

## Supporting Information (Low Reactivity of Non-bridging Oxygen Defects on Stoichiometric Silica Surfaces, Said Hamad and Stefan T. Bromley)

Both systems were first optimised without water molecules using conjugate-gradient energy minimisation of cell parameters and atomic positions with INCAR=4 (EDIFF=10E-6 energy tolerance and EDIFFG=10E-5 force tolerance were used). The use of INCAR=4 allows for relaxations in all directions while conserving the cell volume. Considering the large vacuum gap between the silica slabs in the  $z$  direction the energy and forces associated with cell changes in this direction will be negligible and thus the optimisations will predominantly be intraslab. This procedure was followed for a number of constant volumes until a minimum energy was found with respect to volume change. This mode of energy minimisation was preferred over manual x-y fitting as it allows for arbitrary cell parameter change (i.e. cell lengths and angles) for each volume and thus one can be more confident in finding a true minimum geometry. The optimised dry slabs had the following cell parameters:

System A:  $a=10.050$ ,  $b=10.0500$ ,  $c=18.0000$   $\alpha=90.0000$ ,  $\beta=90.0000$ ,  $\gamma=120.1676$

System B:  $a=7.0880$ ,  $b=6.8700$ ,  $c=23.5032$ ,  $\alpha=85.4653$ ,  $\beta=86.1735$ ,  $\gamma=117.7882$

Following other similar studies (e.g. ref 7) the MD calculations were performed using the NVE microcanonical ensemble. Use of the alternative NVT canonical ensemble was not favoured due to the use of an artificial heat bath during production which the authors feel should be largely unnecessary in relatively large systems such as ours in which a good equilibrium state has been achieved. Preliminary NVT tests of system B show the same result as reported herein i.e. the NBO is not hydroxylated during the run. System A was equilibrated for 5 ps and system B for 2ps. The graphs of energy versus time for these equilibrations can be seen below in figures S1 and S2. For both NVE calculations EDIFF was set to 10E-5.

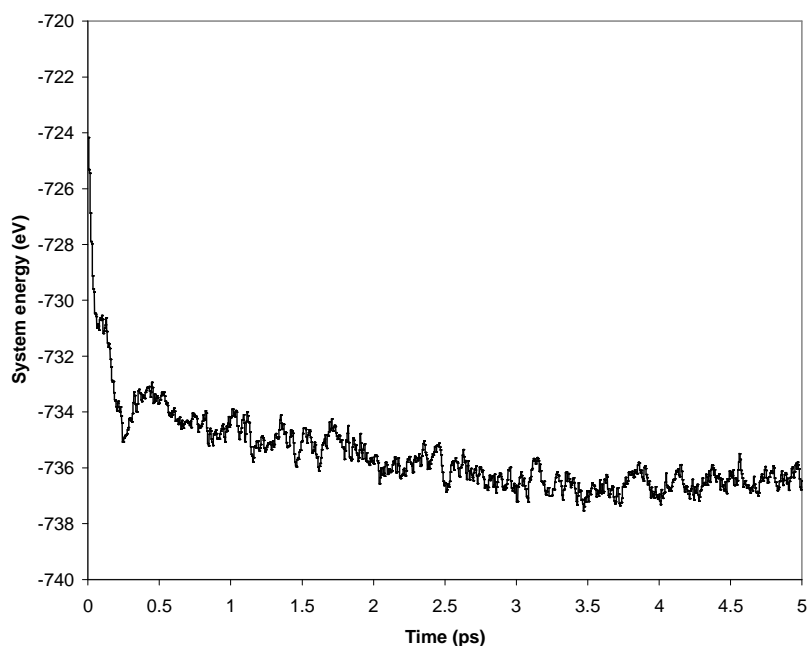


Fig. S1: Equilibration of system A.

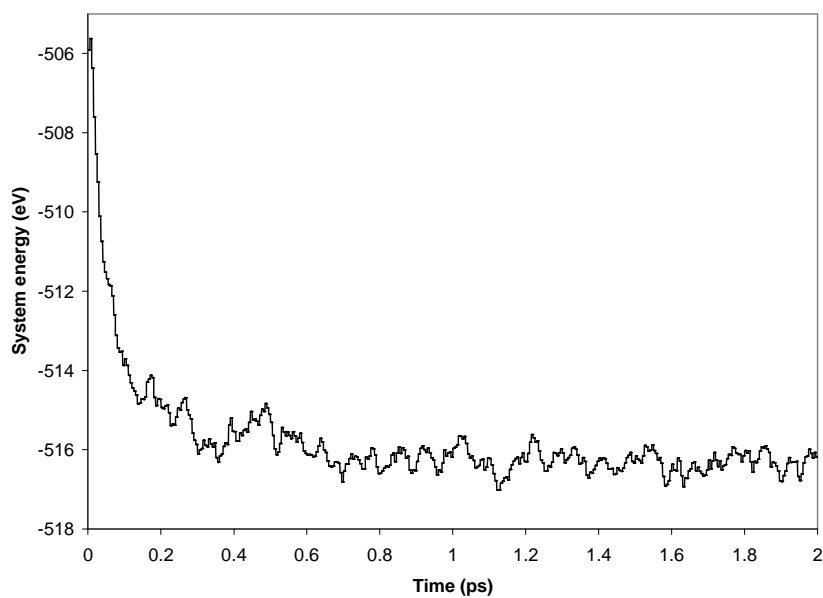
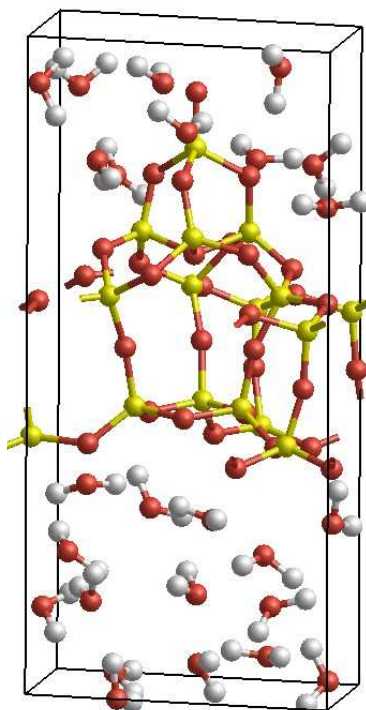
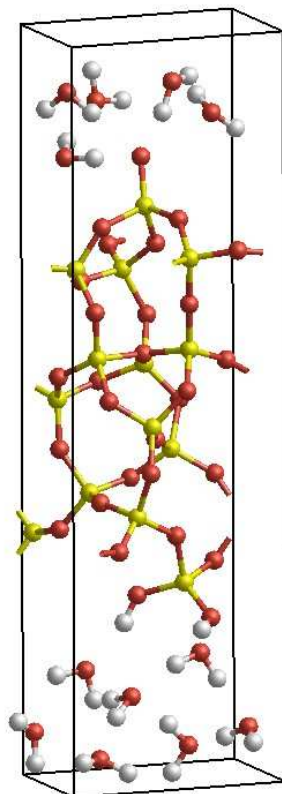


Fig. S1: Equilibration of system B.

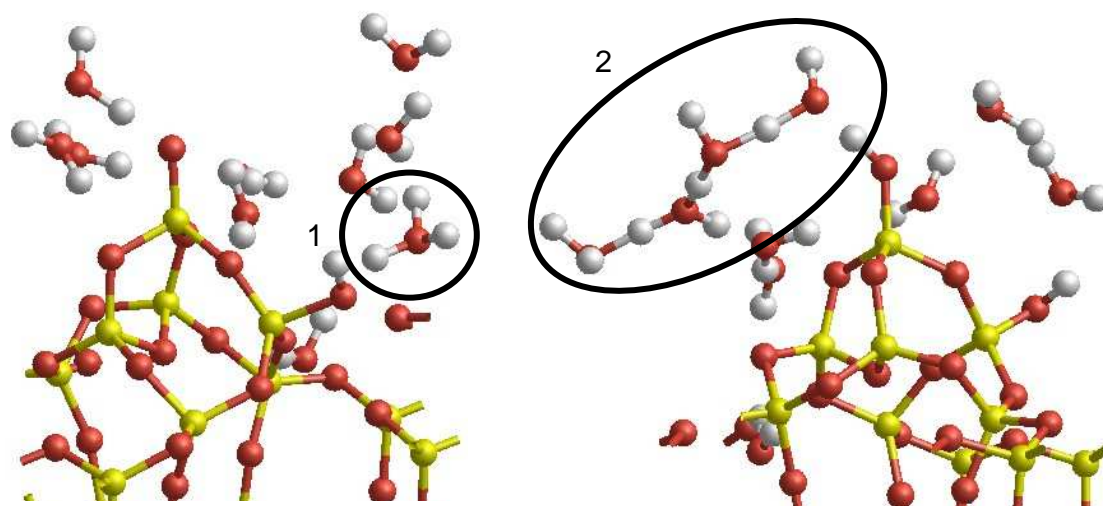
Snapshots of the full hydrated systems from near the start of the MD runs for each system are shown in figures S3 and S4. Figure S5 details the intermediate reaction steps of the hydroxylation reaction observed in system A.



S3: Full cell of hydrated system A.



S4: Full cell of hydrated system B. Note that a water molecule reacts on the underside of the slab to form a geminal silanol early in the MD run which does not affect in the NBO on the other side of the slab (distance 9.3 angstrom).



S5: Intermediate steps of the hydroxylation reaction on system A: (1) after the water has attacked the silicon atom a proton is released to form a  $\text{H}_3\text{O}^+$  ion, (2) the  $\text{H}_3\text{O}^+$  ion induces a grouping of water molecules which donates a proton to the NBO $^-$ .

The program used to calculate the reported Bader charges was by Andri Arnaldsson, Wenjie Tang, and Graeme Henkelman, from the University of Austin, Texas (<http://theory.cm.utexas.edu/bader/>) with grid settings: NGXF=42, NGYF= 42, NGZF=144.