

Surface and Interstitial Ti Diffusion at the Rutile $\text{TiO}_2(110)$ Surface

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Supplementary Information

Figure S1 shows the charge distributions in the A and B Ti adsorption sites from the Hallil QEq model (a) and (d); the modified QEq (c) and (f); and the Bader analysis of the DFT+U results (b) and (e). The visual comparison between the models is reasonable throughout.

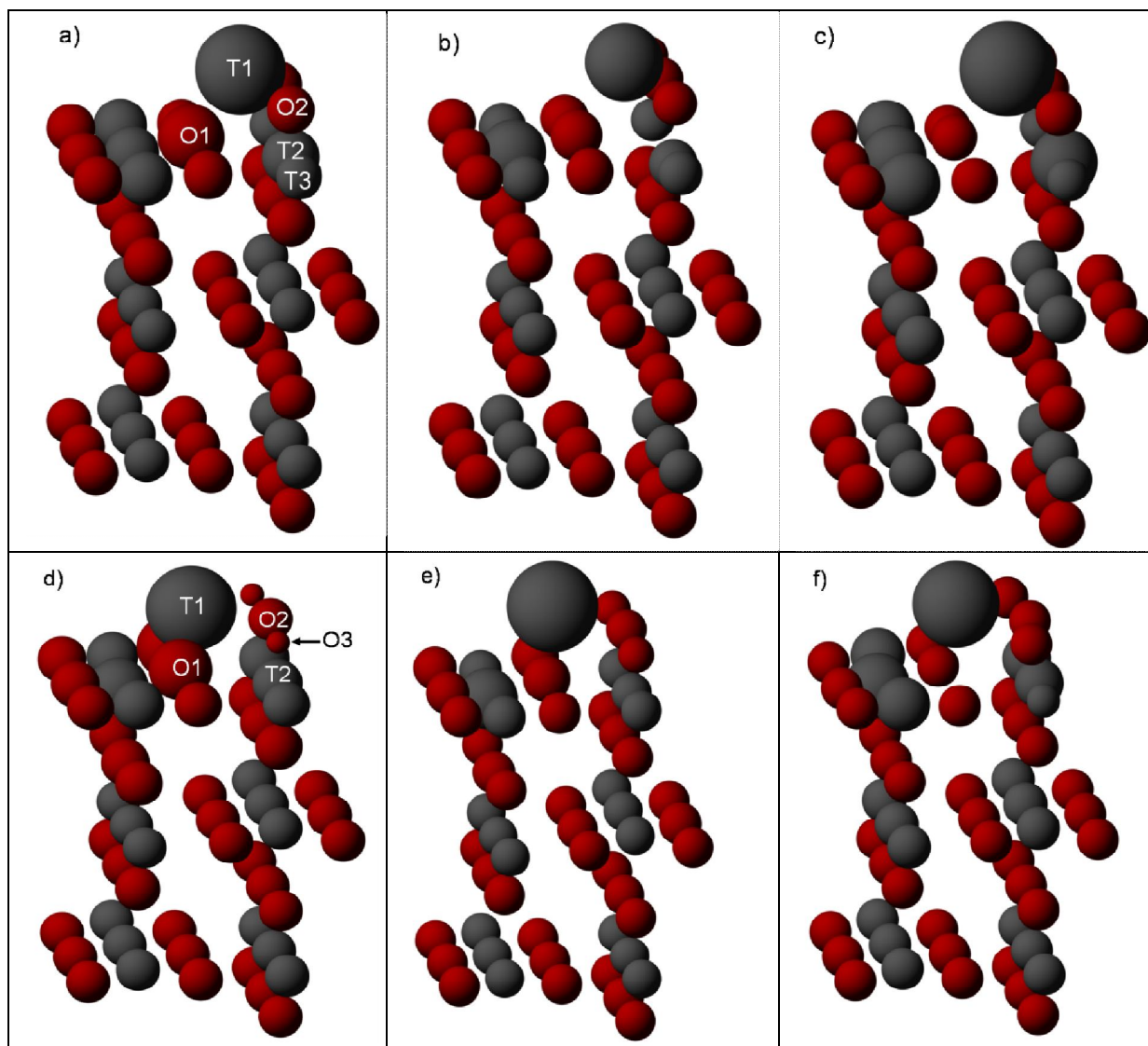


Fig. S1 Adatom sites: (a) Hallil model QEq results for the A site; (b) Bader analysis of the DFT+U A site; (d) Hallil model QEq results for the B site; (e) Bader analysis of the DFT+U B site. The oxygens are light grey and the titanium dark grey. The size of the ions in all images represent how much excess charge dQ (e) is associated with the ion in comparison to its bulk charge (specifically radius scales as $1+1.3dQ$). The values of dQ for the labelled ions are given in Table 1 in the main text. In (c) and (f) the results of the QEq calculations with fixed oxygen charge are also shown for the A and B sites respectively. Only a section of the full cell used in the calculations is show for clarity, with the upper surface being the free one with the exposed bridging oxygen.

Figure S2 shows the charge distributions in the Fi and Bi adsorption sites from the Hallil QEq model (a) and (d); the modified QEq (c) and (f); and the Bader analysis of the DFT+U results (b) and (e). Here we see a marked difference between the models. In particular, the Hallil QEq model (S2a and S2d) shows strong charging of the nearest-neighbour oxygen to the interstitial, which explains the very strong binding of interstitials over adatoms in this model. This behaviour is suppressed when the charge on the oxygen is held fixed (S2c and S2f), which leads to charge distributions more in accord with the DFT+U Bader analysis shown in S2b and S2e.

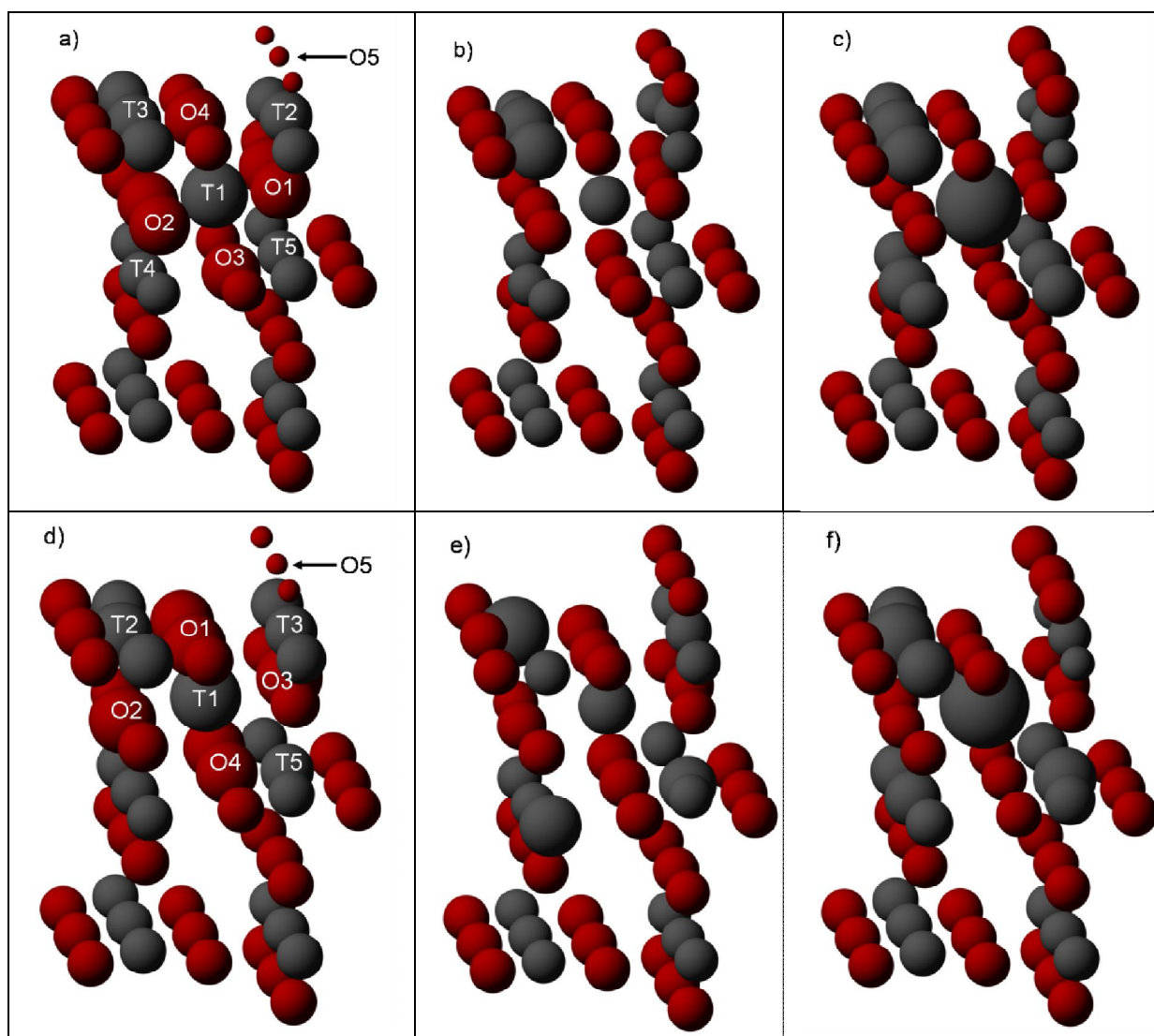


Fig. S2 First-layer interstitial sites: (a) Hallil model QEq results for the Fi site; (b) Bader analysis of the DFT+U Fi site; (d) Hallil et al QEq results for the Bi site; (e) Bader analysis of the DFT+U Bi site. The colours and ion sizes are as in Figure S1. The values of dQ for the labelled ions are given in Table 2 in the main text. In (c) and (f) the results of the QEq calculations with fixed oxygen charge (see main text) are also shown for the Fi and Bi sites respectively.

Another feature of the Hallil QEq model is the charge transfer away from the under-coordinated bridging oxygen O5 seen in figures S2a and S2d. Again this feature is not found in the Bader analysis of the DFT+U calculations shown in S2b and S2e. It is important to note that the fixed oxygen charge modification leaves the bulk properties such as optimised lattice parameters unchanged, but changes the surface calculations by correcting the depleted bridging row ionic charge. We find that whilst this modification changes the absolute values of the surface energies of the low-index rutile surfaces, it leaves the hierarchy unchanged; the modified surface energies are calculated to be 1.33Jm^{-2} , 1.62Jm^{-2} and 1.99Jm^{-2} for the (110), (100) and (001) surfaces respectively. The (110) surface is therefore still correctly predicted to be the most stable.

In support of the physical basis of charge transfer modification to the QEq potential used in this work, we present experimental data which illustrates the low variability of charge transfer to and from the $\text{TiO}_2(110)$ surface oxygen predicted by our calculations. In Figure S3, we show results from an X-ray Photoemission Spectroscopy (XPS) study. The lower trace is from a clean, stoichiometric $\text{TiO}_2(110)$ (1x1) surface. The middle is from doping the surface with 1/8 monolayer of Ti adatoms, and the upper from a (1x2) reconstructed surface which has thermally grown added rows of Ti_2O_3 . These are the surfaces that show Ti core level shifts. If there is much charge transfer to the surface oxygen caused by the excess Ti neighbours compared to the (1x1) bulk termination, core-level shifts would show in these O1s spectra on the *leading edge*; none are evident. (Note that the broadening to higher binding energy is due to differing energy-loss behaviour of the outgoing electrons in reduced samples). We conclude that the levels of charge transfer to and from oxygen in all these surface structures is low, in line with the calculations presented here.

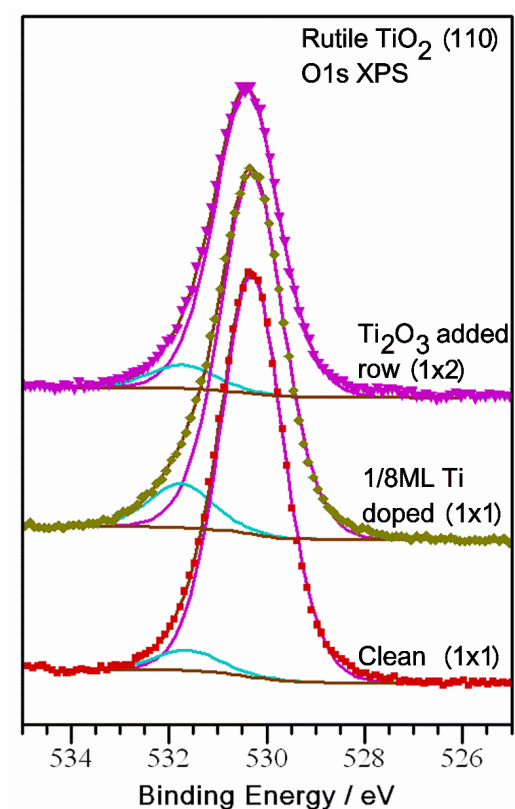


Figure S3 XPS O1s spectra for various rutile $\text{TiO}_2(110)$ surface structures. The lower trace is for a clean, stoichiometric (1x1) bulk terminated surface. The middle trace follows doping with 1/8 monolayer Ti adatoms see ref for details. The upper trace is for the reconstructed (1x2) termination with added-row Ti_2O_3 .