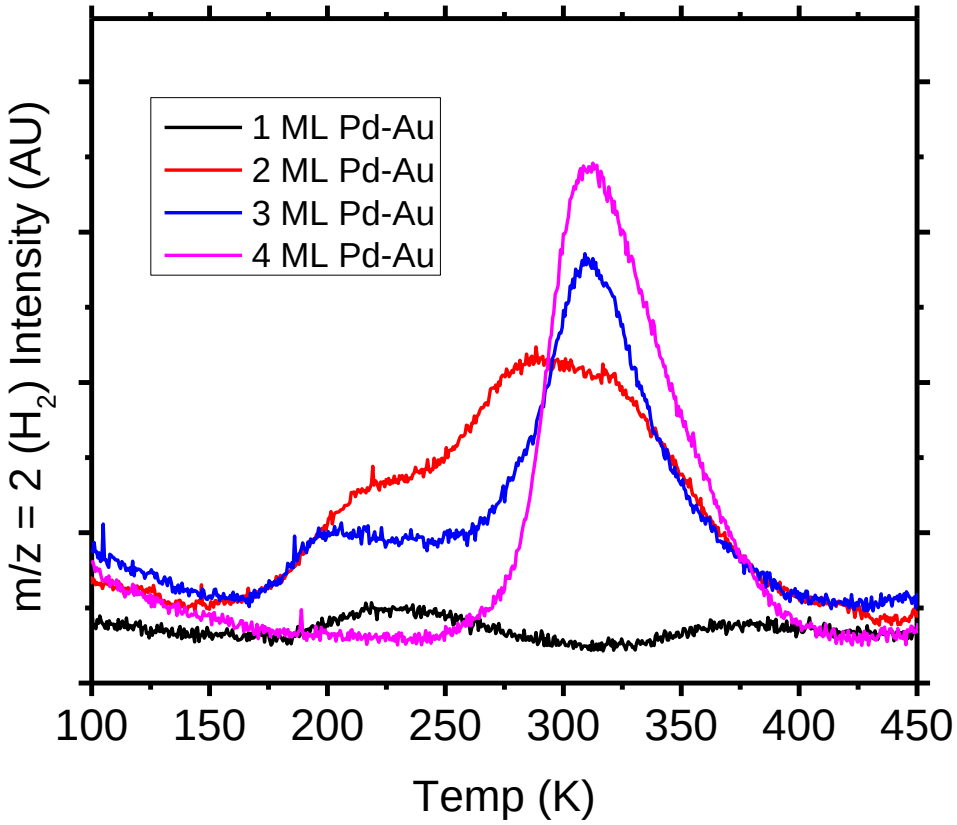

Figure S2. Background-subtracted H_2 Temperature-programmed desorption (TPD) from 1 ML, 2 ML, 3 ML, and 4 ML Pd-Au surfaces.

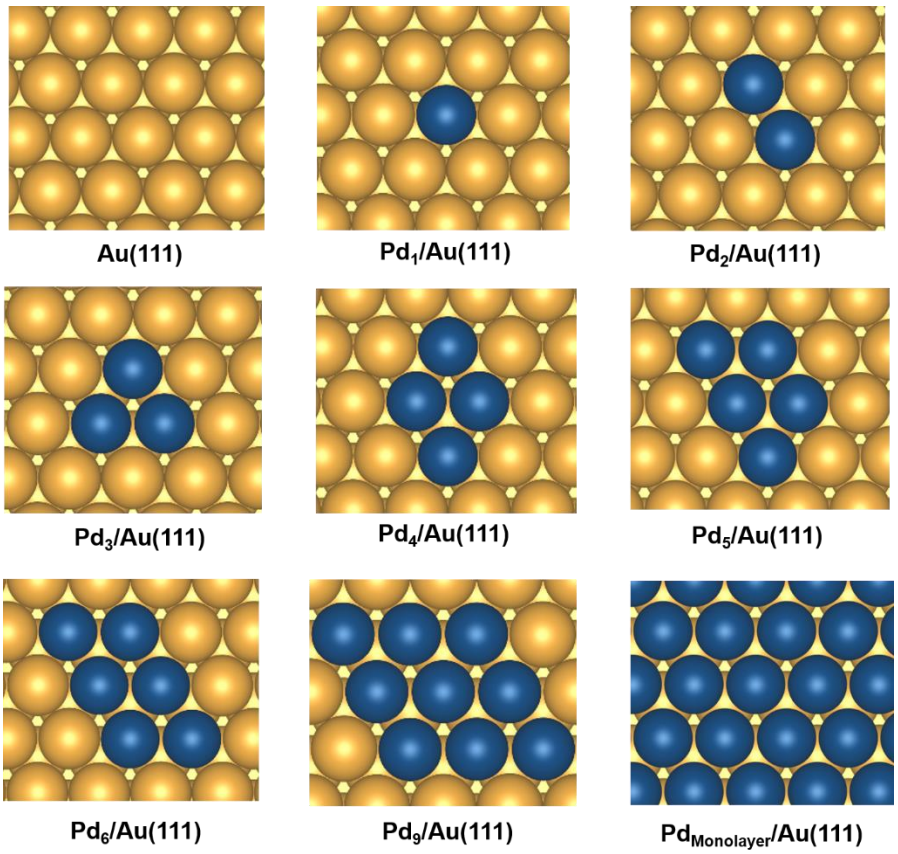

Figure S3. Pd/Au(111) surfaces considered for DFT calculations. Blue and golden spheres represent Pd and Au atoms, respectively.

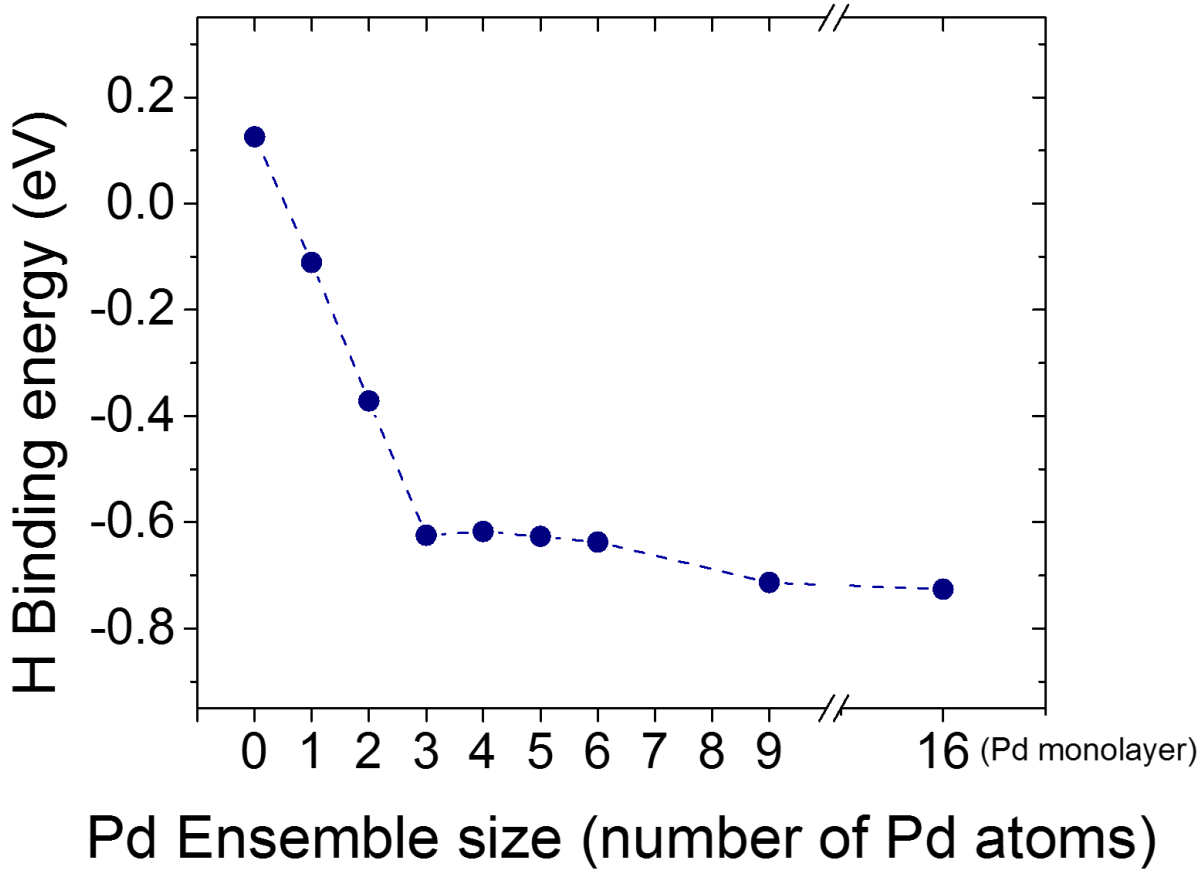

Figure S4. DFT calculations of the H binding energy vs the Pd ensemble size on the Pd/Au(111) surfaces shown in Figure S3.

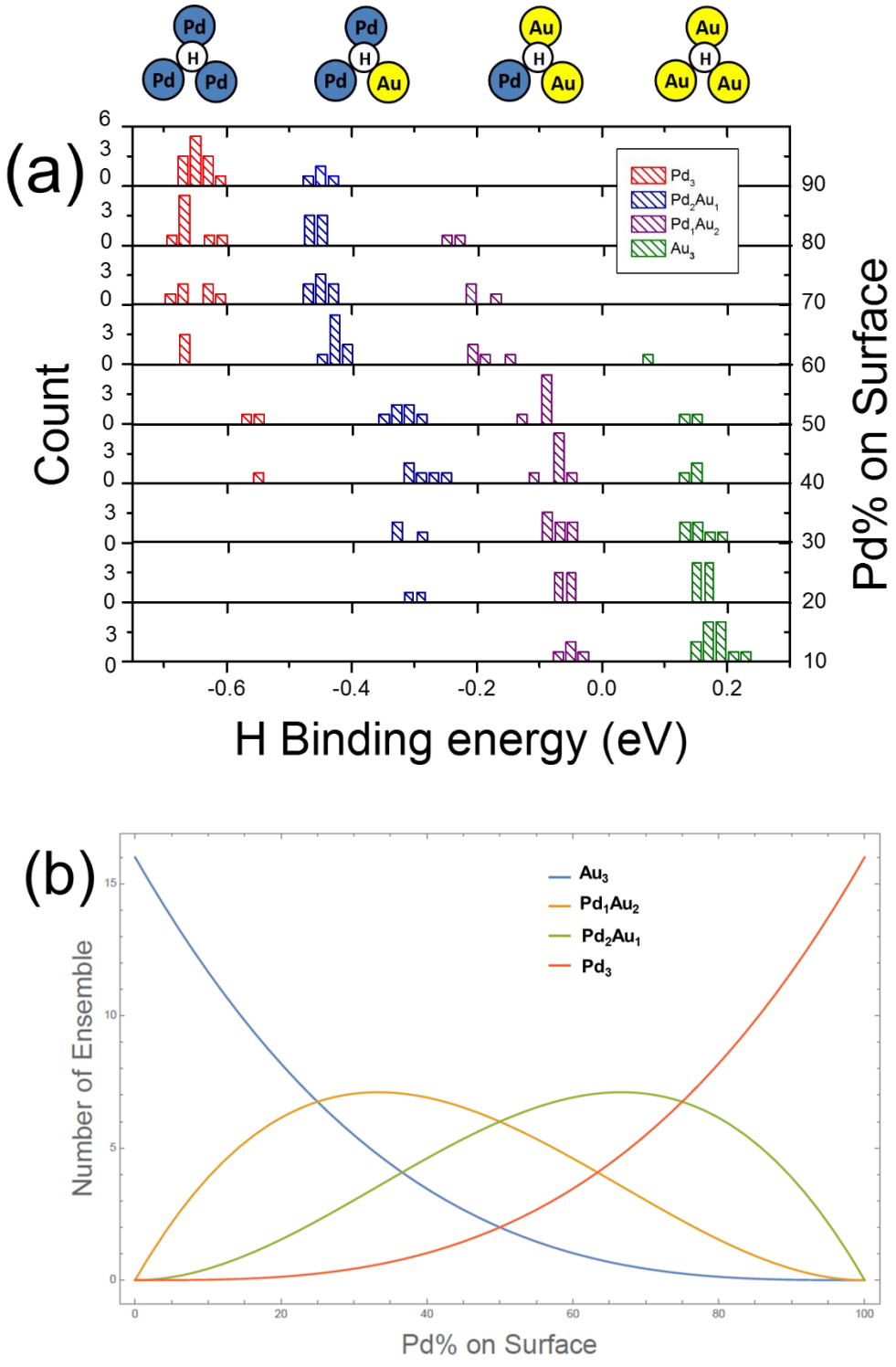

Figure S5. (a) DFT calculations of the H binding energy on 3-fold ensembles created by varying Pd coverage on Pd/Au(111) random surface alloys. (b) Calculated distribution of 3-fold ensembles on

Pd/Au(111) surface alloys with varying compositions, with the assumption that Pd and Au distribute randomly on surface.

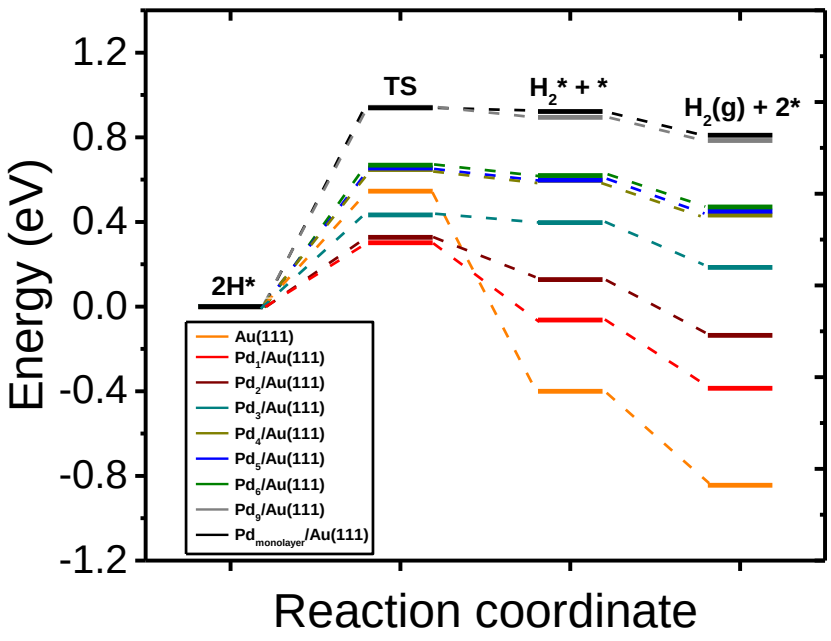

Figure S6. Reaction pathway of H_2 association and desorption on Pd_x/Au(111) surface alloys, where x is the number of atoms of the Pd ensemble, shown in Figure S3. Entropy corrections of H_2 were added with the temperature of 298.15 K.

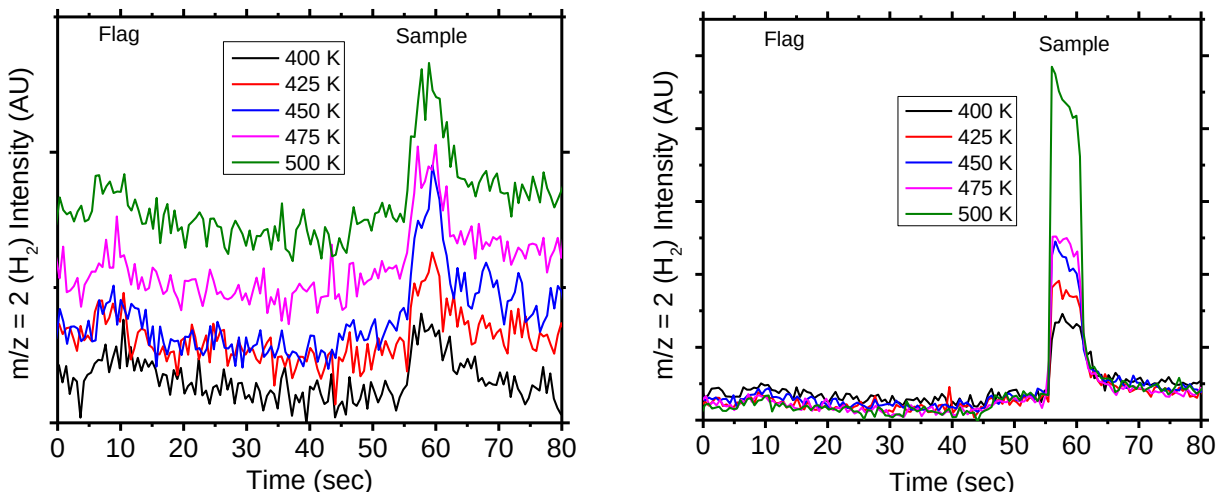

Figure S7. H_2 production on a) 1 ML and b) 2 ML Pd-Au catalyst from EtOH decomposition at varying temperatures. EtOH was impinged on the inert flag from 5-10sec and on the Pd-Au model catalysts from 55-60sec.

Table S2: Turnover Frequency of H_2 production on 1 ML and 2 ML Pd-Au at varying temperatures from 400K to 500K.

Turnover Frequency (H_2/(site*sec))		
Temp	1 ML Pd-Au	2 ML Pd-Au
400	3.37E-03	2.68E-03
425	3.90E-03	3.15E-03
450	5.12E-03	3.76E-03
475	6.42E-03	4.45E-03
500	7.46E-03	8.48E-03

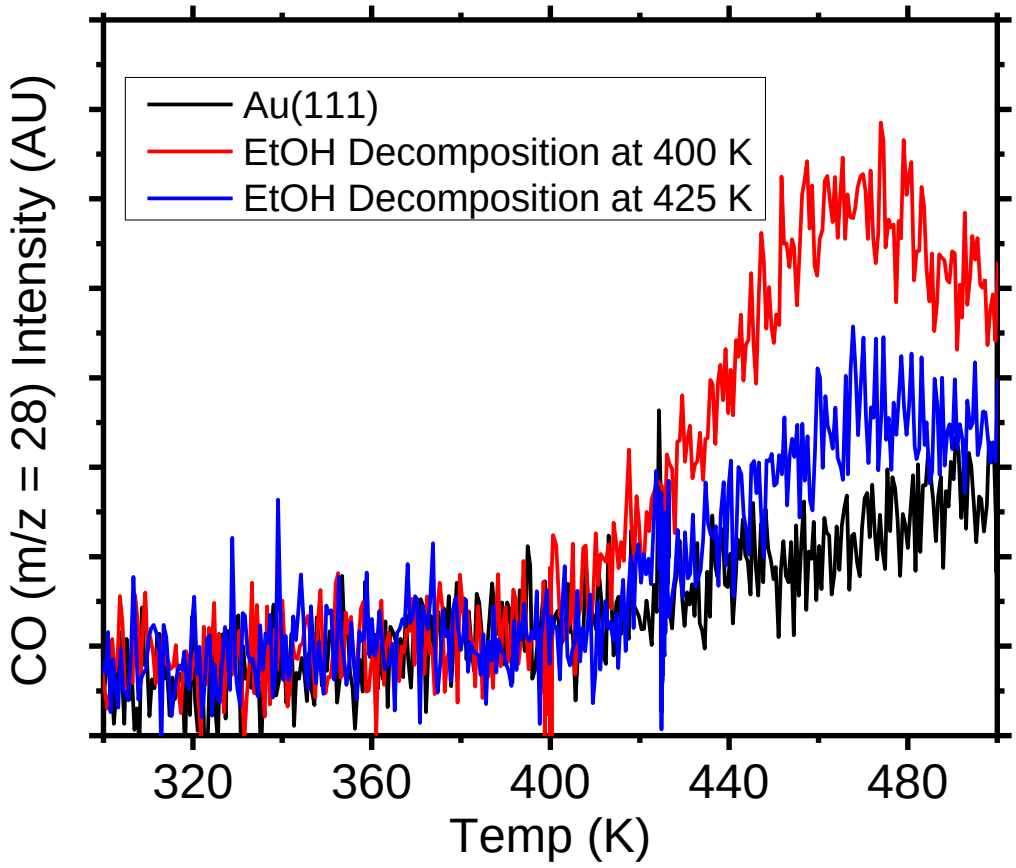

Figure S8. CO production from EtOH on Au(111) and 2 ML Pd-Au at 400K and 425K.

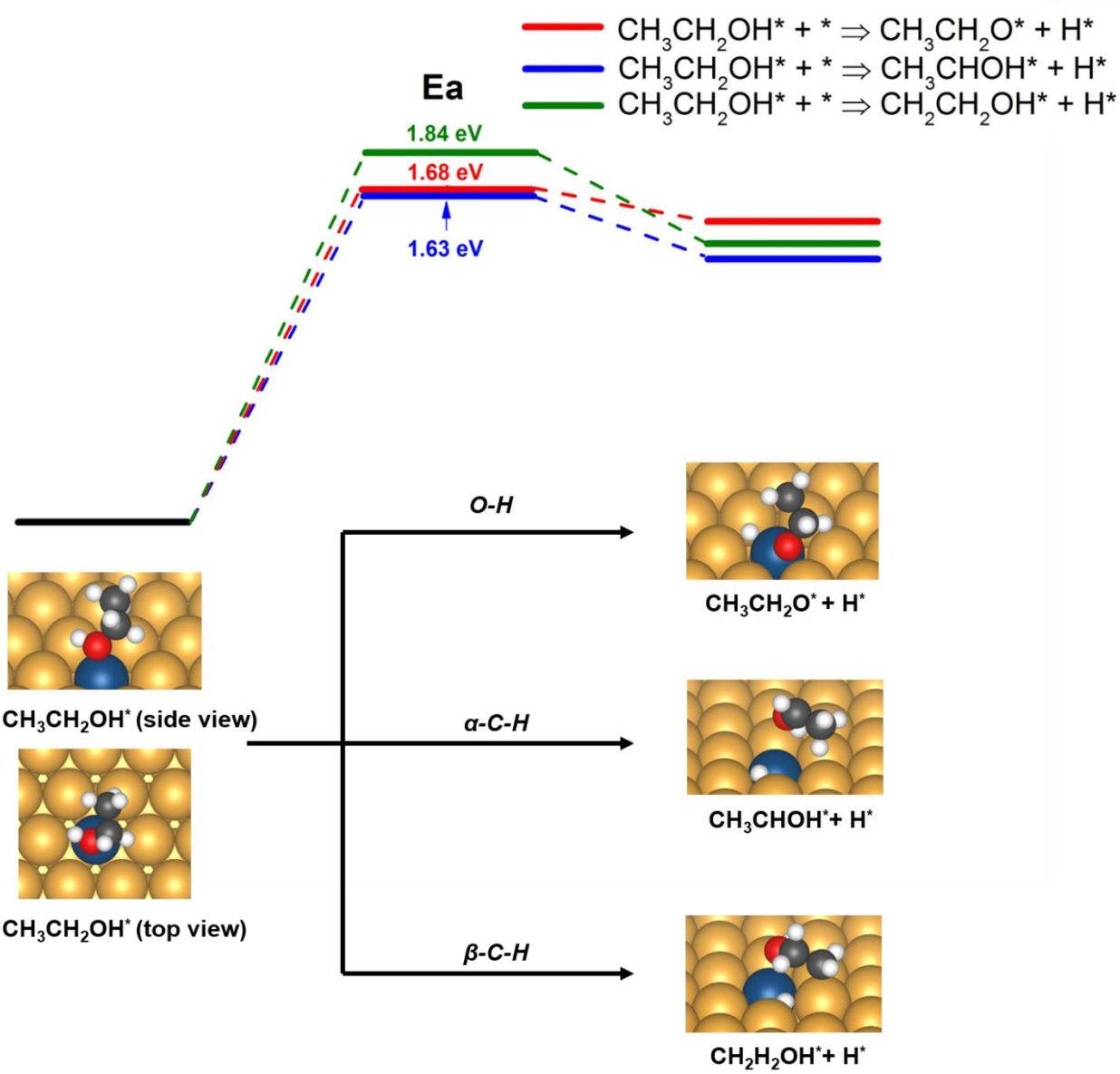

Figure S9. Energy pathways of three initial dehydrogenation steps of EtOH (hydroxyl dehydrogenation, α-carbon dehydrogenation, or β-carbon dehydrogenation) on a $Pd_1/Au(111)$ surface alloy.

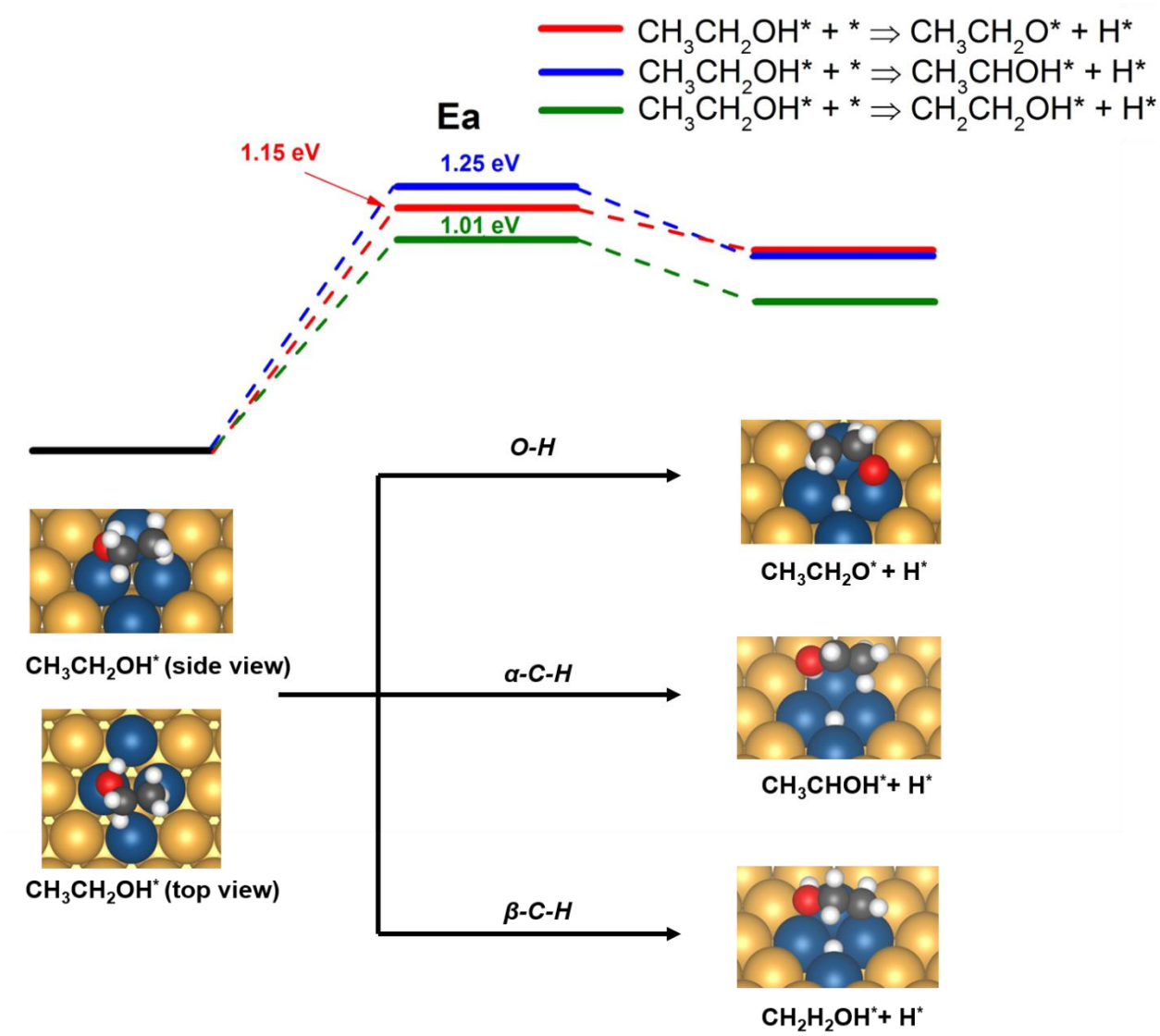

Figure S10. Energy pathways of three initial dehydrogenation steps of EtOH (hydroxyl dehydrogenation, α-carbon dehydrogenation, or β-carbon dehydrogenation) on a Pd_4/Au(111) surface alloy.

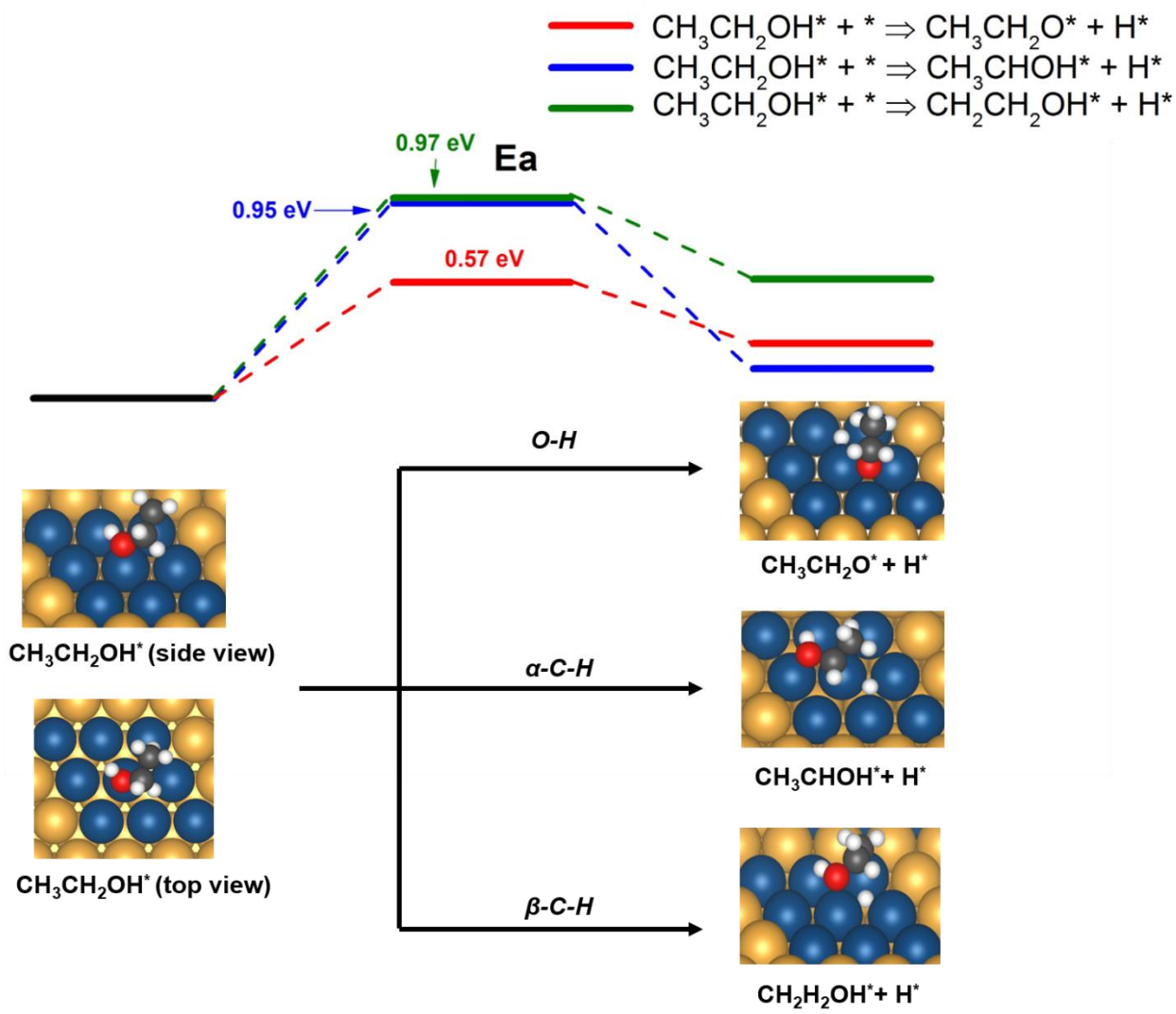

Figure S11. Energy pathways of three initial dehydrogenation steps of EtOH (hydroxyl dehydrogenation, α-carbon dehydrogenation, or β-carbon dehydrogenation) on a $Pd_9/Au(111)$ surface alloy.

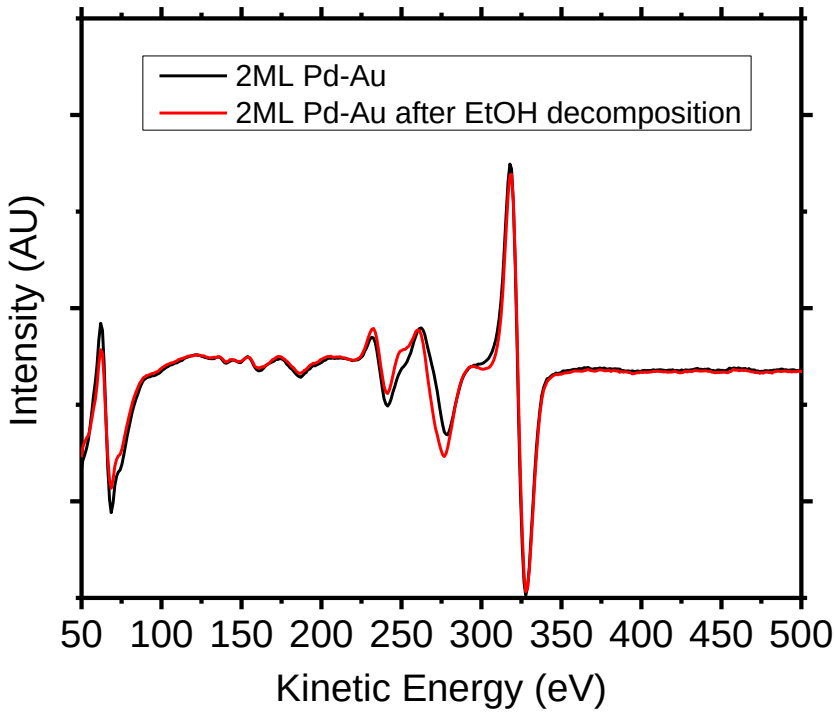

Figure S12. Auger Electron Spectroscopy of untested 2 ML Pd-Au and 2 ML Pd-Au after EtOH decomposition for 60 seconds. The major Pd feature is at 328eV. A second Pd feature at 277eV dwarves the carbon feature that is at 272eV.