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

Supporting Information

Insights into the electronic structure of hydroxyl at Ag(110) under near ambient conditions

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1. Surface reconstruction

This supporting information explores the other reconstruction structures obtained in the free energy plot (figure 1S) which has similar binding energies to the surface reconstruction OH(1x2), the strucutre which has a p-DOS and simulated O K edge in the best agreement with experimental data and which was discussed in the main text.

Figure 1S shows the free energy plot for the Ag(110) surface in equilibrium of O_2 and H_2O with different possible reconstructions. In this DFT simulation we consider (i) the OH adsorbed at different silver surface sites: four-fold hollow (FFH), three-fold hollow (TFH), short-bridge (SB) and long-bridge (LB) and (ii) OH adsorbed with the constrain that the O-H bond is normal to the surface (indicated by the term vertical in the figure) and without the constrain, thereby allowing adsorbed OH to form hydrogen bonds with neighbouring adsorbates. Although the OH(1x2) TFH at chemical potencial bellow 0.9 eV become the lowest energy structure with OH, it is important to analyse other surface reconstructions with closer energies, as the case OH(2x1) with OH at SB site (orange curve), as an attempt to identify the phase obtained in the experiment.

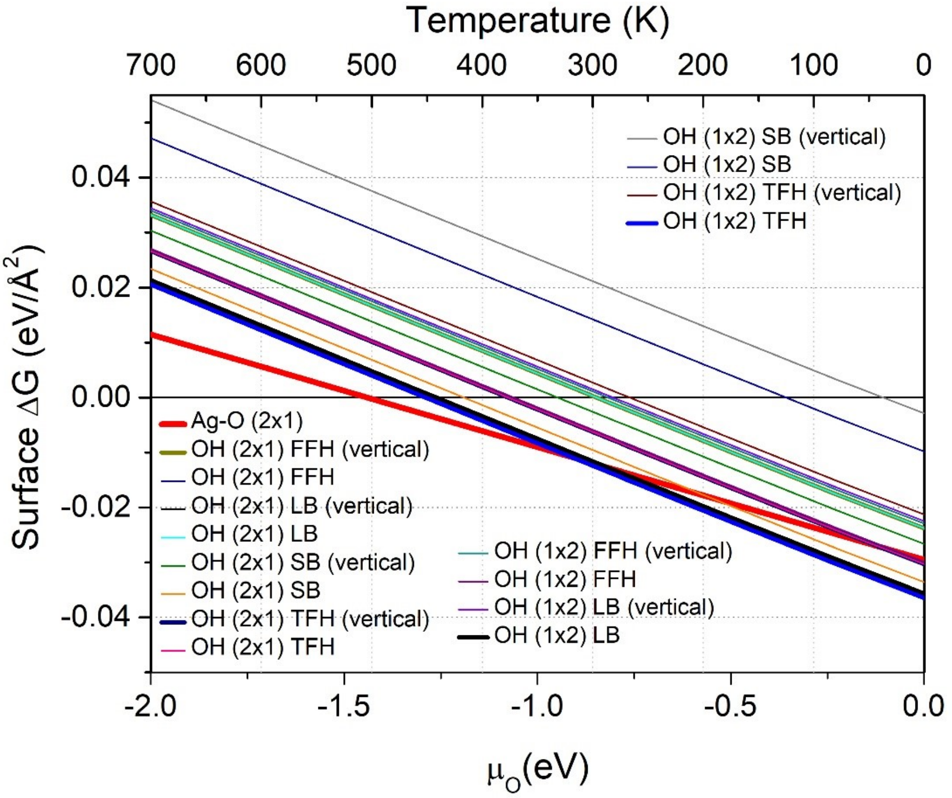

Figure 1S: Surface Gibs free energy for adsorbates on Ag(110) as a function of the oxygen chemical potential at a fixed pressure of 10^{-4} mbar of O_2 and H_2O (1:5) at variable temperature. The simulation considering the OH adsorbed at different surface sites: four-fold hollow (FFH), three-fold hollow (TFT), short-bridge (SB) and long bridge (LB).

Figure 2S presents the structural models obtained by DFT for the phases OH(2x1) and OH(1x2) considering the OH adsorbed at different surface sites without a constrain in OH adsorbate. Figure 3S explores the difference of the constrain imposed on the OH adsorbate for the phase OH(1x2) with the OH adsorbed in a TFH site, in (a) the OH is adsorbed without any constrain, allowing it to form hydrogen bonds with neighbouring adsorbates, in (b) the OH is adsorbed considering the constrain that the O-H bond is normal to the surface and in (c) is presented a 3D image of the structure.

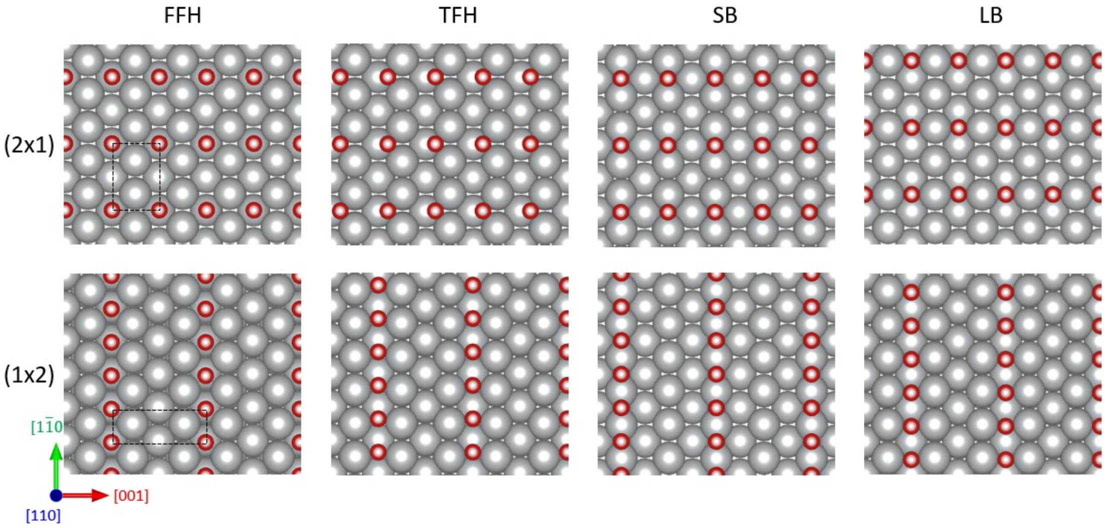

Figure 2S: Ag(110)-OH structural models used for the DFT calculations with OH species adsorbed at different surface sites: four-fold hollow (FFH), three-fold hollow (TFT), short-bridge (SB) and long bridge (LB), forming a (1x2) surface lattice (top) or (2x1) lattice (bottom)

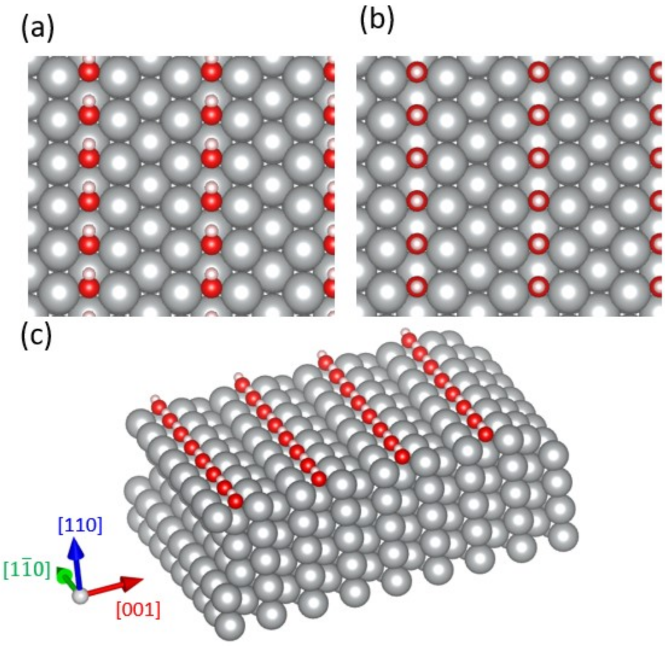

Figure 3S: Ag(110)-OH(1x2) TFH with H-bonding (a) and constraining the H atoms to the vertical (b) to preclude the H-bonding. (c) Minimum energy structure in 3D perspective.

To identify the OH(1x2) as the phase obtained in our experiment, we compare the projected density of states (p-DOS) and the simulated O K edge obtained by DFT of several surface reconstructions with the experimental data. Figure 4S presents the p- DOS of both (a) OH(2x1) and (b) OH(1x2). Comparing the simulations, it is possible to observe that in the case of OH(2x1) the pronounced difference of intensity with bonding state of O-H higher than anti-bonding state of O-Ag is not observed in the experimental data (figure 3b). On the other hand, figure 5S presents a comparison between the simulated O K edge of both phases and the experimental data. The simulated O K edge of the OH(2x1) phase (black curve), presents two pronounced peaks showing even less resemblance to the experiment data (blue dots). Based on the poor agreement between the p-DOS and simulated O K edge of OH(2x1) surface reconstruction with the experimental data, we discard this phase and identify in the main text the surface reconstruction OH(1x2) as the phase obtained in our experiment (combined with a great resemble of experimental data). We reinforce the absence of evidence of long-range order, the similarities between experimental and simulated data allows to identify a local surface order.

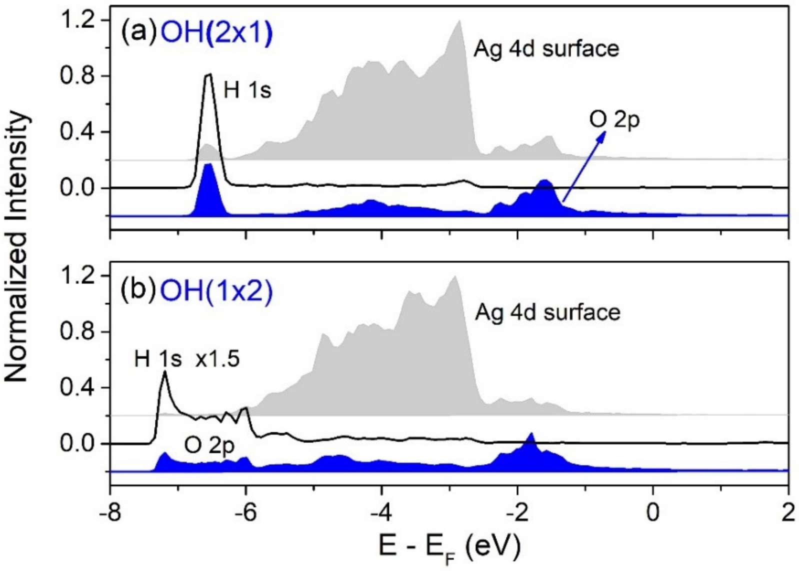

Figure 4S: Calculated projected density of states (p-DOS) for OH adsorbates on Ag(110). (a) p-DOS of O 2p (filled blue curve), H 1s (black curve) and Ag 4d surface (filled grey curve) for OH(2x1)-Ag(110) reconstruction. (b) p-DOS of O 2p (filled blue curve), H 1s (black curve) and Ag 4d surface (filled grey curve) for OH(1x2)-Ag(110) reconstruction.

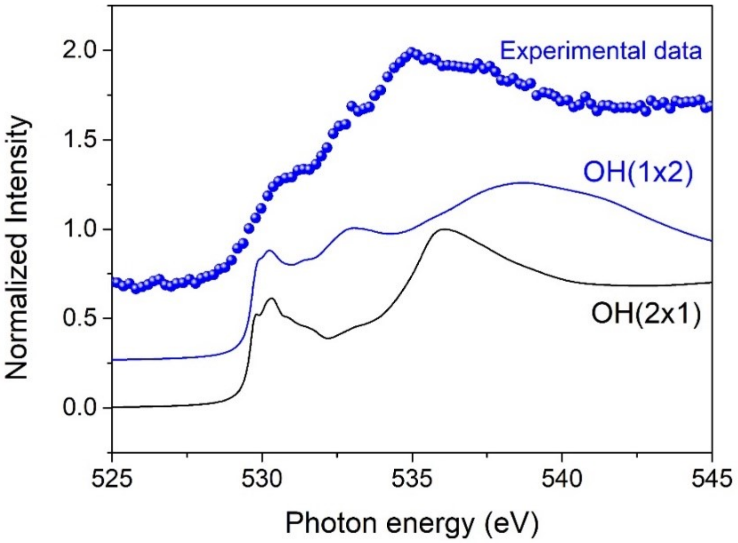

Figure 5S: Experimental O K-edge NEXAFS spectra as a function of photon energy for the Ag(110) surface exposed to O_2 and H_2O (1:5) at 10^{-4} mbar pressure and 423 K (blue dots). Simulated O K-edge spectra for OH(1x2) reconstruction (blue curve) and OH(2x1) (black curve).

Table1: Adsorption energies calculated with (XDM) and without dispersive interactions (XDM) for surface reconstructions with OH species at different sites as represented in figure 2S. The label vertical means the H-atom position was constrained to preclude H-bonding.

Structure	**Eads XDM (eV)**	**Eads PBE (eV)**
Ag-O (2x1)	-0.72	-0.83
OH (2x1) FFH (vertical)	-0.58	-0.53
OH (2x1) LB (vertical)	-0.58	-0.56
OH (2x1) SB (vertical)	-0.65	-0.66
OH (2x1) TFH (vertical)	**-0.74****	**-0.71***
OH (1x2) FFH (vertical)	-0.56	-0.51
OH (1x2) LB (vertical)	-0.55	-0.48
OH (1x2) SB (vertical)	-0.07	-0.06
OH (1x2) TFH (vertical)	-0.52	-0.5
OH (2x1) FFH	-0.58	-0.53
OH (2x1) LB	-0.58	-0.58
OH (2x1) SB	-0.82	**-0.85†**

OH (2x1) TFH	-0.74	-0.71
OH (1x2) FFH	-0.73	-0.71
OH (1x2) LB	-0.87	**-0.84†**
OH (1x2) SB	-0.24	-0.23
OH (1x2) TFH	**-0.89††**	**-0.84†**
OH (1x2) fully relaxed	**-0.89**	**-0.84**

Comparison of the adsorption energies for the different structures in table 1, indicates that without H-bonding, the lowest energy structure is the OH(2x1) TFT and the inclusion of dispersive interactions (XDM) does not change this scenario. However, when H-bonding is allowed, three structures become nearly degenerate (marked with a † in the table) at the lowest energy. But the inclusion of dispersive interactions favors the OH (1x2) TFH (marked with a †† in the table), which has the same energy as the fully relaxed OH(1x2) structure.