

Supporting information

**H₂O-Improved O₂ Activation on the Pd–Au
Bimetallic Surface**

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Experimental section

The experiments were performed in a UHV chamber which has been described previously,¹ however brief details regarding the apparatus and experiments are described below. The Au (111) single crystal sample (12 mm in diameter \times 2 mm thickness) is held in the UHV chamber by a Mo wire that can resistively heat the sample and also provide thermal contact with a liquid nitrogen bath. For the preparation of the Pd–Au bimetallic model surface, we believe the growth of Pd overlayers on Au (111) is governed by a layer-by-layer mechanism, in which the Pd atoms can diffuse in to the bulk of the Au (111) sample upon heating to form a Pd–Au alloy at the surface.² The Pd–Au surface for this study was made by depositing 2.5 ML of Pd atoms from a homemade thermal evaporator onto the Au (111) surface at 77 K, and then the surface was annealed at 500 K for 10 min. All the gas molecules were delivered to the sample surface via a collimated molecular beam, enabling accurate control of the number of target molecules impinging on our model catalyst. We also utilized a Fourier transform infrared (FTIR) spectrometer with a mercury-cadmium-telluride (MCT) detector cooled by liquid nitrogen for reflection-adsorption infrared spectroscopy (RAIRS).

RAIRS spectra of H₂O on various Pd–Au surface

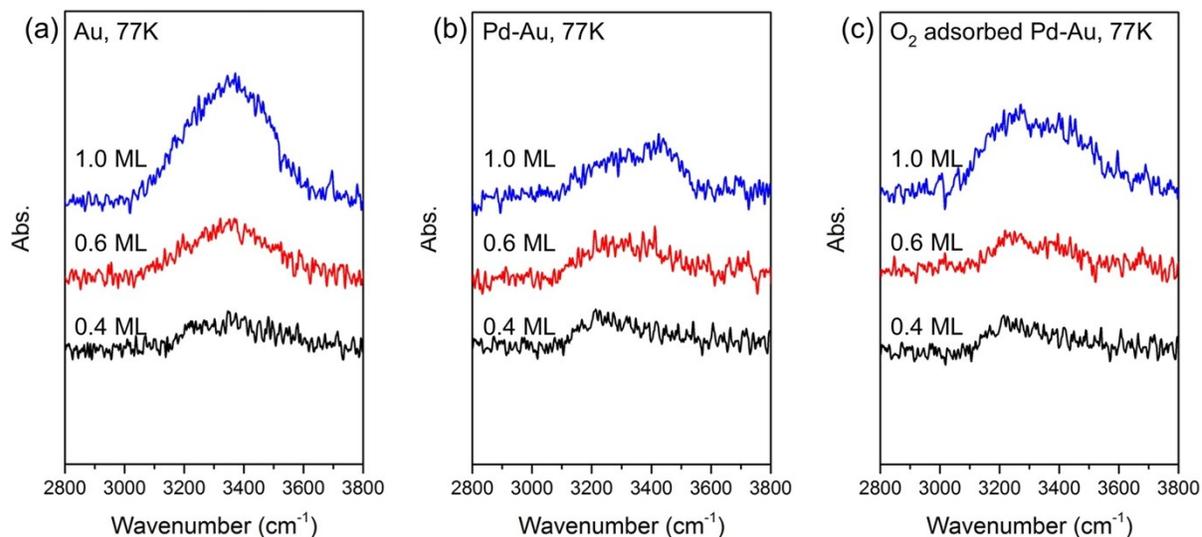


Figure S1. RAIRS spectra measured in the region of O–H bond frequencies for 0.4 ML, 0.6 ML, and 1.0 ML of H₂O impinged on (a) Au (111) (b) Pd–Au (111), and (c) 1.0 ML of O₂ adsorbed Pd–Au (111) surface. All those spectra were measured at 77 K, and the H₂O coverages were controlled based on the results from the H₂O desorption on Pd–Au surface (Figure 1b).

As indicated in Figure S1b, when the Pd–Au surface is covered with 0.4 ML of H₂O, RAIRS shows a peak near 3200 cm⁻¹, but the overall spectrum becomes broader with 0.6 ML of H₂O, and then 1.0 ML of H₂O makes two different regions, 3100 cm⁻¹ – 3360 cm⁻¹ and 3360 cm⁻¹ – 3540 cm⁻¹, corresponding to weaker O–H bonds induced by stronger Pd–H₂O interactions (177 K peak on TPD in Figure 1b) and stronger O–H bonds with weaker Pd–H₂O interactions (160 K peak on TPD in Figure 1b). As a reference, we also measured RAIRS for H₂O on Au (111) where the H₂O molecules are not so strongly interacting with the surface, and here there is just a broad spectrum for the different coverages as shown in Figure S1a. The intensity of each spectrum increases with H₂O coverage since more H₂O molecules make more H-bonds among them. This interpretation is

also supported by the TPD results shown in Figure S2, which shows a peak temperature for each H₂O coverage on Au (111) that is shifted a little bit from near 140 K to 146 K as coverage increases.

Increasing the amount of H₂O coverage on the 1ML of O₂ adsorbed Pd–Au surface, it also shows two different regions for O–H bond frequencies. Different from the H₂O solely adsorbed cases, however, the intensity for the lower frequency region in the 1.0 ML of H₂O / 1ML of O₂ adsorbed Pd–Au surface, 3100 cm⁻¹ – 3250 cm⁻¹ for the relatively weaker O–H bonds (180 K peak on TPD in Figure 2b), is higher than the higher frequency region, 3250 cm⁻¹ – 3500 cm⁻¹ for the relatively stronger O–H bonds (152 K peak on TPD in Figure 2b), depending on the degree of interactions with the adsorbed O₂ on the Pd–Au surface.

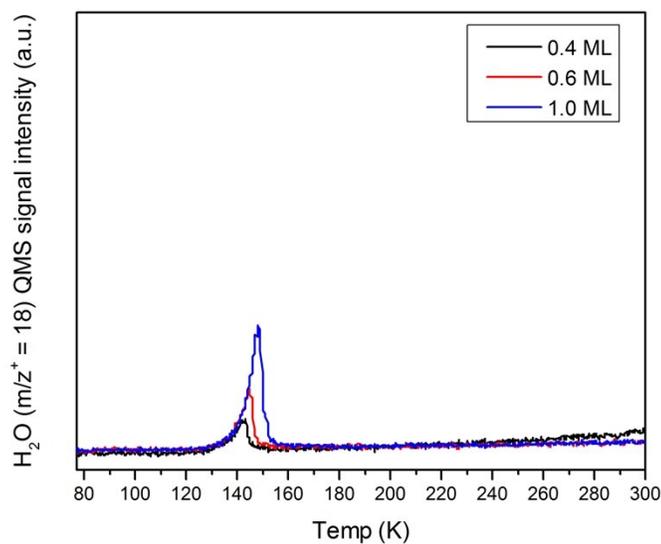


Figure S2. TPD results for H₂O (m/z⁺ = 18) from 0.4 ML, 0.6 ML, 1.00 ML of H₂O adsorbed Au (111).

O₂ adsorption on 1 ML of H₂O covered Pd–Au surface.

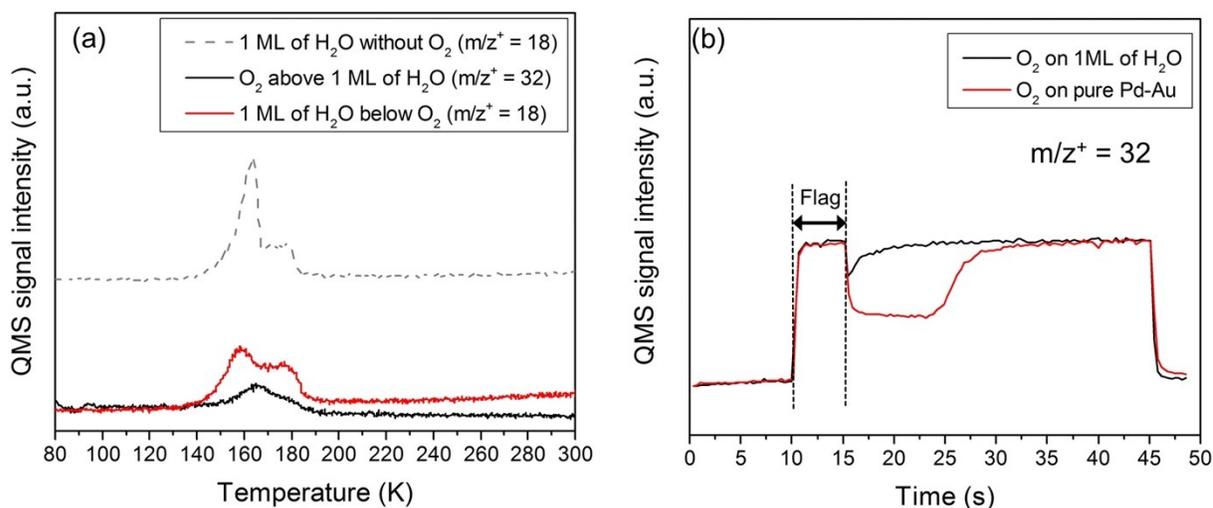


Figure S3. (a) TPD spectra of 1 ML of H₂O without O₂ (gray dotted line) and small amount of O₂ (black solid line) adsorbed above 1 ML of H₂O (red solid line) on the Pd–Au surface and (b) King and Wells measurements of O₂ directly adsorbed on the Pd–Au surface (red solid line) and 1 ML of H₂O pre-adsorbed Pd–Au surface (black solid line).

As described in Figure S3a and S3b, relatively small amount of O₂ molecules are adsorbed on 1 ML of H₂O pre-adsorbed Pd–Au surface compared to the pure Pd–Au surface. However, even this small amount of O₂ admolecules clearly affects the desorption of the pre-adsorbed H₂O molecules, where they simultaneously desorb in the range of 140 K – 190 K.

Isotopically labeled H_2^{18}O used TPD and CO-RMBS

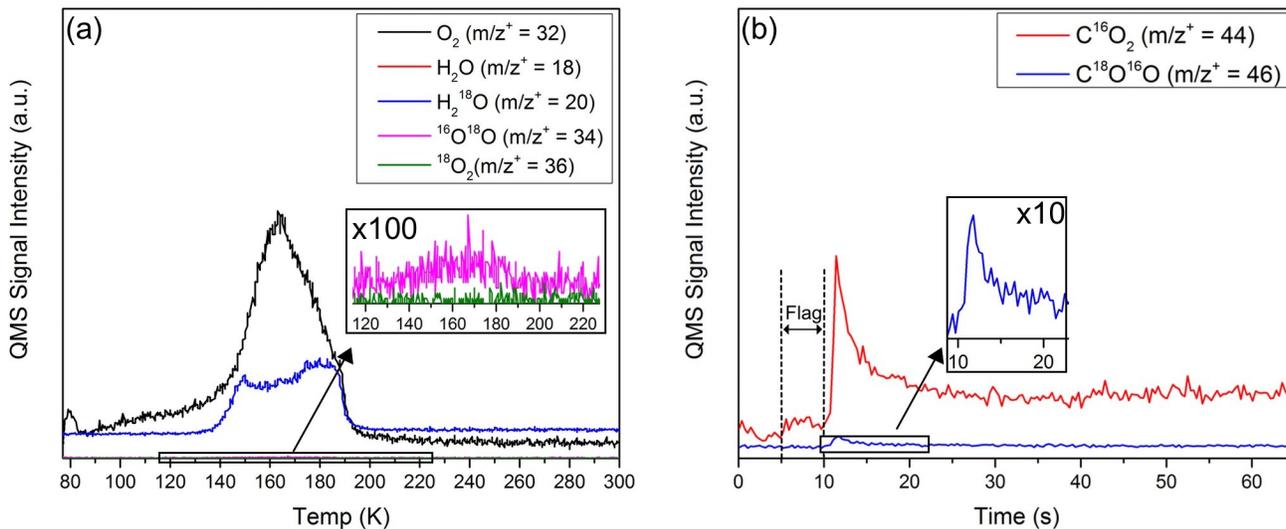


Figure S4. (a) TPD and (b) CO-RMBS results from 1.0 ML H_2^{18}O and 1.0 ML O_2 adsorbed Pd–Au surface. The inset in (a) shows a very low desorption of $^{16}\text{O}^{18}\text{O}$, and the inset in (b) also describes a very low generation of $\text{C}^{18}\text{O}^{16}\text{O}$.

In our TPD experiments for H_2O and O_2 co-adsorbed on the Pd–Au surface, as shown in Figure 2, we do not observe another H_2O desorption peak around 240 K which would be related to the associative desorption of hydroxyl ($-\text{OH}$) groups on the surface, and which has been reported in previous Pd model catalyst studies.^{3,4} For the Pd–Au bimetallic surface case, thus, it is expected that O_2 and H_2O molecules tend to form H-bonded complexes instead of making hydroxyls ($-\text{OH}$) by dissociating $\text{O}=\text{O}$ and $\text{H}-\text{OH}$ bonds. To confirm this, we also conducted TPD experiments using H_2^{18}O with $^{16}\text{O}_2$ co-adsorbed on the Pd–Au model surface to measure the generation of $^{16}\text{O}^{18}\text{O}$ ($m/z^+ = 34$). Based on our previous study regarding co-adsorbed H_2^{18}O with atomic O on an Au (111) surface,⁵ formation of adsorbed hydroxyls ($-\text{OH}$), should generate $^{16}\text{O}^{18}\text{O}$ ($m/z^+ = 34$) during TPD via the associative desorption of O_2 from the coupling of the isotopically labeled hydroxyls ($^{16}\text{OH} + ^{18}\text{OH}$). However, in testing with 1.0 ML of H_2^{18}O and 1.0 ML of O_2 co-adsorbed on the

model Pd–Au surface, we do not observe the generation of $^{16}\text{O}^{18}\text{O}$ (see Figure S3a in which the signal for $m/z^+ = 34$ is very small compared to the $^{16}\text{O}_2$ ($m/z^+ = 32$) signal). Therefore, we conclude that co-adsorbed O_2 and H_2O on the Pd–Au surface are more likely to form a strong H-bonded complex rather than adsorbed hydroxyls ($-\text{OH}$).

Additionally, we also conducted CO-RMBS experiments on a 1.0 ML of H_2^{18}O + 1.0 ML of O_2 co-adsorbed surface to test for the generation of $\text{C}^{16}\text{O}^{18}\text{O}$ ($m/z^+ = 46$). This is another way to check for the formation of hydroxyls from the interactions of adsorbed H_2O and O_2 on the Pd–Au surface.⁶ In Figure S3b, the intensity for $\text{C}^{16}\text{O}^{18}\text{O}$ ($m/z^+ = 46$) is much lower than for the standard CO_2 ($m/z^+ = 44$) signal, and the $m/z^+ = 46$ signal only becomes visible by magnifying the scale by a factor of 10. This very small signal is possibly caused by a tiny amount of ^{18}OH on the surface. Therefore, from these results, it is expected once again that co-adsorbed H_2O and O_2 molecules on our model Pd–Au surface are mainly forming a H-bonded complex, and only a small fraction of them exist as hydroxyls.

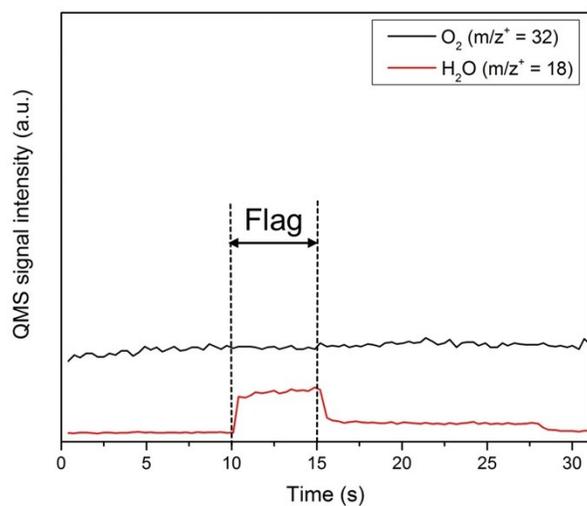


Figure S5. King-Wells measurement of a H₂O beam impinging on 1 ML of O₂ covered Pd–Au surface. From 10 s to 15 s, the H₂O beam was directed to the inert flag and then hit the sample from 15 s to 28 s for impinging 1 ML of H₂O.

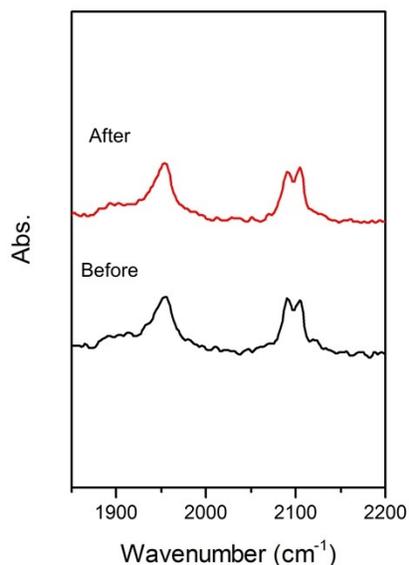


Figure S6. RAIRES spectra of saturated CO on Pd–Au (111) surface before (bare surface, black) and after (red) the adsorption and desorption of 1.0 ML of O₂ and 1.0 ML of H₂O.

As shown in Figure S6, our Pd – Au (111) surface has Pd ensembles, which can be verified from the existence of vibrational frequencies for CO molecules on the continuous Pd sites (ν_{CO} : 1900 – 2000 cm⁻¹). Furthermore, the desorption of 1.0 ML H₂O/ 1.0 ML O₂ negligibly affect the compositions of Pd ensembles because the IR spectra of before and after the desorption of O₂ / H₂O are almost identical to each other.

H ₂ O coverages (ML)	O ₂ desorption ratio in 77 K – 145 K (%)	O ₂ desorption ratio in 145K – 165 K (%)	O ₂ desorption ratio in 165 K – 200 K (%)	Total amount of O ₂ desorption ratio in 77 K – 200 K (%)	Total amount of CO ₂ generation ratio (%)
0	58.4	23.8	17.8	100	32.2
0.6	44.5	24.2	31.3	85.4	65.5
1	28.2	28.9	42.9	81.5	100
1.5	24.2	35.6	40.2	81.7	100.2
2.1	19.6	43.9	36.5	84.8	82.7

Table S1. Estimated percentages for O₂ desorption and CO₂ generation on the basis of H₂O coverages.

References

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