

Supporting Information
Hydrogen oxidation on oxygen-rich IrO₂(110)

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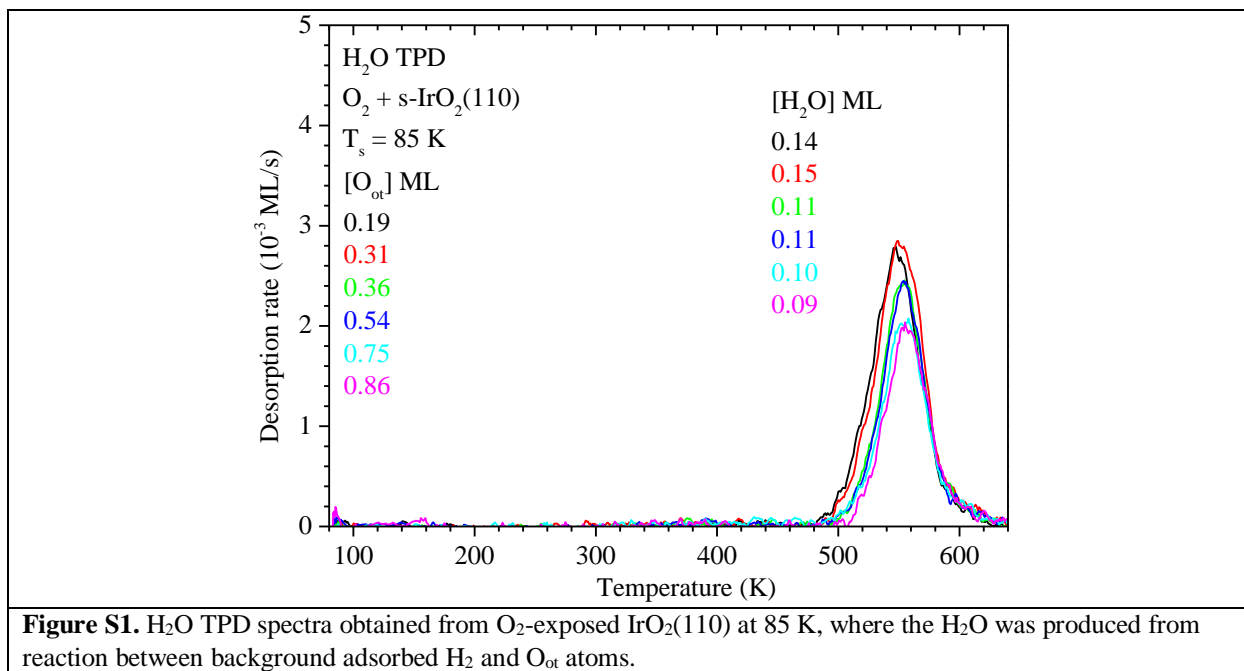
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Estimates of adsorbate coverage and product yields from TPRS

We estimate atomic oxygen coverages by scaling integrated O₂ TPD spectra with those obtained from a saturated (2 × 1)-O layer containing 0.50 ML of O-atoms and prepared by exposing the Ir(100)-(5 × 1) surface to O₂ in UHV [1]. To estimate hydrogen coverages, we scaled integrated hydrogen desorption spectra by an integrated TPD spectrum collected from a saturated Ir(100)-(5 × 1)-H layer containing 0.80 ML of atomic hydrogen that we prepared by adsorbing hydrogen to saturation on the Ir(100)-(5 × 1) surface at 300 K [2]. We performed TPRS experiments of CO oxidation on saturated O-covered Ir(100) to estimate CO₂ desorption yields. Specifically, we collected O₂ and CO₂ TPRS spectra after exposing a (2 × 1)-O layer to a sub-saturation dose of CO and assuming that the CO₂ yield is equal to the difference between the initial (0.50 ML) and final coverages of oxygen as determined from the O₂ TPRS yield. We performed TPRS experiments of hydrogen oxidation on partially O-covered Ir(100) to estimate the H₂O desorption yields. In these experiments, we first collected O₂ and CO₂ TPRS spectra after exposing a (2 × 1)-O layer to a sub-saturation dose of CO and assuming that the oxygen remaining on Ir(100) is equal to the difference between the initial oxygen coverage in the (2 × 1)-O layer (0.50 ML) and the CO₂ yield determined from the CO₂ TPRS spectrum. We then collected O₂ and H₂O TPRS spectra after exposing the partially O-covered Ir(100) surface generated from the first step to a saturation dose of H₂ and assuming that the H₂O yield is equal to the difference between the initial and final coverage of oxygen determined from the O₂ TPRS yield. We repeat these calibration TPRS experiments to ensure accuracy in our estimates of desorption yields.

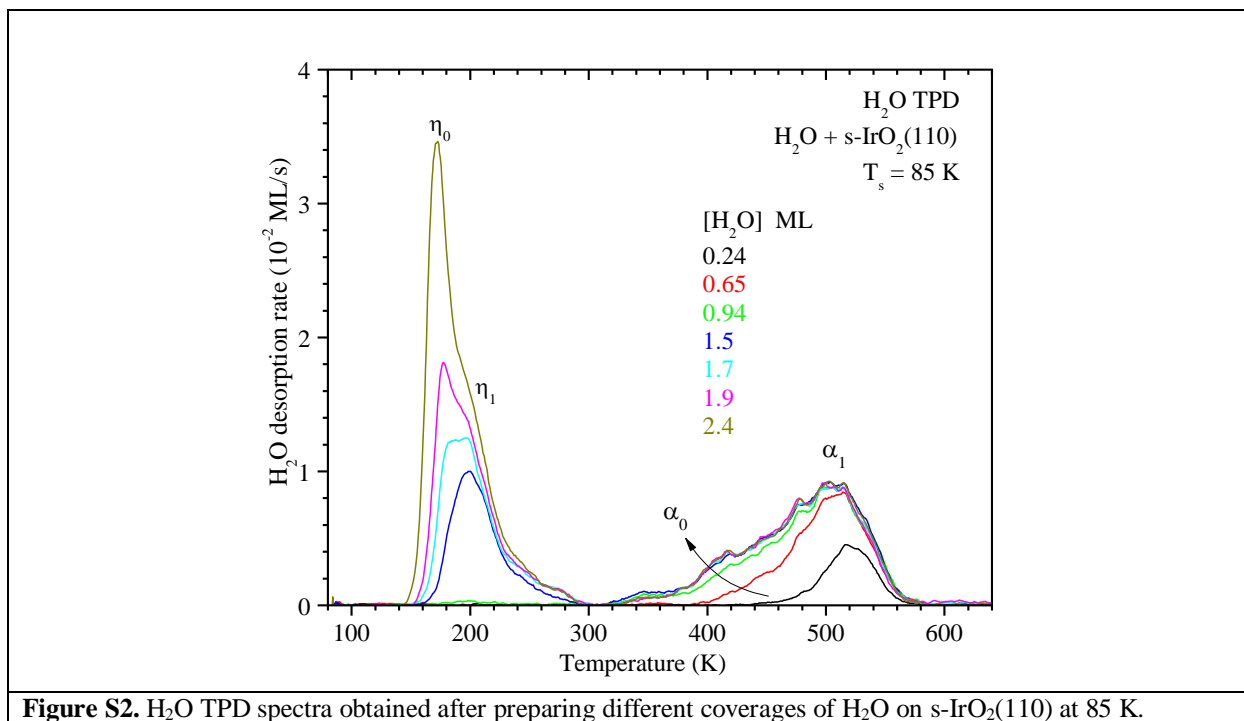
H₂O TPD spectra obtained from O₂-exposed IrO₂(110) at 85 K

Figure S1 shows H₂O TPRS spectra obtained after adsorbing O₂ on IrO₂(110) at 85 K, where the H₂O was produced by reaction between O_{ot} atoms and H₂ that adsorbed from the vacuum background before or during O₂ adsorption. An average of 0.11 ± 0.02 ML of H₂O desorbs from the O₂-exposed surfaces. Because the background-adsorbed hydrogen is the limiting reactant for the O_{ot} coverages studied, we assume that the initial O_{ot} coverage is equal to the sum of H₂O and O₂ that desorbs. Experiments with ¹⁸O_{ot}-covered IrO₂(110) support our approach for computing the initial O_{ot} coverages.



H₂O TPD spectra from s-IrO₂(110) after H₂O adsorption at 85 K

We investigated H₂O adsorption on IrO₂(110) using TPD to aid in interpreting the H₂O desorption features that result from H₂ oxidation on O-rich IrO₂(110) (Figure S2). After adsorbing 2-3 ML of H₂O on IrO₂(110) at 85 K, the H₂O TPD spectrum exhibits a broad feature with a maximum near 500 K as well as sharper peaks at 200 and 170 K. Based on similarities with TPD spectra reported for H₂O-covered RuO₂(110) [3] and PdO(101) [4], we attribute the broad feature (α) to H₂O species chemisorbed either associatively or dissociatively on Ir_{cus} sites while the peaks at 200 K and 170 K are consistent with H₂O adsorbed on O_{br} sites and an initial H₂O multilayer, respectively. Figure 3 shows that the water-Ir_{cus} species on IrO₂(110) desorb in a peak (α_1) at ~520 K at low coverage and that a broad shoulder (α_0) develops on the leading edge of the α_1 peak with increasing H₂O coverage. The α TPD feature saturates at an H₂O coverage of ~1 ML, i.e., one H₂O molecule per Ir_{cus} atom, further supporting the assignment of this feature to water species adsorbed on the Ir_{cus} atoms.



A prior study reports that the TPD feature from chemisorbed H₂O on PdO(101) exhibits a broadening that is similar to that observed here [4]. Those authors report that H₂O molecules prefer to adsorb as H-bonded H₂O-HO dimer complexes on the Pd_{cus} sites, but that a variety of less stable H₂O oligomers can develop on the Pd_{cus} rows at H₂O coverages above 0.50 ML, with desorption from the oligomer structures producing a broad shoulder in the TPD spectra. A preference for H₂O-HO dimer formation has also been reported for water adsorption on s-RuO₂(110)[5,6] and crystalline Fe₃O₄ surfaces [7]. Below, we report DFT calculations which predict that H₂O dissociative chemisorption is moderately favored over H₂O-HO dimer formation on s-IrO₂(110). This prediction suggests that the composition of the water adlayer evolves differently with increasing coverage on IrO₂(110) compared with PdO(101) and RuO₂(110); however, a shared characteristic among these oxide surfaces is that chemisorbed water becomes destabilized with increasing H₂O coverage. Further characterization using surface vibrational and/or photoelectron

spectroscopy is needed to determine the structure and composition of the water adlayer on $\text{IrO}_2(110)$.

TPRS for H_2 oxidation on $\text{IrO}_2(110)$ with O_{ot} -layer prepared at 300 K

Figure S3 shows H_2 and H_2O TPRS spectra obtained after exposing a saturation amount of H_2 to $\text{IrO}_2(110)$ surfaces with different initial O_{ot} coverages. We prepared the O_{ot} -layers by exposing the $\text{IrO}_2(110)$ surface to varying amounts of O_2 at a surface temperature of 300 K. The TPRS traces evolve with the O_{ot} -coverage in a qualitatively similar way as when the O_{ot} -layer is prepared by flashing a saturated on-top oxygen layer to selected temperatures (Figure 3a, main manuscript).

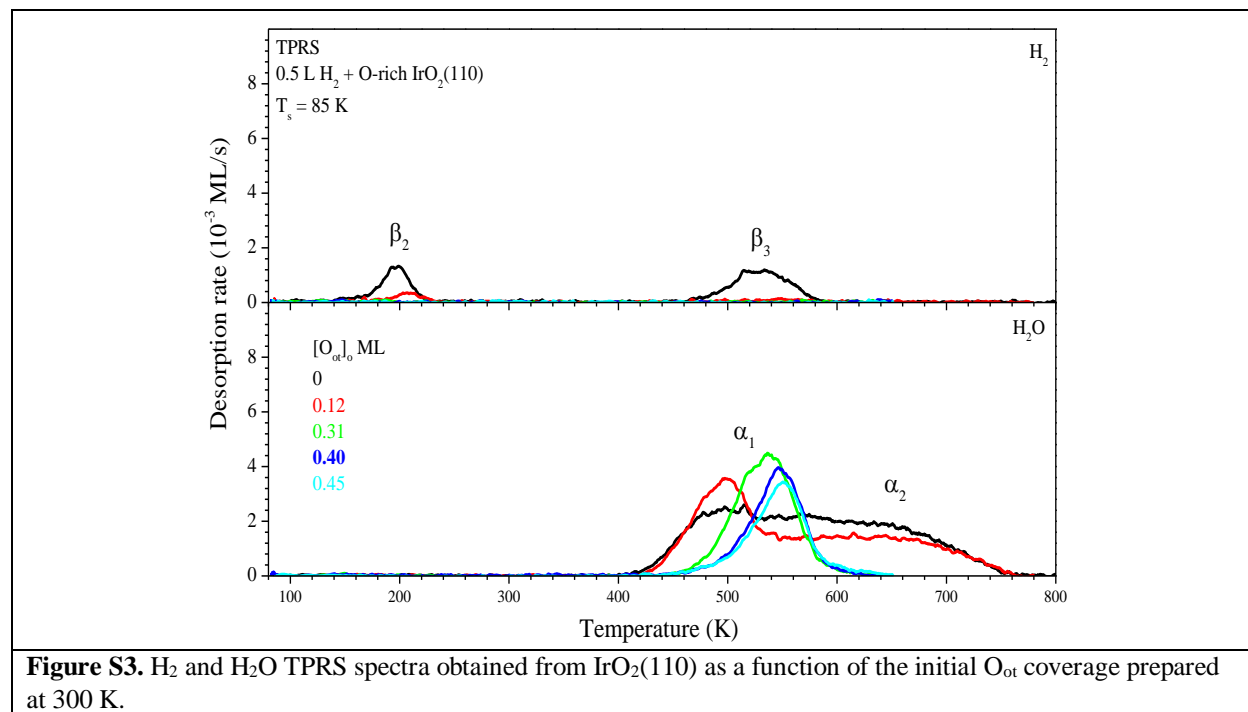
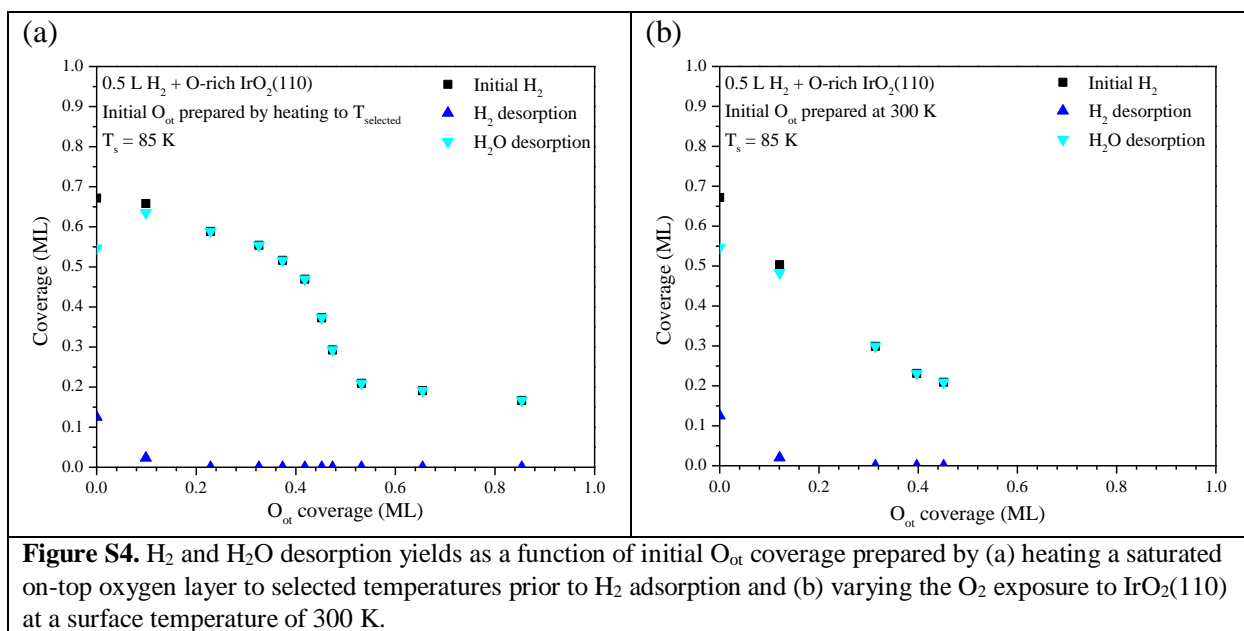


Figure S3. H_2 and H_2O TPRS spectra obtained from $\text{IrO}_2(110)$ as a function of the initial O_{ot} coverage prepared at 300 K.

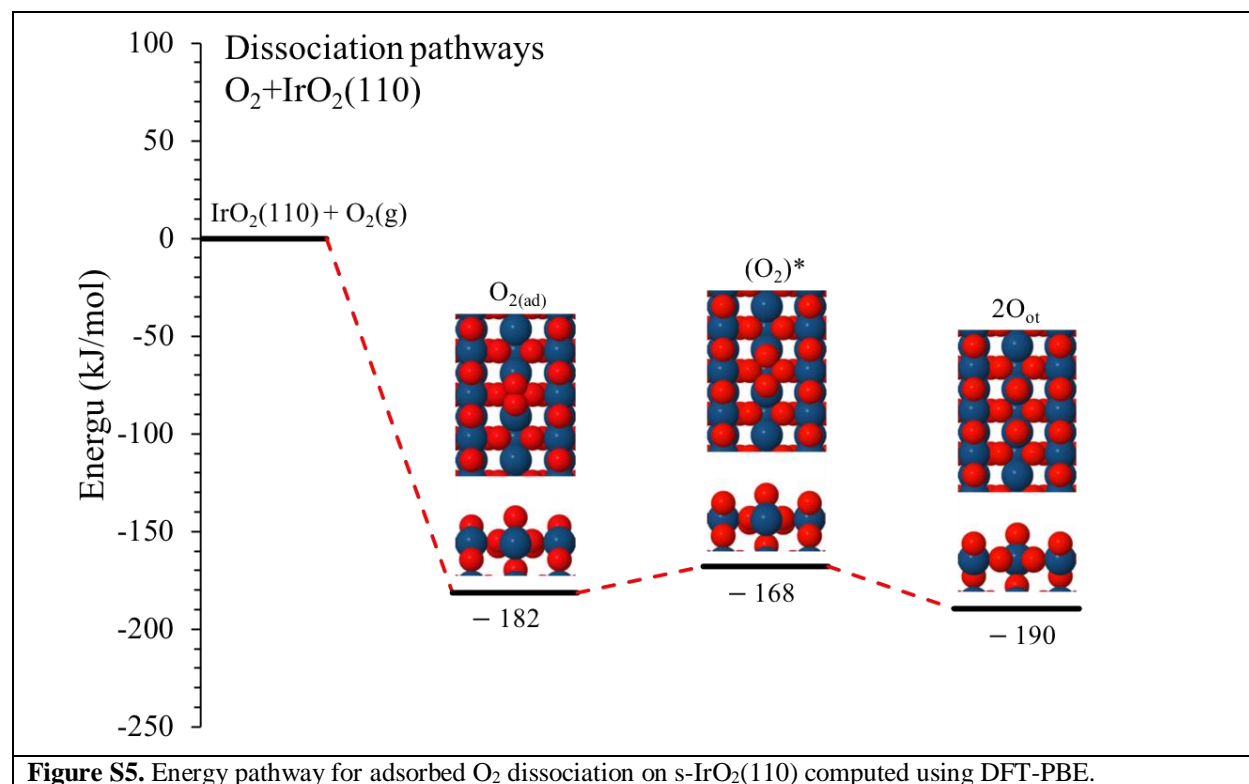
H₂ oxidation yields as a function of initial O_{ot} coverage prepared by heating to selected temperatures vs. O₂ adsorption at 300 K

Figures S4a and S4b show H₂ and H₂O TPRS yields as a function of the initial on-top oxygen coverage for two methods of preparing the oxygen layer, namely, heating a saturated oxygen layer to selected temperatures (Fig. S4a and Fig. 4c) and varying the O₂ exposure to IrO₂(110) at a surface temperature of 300 K. The H₂ uptake decreases continuously when the O_{ot}-layer is prepared at 300 K (Figure S4b), rather than exhibiting an abrupt decrease near ~0.4 ML as seen when the layer is prepared by heating (Figure S4a). The H₂ uptake is also lower for the O_{ot}-layer prepared at 300 K vs. the layer prepared by heating. This behavior strongly supports the interpretation that H_{ot} atoms, resulting from H₂ adsorption from the background, block subsequent H₂ adsorption at 85 K and that heating the initial O_{ot}-layer above ~450 K causes an abrupt increase in the coverage of empty Ir_{cus} sites by promoting the conversion of Hot atoms to OH groups.



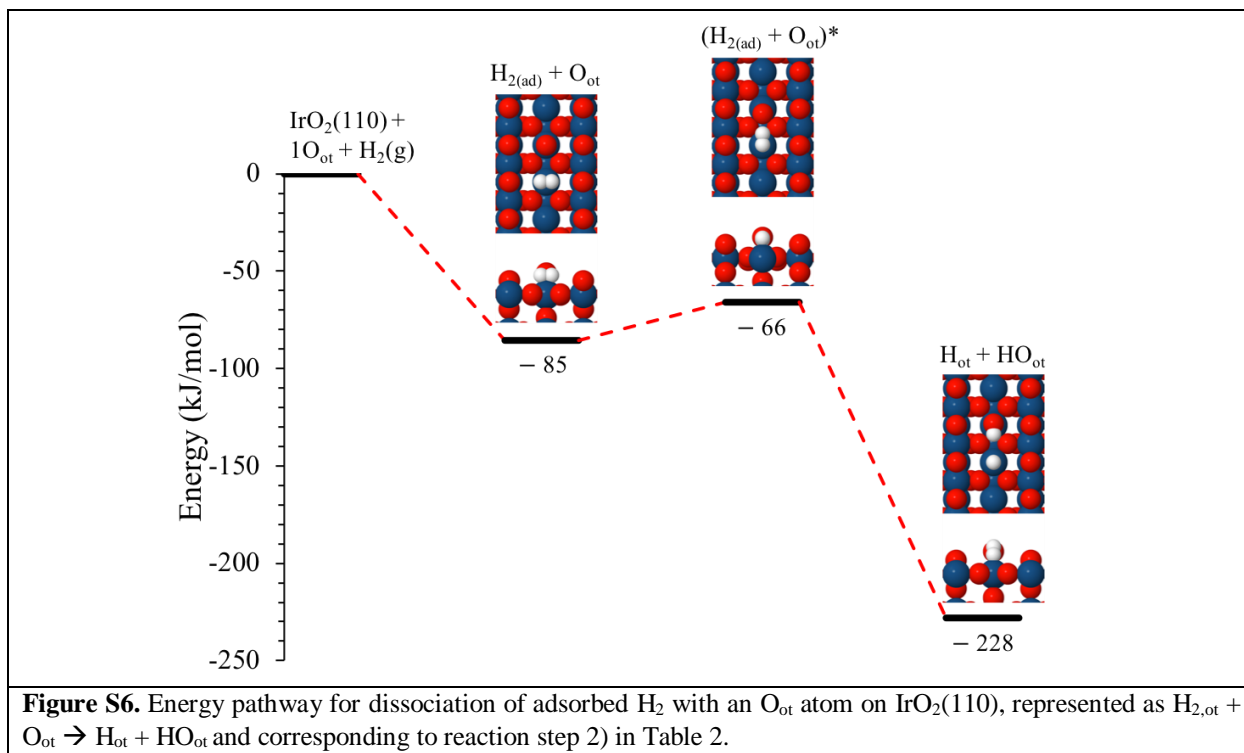
O₂ dissociation pathway on s-IrO₂(110)

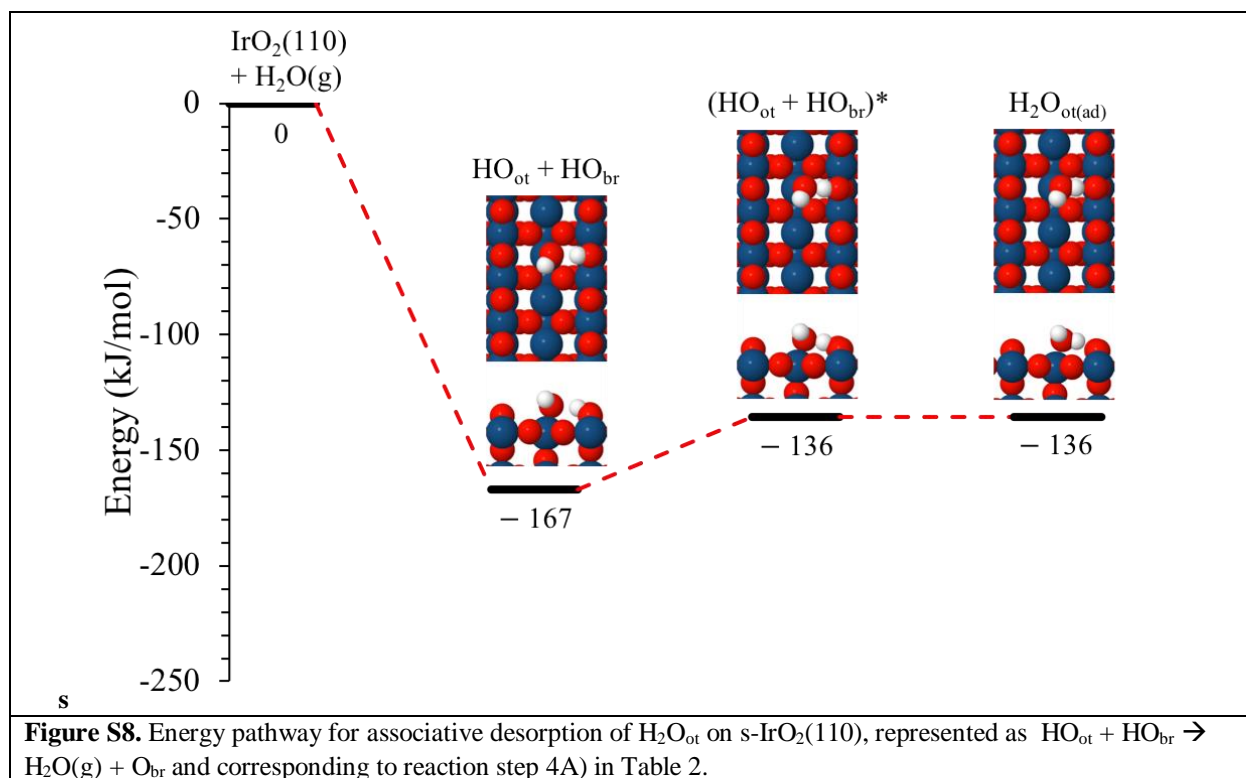
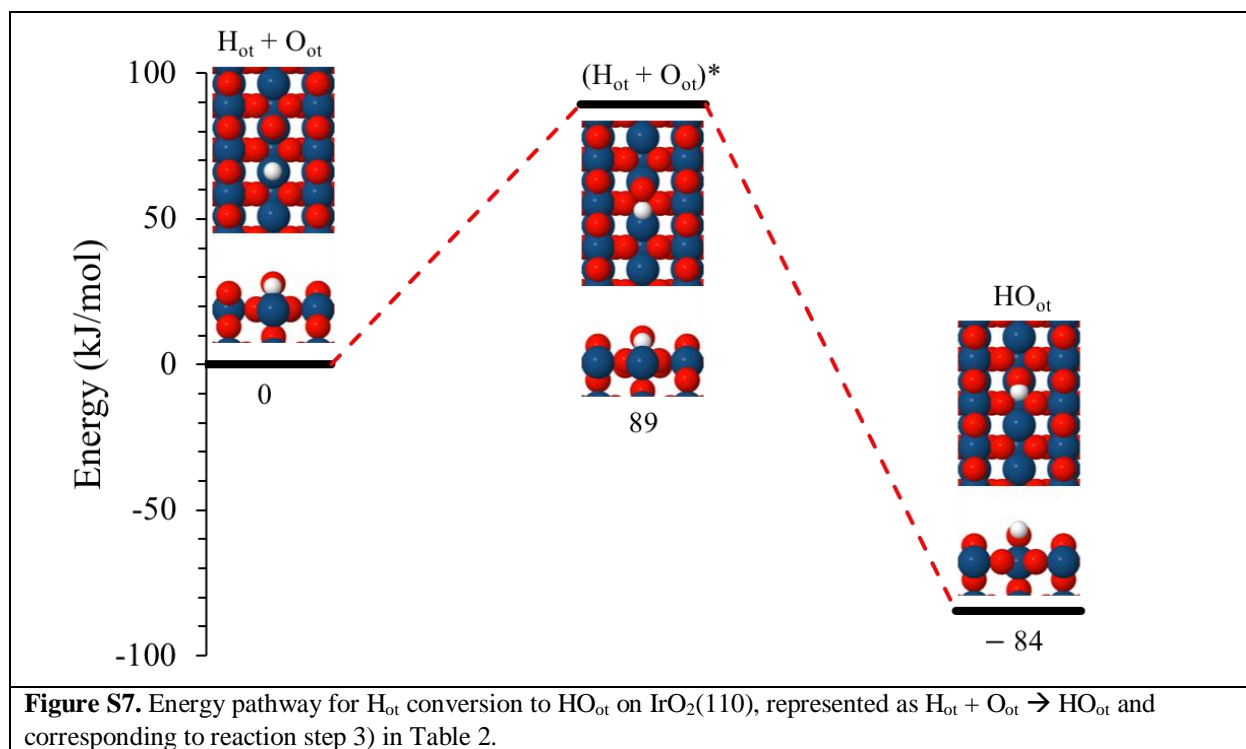
Figure S4 shows the computed energy diagram and molecular images for dissociation of molecularly adsorbed O₂ on IrO₂(110).

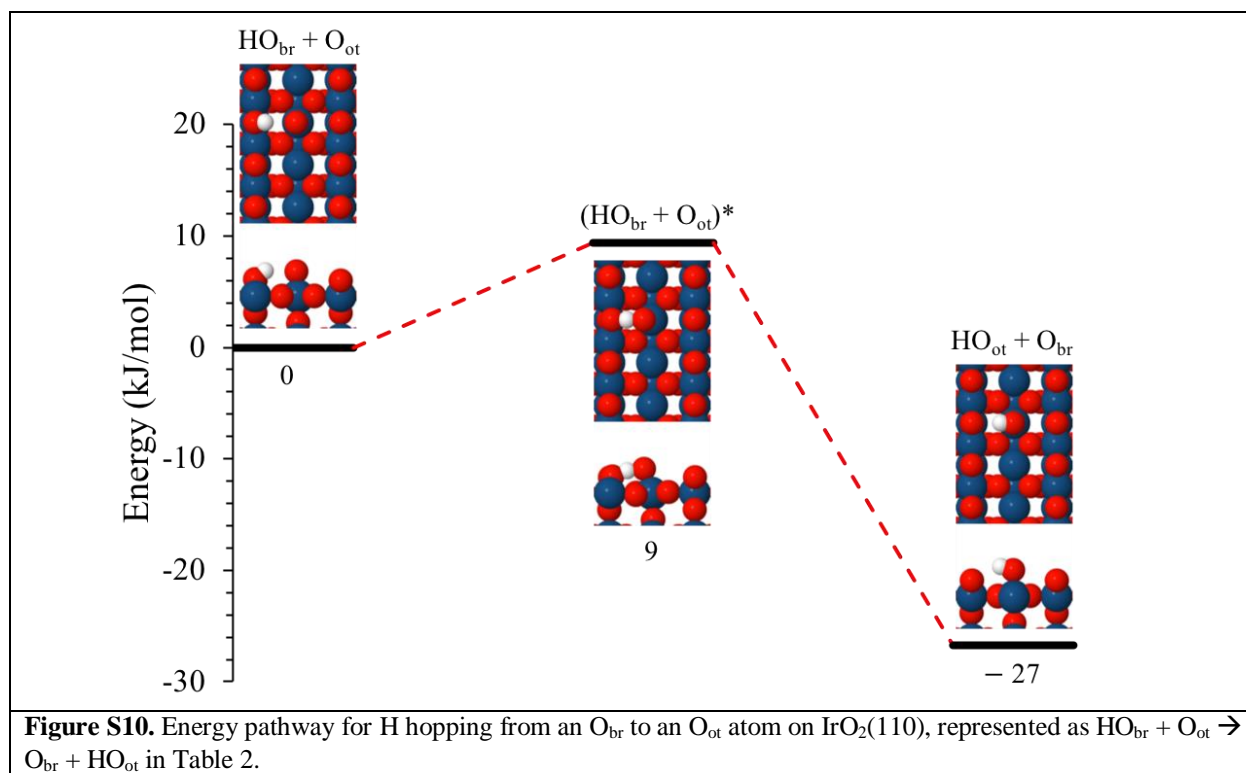
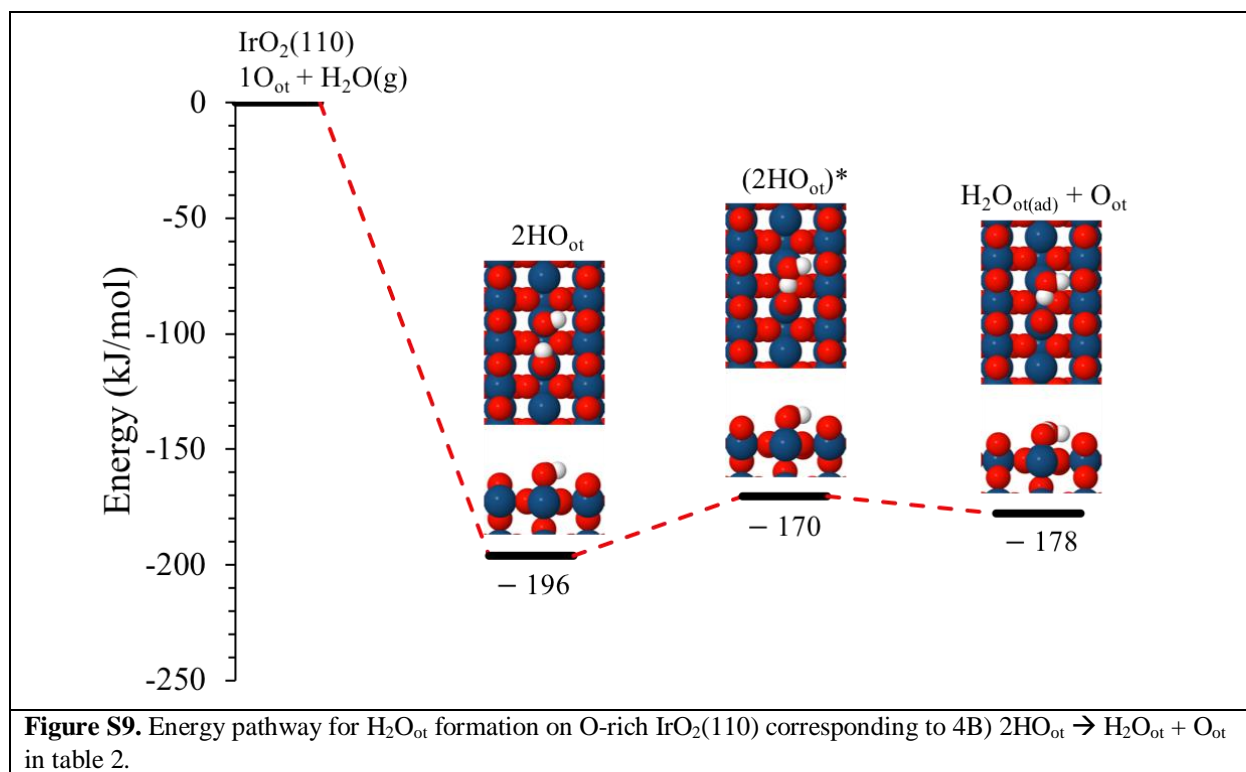


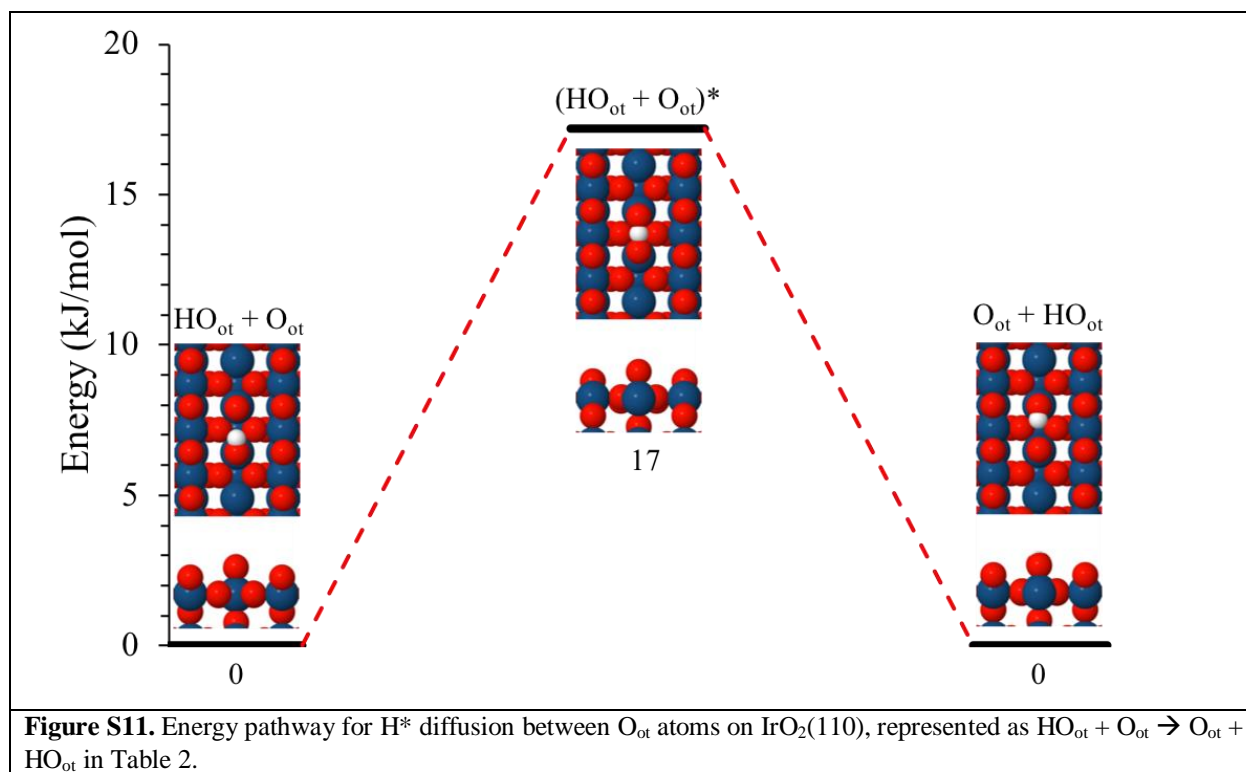
Energy diagrams and molecular images for reactions in H₂ oxidation on O-rich IrO₂(110)

Figures S6-S11 show energy diagrams and molecular images for the reaction steps identified as governing H₂ oxidation on O-rich IrO₂(110) and summarized in Table 2 of the main manuscript.









References

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