Computational investigation of α-SiO$_2$ surfaces as a support for Pd

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Supplementary Information

S1. Water reference structure molecular dynamics

The calculation of water adsorption energy and the surface energy of hydroxylated surfaces requires a reference state for the water molecule. In this work we compare results using a gas phase water reference and a liquid phase water reference.

For the liquid phase 64 molecules of water were placed in a cubic simulation box with a side length of 12.4 Å with the water molecules placed in a regular 4×4×4 array. This produces a system with the expected density of liquid water of 1.00 g cm^{-3}. The periodic water model was first subjected to a high temperature (T=500 K) molecular dynamics (MD) simulation, using an NVE ensemble to maintain the density. For this phase of the calculation the TIP4P[1,2] potential in the DL-POLY[3] package was used with a 1 fs timestep. After 20 ps equilibration (velocity scaling) the simulation switched into the designated ensemble for a further 30 ps. This was sufficient to produce a randomised hydrogen bonded network model. The resulting structure was then used as input for a CASTEP MD simulation run using the NVT ensemble with a Nose-Hoover thermostat. The functional and basis set cut-off were the same as used for the SiO$_2$ slab calculations (PBE, E_{cut} = 700 eV) and TS dispersion corrections were included. The MD calculations were carried out at the Γ-point (k sample (1×1×1)). This DFT MD was run at a simulation temperature of 300 K for a total run time of 3.5 ps.

Figure S1 shows the temperature and potential energy of the system as a function of time over the DFT MD calculation. It can be seen that after an initial sharp drop the calculated potential energy fluctuates around a constant value and the calculated temperature remains
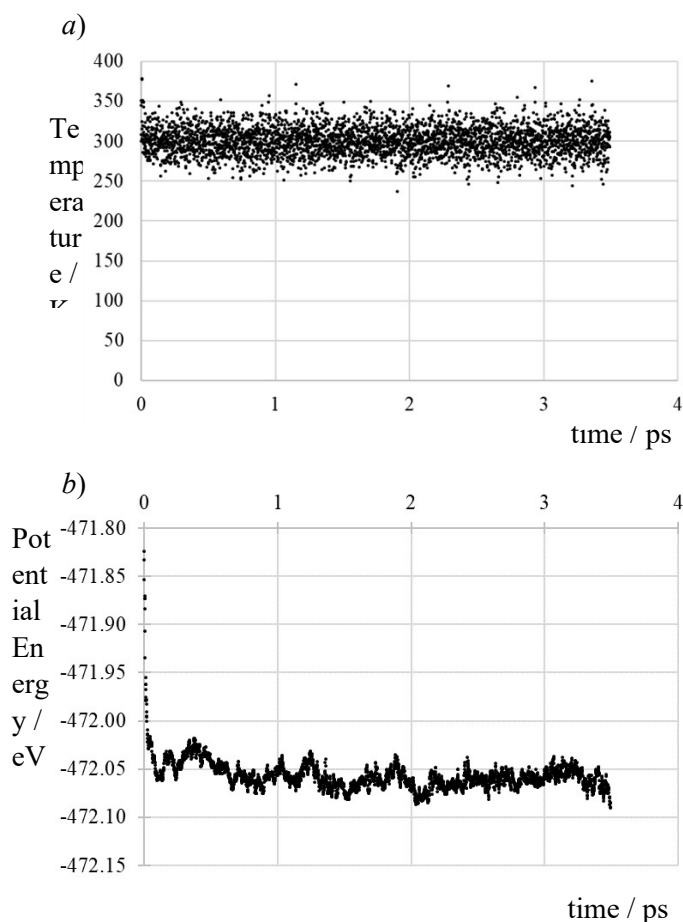
a)

b)

Figure S1. a) Temperature and b) potential energy as a function of time over the DFT molecular dynamics simulation for 64 water molecules at a density of 1.00 g cm^{-3}.

well within ±50 K of the target temperature. To obtain the water reference energy 14 structures were taken at regular intervals from the trajectory of the simulation between 1 ps and 3.5 ps. Each structure was optimised using a fixed cell procedure and the same convergence criteria as used for simulation of the silica bulk and slab models. This gave liquid water reference energies of -472.0026 ± 0.0074 eV for the PBE functional alone and -472.1507 ± 0.0052 eV when dispersion is included. The error estimates here are the standard deviations calculated from the 14 optimised structure energies.

References

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