ORIGINAL PAPER

Revisiting the hydroxylation phenomenon of SiO$_2$: a study through "hard-hard" and "soft–soft" interactions

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Abstract

Surface hydroxylation has been extensively studied over the years for a variety of applications, and studies involving hydroxylation of different silica surfaces are still carried out due to the interesting properties obtained from those modified surfaces. Although a number of theoretical studies have been employed to evaluate details on the hydroxylation phenomenon on silica (SiO$_2$) surfaces, most of these studies are based on computationally expensive models commonly based on extended systems. In order to circumvent such an aspect, here we present a low-cost theoretical study on the SiO$_2$ hydroxylation process aiming to evaluate aspects associated with water-SiO$_2$ interaction. Details about local reactivity, chemical softness, and electrostatic potential were evaluated for SiO$_2$ model substrates in the framework of the density functional theory (DFT) using a molecular approach. The obtained results from this new and promising approach were validated and complemented by fully atomistic reactive molecular dynamics (FARMD) simulations. Furthermore, the implemented approach proves to be a powerful tool that is not restricted to the study of hydroxylation, opening a promising route for low computational cost to analyze passivation and anchoring processes on a variety of oxide surfaces.

Keywords Molecular modeling · DFT · SiO$_2$ · Hydroxylation · Chemical reactivity

Introduction

Involved in surface modification processes [1], the hydroxyl groups (OH) may even exist spontaneously on the surfaces of various oxides [2–4]. Currently, there are a number of techniques and approaches to control, improve the formation of these groups on surfaces and even prevent their spontaneous formation [4–8]. The amount of studies involving hydroxyls is meaningful, since it can used in combination for the most diverse applications, such as in catalysis/photocatalytic processes [6, 9, 10], control of surface wettability [11], anchoring sites for surface functionalization to obtain properties of

interest [1], which is of great interest in research areas for biomaterials/implants, for instance [12, 13].

The study of OH groups on oxide surfaces has been reported since the 1960s [2], and the results of these pioneering works have been used for varied applications, as described previously. These groups can be naturally present on surfaces or be added through external chemical or physical stimuli [3, 4]. In general, hydroxyl groups are created on a surface due to water dissociation. In this process, H$_2$O is split into OH$^-$ and H$^+$ species [4]. OH$^-$ species adsorb on the metal or metalloid atoms, while H$^+$ attaches to the exposed oxygen. The water molecules involved in this process can be present in air or in a solution. The formation of hydroxyls on the surfaces is usually dependent on the total number of defects [2, 14, 15] and generally independent of the metal or metalloid's valence, since it was reported that different oxides present similar hydroxylation levels [4].

Hydroxyl groups generated via external stimuli (chemical or physical) generally lead to the formation of more effectively functionalized surfaces than those from natural processes. This is the case of UV-irradiated TiO$_2$ surfaces [6]. The irradiation of this material

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leads to the formation of free charge carriers (electrons and holes), which should promote the cleavage of some metal–oxygen bonds, coordinating water molecules on the surface. These coordinated water molecules release a proton for charge compensation, leading to the formation of OH^- species and increasing the number of hydroxyls on the surface. As this effect improves the hydrophilicity of the material, it is known as photoinduced hydrophilicity process [6, 16]. Despite the high efficiency of this process, the photoinduced hydroxyls commonly exhibit less thermodynamic stability than their naturally formed analogues [6].

Among the available oxides, silica (SiO_2) is one of the most abundant materials on the surface of the Earth and the most studied for its hydroxylation and other features [2, 14, 15]. Due to its abundance, inexpensiveness, and interesting properties, many scientists and engineers have studied silica and silicon related systems [17–20]. In particular, a number of studies have been conducted to understand the interfacial surface chemistry of silica/water systems, such as the role of silicon-hydroxyl bonds in interfacial properties [1, 21, 22] and the effect of tensile or compressive stresses on the silica/water reactions [23].

In the SiO_2 hydroxylation process, the water hydrolysis reaction is initiated by physisorption of water molecules onto the silica surface, followed by water splitting and chemisorption of the hydroxyl groups [2, 18]. After hydroxylation, the silica becomes silanol (Si–OH), which can exist in three different forms (Fig. 1). The hydroxyls greatly modify the surface properties due to their unique ability to form hydrogen bond networks, allowing a variety of applications [1, 2, 24].

Although the hydroxylation process of the silica surface is well known, from both experimental and theoretical point of views [2, 14, 18, 25–29], most of the theoretical studies are based on computationally expensive approaches, involving extended periodical systems [14, 15, 30].

Aiming to circumvent such an aspect here, we propose the use of low-cost (molecular-based) DFT-based approach to evaluate the local reactivity of simplified $(SiO_2)_n$ model systems and interpret mechanisms involved in the SiO_2 hydroxylation at nanoscopic scale. Electronic descriptors based on condensed-to-atoms Fukui indexes (CAFI), local chemical softness and molecular electrostatic potential (MEP) maps were evaluated in the framework of the density functional theory (DFT) to investigate details on the oxide–water interactions, while full atomistic reactive molecular dynamics simulations (FARMD) were conducted to validate the DFT results and investigate the adsorption processes in more extended systems.

The obtained results indicate that the use of such descriptors allows the identification of relevant SiO_2-water interactions and mechanisms associated with silica hydroxylation in aqueous solutions, which is reinforced by FARMD simulations [28]. We consider that the proposed approach can be employed to revisit and interpret a number of experimental data as well as being employed for the study of other similar systems.

Materials and methods

Preparation of $(SiO_2)_n$ model and its derivatives

Aiming to reproduce some basic electronic properties of the substrate and maintain the molecular approach and reasonable computational costs, $(SiO_2)_n$ clusters were designed as silica model structures (for $n = 3, 4, 5,$ and 6), as proposed by Nayak et al. [31] (Fig. 2). Terminal hydroxyl groups were included on the non-passivated oxygens to simulate hydroxylated structures (expected from the oxide–water interactions) [2, 4]: (i) partially hydroxylated (OH groups at one extremity) and (ii) fully hydroxylated (OH at both extremities) (see Fig. 2). It is worth emphasizing that, even though the hydroxylation process is well known in the literature, the computational approach used here is unprecedented.

Computational methods

The initial geometries were designed with the aid of the Gabedit [32], Molden 5.0 [33], and Gaussview [34] computational packages. The molecules were then pre-optimized in a Hartree–Fock approach with the PM6 semiempirical Hamiltonian, implemented in the MOPAC2016 computational package [35]. The obtained structures were subsequently fully optimized in the framework of the density functional theory (DFT), with the aid of the Gaussian 16 computational package
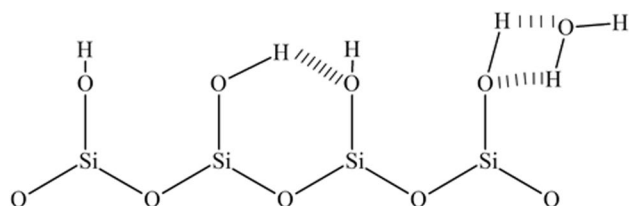
Fig. 1 Different forms of hydroxyl groups chemisorbed on silica surface

Fig. 2 Equilibrium $(SiO_2)_n$ geometries (n ranging from 3 to 6) for non-passivated, partially hydroxylated, and fully hydroxylated geometries. Geometries optimized in the framework of the density functional theory (DFT), with B3LYP functional and 6-31G(d,p) basis sets

$(SiO_2)_n$ geometries

n = 3   n = 4   n = 5   n = 6

Partially hydroxylated geometries

Hydroxylated geometries
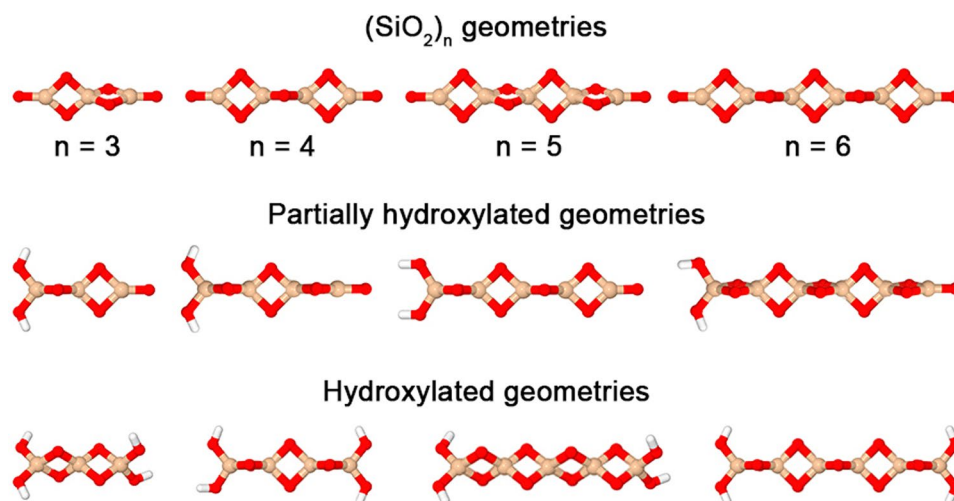
[36]. The B3LYP hybrid XC functional [37–40] and 6-31G(d,p) polarized basis sets were employed. As the hydroxylation process occurs in the presence of water molecules (liquid or vapor) [2–4], the presence of this solvent was simulated via polarizable continuum model (PCM) [41]. Despite its simplicity, PCM presents a reasonable cost–benefit ratio, which is successfully employed in the study of most diverse SiO_2 based systems [42–45].

The local reactivities of the structures were evaluated via condensed-to-atoms Fukui indexes (CAFI) [46, 47] to identify which molecular sites are prone to interact with electrophilic (f^-) and nucleophilic (f^+) agents. These indexes provide significant insights about the reactivity of distinct systems [43, 48–50]. Once CAFIs are obtained from the finite difference of the atomic populations of charged and neutral systems (i.e., from relaxed orbitals), it can be considered more effective descriptors for chemical reactivity than the analysis of the frontier orbitals, mainly due to the fact that lower-lying energy molecular orbitals effects are considered in some degree [51].

To better estimate the interactions between the SiO_2-based structures and water molecules, the local chemical softness ($s^{+/-}$) of the compounds were also evaluated. These indices correlate the local information provided by CAFI, with the global softness (S) of the molecule, indicating the most likely pair of atoms associated with a specific chemical reaction/interaction. According to the principle of hard-soft acids-bases (HSAB) [52], electrophilic/nucleophilic and radical/radical interactions are favored when the involved atoms present similar chemical softness. Details on CAFI and local chemical softness estimation are described in our previous work [43].

Given their definition, CAFI and local softness analyses allow the rationalization of "soft–soft" interactions, i.e., those associated with deformations induced on the frontier orbitals during chemical reactions [46, 47, 52]. To elucidate the effect of electrostatic effects, associated with "hard-hard" interactions [53], molecular electrostatic potential (MEP) maps were also evaluated. MEPs were obtained via CHelp partition charge scheme [54].

To validate and complement the DFT analysis, additional adsorption studies were conducted via fully atomistic reactive molecular dynamics (FARMD) simulations, by considering interaction between SiO_2 crystalline substrate and water molecules (Fig. 6b). For this purpose, two different 5×5 α-quartz (001) structures were built and inserted in water: (i) with only one oxygen atom bound to the Si atom at the surface (non-passivated Si surface) and (ii) with two oxygen atoms bound to the Si (passivated Si surface). The non-passivated surface was built to reproduce the terminal sites of $(SiO_2)_n$ models.

The number of water molecules in the simulation box was estimated from the normal conditions for pressure and temperature, considering a pre-defined volume of a hexagonal system (a = b = 24.58 Å and c = 24.89 Å) (see Fig. 6a). The systems were allowed to evolve at room temperature in an NVT ensemble for 0.6 ns. During the simulations, water molecules and only the silicon and oxygen atoms from the surface of the substrates were allowed to evolve, while the bulk atoms were kept frozen. The molecular dynamics simulation was performed using the ReaxFF reactive force field [55], with the aid of the LAMMPS [56] computational package, considering a timestep of 0.1 fs. As the systems were thermally equilibrated

after 0.3 ns, the average values were evaluated only for the last 0.3 ns of simulation. The radial pair distributions (g(r)) involving water hydrogen (H_w) and surface oxygen (O_{SiO2}), and the water oxygen (O_w) and surface silicon (Si_{SiO2}) were analyzed. The g(r) values were normalized, and the B-spline curve fit was applied to facilitate the visualization. In general, ReaxFF reactive force fields are developed to simulate large systems ($> 10^6$ atoms) with relatively small computational cost and tantamount accuracy when compared to quantum based simulation results [28, 55, 56]. Unlike the force fields from classical molecular dynamics, ReaxFF employs a bond-order dependent concept, allowing formation and breaking of bonds, which are fundamental aspects for the present study.

Results and discussion

Electronic structure calculations

The optimized geometries of $(SiO_2)_n$ clusters are presented in Fig. 2. After geometry optimizations, reactivity studies were conducted to identify the most reactive sites on these structures. Molecular electrostatic potential (MEP) maps were also analyzed to evaluate whether the reactive regions (coming from CAFI) are consistent with the position of water adsorption centers (guided by electrostatic interactions), and if these could guide the hydroxylation process. According to the literature, some oxide surfaces can immediately react with water molecules, both in aqueous solutions and moisture in the air. This reaction occurs due to

Fig. 3 Optimized structures, CAFI (f^+ and f^-) and MEP maps of non-passivated, partially hydroxylated, and fully hydroxylated structures of $(SiO_2)_n$ (n ranging from 3 to 6)
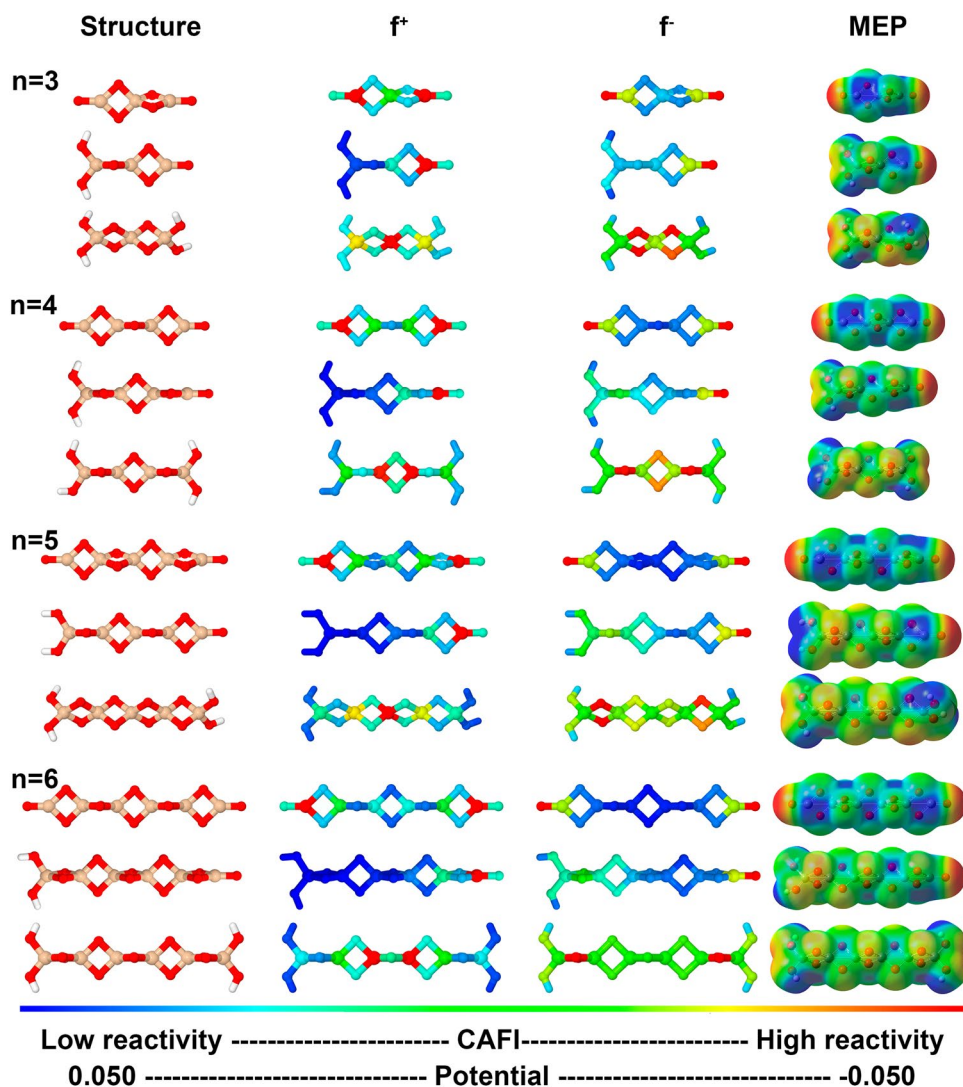
the attraction of water molecules to the oxide surface followed by the interaction through hydrogen bonds, adsorption (hydration), and finally the formation of terminal and bridge -OH groups [3, 4].

Figure 3 shows colored maps from CAFI (MEP) analyses. Blue and red colors indicate inert (positively charged) and reactive (negatively charged) sites. The other colors are regions with intermediate reactivities (charge concentrations) following a RGB scale. The same quantitative scale was used for the MEP for comparison purposes.

In general, the CAFI analysis indicates interactions involving the frontier orbitals in relation to nucleophilic (f^+) and electrophilic (f^-) species. Such interactions are commonly defined as "soft–soft" interactions, since they are associated with deformations in the frontier orbitals, which are induced by external chemical species. On the other hand, MEP shows possible electrostatic interactions, known as "hard-hard"

ones, with little deformation of the electronic orbitals [53]. The analysis of such indices in conjunction allows, in principle, the identification of expected interactions between $(SiO_2)_n$ structures and water molecules.

Figure 3 illustrates the high reactivity on the Si=O bonds for all $(SiO_2)_n$ structures, especially in relation to f^-. These regions also have high electron density, according to the MEPs. Such results suggest that these sites act as adsorption centers for water molecules (via electrostatic interactions) and, eventually, lead to the formation of hydroxyl groups. Partially and fully hydroxylated structures present low reactivity around hydroxyls (partially hydroxylated models still maintain high reactivity on the Si=O). Note that $(SiO_2)_n$ structures with distinct sizes show high reactivity on Si=O bonds (i.e., without strong dependence on n).
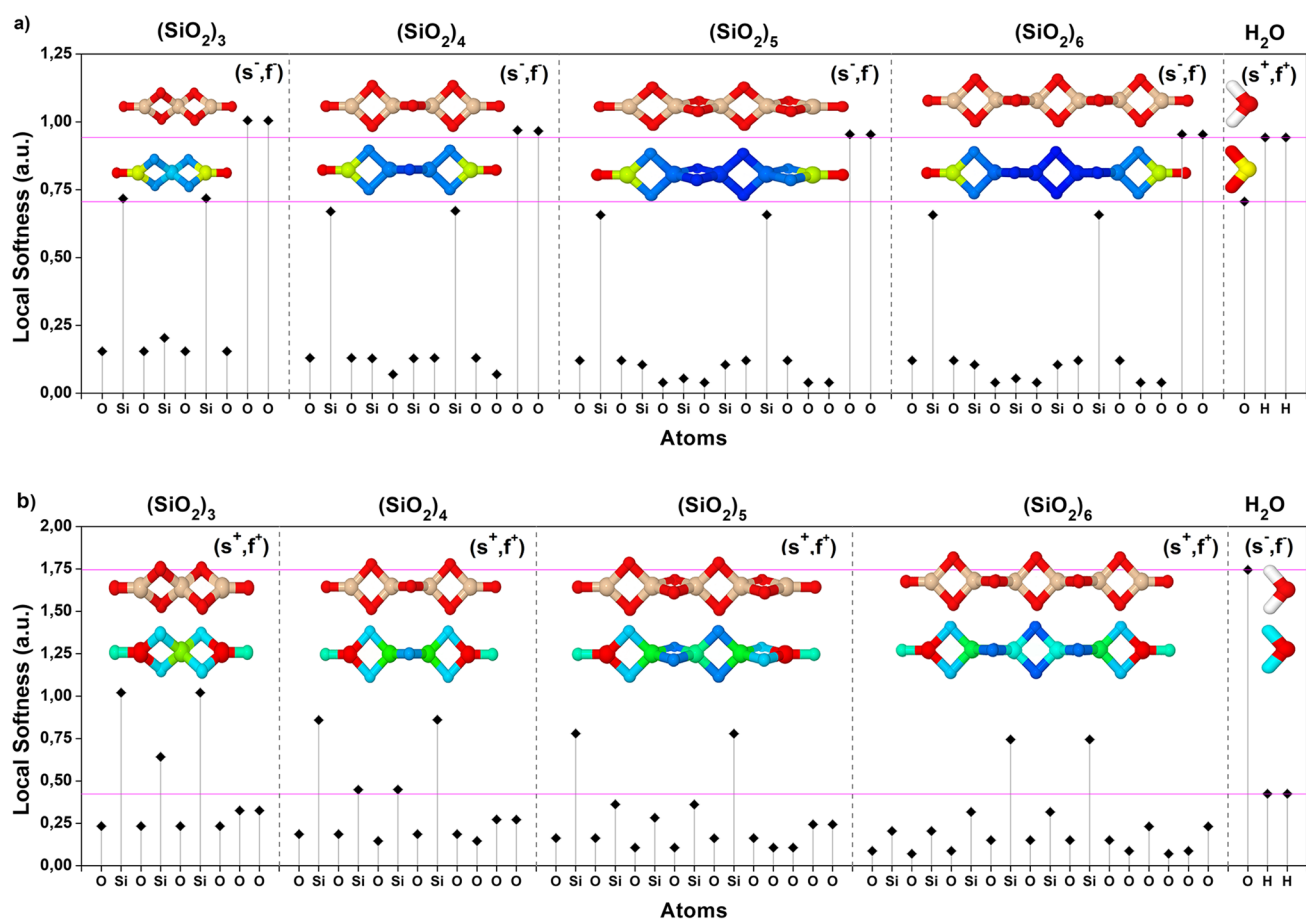
Fig. 4 Comparative analysis between the $(SiO_2)_n$ structure, with n ranging from 3 to 6, for **a** (s^-,f^-) and **b** (s^+,f^+) in relation to H_2O **a** (s^+,f^+) and **b** (s^-,f^-)

To validate the CAFI results, local softness data were evaluated to analyze the chemical affinity between reactive regions and water molecules. Structures with distinct sizes ($n = 3$ to 6) were considered to identify possible saturation effects (see Fig. 4). The respective CAFI maps are presented for each index (i.e., f^- for s^-, and f^+ for s^+). The last column presents the complementary chemical softness indexes predicted for water molecules to allow the evaluation of the chemical softness similarities (chemical affinity) through electrophilic/nucleophilic interactions, according to the HSAB principle [52].

In general, small variations of s^- values are noticeable with a number of SiO_2 basic units. The symmetry of the optimized structure and the spatial distribution of reactive sites is not so sensitive to n. The terminal atoms (Si=O bonds) present a high degree of similarity (affinity) in terms of chemical softness with water atoms: (i) oxygen atoms (O_{SiO2}) show affinity for hydrogen atoms from water (H_w),

while (ii) silicon atoms (Si_{SiO2}) present affinity for the oxygen atom from water (O_w). Moreover, the degree of similarity increases as the number of SiO_2 repetition units increases. Such results, in conjunction with MEP data, indicate that the Si=O region of $(SiO_2)_n$ structures are supposed to effectively react with water molecules, forming hydroxylated surfaces, as predicted in the metal oxide hydroxylation process described in the literature [2–4].

The results presented in Fig. 4b are not as conclusive as those shown in Fig. 4a. However, the symmetry of the optimized structures and the spatial distribution of reactive sites are maintained for distinct n. Such results suggest that the SiO_2 hydroxylation process in water is governed by the tendency of the silica to donate electrons (i.e., interact with electrophiles).

Aiming to investigate whether the structures after the hydroxylation process would still interact with water molecules, additional studies were carried out for (partially or fully) hydroxylated analogues of
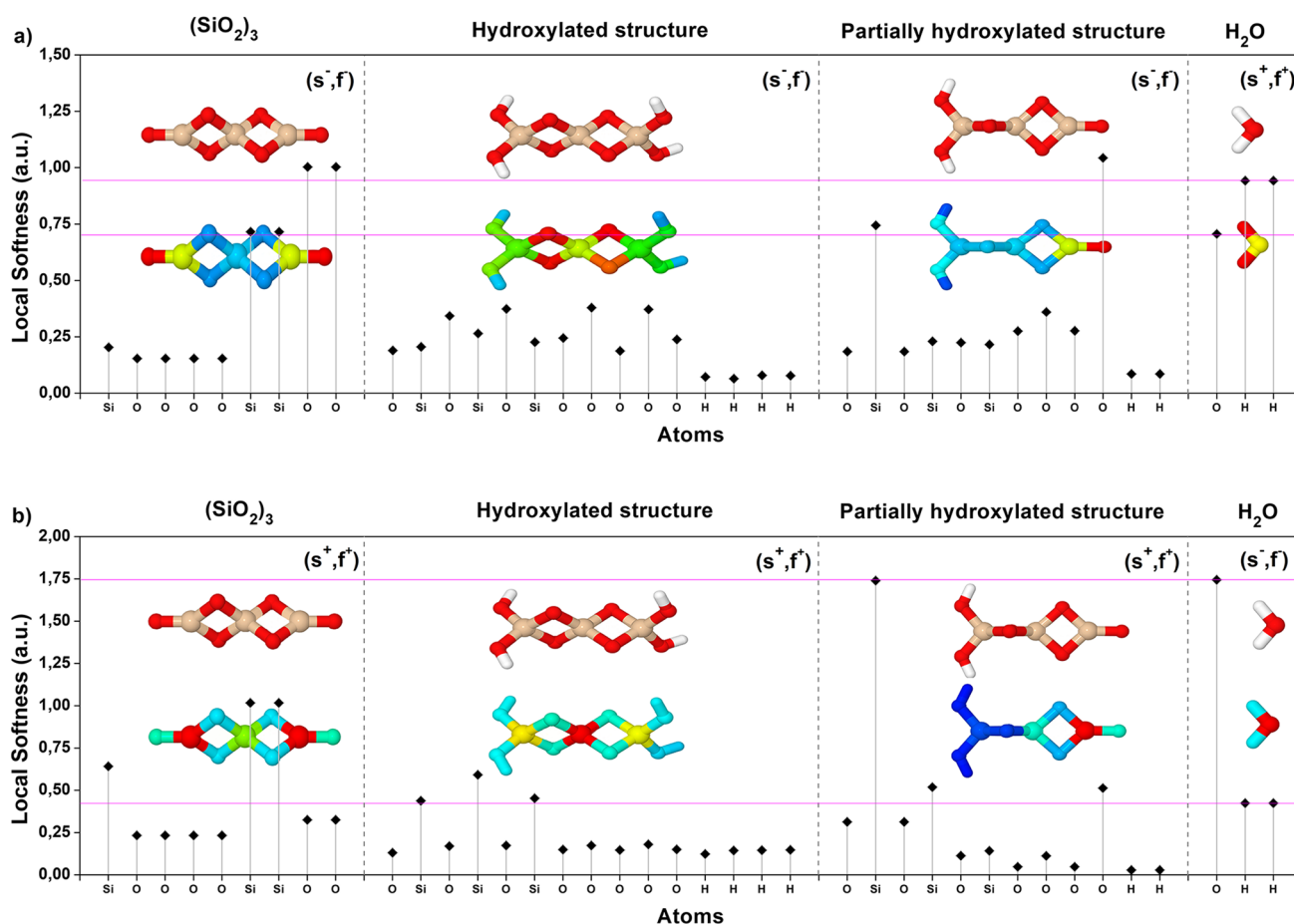
Fig. 5 Comparative analysis between the $(SiO_2)_3$ structure, its hydroxylated and partially hydroxylated structures for **a** (s^-, f^-) and **b** (s^+, f^+) in relation to H_2O **a** (s^+, f^+) and **b** $(s^-, f-)$

Fig. 6 a Representation of the simulation box for FARMD calculations. Analysis of the normalized g(r) distribution coming from the simulations for the interactions between water and: **b** non-passivated; and **c** passivated 5×5 α-quartz (001) surfaces
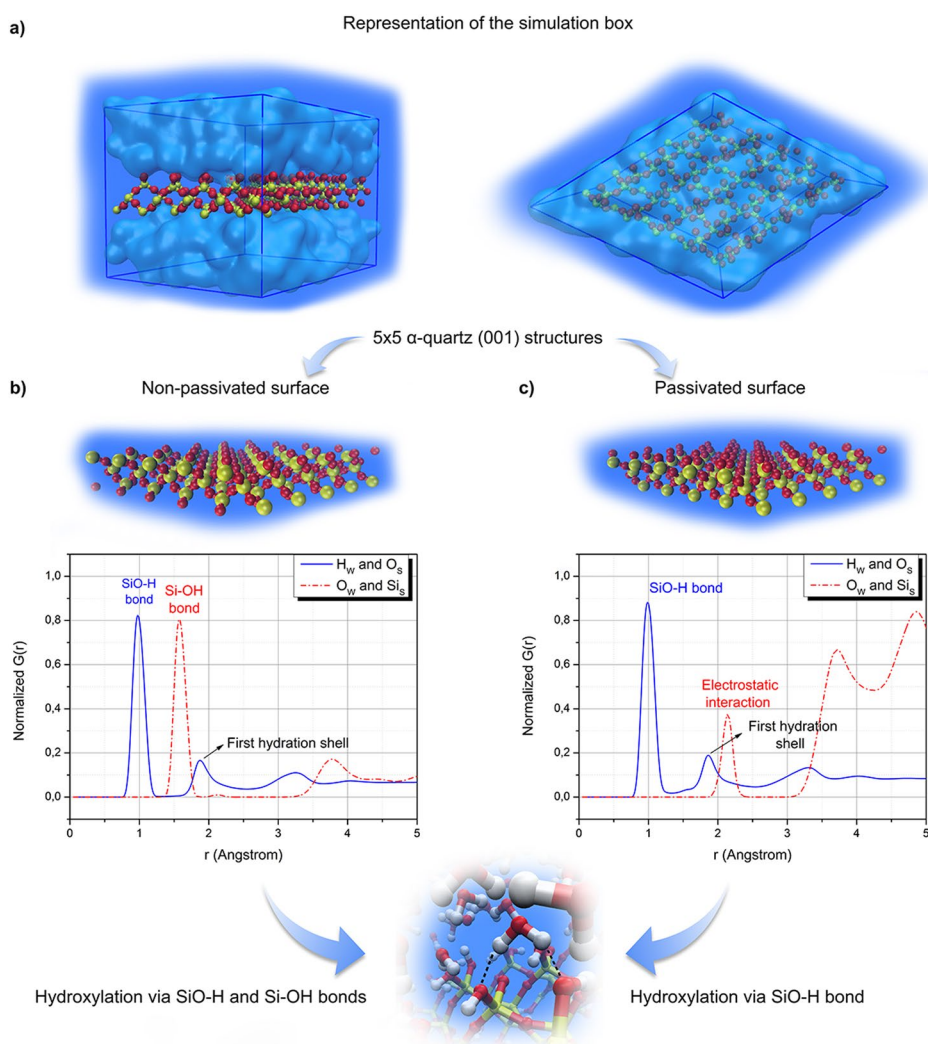
$(SiO_2)_3$ model system. In Fig. 5, the fully hydroxylated structure presents low affinity with water atoms while higher affinity is notable for partially hydroxylated clusters only at non-hydroxylated terminals. This suggests that the $(SiO_2)_n$ structures tend to be fully hydroxylated in water.

Fully atomistic molecular dynamics simulations

Fully atomistic reactive molecular dynamics simulations were conducted to validate and complement the DFT results. These simulations also aimed to assess details on the chemical/electrostatic interactions between water molecules and SiO_2 surfaces. Figure 6 shows the normalized g(r) functions for H_W and O_{SiO2} and O_W and Si_{SiO2} atoms from panel "b" non-passivated and panel "c" passivated SiO_2 surfaces.

The results show that hydroxylation occurs on both SiO_2 surfaces. However, the water hydroxyl bonds only to the non-passivated SiO_2. Complementally, Fig. 7 shows that the non-passivated surface also leads to a greater formation of H_W-O_{SiO2} bonds when compared to the passivated one. Therefore, the non-passivated SiO_2 surface reacts with water in a complete reaction, i.e., OH^- bonds to the Si_{SiO2} atom while H^+ bonds to the O_{SiO2}, similar to $(SiO_2)_n$ clusters evaluated in this work. Thus, despite the simplicity of these $(SiO_2)_n$ model structures, they define reasonable models for the evaluation of SiO_2 hydroxylation processes and can be considered as effective molecular models for silica, as found in our previous work [43].

In summary, the FARMD analysis validates our low-cost DFT-based approach for the evaluation of SiO_2 hydroxylation. These results suggest that CAFI
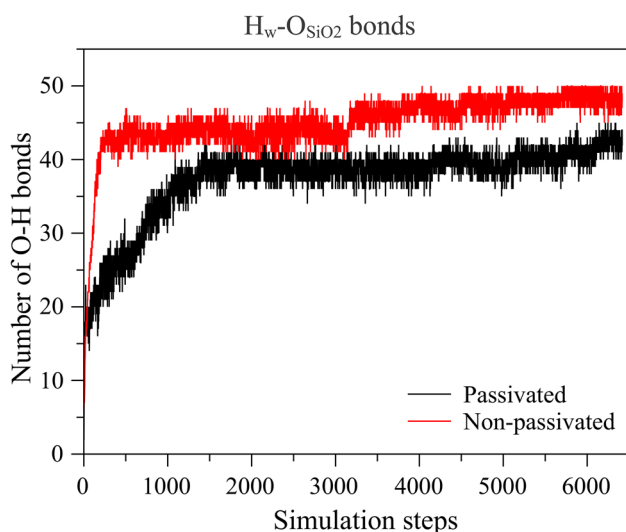
Fig. 7 Number of H_W-O_{SiO2} bonds formed along the FARMD simulation for the passivated (black) and non-passivated (red) 5×5 α-quartz (001) surfaces

and local softness could be, in principle, applied for other similar or even more complex systems to evaluate basic mechanisms of chemisorption at nanoscopic scale, which will be better evaluated in future works.

Conclusions

The local reactivity and electronic properties of $(SiO_2)_n$ model systems were evaluated via DFT calculations to identify features associated with hydroxylation processes of passivated and non-passivated SiO_2 surfaces in water. Additional FARMD simulations were conducted to validate the results.

Our data suggest that simple electronic descriptors can be used to understand how $(SiO_2)_n$ structures behave in terms of reactivity, chemical affinity, and interaction with water molecules. The results suggest that the hydroxylation process of SiO_2 surfaces can be evaluated by the analysis of f^- (and s^-) descriptors of simplified $(SiO_2)_n$ clusters, which is in line with the literature. The proposed methodology combined with an appropriate structural approach opens a promising route for low computational cost to analyze passivation and anchoring processes on a variety of oxide surfaces.

Declarations

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