Supporting information for manuscript

Reactivity of sub 1nm supported clusters: \((\text{TiO}_2)_n\) clusters supported on rutile \(\text{TiO}_2\) (110)

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The supporting information for this manuscript is four figures: S1 to S4.

Figures S1 and S2 show the DFT and DFT+U \((U = 4.5 \text{ eV in Ti 3d states})\) spin density plots for oxygen vacancy structures for supported \(\text{Ti}_2\text{O}_4\) (figure S1) and \(\text{Ti}_4\text{O}_8\) (figure S2)

Figure S1: Comparison of DFT and DFT+U spin density for oxygen vacancy structures for \(\text{Ti}_2\text{O}_4\) and supported on \(\text{TiO}_2\). (a): DFT, (b): DFT+U, as described in the text. Different slab thicknesses are shown to highlight the DFT delocalisation

Figure S2: Comparison of DFT and DFT+U spin density for oxygen vacancy structures for \(\text{Ti}_4\text{O}_8\) and supported on \(\text{TiO}_2\). (a): DFT, (b): DFT+U, as described in the text. Different slab thicknesses are shown to highlight the DFT delocalisation
Figure S3 shows the relaxed structures for oxygen vacancy sites 2 and 4 in supported Ti$_3$O$_6$

![Figure S3](image)

**Figure S3:** Relaxed atomic structures for oxygen vacancy sites 2 and 4 in reduced Ti$_3$O$_6$ supported on TiO$_2$. (a): site 2, (b): site 4

Figure S4 shows the relaxed structures for oxygen vacancy sites 1 and 2 in supported Ti$_4$O$_8$

![Figure S4](image)

**Figure S4:** Relaxed atomic structures for oxygen vacancy sites 1 and 2 in reduced Ti$_4$O$_7$ supported on TiO$_2$. (a): site 1, (b): site 2