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

# Supporting information for:
# Hydrogen adsorption on $In_2O_3(111)$ and $In_2O_3(110)$

Alvaro Posada-Borbón* and Henrik Grönbeck*

*Department of Physics and Competence Centre for Catalysis, Chalmers University of Technology, SE-412 96 Göteborg, Sweden*

E-mail: palvaro@chalmers.se,ghj@chalmers.se

## Effect of Hubbard-U correction on $O_v$ and surface hydrogenation

To analyze the sensitivity of the results on the chosen U-value, calculations using Hubbard-U values of 0, 3, 5 and 7 eV are compared with benchmark calculations using a functional with exact exchange (HSE06).[S1] The $E_f(O_v)$ for $O_3$ and $O_6$ on the $In_2O_3(110)$ facet is here calculated at the experimental lattice constant[S2] (Figure S1 (top)). Additionally, the hydrogen adsorption energy at 16% coverage is calculated for the same surface (Figure S1 (bottom)).

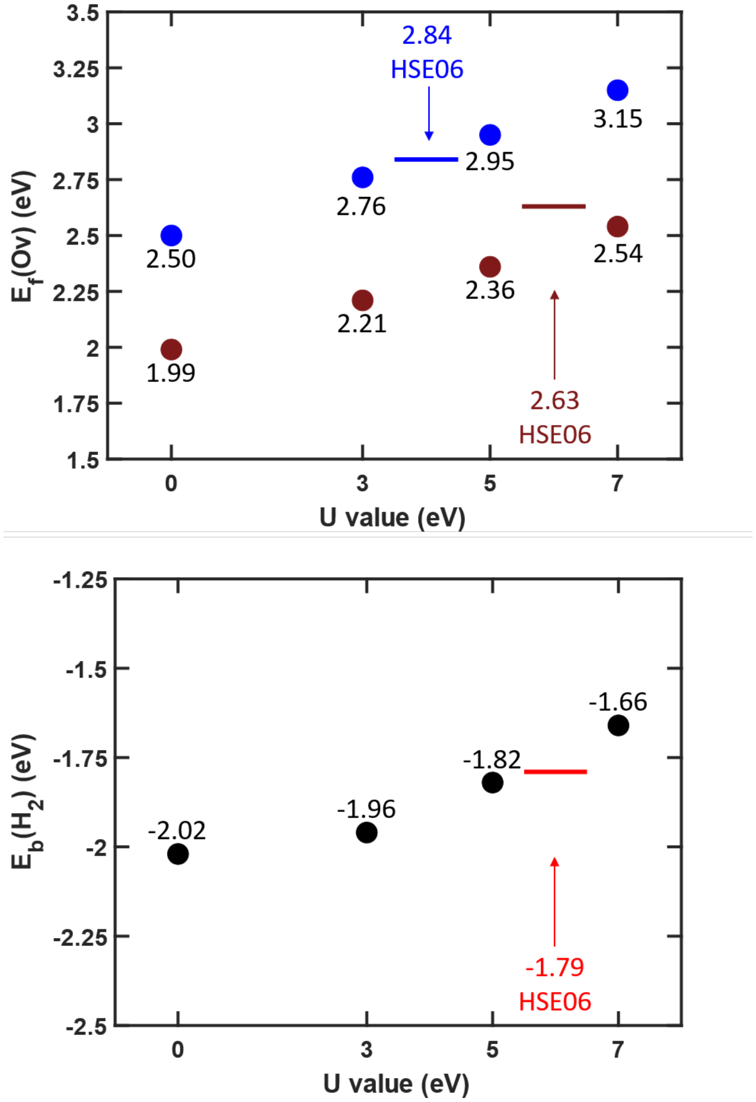


Figure S1: Calculations with different Hubbard U-values for $In_2O_3(110)$. (Top) Oxygen vacancy energy of formation for $O_3$ (blue) and $O_6$ (brown). (Bottom) Hydrogen adsorption energy at 16% coverage. Calculations are performed using the experimental lattice constant.[S2]

We find that using a Hubbard correction U = 7 eV gives results in good agreement with the hybrid functional. The Hubbard correction (U = 7 eV) underestimates the $E_f(O_v)$ for $O_6$ with respect to the hybrid, whereas the vacancy formation energy is overestimated for $O_3$. The hydrogen adsorption energy is underestimated by 0.13 eV with respect to the HSE06 calculation using U=7 eV. We note that the hydrogen adsorption results are affected by the use of the experimental lattice constants. However, complete relaxation is currently computationally expensive.

To further investigate the effect of the Hubbard-U correction on the description of the surface properties, we calculated the formation energy for oxygen vacancies [$E_f$ ($O_v$)] with and without the correction. The energy ($E_f(O_v)$) is calculated forming either $O_2$ (thermal desorption), $H_2O$ or $CO_2$ in the gas phase. The results using U=7 eV is given in Figure S2. We find that PBE predicts reduction of the surface with both $H_2$ and CO. Using PBE+U, the formation of oxygen vacancies is energetically less preferred by about 1 eV.

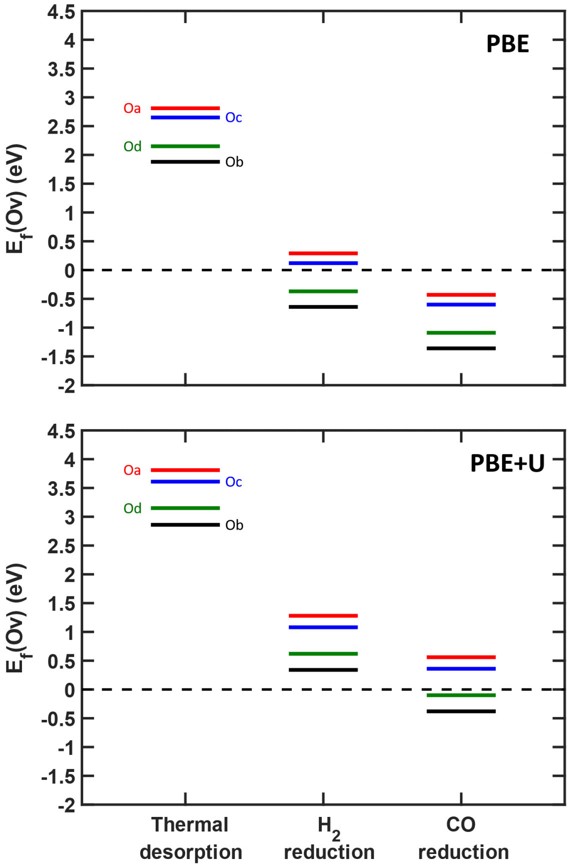


Figure S2: Oxygen vacancy energy of formation for non-equivalent sites on $In_2O_3(111)$ using PBE (top) and PBE+U (bottom) (U= 7 eV).

## Effect of oxygen vacancy concentration

We investigated the effect of a higher concentration of oxygen vacancies on surface stability as a function of hydrogen chemical potential (Figure S3). Three oxygen vacancy situations are considered, namely having one, two and three $O_v$ on the surface. These calculations were done using PBE. For comparison, we include the results for the 16% hydrogen covered surface. Adsorption of hydrogen is thermodynamically preferred at relevant experimental conditions. We find that the vacancies always are located close to the $In_b$-site. The structure of the surface with three $O_v$ is shown as an inset in Figure S3.

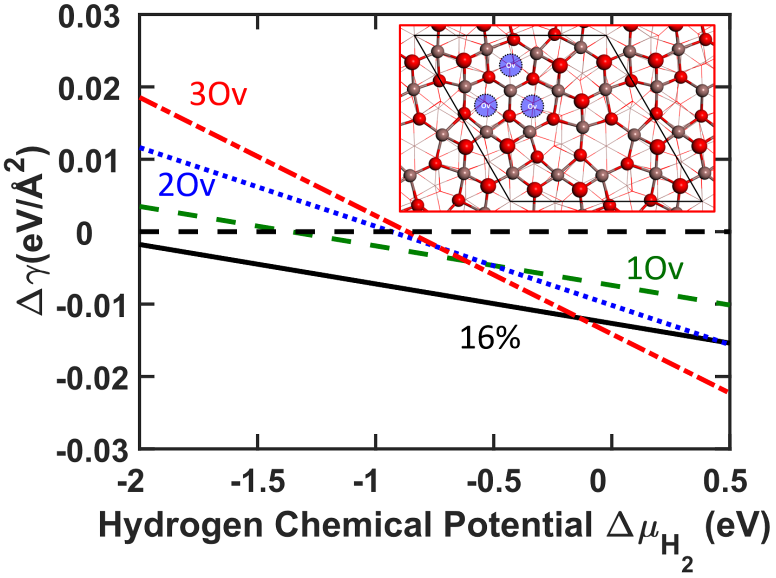


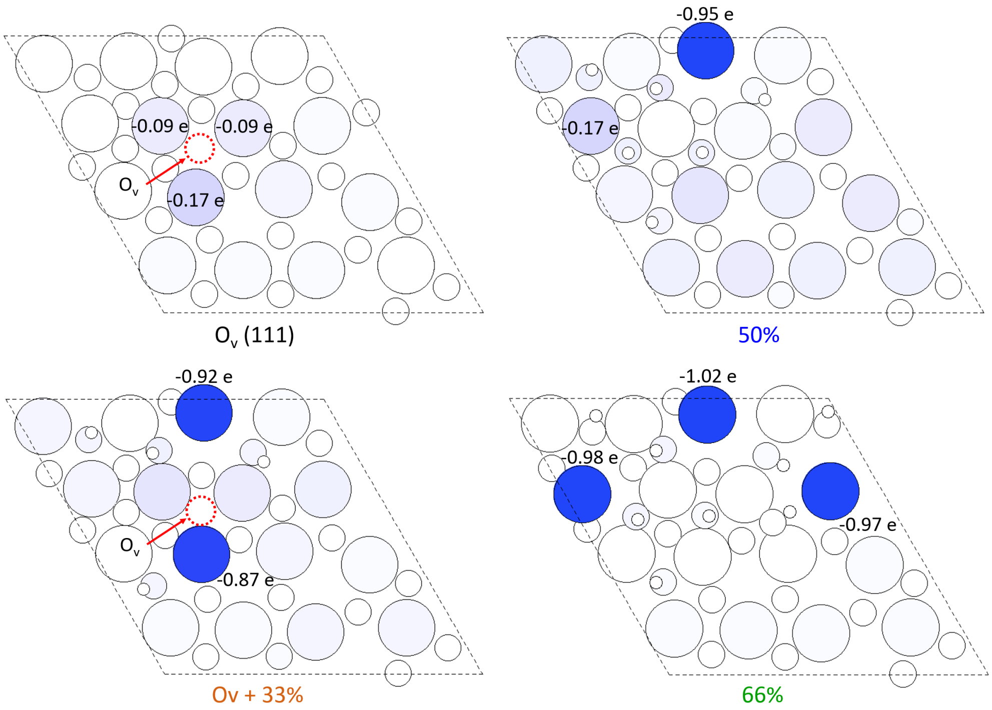
Figure S3: Surface stability of $In_2O_3(111)$ as a function of hydrogen chemical potential ($\mu_{H_2}$) at a temperature of 573 K and $H_2O$ partial pressure of 1 bar.

## Hydrogen adsorption energies with PBE+U (U = 7 eV)

Here we report the average hydrogen adsorption energies at various coverages for the Hubbard corrected calculations of $In_2O_3(111)$ and $In_2O_3(110)$. For the (111) orientation, the average binding energy of hydrogen is, -1.64, -0.71, -0.27, -0.30, 0.02, -0.08 and 0.11 eV for 16%, 33%, 33%+$O_v$, 50%, 50%+$O_v$, 66% and 100 %, respectively. For the (110) orientation, the average hydrogen binding energy is -1.52, -0.91, -0.65, -0.70, -0.63 and -0.39 eV for 16%, 50%, 66%, 83%, 83%+$O_v$ and 100% coverage, respectively. For both surface orientations, the inclusion of the Hubbard-U correction shifts the binding energies by $\sim 0.8$ eV to higher values, with respect to the PBE case.

# Bader charge analysis PBE+U

A Bader charge analysis is performed on the relevant hydrogen covered $In_2O_3(111)$, with Hubbard correction (Figure S4). The results are in quantitative agreement to the findings reported in the main text without the U-correction. We find a change in oxidation state, from +3 to close to +1, on $In_e$ and $In_f$ upon hydroxylation. On the $O_v$ surface, we find the reduction of the surrounding In-ions to be modest. The largest change is observed for the $In_e$ site at the vacancy. This site changes its charge from 11.24 electrons in the pristine to 11.41 electrons on the $O_v$ surface. The reminding of the charge is distributed on the rest of the In-ions in the slab, which charge changes by less than 0.1 e. This result further suggests that the creation of an oxygen vacancy does not lead to the reduction of the In-ions. Similarly as reported with PBE, change in oxidation state occurs on the 33%+$O_v$ surface, at moderate hydrogen coverages. Here, the combination of hydroxylation and $O_v$ creation leads to two $In_e$ changing charge from 11.24 electrons in the pristine surface to 12.16 and 12.11 electrons upon hydroxylation. On the 50 % covered structure, one $In_e$ changes oxidation state upon hydroxylation. The charge on the $In_e$ changes from 11.24 electrons on the pristine to 12.19 electrons on the hydroxylated surface. On the 66 % covered structure, three In-ions change oxidation state upon hydroxylation. Two $In_e$ and a $In_f$ go from having 11.24 electrons on the pristine surface to having 12.26, 12.21 and 12.22, respectively. The results are in agreement with the experimentally measured change in the oxidation state of In-ions during reaction.[S3]



O$_v$ (111)

50%

Ov + 33%

66%

Figure S4: Bader charge analysis of relevant $In_2O_3$(111) structures with Hubbard correction. Degree of charge localization is shown in blue.

# O 1s Core-level shifts

A graphical representation of the O 1s CLS for $In_2O_3$(111) without (a) and with (b) oxygen vacancy is shown in Figure S5.

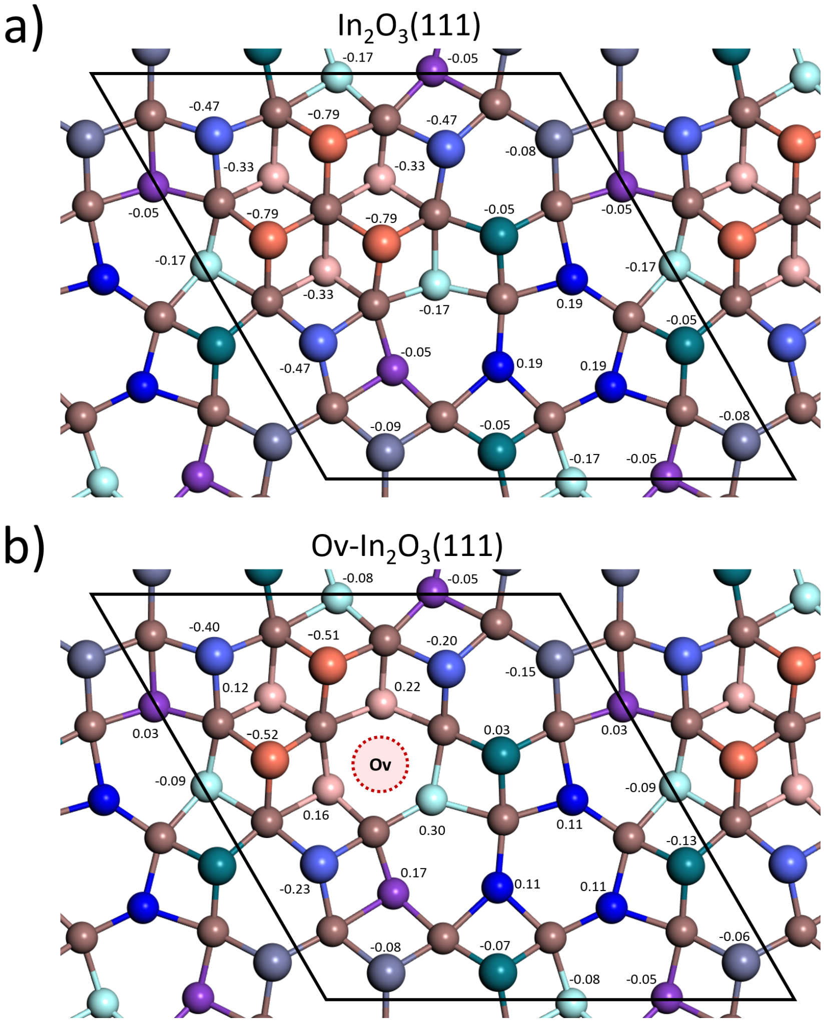


Figure S5: Calculated O 1s core-level shifts of surface oxygen on pristine and $O_v$ $In_2O_3(111)$. Calculated O 1s CLS in eV is shown next to each O-site. Topmost oxygen are shown slightly larger to help with perspective. Same color indicates semi-equivalent O-sites.

The effect of Hubbard correction on the O 1s CLS is investigated on $In_2O_3(111)$ and $In_2O_3(110)$, respectively (Figure S6). We find that the Hubbard correction has a negligible effect on the overall trend of the calculated O 1s CLS. The results are in close to the PBE results. The results suggest that the experimentally assigned peaks at 531.7 eV and at 532.5 eV[S4] are likely caused by OH groups on In-ions and OH groups in oxygen lattice position, respectively.

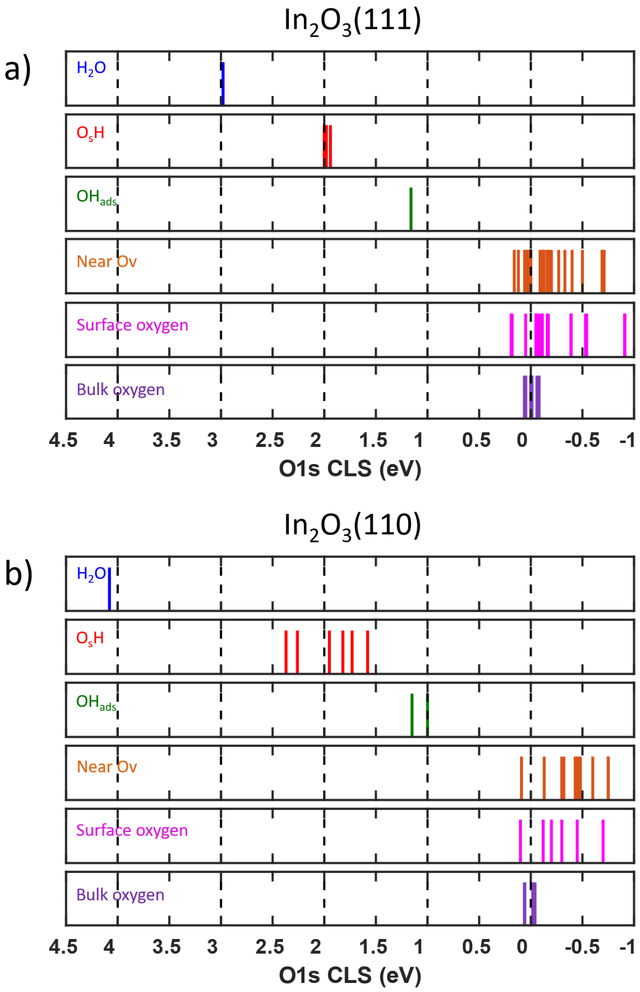


Figure S6: Calculated O 1s core-level shifts of hydroxylated $In_2O_3(111)$ and $In_2O_3(110)$ with Hubbard correction. CLS are calculated with respect to a bulk O-site, in the middle layer of the slab, for each surface.

The structural models of $O_sH$ and $OH_{ads}$ on $In_2O_3(110)$ are shown in Figure S7.

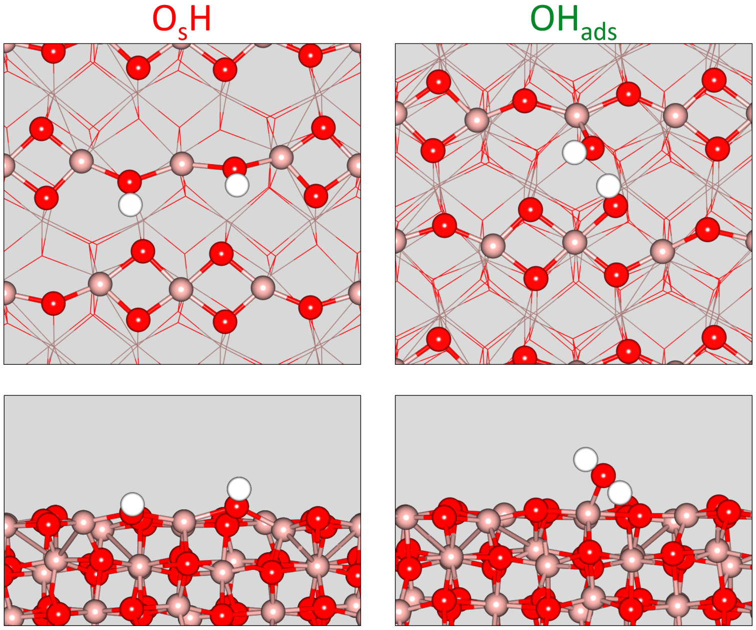


Figure S7: Structural models of $O_s$H(left) and $OH_{ads}$(right) on $In_2O_3$(110). Atomic color code as in Figure 2 in the main text.

# References

(S1) Krukau, A. V.; Vydrov, O. A.; Izmaylov, A. F.; Scuseria, G. E. Influence of the exchange screening parameter on the performance of screened hybrid functionals. *J. Chem. Phys.* **2006**, *125*, 224106.

(S2) Gonzalez, G.; Cohen, J.; Hwang, J.; Mason, T.; Hodges, J.; Jorgensen, J. Neutron diffraction study on the defect structure of indium-tin-oxide. *J. Appl. Phys.* **2001**, *89*, 2550–2555.

(S3) Tsoukalou, A.; Abdala, P. M.; Stoian, D.; Huang, X.; Willinger, M.-G.; Fedorov, A.; Mueller, C. R. Structural evolution and dynamics of an $In_2O_3$ catalyst for $CO_2$ hydrogenation to methanol: An operando XAS-XRD and In situ TEM study. *J. Am. Chem. Soc.* **2019**, *141*, 13497–13505.

(S4) Martin, O.; Martin, A. J.; Mondelli, C.; Mitchell, S.; Segawa, T. F.; Hauert, R.; Drouilly, C.; Curulla-Ferre, D.; Perez-Ramirez, J. Indium oxide as a superior catalyst for methanol synthesis by $CO_2$ hydrogenation. *Angew. Chem. Int. Ed.* **2016**, *55*, 6261–6265.