

Low reactivity of non-bridging oxygen defects on stoichiometric silica surfaces†

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Using *ab initio* molecular dynamics simulations we demonstrate that surfaces of stoichiometric silica exhibiting non-bridging oxygen defects can be surprisingly resistant to attack by water.

Silica is increasingly being employed in a wide array of functionalised nanostructures¹ and bio-inspired (nano)materials² where hydroxylation reactions at its surfaces are key. Computational modelling methods have contributed greatly to the understanding of the complex silica–water system with uniquely detailed microscopic insights into the mechanisms of silica hydroxylation reactions.³ From such studies, water molecules are generally predicted to preferentially attack the surfaces of bulk silica at terminating point defects and strained Si–O–Si sites with modest reaction barriers.^{4–8} On the contrary, regular non-defective crystalline silica surfaces are known from experiment to be often very resistant to reactions with water (*e.g.* thin ordered films,⁹ zeolite interiors¹⁰). From such evidence it is chemically reasonable to equate the observation of low reactivity/hydrophobicity with the presence of an underlying unstrained defect-free silica surface. Taking inspiration from structural reconstructions in low-energy silica nanoclusters and using *ab initio* molecular dynamics (AIMD) simulations, we show, conversely, how stoichiometric silica surfaces displaying under-coordinated terminating oxygen defects can be surprisingly unreactive with water.

Defects in silica are typically regarded as a minority species with respect to a dominant perfectly tetrahedrally coordinated oxygen-bridged ($\equiv\text{Si}-\text{O}-\text{Si}\equiv$) network. Although generally true for bulk systems, for silica surfaces and nanostructures, the high proportion of terminating sites increases the probability for the presence of defects. In the extreme case of silica nanoclusters of only a few tens of SiO_2 units, nearly all atoms can be considered to be at the surface. Intensive global optimisation searches of the most stable silica nanoclusters of this size have shown that many (and often most) surface atoms in such nanoclusters are directly involved in defects as opposed to bulk-like tetrahedral linkages.^{11–13} In Fig. 1, the lowest energy silica nanoclusters for $(\text{SiO}_2)_{13}$ ¹² and $(\text{SiO}_2)_{17}$ ¹³ are shown as

typical examples. Considering these nanoclusters, it is evident that it is a poor approximation to view silica at this scale as a simple cut from an extended tetrahedral network. Instead, small low energy silica clusters stabilise themselves most effectively by adopting non-bulklike structures that are optimally adapted to the confines of the nanoscale. Although the nanoclusters in Fig. 1 differ in size by only four SiO_2 units their structures are remarkably distinct. The ground state for $(\text{SiO}_2)_{13}$ has a symmetric radial structure (C_{3v}) whereas that for $(\text{SiO}_2)_{17}$ adopts an unsymmetric elongated structure. Both clusters are highly defective with silanone ($\text{Si}=\text{O}$), two-ring (Si_2O_2), and non-bridging oxygen (NBO) defects highlighted in Fig. 1.

The interaction of water with each of these exhibited defect types have been studied by a number of quantum mechanical (QM) and classical calculations. The widely studied Si_2O_2 two-ring shows relatively facile, although possibly strain dependent,^{4,5} ring breaking with water to give two oxygen-bridged silanol (SiOH) groups.^{6,7,14} Closed-shell $\text{Si}=\text{O}$ defects react with water with a low energy barrier to yield geminal silanols *i.e.* $\text{Si}(\text{OH})_2$.^{5,8,14,15} QM studies have further shown that the presence of nearby water molecules can assist hydroxylation by providing a proton transfer channel.⁷ The predicted relative ease of $\text{Si}=\text{O}$ and two-ring hydroxylation, however, contrasts with mixed results on NBO defects.^{5,8,16,17} Employing large-scale AIMD calculations with numerous explicit water molecules, we clarify the susceptibility of NBOs, with well-defined electronic states, to water attack.

Although no quantitative experimental data exist on the local atomic structure of NBO defects and their immediate vicinity, we created two stoichiometric silica nanoslab models inspired by the structures of low energy NBO-exhibiting silica nanoclusters. We note that all low energy clusters with NBO centres also contain proximal three-coordinated oxygen ($\equiv\text{O}$) centres (see D in Fig. 1) which we incorporated into our nanoslab models. System A can be thought of as a

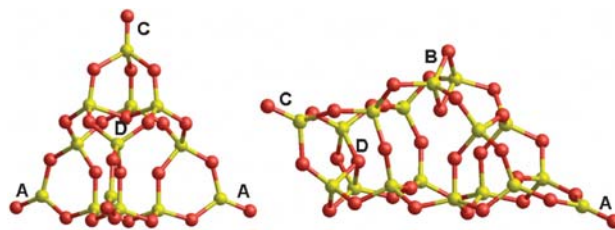


Fig. 1 Ground state silica clusters for $\text{Si}_{13}\text{O}_{26}$ (left) and $\text{Si}_{17}\text{O}_{34}$ (right) showing a range of defects: (A) silanone ($\text{Si}=\text{O}$), (B) two-ring (Si_2O_2), (C) non-bridging oxygen (NBO), (D) three-coordinated oxygen centre ($\equiv\text{O}$). In all figures oxygen is red and silicon is yellow.

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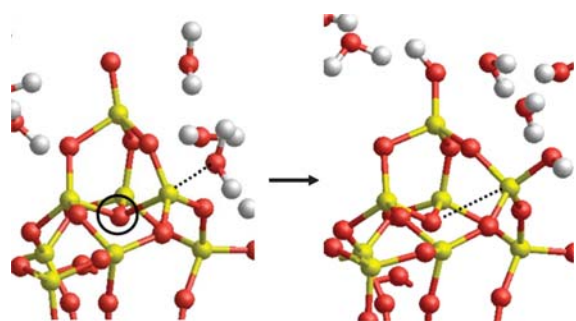


Fig. 2 MD run A snapshots showing the rapid attack of the silicon atom coordinated to a $\equiv\text{O}$ centre (black circle). Dotted lines show bond breaking/forming (proton transfer occurs *via* two water molecules).

two-dimensional network of Si–O–Si-linked $(\text{SiO}_2)_{13}$ ground state clusters (see Fig. 2) with inter-NBO separations of 10 Å and $\equiv\text{O}$ –NBO distances of 4.5 Å. The unit cell of model B has 14 SiO_2 units giving an extended system with NBO centres separated by ~ 7 Å and $\equiv\text{O}$ –NBO distances of 6.1 Å (see Fig. 3). Both nanoslabs are approximately 10 Å thick and separated by > 10 Å in the z -direction. To initialise, both slabs were optimised with respect to both internal atomic coordinates and cell parameters using constant volume energy minimisations. As the NBO terminations were only on one side of the slabs, dipole corrections were applied to all calculations. To both systems, explicit water molecules (25 for A and 13 for B) were then added in random positions to achieve a water density close to that at 300 K at 1 atm. Microcanonical NVE (constant number of atoms, volume and energy) Born–Oppenheimer AIMD simulations were carried out at the gamma point with a timestep of 0.5 fs within the framework of density functional theory. The PBE functional¹⁸ was used with inner core electrons described by the projector-augmented-wave method and a 400 eV cut-off energy. Equilibrations were for 5 ps (system A) and 2 ps (system B), with velocity rescaling every ten steps to reach a temperature of 300 K. Productions were for 5 ps (system A) and 8 ps (system B). The VASP code¹⁹ was used throughout.

In system A, NBO hydroxylation happens very quickly (< 1 ps). First a water molecule attacks a silicon atom co-

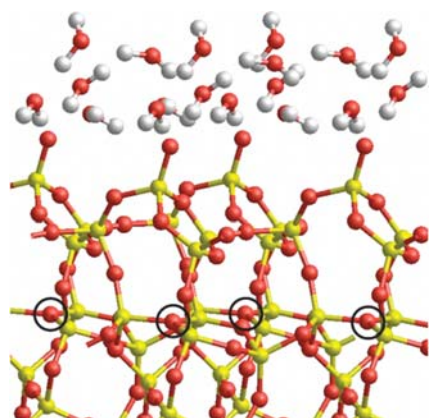


Fig. 3 A snapshot from MD run B showing the non-reacting NBO-terminated surface and the sub-surface $\equiv\text{O}$ centres (black circles).

ordinating to the $\equiv\text{O}$ centre. This leads to the breakage of the bond between the silicon atom and $\equiv\text{O}$ centre, the latter becoming a typical bridging oxygen atom (Si–O–Si). The water molecule attached to the silicon atom then dissociates to form a silanol while releasing a proton. Proton transfer to the NBO then occurs *via* two intermediate water molecules. The initial and final steps of this reaction are shown in Fig. 2.

Intriguingly, the small difference in $\equiv\text{O}$ –NBO separation in system B (~ 1.6 Å more than system A) makes a large change to its reactivity. During the full 8 ps run the NBO centres are not attacked and hydroxylation never occurs (a typical snapshot is shown in Fig. 3). In system A, the silicon atoms coordinated to the $\equiv\text{O}$ centre are very reactive and accessible and act as the initiators for the eventual NBO hydroxylation. In system B, however, these silicon sites are hidden and thus even though the NBO is exposed it is not attacked.

To understand these results, we must consider the nature of the NBO defects in our systems. NBOs can exist as: (i) as open-shell paramagnetic species (NBO^\bullet) resulting from the homolytic breakage of the Si–O bond (*e.g.* by cleavage of dry silica, or radiation), or (ii) negatively charged closed-shell centres (NBO^-) which may result from the deprotonation of silanols on hydroxylated silica surfaces under basic conditions,²⁰ or from electron trapping by NBO^\bullet defects.²¹ In either case, assuming we have stoichiometric silica, we should also expect the presence of NBO centres to be accompanied by three-coordinated silicon surface $\equiv\text{Si}$ defects ($\equiv\text{Si}^\bullet$ in the case of NBO^\bullet and $\equiv\text{Si}^+$ for NBO^-). Although NBOs are necessarily terminating species, $\equiv\text{Si}^\bullet$ centres may occur within bulk silica. Open-shell $\equiv\text{Si}^\bullet$ centres, for example, are considered to be the basic constituent of paramagnetic E' defects within bulk silica. Near-surface bulk $\equiv\text{Si}^\bullet$ centres and surface NBO^\bullet centres, if relatively close to one another, may be stabilised by the transfer of an electron to form a $\equiv\text{Si}^+/\text{NBO}^-$ defect pair.^{21,22} The charged defect pair is electrostatically stabilised over the neutral pair and further favoured energetically due to the known propensity of NBO to bind an electron.²¹ In the bulk, $\equiv\text{Si}^+$ centres are also created in E' formation and it has been suggested that energy-lowering can occur *via* coordination with a nearby bridging oxygen atom ($\equiv\text{Si}^+\cdots\text{O}$) in the surrounding silica network.²³ Such relaxation restores the four-coordinated oxygen environment of the $\equiv\text{Si}^+$ centre whilst forming a three-coordinated oxygen centre ($\equiv\text{O}$). Stabilisation by this mechanism for $\equiv\text{Si}^+$ centres in $\equiv\text{Si}^+/\text{NBO}^-$ defect pairs, gives defect pairs characterised geometrically as surface-terminating undercoordinated oxygen centres (NBO) close to non-surface over-coordinated oxygen centres ($\equiv\text{O}$). Such combined stabilised $\equiv\text{O}/\text{NBO}$ defect pairs are exactly that found in low energy clusters^{11–13} (*e.g.* see the D/C combinations in Fig. 1) and thus, by construction, also in our cluster-inspired nanoslab models. In extended crystalline silica, defective $\equiv\text{Si}^+$ centres coordinate with nearby oxygen atoms by distorting the lattice, forming geometrically asymmetric $\equiv\text{O}$ centres. In less restrictive topologies (*e.g.* nanoclusters), $\equiv\text{O}$ centres can be coordinated more symmetrically (*i.e.* with less energetically unfavourable distortion) to three $\equiv\text{Si}^{\delta+}$ centres (see Fig. 1–3).

With respect to the electronic state of the NBOs in our systems, we first note that our calculations were carried out in a closed-shell manner (initial nanoslab systems were less stable

by ~ 1 eV after open-shell optimisation) already suggesting that our NBO centres are negatively charged. To further characterise our systems, Bader atomic charges²⁴ of the NBO and $\equiv\text{O}$ centres were taken periodically throughout the MD run for system B and their averages compared with the corresponding average charges from bridging oxygen atoms. The resulting NBO and $\equiv\text{O}$ charges were -1.81 and -2.08 e, respectively, with the bridging oxygen atoms having average atomic charges of -2.01 e (all standard deviations < 0.04). Although slightly less negative than oxygens atoms in the slab interior the NBO^- is well characterised as carrying an excess electron. The length of the Si–O bonds in NBO defects also provide a geometric characterisation. Although the terminal Si–O bond in a NBO^\bullet defect is known to be close to 1.69 Å, the corresponding bond distance, averaged over the simulation, in the NBO^- centre has the characteristically shorter average length of 1.55 Å (standard deviation 0.017).^{21,25} Conversely, the three silicon atoms coordinated to the $\equiv\text{O}$ centres have longer average Si–O distances of 1.77 Å (standard deviation 0.018). Clearly our nanoslabs are well characterised as possessing closed-shell $\equiv\text{O}/\text{NBO}^-$ defect pairs, which we term “compensated-NBOs” (CNBOs).

The reactivity of NBO defects with water has been previously studied by a few other classical MD and QM studies. The lack of electronic degrees of freedom precludes distinguishing between open-shell and charged closed-shell species in classical simulations and under-coordinated classically-treated defects resemble charged species. Using the pre- and post-hydroxylated energies of NBO^- and $\equiv\text{Si}^+$ centres to calculate reaction energies, classical MD studies show that hydroxylation stabilises dry silica surfaces exhibiting both NBO^- and $\equiv\text{Si}^+$ defects in the presence of water.¹⁶ Classical MD studies allowing for an explicit representation of water dissociation report rapid hydroxylation of NBO^- sites, either initiated by protonation of the NBO^- and then hydroxylation of a nearby $\equiv\text{Si}^+$, or *vice versa*.¹⁷ QM studies of the water–NBO system in principle have more control over the electronic state. In the two reported studies of this type a QM transition state search⁵ appears to have used the open-shell NBO, whereas in another QM MD⁸ study the state of the NBO is less clear. Both studies suggest that NBOs are rather inert to direct attack by water. The main reasons for the different predictions by classical and QM methods are likely due to the fact that the QM studies only probed a local region close to an isolated NBO with one or two water molecules, whereas the classical systems were larger and included both NBO^- and $\equiv\text{Si}^+$ sites and more water molecules. Our large scale AIMD calculations further show that NBO^- s are hydroxylated only if water dissociation occurs first elsewhere (*e.g.* at charged silicon sites).

Due to the relatively short simulation times currently possible using AIMD, we cannot guarantee that the CNBO in system B is resistant to attack over macroscopic timescales. Comparing with the rapid reaction in system A, however, it appears that the reactivity of the CNBO in system B is considerably lower. Energy minimisation of slab B with a single water molecule constrained to lie at a range of distances from the CNBO shows no tendency for dissociation. Deliberately protonating the NBO^- (to form a silanol) with an OH^- fixed at various distances shows that OH^- deprotonation to form H_2O and NBO^- is barrierless and

energetically favoured by ~ 2 eV and spontaneously occurs when the OH^- is initially within at least 2 Å of the SiOH. This calculation is reminiscent of the known deprotonation of silanols under strongly basic conditions. NBO^- species formed in this manner are thought to polarise, and order, nearby water molecules.²⁰ By analogy we expect CNBOs to have a similar capacity to order water at low temperature but at neutral conditions.

In summary, our calculations strongly point to an asymmetry in the reactivity of $\equiv\text{Si}^+$ (or $\equiv\text{Si}^+\cdots\text{O}$) sites with respect to that of corresponding NBO^- centres. Following the way NBO^- sites are exhibited in low energy nanoclusters, we constructed model stoichiometric silica nanoslab systems with CNBO defects (*i.e.* NBO^- terminated with interior $\equiv\text{O}$ sites). When the $\equiv\text{O}$ centres are sufficiently deep within the nanoslab, the NBO^- -terminated surface is observed to be unreactive with water. Due to the common occurrence of CNBOs in low energy nanoclusters, we argue that they are likely to be found in many nanosilica systems. Our results may suggest alternative interpretations of experimental data and new ways to manipulate SiO_2 –water interfaces in nanosilica applications.

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