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Abstract
We have performed first principles metadynamics simulations of the grafting process of tetraethoxysilane (TEOS) at two surface sites of dry amorphous silica: the two-membered silicon ring and the isolated silanol. The *ab initio* activation energies for the grafting reaction are 0.2 eV and 1.4 eV, at the 2M and SiOH sites, respectively. The simulations support the experimental evidence based on IR vibrational spectroscopy that the ring is more reactive than the surface SiOH group for the grating of organosilanes.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Many technological applications of amorphous silica (a-SiO_2) rely on its specific surface properties [1, 2]. Understanding the nature of silica surface sites available for physisorption and chemisorption of gas phase molecules is crucial to understanding the behavior of silica in a wide range of applications [1]. On the normal silica surface exposed to air, silanols (Si–OH groups) are known to represent the main adsorption sites. In contrast, the precise nature of surface reactive sites on the dry (dehydroxylated) surface of silica is still uncertain. In the current literature, it is customarily proposed that metastable two-membered (2M) silicon rings could constitute the main reactive sites on the surface of dry silica [3–9]. Supporting evidence comes from IR spectra of dry silica which exhibit two strong bands at 888 and 908 cm^{-1} (where bulk silica is transparent) assigned to vibrations of the 2M ring. These IR peaks appear upon dehydroxylation above 500 °C and disappear upon adsorption of water and other chemical species such as ammonia and methanol [4–7]. It is therefore conceivable that the surface structures responsible for the new IR bands could arise by condensation of neighboring silanols (Si–OH) on the hydroxylated surface. The fast reaction of water with the dry surface observed experimentally from the

depletion of the two IR bands is also intriguing since normal siloxane bridges (belonging to larger rings) are believed to be hydrophobic [10, 11].

Among the many technological applications of dry silica which would benefit from a compelling identification of the most reactive site, we here focus on the coating of the optical fibers which involves the adhesion to silica of organosilane molecules used as silica–polymer coupling agents [12]. Although for a long time it has been generally assumed that adhesion occurs on the few residual hydroxyls still present on the surface of optical fibers, IR absorption measurements have later shown that the silane adhesion proceeds without the attenuation of the IR signal due to the OH stretching of surface silanols [8, 9]. Instead, the organosilane chemisorption is accompanied by the disappearance of the IR doublet assigned to the 2M ring. Since the organosilane presently used as silica–polymer coupling agents in the optical fibers technology are designed to react with silanols, a compelling identification of the 2M ring as the most reactive site is obviously of crucial importance to design better performing coupling agents [12].

Classical molecular dynamics simulations [13, 14] have shown indeed that 2M rings can appear at the surface of dry a-SiO_2. Models of dry a-SiO_2 surfaces displaying a 2M ring at a concentration of 0.5 nm^{-2} (close to the experimental estimate of 0.2–0.4 nm^{-2} [9]) have also been investigated from first principles [15]. The calculated IR spectrum shows two peaks at 849 and 856 cm^{-1} due to vibrational modes of the

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2M ring, strongly supporting the experimental assignment of the IR doublet at 888 and 908 cm^{-1} [15]. Reactivity of 2M ring with water and ammonia has also been studied from first principles [11, 16–18].

In this work, to get insight onto the reactivity of the 2M ring with organosilanes, we simulate from first principles the reaction of tetraethoxysilane (Si(OCH$_2$CH$_3$)$_4$, TEOS) with a 2M ring or a surface silanol to assess the difference in reactivity of the two surface sites toward organosilanes as inferred from IR spectroscopy. We have chosen TEOS as a prototypical organosilane, since it has the same functional groups (ethoxy) as most organosilanes used in the optical fibers technology. A model of the a-SiO$_2$ surface is generated by quenching from the melt within classical molecular dynamics simulation [22]. To study the adhesion of TEOS at the surface of a large slab (2592 atoms) we make use of a quantum mechanics/molecular mechanics (QM/MM) scheme recently developed for silica [19]. First principles metadynamics simulations [20, 21] have been performed to identify the reaction paths for TEOS adhesion.

2. Method

The model of amorphous silica has been obtained by quenching from the melt by classical molecular dynamics (MD) using the potentials of van Beest *et al* (BKS) [22] which is known to reproduce with good accuracy the structural and dielectrical properties for the bulk [23, 24] and the dry surface of a-SiO$_2$ [13, 25]. A bulk sample of β-cristobalite made of 216 SiO$_2$ units has been heated up to 4000 K in a constant pressure–temperature (NPT) simulation and then cooled down to 300 K in a MD run 4 ns long. Temperature on ions has been enforced by a Berendsen thermostat [26]. The Parrinello–Rahman scheme has been used to perform MD at atmospheric pressure allowing only isotropic fluctuation of the simulation cell with a fixed cubic shape. The equilibrium density of the amorphous silica model obtained by NPT simulations is 2.46 g cm^{-3}, a value slightly higher than the experimental density of 2.25 g cm^{-3} [27]. A slab of amorphous silica is then obtained by cutting a larger supercell (2 × 2 × 1) of the amorphous bulk model. The slab is made of 864 SiO$_2$ units with 3D periodic boundary conditions and a vacuum 15 Å wide. The surface supercell is 41.2 Å × 41.2 Å large. Then the slab has been heated up again to 4000 K in a NVT MD simulation for 1 ns and quenched from 4000 to 1000 K in five MD simulations each 1 ns long at different temperature (3500, 3000, 2500, 2000 and 1000 K). The system has been finally optimized at 0 K. As expected, the annealed surfaces are nearly fully self-passivated with very few undercoordinated or overcoordinated atoms [13, 25]. Indeed, the slab has only eight defects: one fivefold-coordinated silicon and one threefold-coordinated oxygen in the bulk, three onefold and three threefold-coordinated oxygen atoms at the surface. There are nine two-membered (2M) rings, three on the top surface of the slab and six on the bottom surface. On average a single 2M ring is present in an area of 3.8 nm^2 which corresponds to a density of 0.26 nm^{-2} close to the experimental estimate of 2M rings density on dehydroxylated amorphous surfaces

(0.2–0.4 nm^{-2} [9]). The 2M rings are perpendicular to the surface plane as found in previous first principles [15] and classical [25] simulations.

The surface chemical reactions have been investigated by first principles molecular dynamics simulations within the QM/MM scheme for silica that we have recently developed [19]. The method is based on a multi-grid technique for computing the electrostatic potential due to the MM atoms and on the Quickstep approach for the description of the quantum region treated at the density functional theory (DFT) level. In Quickstep the Kohn–Sham orbitals are expanded in Gaussian type orbitals (GTOs) and the charge density is represented with an auxiliary plane waves basis to efficiently solve the Poisson equation [28, 29]. We have used the generalized gradient functional BLYP-GGA [30], Gaussian based pseudopotentials [31] with a DZVP atomic basis set for Si, O, C atoms, SZV atomic basis set for H atoms and an expansion in plane waves of the electron density up to an energy cutoff of 280 Ryd. This computational framework has been validated in our previous study of point defects in silica [19].

We have studied the grafting of TEOS at two surface sites. Firstly, we have considered the 2M ring by choosing the 2M ring furthest from the other defects. Secondly, we have considered a surface silanol. This has been obtained by adsorbing a water molecule which formally dissociates at the surface transforming a threefold-coordinated oxygen and a non-bridging oxygen into two SiOH groups 8.8 Å far apart.

The QM silica region is made of 45 atoms or 81 atoms around the 2M ring (figure 1(a)) or the silanol (figure 1(b)), respectively. Preliminary metadynamics simulations with a smaller QM region (36 atoms) have also been performed for the 2M ring. As described in [19], the QM region is chosen in such a manner that the boundary QM atoms are always oxygen atoms. The pseudopotential of these atoms (hereafter refereed to as O*) is the ordinary one. To saturate the valence of the boundary oxygen atoms we add one electron for each O*, which would ideally come from the neighboring MM Si. In order to enforce global charge neutrality, we change the ionic charge of the boundary oxygen pseudopotential from 6 to 6.4. Hence, the total charge of the QM system is $(0.4-1)n_{O^*} = -0.6n_{O^*}$ which is equal to the total charge of the classical atoms that have been replaced by the QM atoms, given that the charges of Si and O atoms in the BKS potential are 2.4 and −1.2 (in au), respectively. In the QM/MM scheme there is no short range interaction between the quantum TEOS and the classical amorphous surface. We have always checked on-the-fly that the TEOS did not approach the classical surface too closely (below 3–4 Å). The cell parameters of the quantum simulation cell are $a = b = 18$ Å, $c = 22$ Å and $a = b = 22$ Å, $c = 24$ Å for the QM regions around the 2M ring or the silanol, respectively. The cell parameters of the classical cell are $a = b = 41.2$ Å and $c = 60$ Å with a vacuum 35 Å wide. The interactions between the replica of the QM region are coupled with the periodicity of the MM cell as described in [32].

We have optimized the geometry of a TEOS molecule far from the surface (6 Å) with its ethoxy groups initially rotated
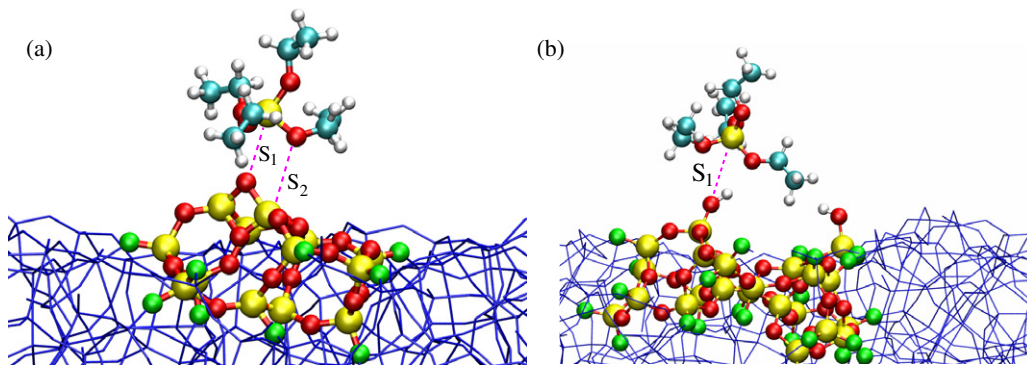
Figure 1. Starting geometry of the simulation for the grafting reaction of TEOS (a) with a 2M ring and (b) with a silanol at the surface of dry amorphous silica. The atoms in the QM region are depicted by spheres in light gray, dark and gray (yellow, red, and green on line) representing Si, O and O*, respectively (body text). The bonds in the MM region are depicted by dark (blue) lines. O* indicates boundary oxygen atoms. The dotted lines indicate the collective coordinates used in the metadynamics simulation: (a) the coordination number between the Si atom of the TEOS and the O atom of the 2M ring (S_1) and the coordination number between one O atom of the TEOS and a Si atom of the ring (S_2), (b) the coordination number between the Si atom of the TEOS and the O atom of the silanol (S_1).

around the Si–O bonds in order to reduce the steric repulsion by the surface.

The reactions we address here turn out to be activated processes. Actually a reaction would not occur spontaneously during the short span of a first principles MD run whenever the activation barrier was much larger than the thermal energy. To overcome this limitation we have used the recently devised metadynamics technique which allows large barriers to be overcome in an affordable simulation time (few picoseconds) [20, 21, 33, 34]. The method is based on a coarse-grained, non-Markovian dynamics in the manifold spanned by few reaction coordinates, biased by a history-dependent potential, which drives the system towards the lowest saddle point. The main assumption is that the reaction path could be described on the manifold of few collective coordinates $S_\alpha(\{\mathbf{R}_I\})$, function of the ionic coordinates $\mathbf{R}_I$. Following the scheme of [35], the first principles Lagrangian is supplemented by a history-dependent external potential $V(t, S_\alpha(\{\mathbf{R}_I\}))$ which acts on the ionic coordinates. The history-dependent potential is constructed by the accumulation of Gaussians, centered at the positions of the $\{S_\alpha\}$ already visited along the trajectory. The potential discourages the system from remaining in the region already visited and pushes it over the lowest energy barrier towards a new equilibrium basin. This method has been applied previously to study chemical reactions at surfaces, in the gas phase and in the bulk [34–41].

In the simulation of the grafting reaction at the 2M ring we have chosen two collective variables: the coordination number between the Si atom of the TEOS and the O atom of the 2M ring (S_1) and the coordination number between a selected O atom of the TEOS and the Si atom of the 2M ring (S_2), as shown in figure 1(a). In the simulation of the grafting reaction at the silanol site we have used a single collective variable (S_1), the coordination number between the Si atom of the TEOS and the O atom of the surface silanol. In this way, we impose that the bond broken in the adhesion is the Si–O bond of the TEOS in analogy with the description of the hydrolyzation reaction of TEOS in water [42].
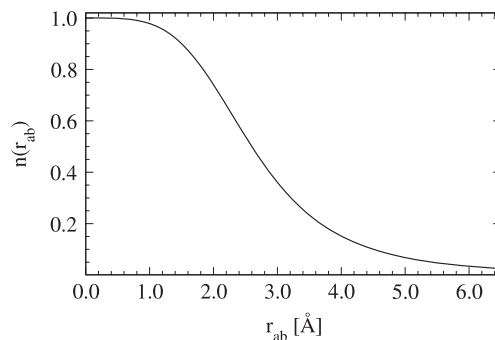

Figure 2. Coordination number (equation (1)) as a function of distance between the Si atom of the TEOS and the oxygen atom of the ring (S_1) or the Si atom of the ring and the O atom of the TEOS (S_2).

Following [21], the coordination number between atom a and atoms b is defined as

$$n_{\mathrm{a}} = \sum_{\mathrm{b}} \frac{1 - (\frac{r_{\mathrm{ab}}}{d})^p}{1 - (\frac{r_{\mathrm{ab}}}{d})^q}, \tag{1}$$

where r_{ab} is the distance between the two atoms. The coordination number n_{a} estimates the number of atoms b within the bond cutoff distance to atom a and decays smoothly for larger distances. The exponents p and q have been chosen as 4 and 8 and $d = 2.6$ Å for S_1 and S_2, for both the simulations of the 2M ring and silanol. This choice of parameters for the coordination number produces the function shown in figure 2 which displays a large derivative in the appropriate range of distances including non-interacting and grafted TEOS. A different choice of the parameters resulting in a very different function might imply the need of longer simulation time for the reaction to occur.

The history-dependent potential is made of isotropic Gaussian functions with parameters $\delta\sigma = 0.05$ and $W = 54$ meV. Gaussian functions are added every 30 fs. We imposed a wall to prevent the molecule leaving from the surface.
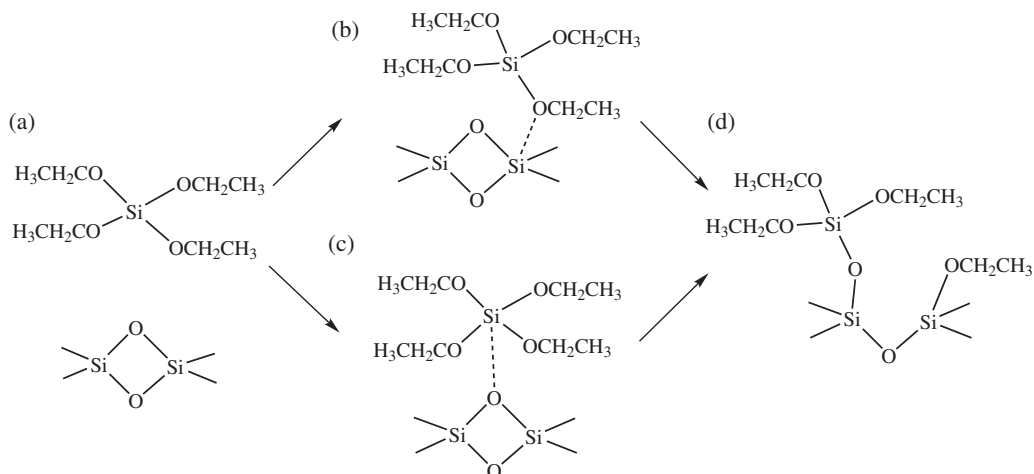
Figure 3. Sketch of the reaction mechanism of TEOS adhesion at the 2M ring: (a) reactants, (b) the oxygen atom of the ethoxy group of the TEOS reacts via a nucleophilic attack to a silicon atom of the ring, (c) the silicon atom of the TEOS reacts via an electrophilic attack to the oxygen atom of the 2M ring, (d) grafted TEOS.

Constant temperature is enforced by velocity rescaling at the target temperature of 300 K with a tolerance of 80 K. The time step is 1 fs and the deuterium mass for hydrogen atoms is used.

Although the metadynamics allows computing activation energies from a finite temperature simulation, long simulation time (with small Gaussian height W) are needed to obtain accurate estimates of activation free energies. Actually, our metadynamics simulations are aimed at just obtaining a good starting guess for the transformation path. Then, the geometry and activation energy of the transition state identified along the dynamical trajectory have then been further refined by using constrained molecular dynamics simulations [43, 44] as better described in the next section.

3. Results

We discuss the reaction on the 2M ring first. The reaction mechanism may follow two possible routes: a nucleophilic attack of the oxygen atom of the TEOS toward a silicon atom of the 2M ring (figure 3(b)) or an electrophilic attack of the silicon atom of the TEOS toward the oxygen atom of the 2M ring (figure 3(c)). Our choice of the collective variables (S_1 and S_2, cf section 2) allows the path with the minimum activation energy to be spontaneously chosen among the nucleophilic attack, the electrophilic attack but also a concerted four centers mechanism (along the diagonal of the corresponding Morrel–O'Ferral–Jenks diagram [45]). We have observed the occurrence of the reaction after 5.8 ps of simulation. The reaction mechanism turns out to be a nucleophilic attack of the oxygen of the TEOS to the silicon atom of the 2M ring. The grafting leads to ring opening with an energy gain of 2.3 eV with respect to reactants (TEOS at 6 Å above the surface). The basis set superposition error in the calculated reaction and activation energies is estimated to be less than 0.1 eV. The optimized geometry of the product is reported in figure 4(c).

For sake of completeness we have also tried to enforce the other mechanism, the electrophilic attack by using the collective variable S_1 alone. In a MD simulation 2.2 ps long

we have observed the grafting process sketched in figure 3(c). As expected, the activation energy roughly estimated from the total biasing potential for the electrophilic attack is larger than the activation energy for the nucleophilic attack identified in the first simulation (with two CVs).

To get a quantitative estimate of the activation energy (neglecting entropic contributions) we have refined the geometry of the transition state for the nucleophilic attack by a constrained molecular dynamics simulation [43, 44]. We have first identified a physisorbed state with the oxygen of the TEOS bound to the Si atom of the 2M ring as sketched in figure 4(a). The physisorption energy due to the interaction of the acidic Si atom of the ring and the basic O atom of the TEOS is 0.1 eV which is most probably an underestimation due to the lack of van der Waals interaction at our level of theory (DFT-GGA).

We then performed eight simulations by constraining at different values the S_2 collective variable (i.e. the distance between the O atom of TEOS and the Si atom of the 2M ring) in the range 1.72–1.93 Å. The ground state geometry for each value of the constraint is reached by decreasing the ionic temperature down to zero in 2–4 ps. We have identified the transition state geometry as the configuration with the smallest Si–O distance (1.736 Å) below which the system evolves spontaneously into the products. The transition state geometry is sketched in figure 4(b). The energy of the transition state is 0.1 eV above the energy of the reactants and 0.2 eV above the physisorbed state (figure 4(d)).

Secondly, we have simulated the grafting of TEOS at the surface silanol. The trajectory obtained from the metadynamics simulation has been used as initial configuration for constrained molecular dynamics simulations. In this case, we have constrained the distance between the Si atom of the TEOS and the oxygen atom of the surface silanol to six different values. Also in this case we have identified a physisorbed state whose geometry is sketched in figure 5(a). The physisorption energy mostly due to H bonding is 0.4 eV. The activation energy from the physisorbed state is 1.4 eV from the physisorbed state or 1.0 eV from the free reactants
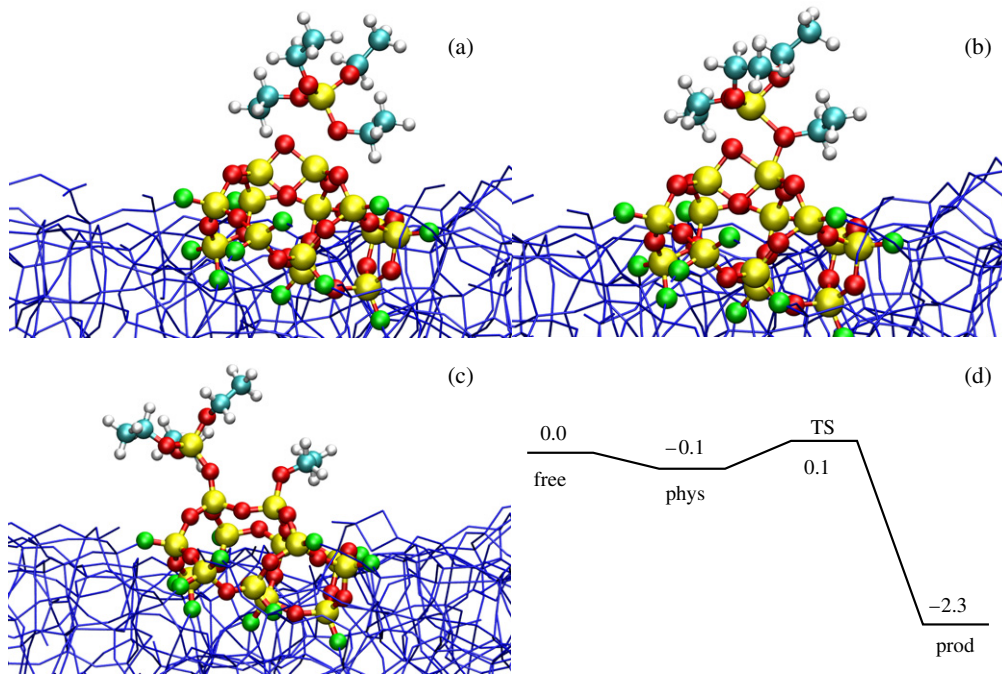
Figure 4. (a) Physisorbed state (phys) geometry of TEOS at the 2M ring. The color code is the same as in figure 1. (b) Transition state (TS) geometry as identified in the constrained molecular dynamics simulations. The distance between the Si atom of the 2M ring and the oxygen atom of the TEOS is 2.048 Å and 1.736 Å in panel (a) and (b), respectively. (c) Optimized geometry of the grafted TEOS. (d) Energetics (eV) of the grafting process.
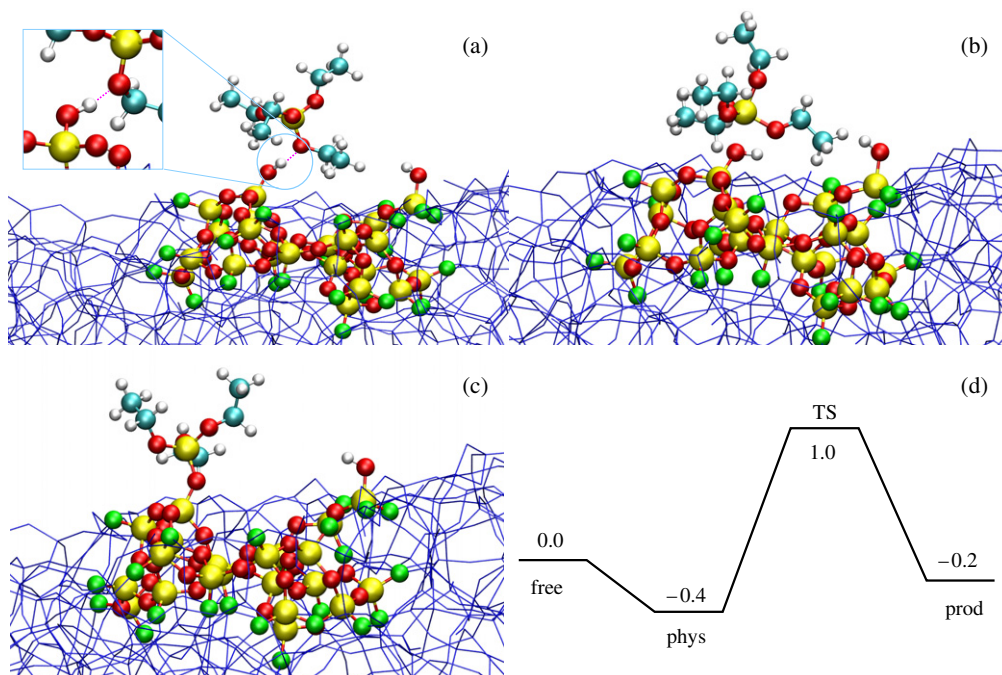

Figure 5. (a) Physisorbed state (phys) geometry of TEOS at the surface silanol. There is a hydrogen bond between the O atom of the TEOS and the H atom of the SiOH group. The color code is the same as in figure 1. The distance between the Si atom of the TEOS and the oxygen atom of the SiOH and the O atom of the TEOS and the H atom of the SiOH are 3.757 Å and 1.602 Å, respectively. (b) Transition state (TS) geometry as identified in the constrained dynamics simulations. The distance between the Si atom of the TEOS and the oxygen atom of the SiOH and the O atom of the TEOS and the H atom of the SiOH are now 2.030 Å and 1.510 Å, respectively. (c) Optimized geometry of the grafted TEOS with the release of an ethanol molecule (not shown). (d) Energetics (eV) of the grafting process.

(figure 5(d)). The reaction products correspond to the grafted molecule (figure 5(c)) and a released ethanol molecule (situated 8 Å above the surface and 5 Å far from the TEOS in total energy calculations). The calculated activation energy is lower than the value obtained previously (1.6 eV, with respect to the energy of the free reactants) [46] for the same reaction

on a model of the hydroxylated surface of β-cristobalite. The higher activation energy obtained for the crystalline surface is presumably due to a larger steric hindrance between the TEOS and the surface in the presence of a high density of surface silanols. The isolated silanol modeled here within the QM/MM scheme is obviously a more reliable description of the few residual silanols on the dry amorphous surface than the crystalline models used previously. Nevertheless, the activation energy for the grafting on the isolated silanol is still sizably larger (by 1.2 eV) than the barrier for adhesion of TEOS on the 2M ring. As a final word of caution, we remark that due to the neglect of van der Waals interaction, basis set superposition error and to uncertainties in the location of the transition states within constrained dynamics (besides uncertainties intrinsic to the GGA-DFT level of theory), errors in the activation energy mostly probably of the order of 0.1 eV are well to be expected. Still these uncertainties are much smaller indeed than the difference in activation energy of the two grafting processes at 2M ring and isolated silanol.

4. Conclusions

On the basis of density functional, QM/MM calculations, we have investigated the grafting process of a prototypical organosilane, TEOS, at an isolated silanol or at a two-membered silicon ring at the surface of amorphous silica. TEOS physisorbs with physisorption energy of 0.1 or 0.4 eV at the 2M ring and silanol sites, respectively. Starting from reactive trajectories identified by metadynamics simulations, we have computed the activation energies by constrained molecular dynamics for the two processes. The TEOS grafts at the 2M ring via a nucleophilic attack to the Si atom of the ring with an activation energy of 0.2 eV, while the activation energy for the grafting to the silanol is high as 1.4 eV. The calculations confirm that the 2M ring is much more reactive than silanols for the grafting of organosilanes as inferred experimentally by IR vibrational spectroscopy.

Acknowledgments

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