

Adsorption of atomic oxygen and nitrogen at β -cristobalite (100): a density functional theory study

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ABSTRACT

The adsorption of atomic oxygen and nitrogen on the β -cristobalite (100) surface is investigated from first principles density functional calculations within the generalized gradient approximation. A periodic SiO_2 slab model (6 layers relaxing 4 or 6) ended with a layer of Si or O atoms is employed throughout the study. Several adsorption minima and diffusion transition states have been characterized for the two lowest spin states of both systems. A strong chemisorption is found for either O or N in several sites with both slab endings (e.g., it is found an average adsorption energy of 5.89 eV for O (singlet state) and 4.12 eV for N (doublet state) over the Si face). The approach of O or N on top O gives place to the O_2 and NO abstraction reactions without energy barriers. Atomic sticking coefficients and desorption rate constants have been estimated (300 - 1900 K) by using the standard transition state theory. The high adsorption energies found for O and N over silica point out that the atomic recombination processes (i.e., Eley-Rideal and Langmuir-Hinshelwood mechanisms) will play a more important role in the atomic detachment processes than the thermal desorption processes. Furthermore, the different behavior observed for the O and N thermal desorption processes suggests that the published kinetic models for atomic O and N recombination reactions on SiO_2 surfaces, based on low adsorption energies (e.g., 3.5 eV for both O and N), should probably be revised.

Keywords: Chemisorption, physisorption, adsorption, density functional theory, atomic oxygen, atomic nitrogen, silica, cristobalite, adsorption energy, sticking coefficient, desorption rate constant, spin state, recombination, diffusion.

Tables: 8
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I. Introduction

Modeling of the different heterogeneous processes involved in nonequilibrium vibrational kinetics of air hitting over silicon dioxide surfaces is necessary for the study and the design of new thermal protection systems (TPS) to be used in atmospheric terrestrial re-entry vehicles ¹. TPS coatings for space vehicles must have very low catalytic efficiency to reduce the surface heat flux due to atomic recombination effects.

Forthcoming development of reusable launch vehicles (RLV) is a prerequisite for guaranteeing long-term access to space. New materials that allow the reduction of launch mass, improved modeling of aerothermodynamic phenomena, increased performance and reliability of propulsion systems and innovative TPS are required to fulfill RLV objectives. The mastering of the detailed chemical physics phenomena associated with TPS catalysis is therefore a key element in this context. Therefore, theoretical, numerical and experimental developments are necessary in order to model more accurately the corresponding gas-surface interactions.

Currently, silica-based materials (e.g., reaction-cured glass (RCG) with 94 % of SiO₂, 4% of B₂O₃ and 2 % of SiB₄) are primarily used in TPS surfaces, where catalytic atomic recombination of oxygen and nitrogen (via Eley-Rideal (ER) or Langmuir-Hinshelwood (LH) mechanisms) play an important role in re-entry heating at thermal nonequilibrium conditions. However, another elementary processes need to be also included in the global kinetic modeling in these conditions ^{1,2}: atomic adsorption-desorption, molecular adsorption-desorption, atom-molecule ER or LH reactions,.. Among the different elementary steps involved in the heterogeneous catalysis: 1) diffusion of reactants to the surface, 2) adsorption of reactants on surface, 3) chemical reactions on surface, 4) desorption of products from surface, and 5) diffusion of products away from the surface, steps 1 and 5 are usually fast, and the rate determining step has to be found among steps 2,3 and 4.

The main goal of our research in progress is the theoretical study from first principles of the steps 2, 3, and 4 with several models of a silica surface in order to provide kinetic and dynamical data useful for Computational Fluid Dynamics (CFD) simulations. Published kinetic models for air recombination over SiO₂-based materials incorporate rough estimates of several important physiochemical quantities (sometimes used as adjustable parameters), such as, for example, atomic adsorption energies, atomic sticking coefficients, the number of adsorption sites by unit area and others. We believe that a deep theoretical understanding on these processes will permit the proposal of new less catalytic materials to be used as TPSs.

In a first step of the work we have to study the O and N adsorption processes. Nevertheless, scarce experimental data are available on both processes, which are usually treated in a similar way

by means of an average adsorption energy of 3.5 eV¹ regardless of the kind of silica surface (e.g., pyrex, quartz, RCG,..), although several used values are within the range of 2.6-5.5 eV²⁻⁶. These data are indirectly derived from kinetic modeling of atomic recombination on SiO₂ surfaces to fit some experimental data. Thus, for instance, initial surface sticking coefficients S_o of 0.05 e^{-0.002T} (on SiO₂) or 1.0 e^{-0.002T} (on RCG) and an adsorption energy of 3.5 eV were reported for oxygen in both surfaces¹; for nitrogen on RCG the reported data were S_o = 0.95 e^{-0.002T} and an adsorption energy of 3.4 eV¹.

Among the different forms of silicon dioxide to be studied, either amorphous or crystalline (e.g., quartz, tridymite, cristobalite,..), the β-cristobalite is the most stable polymorph at high temperatures up to the melting point of 1983 K; these elevated temperatures are achieved during the Earth's atmospheric re-entry phase. Moreover, β-cristobalite is the crystalline phase of silica with properties closest to those of amorphous silica (e.g., density, refractive index, band structure,..). Recent experimental measurements⁷⁻⁸ of the oxygen recombination coefficient γ_O over silica have shown that this coefficient is four times higher for β-cristobalite than for quartz. Another related theoretical work⁹ has also studied the kinetics and dynamics of the atomic oxygen recombination (ER and LH mechanisms) over β-cristobalite. They used a semiempirical interaction potential for oxygen on β-cristobalite along with a semiclassical collisional model, which allow ascertain the importance of both mechanisms depending on the surface temperature. This potential energy surface, as the authors recognize, seems a crude approximation to the real interaction forces, although theoretical and experimental γ values are in reasonable agreement.

In this paper we present a wide theoretical study based on periodic density functional theory (DFT) calculations for the O and N adsorption at β-cristobalite (100), with both O or Si as a first layer. We have considered dehydroxylated β-cristobalite as a first approximation to the real amorphous TPS materials used at high temperatures to simplify the theoretical study and to facilitate its comparison with previous and related theoretical⁹ and experimental studies⁷⁻⁸, which used α-quartz or β-cristobalite. For instance, the experimental results for γ_O over RCG are quite similar as for α-quartz⁸. Up to our knowledge, this is the first attempt to quantify from first principles these elementary processes, and it is a first stage in the construction of the *ab initio* potential energy surfaces needed to study the dynamics of the O and N recombination processes over β-cristobalite surfaces (i.e., O + O_{ad}, N + N_{ad}, O + N_{ad}, N + O_{ad},..).

2. COMPUTATIONAL METHOD

We have performed DFT calculations by means of the VASP code¹⁰⁻¹³, which uses plane wave basis set. The calculations are based on the generalized gradient correction (GGA) functional Perdew-Wang 91 (PW91)¹⁴⁻¹⁵. The electron-ion interactions were described by using the projector-augmented-wave (PAW) technique¹⁶⁻¹⁷, particularly good for transition metals and oxides, and giving similar results as the FLAPW all-electron method. We checked widely the appropriate energy cut-off in several bulk and slab calculations. Thus, our previous bulk calculations to obtain several properties (e.g., bulk modulus, cell lattice parameters, cohesive energy,..) of some silica polymorphs (e.g., α -quartz, β -quartz, β -tridymite or β -cristobalite) showed that an energy cut-off of 400 eV was accurate enough to obtain converged properties. We have also confirmed this value with some extra slab calculations.

Spin-polarized calculations were carried out to check the ground electronic state of the total system, as both atomic adsorbates (i.e., O(³P) and N(⁴S)) are open-shell systems. Integration over the Brillouin zone was performed by using a 3x3x1 (in slab calculations) or 9x9x9 (in bulk calculations) k-points mesh by means of the Monkhorst-Pack method¹⁸. Geometrical optimizations and vibrational frequencies were computed with an energy accuracy of 10⁻⁶ eV.

For adsorption studies we use a 1x1 surface unit cell and several slab models (4, 6 or 8 layers of SiO₂) for the β -cristobalite (100) face with either an oxygen or a silicon first layer. An additional hydrogen back layer was added to saturate the Si or O dangling bonds as is commonly accepted for silica and silica-containing oxides¹⁹⁻²¹. Thus, to ensure this behavior, the two last layers were always kept fixed while the others were fully or partially relaxed depending on the slab model used. The distance between slabs (ca. $z = 17-18$ Å) was large enough to prevent significant interactions between them.

In spite of the large lattice parameter of β -cristobalite, we have also carried out some supplementary adsorption calculations with a 2x2 supercell to check that the atomic coverage effect was very small in the calculated properties.

Several adsorption sites were characterized for O and N adatoms (see next section for details). Once determined the optimal geometry for each adsorption site, we calculated the Hessian matrix and its corresponding harmonic vibrational frequencies (ν_i) for the adatom (i.e., these can be approximately classified as two parallel and one perpendicular movements), keeping fixed the optimized slab geometry. Several calculations introducing a slab relaxation (i.e., 2 or 4 layers) were carried out to verify that the vibrational frequencies were essentially the same. This analysis

allowed the complete characterization of minima (i.e., 3 real v_i) and surface diffusion transition states (i.e., 1 imaginary frequency (1st-order saddle point) or 2 imaginary frequency (2n-order saddle point)).

The adsorption energy (E_{ad}) was defined as

$$E_{ad} = E(\text{atom}) + E(\text{slab}) - E(\text{atom+slab}) \quad (1)$$

where $E(\text{atom})$ is the total calculated ground state energy of the atom in gas phase (i.e., $O(^3P)$ or $N(^4S)$), $E(\text{slab})$ is the value for the relaxed clean slab in its singlet state and $E(\text{atom+slab})$ is the value of the full relaxed slab containing the adatom. Therefore, when we report a positive adsorption energy for a particular site (e.g., in tables) it means that this site is a minimum (stationary point), which is more stable than the atom + slab asymptote; on the contrary, a negative adsorption energy corresponds to another stationary point (usually a transition state) less stable than the atom + slab asymptote. Thus, minima should be considered as the true adsorption sites.

The atomic energies were calculated with the atom inside large broken symmetry boxes (i.e., $8 \times 7.5 \times 7.6 \text{ \AA}^3$); we used some higher boxes (e.g., $16 \times 16.5 \times 16.6 \text{ \AA}^3$) to be sure that we obtain the same converged energies. In spite of the well known problem about the uncertainty in the DFT energy of systems with a degenerate ground state (e.g., B, N or O atoms) owing to the usual density functionals for the exchange-correlation energy are not invariant over the set of ground state densities²², the small uncertainty (0.1-0.2 eV for second and third period group elements²³) compared with the large adsorption energies makes sure that the main conclusions of the present study will be unaltered. Moreover, this uncertainty is lower or similar to the differences that can be derived from the use of other functionals (e.g., Perdew-Burke-Ernzerhof (PBE)²⁴); thus, for instance, our calculated dissociation energies (D_e) of N_2 and O_2 molecules in gas phase were 0.23 and 0.22 eV lower for the PBE than for the PW91 functional, respectively. A recent study comparing the chemisorption energetics of atoms and molecules on transition-metal surfaces²⁵ with different GGA functionals (i.e., PW91, PBE, revPBE and RPBE) reveals that for O, CO and NO over Ni, Rh and Pd (with several faces and sites) the maximum average difference between calculated chemisorption energies with different functionals is approximately of 0.5 eV, and the maximum average difference between calculated and experimental values is about 0.6 eV.

3. RESULTS AND DISCUSSION

3.1 Bulk and slab calculations for the β -cristobalite

β -cristobalite is formed by extended layers with SiO_4 tetrahedral units with a fourfold-coordinated Si at the center and twofold-coordinated O atoms at the corners, although some controversial remains about its most stable crystal structure. Thus, ordered cubic structures (Fd3m and P2₁3) ²⁶⁻²⁷ as well as a disordered model (formed by small domains of symmetry distributed in six orientations) with an average pseudocubic Fd3m structure ²⁸⁻²⁹ have been experimentally proposed. Recent bulk DFT (LDA and GGA) calculations ³⁰ have been carried out for β -cristobalite using a cubic cell containing eight SiO_2 units with Fd3m and P2₁3 spatial symmetries, although a smaller cell with 4 SiO_2 units would be enough to reproduce Fd3m (cubic) and (tetragonal) structures. In this study the authors concluded that these structures were energetically almost degenerate over a wide interval of densities. A previous DFT study ³¹ supports that the pseudocubic structure is the most stable ((or) < Fd3m < P2₁3) even though the energy difference for the two first is very small (i.e., ~ 0.05 eV). Moreover, they considered a bigger unit cell () instead of the equivalent one.

We have also studied the properties of these structures to check the reliability of the present DFT method to reproduce β -cristobalite in bulk and slab models. Thus, Table 1 presents the calculated internal parameters and the cohesive energy of these bulk structures in comparison with available experimental data for the ordered structures. The calculated structural parameters compare well with earlier DFT results ³⁰⁻³¹ and with experimental data. The major discrepancy is observed for d_{SiO} in the Fd3m symmetry, where the calculated value is somewhat higher (i.e., 0.064 Å) than the experimental one. Respect the energy stability, we found that P2₁3 is the less stable structure in agreement with some preceding results ³¹, although on the contrary we find that Fd3m is a bit more stable than the structure. Nevertheless, the differences are within the expected error of the present DFT method, as it was previously discussed in section II (e.g., due to the O atom energy). In addition, we have performed a Fd3m structure optimization using the PBE functional obtaining that the structural parameters (e.g., $a=b=c= 7.461$ Å, $d_{\text{SiO}}=1.615$ Å,..) are in close agreement with those obtained with the PW91 functional, though the cohesive energy decreases in ~ 0.5 eV (i.e., $E_0 = 19.11$ eV/ SiO_2 molecule), approaching more to the experimental value. In general silica polymorphs (α - and β -quartz, α and β -cristobalite, β -trydimite, stishovite,..) present theoretical (and experimental) cohesive energies very close each other (i.e., <

0.1 eV in DFT studies ³⁰⁻³³), which illustrates the difficulty of the standard DFT methods to be accurate enough to achieve unambiguous conclusions for silica polymorphs.

We have made several slab calculations on singlet state β -cristobalite (100) using 4, 6 or 8 layers (full relaxed arising from the initial Fd3m bulk geometry) of silica to compared with bulk results and to see the validity of the slab model. The results show essentially the same internal parameters for the three models. Thus, we have obtained the following global maximum intervals for the slab structural parameters: d_{SiO} : 1.612-1.650 Å, $\langle \text{SiOSi} \rangle$: 176.3-179.1° and $\langle \text{OSiO} \rangle$: 108.1-111.2°. These values would match bulk properties in between the Fd3m and the structures. Inter-layer relaxation (i.e., Δd_{12} , Δd_{23} ,...) analysis shows a significant outward relaxation of the surface plane (approx. 9.3%) together with smaller inward (approx. -1.2 %) or outward relaxations (approx. 1.8 %) of the lower layers that partially compensate themselves. Concerning the slab thickness dependence, results for the six-layer slab are well converged within 0.3 % (0.007 Å) for the inter-layer relaxation, within 0.8 % (0.01 Å) for the interatomic distances and 0.7 % (0.7°) for the angles.

We have also studied the lowest triplet state to confirm that singlet state was the ground state in the different slab models. Thus, the calculated excitation energies (i.e., singlet-triplet splitting energy defined as $E_{\text{exc}} = E_{\text{triplet}} - E_{\text{singlet}}$) for fixed structures involving 4, 6 or 8 layers were 2.97, 2.99 and 3.01 eV, respectively, compared with 6.42 eV for the bulk calculation. These results corroborate that the singlet state is the ground state for silica. On the other hand, it is observed that the slab models underestimate this energy splitting. This fact agrees with the conclusions derived in an earlier study ³⁴ on self-trapped excitons in α -quartz, which were triplet excited states that distort the crystal locally. The authors concluded that the PW91 functional underestimates the S-T splitting in cases where the triplet state is delocalized, as would correspond to our calculation.

3.2 Atomic oxygen adsorption on β -cristobalite

Firstly, we have studied the atomic oxygen adsorption on the ideal β -cristobalite (100) surface, with a first layer formed by Si atoms. Four different sites have been considered: on top Si (T1), a hollow (H) and two bridges (B1 and B2), as shown in Figure 1. Table 2 presents the results for the atomic adsorption on top Si (site T1) as a function on the slab size. It is observed that the results are almost identical regardless of the number of layers of the slab model, which is consistent with the results about the β -cristobalite models shown in previous section. Thus, Si-O_{ad} distances

are within 0.001 Å, excitation energies within 0.03 eV and adsorption energies within 0.01 eV for full relaxed structures in models with 6-8 layers. This means that the errors due to finite slab thickness will probably not be relevant. Hence, we have finally chosen the 6-layer slab model (relaxing the first-four layers) to be used in the rest of the work unless in one case shown later.

Table 3 summarizes the results for the 4 sites. Two strong chemisorptions are found for T1 and B1 sites. In both cases, singlet and triplet states give place to large adsorption energies. Moreover, the singlet state is much more stable than the triplet state in T1 site, whereas a slight opposite behavior is found in B1 site, though with much closer energies in this latter case. This change on the ground spin-state of the system depending on the adsorption site has been also reported for atomic oxygen adsorption over oxides (e.g., MgO(001)³⁵), metals (e.g., Pt(111)³⁶) or alloys (e.g., Pt/Ni(111)³⁷).

T1 and B1 structures are truly minima as we have verified by the analysis of harmonic vibrational frequencies (Table 3). The different values observed for their vibrational frequencies show the different curvatures of the potential energy surface at these geometries, and can be explained analyzing the position of the adatom in each site and its interactions when the adatom is vibrating along the corresponding normal mode. Thus, for O adsorption on T1 site it is observed that the perpendicular frequency is much higher than the two parallel ones (Table 3) whereas on B1 site the perpendicular is lower than one of the two parallel frequencies, in both spin states. In T1 minimum, the O adatom is very far from the first Si layer ($z \approx 1.4-1.5$ Å) and the perpendicular movement approaches O to the Si atom in the direction of the strong SiO bond. The parallel movements are carried out along the lines T1-B2 and T1-B1 (Figure 1), where the interactions with the neighbor atoms (in the same or in the deeper layers) are clearly minor; therefore, the perpendicular frequency has to be the highest. However, in B1 site the situation is almost the reverse; the O adatom is very close to the first Si layer ($z \approx -0.5-0.2$ Å) and now one of the parallel movements goes into the SiO bond direction (line B1-T1 in Figure 1), which implies a higher frequency, while the another parallel movement corresponds to a direction with less interaction (line B1-H in Figure 1), in a similar way as also occurs for the perpendicular movement.

The $d_{\text{Oad-Si}}$ values for T1 and B1 minima (Table 3) are quite close to the bulk β -cristobalite values (Table 1). However, only a slight relaxation of the silica slab is produced in T1, but an important reconstruction is observed in B1. In this latter case, the Si-Si distance decreases from 5.196 Å (clean slab) to 3.416 Å (singlet state) or 3.179 Å (triplet state), and the d_{12} interlayer-distance changes from 1.007 Å (clean slab) to 0.708 Å (singlet state) or 0.516 Å (triplet state).

The calculated adsorption energies for T1 and B1 sites (in this latter case its half value can be taken as the binding energy due to the formation of two SiO bonds) are slightly lower than the usual SiO bond dissociation enthalpies in gas phase (e.g., 6.50 eV in SiO₂ or 8.29 eV in SiO at 25 °C³²) or in β-cristobalite (e.g., 9.61 eV derived from its cohesive energy (Table 1)). In spite of the absence of direct experimental adsorption (or desorption) energies for the present system³⁸, the comparison with previous DFT studies for the O adsorption over several crystalline surfaces (e.g., E_{ad} equal to 2.0-2.5 eV on MgO(001)³⁵, 3.5-5.0 eV on Pd or Ni(100)²⁵ or 4.2-6.4 eV on GaN(0001)³⁹) supports the magnitude of the chemisorption found. The differences observed in O-SiO₂ with O-MgO adsorption energies could be initially accounted for in terms of their different bond strengths. Thus, the bond dissociation enthalpies at 298 K for SiO and MgO gas phase diatomic molecules are 8.29 and 3.50 eV³² respectively, which would be in agreement with the tendency observed in the O adsorption energies over β-cristobalite and periclase (MgO)³⁵. Moreover, the Mg and O surface atoms of periclase can compete simultaneously to adsorb the incoming O atom, while in β-cristobalite it is more difficult as Si and O atoms are distributed in different layers. In MgO (an ionic solid) it is observed that strongest bonds are formed with lattice O ions (e.g., $E_{ad} = 1.43-2.04$ eV for flat MgO (001)³⁵) to form a peroxide ion (O₂²⁻), whereas O is less adsorbed on Mg lattice ions (e.g., $E_{ad} = 0.84$ eV³⁵) with a O_{ad}-Mg distance (ca. 2.0 Å) similar to the MgO distance in the bulk crystal (i.e., 2.109 Å), and with a O_{ad}-O distance within the range 1.55-2.27 Å (depending on the site). This is also in agreement with the higher bond dissociation enthalpy of O₂ (i.e., 5.16 eV at 298 K³²). Therefore, in both cases (SiO₂ and MgO) the O adatom try to be incorporated into the bulk (like a growing of the crystal) achieving similar geometrical and energy properties as in the lattice. In SiO₂ (a rather covalent solid) the O atom bonds to the Si dangling bonds, on top a Si (in T1 site) or forming a bridge (in B1 site), in such a way that neighboring silicon atoms share the O (oxygen bridging), in both cases with stronger (covalent) bonds than in MgO.

In order to understand better the differences observed in the chemical bonding for T1 and B1 sites in both electronic states, we have analyzed their α and β density of states (DOS) and their projected DOS onto the O adatom and the two underneath Si atoms of the first layer (labeled as Si_{1a} and Si_{1b}), which are involved in the bonding of these minima with different extent. Their plots are shown in Figure 3 along with the pDOS for free O atom and for the clean SiO₂ slab. In this latter case it is observed the existence of the Si dangling bond states (approx. in -0.5 → 0 eV region). These electronic states are changed in the T1 (singlet) structure and appear now at more negative energies (approx. in -4 → -2 eV region) due to their participation in a σ bonding with the O_{ad}. It is

also observed their contribution to the σ^* states at positive energies. Small shifts are observed for the DOS of both silicon atoms, with lower energies for the Si_{1a} states due to its major contribution to the bond. Moreover, as the total state is a singlet, a π bond can be established between O_{ad} and Si_{1a} , involving p_x or p_y orbitals (approx. in $-7 \rightarrow -4$ eV region). Thus, the O_{ad} passivates the two Si dangling bonds. Si_{1a} is also bonded to two oxygen atoms of the second layer with similar SiO distances, keeping the four atoms in the same plane. For the T1 (triplet) structure, the O_{ad} projected DOS present a strong α polarization, which is also appreciated for Si_{1a} atom. On the contrary, Si_{2a} shows almost equal density of α and β states. Thus, this could be explained considering that both O_{ad} and Si_{1a} tend to keep one unpaired electron to produce the total triplet state. This fact would prevent the possibility to form a π SiO bond as it occurs in T1 (singlet) structure. Hence, this could justify the higher binding energy obtained for the singlet structure ($E_{ad}(\text{singlet})= 5.97$ eV) compared with the triplet one ($E_{ad}(\text{triplet})= 3.18$ eV). In T1 (singlet and triplet) structures the O_{ad} is quite above the first Si layer ($z=1.4-1.5$ Å) and the deactivation of two Si_{1a} dangling bonds reduces the possibility of a significant relaxation of the slab. Thus, very similar geometries are obtained for both T1 structures (Table 3) and the slab changes are minor in comparison with the clean slab geometry.

In B1 (singlet) structure, the adatom makes an oxygen bridging between two surface Si atoms. Thus, O_{ad} tends to become like an O of the slab. Their pDOS are very similar. Moreover, both Si atoms under the O_{ad} (i.e., Si_{1a} and Si_{1b}) present equivalent pDOS. The bonding between each Si and O_{ad} passivates one of the two initial Si dangling bonds as can be shown in Figure 3 (shifted to $-6 \rightarrow -5$ eV region). The remaining Si dangling bond of each Si can react to form the reconstructed final structure as a consequence of the trend to bond pairing up, which is observed in semiconductor surfaces. This is also in agreement with the important reconstruction observed in both B1 structures, where in the final geometry the Si achieves a pyramidal structure (SiO_3), with Si very close to the surface ($z=-0.5$ to 0.2 Å). B1 structures (singlet and triplet) present similar binding energies (ca. $5.80/2$ eV (singlet) and $6.56/2$ eV (triplet)), which could be understood taking into account that now oxygen keeps two lone pairs and forms only a σ SiO bond with both Si atoms, regardless of the total spin of the system. The pDOS in B1 (triplet) structure indicate a spin polarization due to O_{ad} and both Si atoms, which would mean some delocalization of two unpaired electrons.

The B2 and H structures correspond to very small adsorptions, mainly in the triplet state, even though these stationary points are not truly minima but transition states (i.e., first-order saddle points). In these structures there is no any significant geometrical relaxation with respect the clean

slab geometry. We have also checked that the H structure seems to be a diffusion transition state that connects two equivalent B1 minima. Nevertheless, as surface reconstruction is important in B1 minimum, the analysis of the vibrational frequencies in H structure has to be taken as approximate due to the vibrational frequencies were calculated keeping fixed the slab geometry in both stationary points. In B2 structure this problem was not found and it was much easier to establish that it corresponds to a diffusion transition state for the T1 interconversion.

The corresponding diffusion energy barriers are: 5.99 eV (singlet state) and 2.74 eV (triplet state) for $T1 \rightarrow B2^\ddagger \rightarrow T1$, and 6.24 eV (singlet state) and 6.40 eV (triplet state) for $B1 \rightarrow H^\ddagger \rightarrow B1$. These high energy barriers should be taken carefully as they imply two lateral migrations of the O adatom between equivalent sites that are quite distant each other. It can be expected than much lower barriers should exist for the interconversion between B1 and T1 minima; these structures are very close (along the T1-B1-T1 diagonal in surface cell shown in Figure 1) in geometry and energy, hence that another transition state (possibly located between T1 and B1 and involving some relaxation of the slab) with a lower energy barrier would allow an easier diffusion. This fact along with the possibility of another internal diffusions (not studied here) would be in better agreement with recent DFT values calculated for O diffusion inside α -quartz (i.e., 1.3 eV assuming a singlet state^{21, 40}) or to the O migration (diffusion) energy (i.e., 1.65 eV) used in kinetic modeling of O and N recombination over silica re-entry thermal protection systems⁵. However, for the study of O atomic collisions over silica the initial direct adsorption in B1 and T1 minima will be more relevant because the initial slight adsorption in H or B2 sites will evolve to the T1 and B1 minima.

In previous section we discussed the bulk and slab models for clean β -cristobalite, and we proposed a slab model (relaxed) derived from a Fd3m bulk structure. To see the possible influence of the SiOSi angles of the slab in the O adsorption energies we have also made calculations by using a slab model derived from a Fdd2 bulk structure (Table 1), which essentially means that the SiOSi angles are close to 147° instead of 180° . The results are presented in Table 4. The comparison with the results shown in Table 3 indicates that the adsorption energies and the geometries are very similar for all structures, and both slabs seem to be almost equivalent for the present study.

We have also studied the possible adsorption of oxygen on the β -cristobalite (100) face terminated with O atoms. Three several sites were finally considered: on top O (T2) and two bridges (B3 and B4), as shown in Figure 2. In this case we had to use the 6-slab model with full relaxation to obtain converged results, which are shown in Table 5. In the first site (T2) we did not find an atomic adsorption but the abstraction reaction to produce the O_2 molecule without energy

barrier. In both bridge sites a chemisorption was obtained either in the singlet or in the triplet state, with similar adsorption energies and very small geometrical relaxation in comparison with the clean slab geometry. The stability of both B3 structures (singlet and triplet) is coherent with the most stable Lewis structures, with two electron lone pairs in each O atom for the singlet B3 structure and with two unpaired electrons in two of the three oxygen atoms for the triplet.

The B4 stationary point is a diffusion transition state which connects two equivalent B3 (singlet) minima (i.e., for $B3 \rightarrow B4^\ddagger \rightarrow B3$) with a small energy barrier ≤ 0.46 eV (singlet state). Nevertheless, B4 has two imaginary frequencies in both states, and it could be expected that a first-order saddle point should be close to the reported geometries. We have also calculated the vibrational frequencies for B4 structure (triplet state), relaxing the two first layers of the slab. All calculated frequencies were real excepting two, which were associated with parallel movements of O adatom (183.7i, 356.9i). The perpendicular movement of the O adatom was approximately associated with a vibrational frequency of 373.5. These results are in agreement with the values reported in Table 5 (i.e., 547.7, 136.7i, 206.3i) and show that the existence of two imaginary frequencies is possibly due to the true transition state is slightly shifted from the reported geometry. Therefore, the rigid slab approximation for the vibrational frequency calculations seem to be appropriate enough to characterize the stationary points.

The number and the energy of the stationary points found points out that the Si face on β -cristobalite (100) will be more important than the O face for oxygen adsorption processes and probably also for the successive Eley-Rideal or Langmuir-Hinshelwood reactions, such as it has been assumed up to date in all kinetic modeling studies on air chemical processes over silica materials¹.

3.3 Atomic nitrogen adsorption on β -cristobalite

We have carried out a similar study as for oxygen using now atomic nitrogen. The same sites (Figures 1 and 2) were initially considered for this system in the two lowest spin states derived from the $N(^4S)$ (i.e., doublet and quartet states). Table 6 summarizes the results for the β -cristobalite (100) with a first Si layer. First of all, it is not observed any adsorption (i.e., zero or negative E_{ad}) for H and B2 sites in whichever of both spin states. On the contrary, T1 and B1 sites correspond to important chemisorptions as it took also place for O adsorption, mostly in the doublet state. Both stationary points are really minima as the harmonic vibrational frequencies prove. Their

$d_{\text{Nad-Si}}$ values, shown in Table 6, are within the range of the usual N-Si distances in silicon nitrides in gas phase (e.g., 1.57 Å in SiN ($^2\Sigma^+$) or 1.70 Å in Si₂N ($^2\Pi_g$)³²) or in nitride films on silicon (e.g., 1.62-1.76 Å⁴¹). Though a very small relaxation is observed for the slab in T1 site, there is a considerable reconstruction of the slab in the B1 site as it also happened for the O adsorption on the Si face. Thus, the Si-Si distance decreases from 5.196 Å (clean slab) to 3.256 Å (doublet state) or to 3.311 Å (quartet state), and the d_{12} interlayer-distance changes from 1.007 Å (clean slab) to 0.465 Å (doublet state) or 0.557 Å (quartet state).

The DFT adsorption energies for T1 and B1 sites are slightly lower than the typical Si-N bond dissociation enthalpies in gas phase (e.g., 4.41 eV in Si₂N or 5.71 eV in SiN at 25 °C³²). Although no direct experimental data are available for N adsorption on silica³⁸, the present results compare reasonably well with earlier theoretical or experimental studies on the N adsorption over several solids (e.g., E_{ad} equal to 2.6-4.6 eV on Si(100), with similar values for doublet and quartet states⁴¹, or 3.35-5.65 eV on several Cu planes⁴²). Moreover, a very recent cluster B3LYP-DFT study⁴³ on the N adsorption on Si_xO_y (silica clusters) reports an adsorption energy for the T1 site (i.e., 2.84 eV) and a N-Si distance (i.e., 1.7 Å) quite similar to our present values (Table 6), which is nonetheless based on periodic (slab) DFT-GGA/PW91 calculations.

The difference between doublet and quartet SiN binding energies in T1 structures (Table 6) could be justified in a similar way as it was made for O adsorption structures. Thus, the doublet state allows the possibility of a Si=N double bond as N can keep one unpaired electron; conversely, the quartet state makes even difficult the formation of a single bond due to the difficulty for N or Si (Si is also bonded to two O atoms of the slab) to have three unpaired electrons and simultaneously to make a bond, which is consistent with the unimportant bonding in quartet state for T1 structure. Similar arguments can be valid for B1 structures.

The stationary point corresponding to N adsorption in H site is a diffusion transition state that connects both equivalent B1 minima (i.e., B1 → H[‡] → B1) with high energy barriers of 3.60 eV (doublet state) and 6.61 eV (quartet state). The B2 structure turns out to be a diffusion transition state connecting both equivalent T1 minima (i.e., T1 → B2[‡] → T1) with energy barriers of 3.96 eV and 0.04 eV for doublet and quartet states, respectively. This behavior is similar as we observed for O adsorption, and does not exclude the existence of even minor diffusion energy barriers for another directions (e.g., line T1-B1 in Figure 1).

The adsorption of N into the first oxygen face on the β-cristobalite (100) shows as well similar sites (Figure 2) and behavior as for O adsorption, and its results are indicated in Table 7. Thus, it is also observed a molecular formation (i.e., NO) in T2 site for both spin states instead of

the N adsorption process, with energy barrierless in both cases. Moreover, an important chemisorption is obtained in B3 site (true minimum) for both spin states. Their corresponding NO binding energies (6.10/2 eV and 5.66/2 eV in doublet and quartet states, respectively) are within the ordinary range of the NO bond dissociation enthalpies in gas phase (e.g., 3.18 eV in $\text{NO}_2(^2\text{A}_1)$ or 6.55 eV in $\text{NO}(^2\Pi)$ at 25 °C ³²). The $N_{\text{ad}}\text{-O}$ distances (1.336 Å and 1.442 Å in doublet and quartet states, respectively) are rather longer than the NO distances in small gas phase molecules (e.g., 1.197 Å in $\text{NO}_2(^2\text{A}_1)$ or 1.151 Å in $\text{NO}(^2\Pi)$ ³²); only a very small slab relaxation is produced as in the case of O adsorption. In B3 minima, N is bonded to two oxygen atoms, which are also bonded to the same tetra-coordinated Si atom (i.e., SiO_4 group in Figure 2). The slight difference in their binding energies (derived from E_{ad} values shown in Table 7) can be explained again taking into account the major facility of the N atom to keep one unpaired electron (and a lone pair) when is also simultaneously making two NO bonds in the doublet state, which seems a bit more difficult for the quartet state.

The B4 stationary point corresponds to a diffusion transition state for the B3 interconversion (i.e., for $\text{B3} \rightarrow \text{B4}^\ddagger \rightarrow \text{B3}$), with a very small energy barrier of 0.18 eV for the quartet state. However, this transition state has a slightly lower energy than B3 minima for the doublet state; even though B3 minimum should be deeper than B4 transition state, the closeness of their energies could point out that B3 is a local minimum and the most stable one should be located not very far.

3.4 Atomic sticking coefficients and desorption rate constants

The heat of chemisorption on a polycrystalline surface represents an average of the binding energies of the different surface sites weighted according to the relative concentrations of these sites. In a single-crystal surface as the β -cristobalite (100), either terminated with Si or O, we can also estimate an average adsorption energy taking into account the active site concentration of a completely free surface (i.e., n_s^0 will be the number of true adsorption minima by surface cell area), assuming the same initial sticking coefficient for these sites and a small effect of the coverage on the adsorption energies as we have checked using some 2 x 2 surface cell calculations. Thus, n_s^0 becomes equal to 3.6×10^{18} sites /m² for T1, B1 or B3 sites (see Figures 1 and 2) and the average adsorption energies for O and N adsorption on the Si (or O) first face of β -cristobalite (100) are compared in Table 8. These values can easily corrected for vibrational zero point energy using the harmonic vibrational frequencies shown in the previous tables, although the effect will be very

small (i.e., a reduction less than 0.1 eV in the E_{ad}). These results show that O adsorption is preferred on the Si face of β -cristobalite (100) in comparison with the O face, and that the reverse behavior is observed for N adsorption. On the other hand, the stronger chemisorption of O over β -cristobalite (100) than for N in the Si face is in total agreement with the usual assumption (see introduction) made in kinetic modeling for hypersonic reactive air flows over silica materials ¹. A study in progress about the adsorption over the (111) first Si face of β -cristobalite shows similar conclusions as for the (100) face (e.g., $E_{ad-O} = 5.45$ eV (singlet) or 2.72 eV (triplet), and $E_{ad-N} = 3.08$ eV (doublet) or 1.00 eV (quartet), for an equivalent T1 site). Thus, these results could also suggest that the existence of terraces, steps or corners on silica would not give much higher adsorption energies than on the flat β -cristobalite (100) surface.

In order to see the influence of these adsorption/desorption energies on the aforementioned kinetic models, we have also calculated the atomic initial sticking coefficients ($S_{o(A)}$) and desorption rate constants ($k_{des(A)}$) by means of the standard transition state theory (TST) ⁴⁴ expressions used in this kind of studies ^{1,6} for non-activated adsorptions and thermal equilibrium between the colliding A atoms and the wall (i.e., $T_g = T_w = T$):

$$(2)$$

and

$$(3)$$

where m_A is the A atom mass, $v_{||}$ and v_{\perp} are the two parallel and one perpendicular vibrational frequencies of the adatom A, respectively, and the rest of symbols have their usual meanings. In both equations we do not introduce the catchall factor (i.e., $P_{des} = 1$), which often is taken as an adjustable parameter in some kinetic models ¹.

Figure 4 illustrates the calculated initial sticking coefficients for O and N over a first Si face of β -cristobalite (100) against the temperature taking into account both minima (B1 and T1). The current DFT-TST results correspond to the ground electronic state in both systems (i.e., highest adsorption energies). The results of two empirical kinetic models (model I ³ and model II ⁶) are also added for comparison. The model I takes into account the O adsorption, the O thermal desorption and the O₂ formation by recombination of atomic oxygen (ER mechanism) by means of the

corresponding time-dependent rate equations and using the following empirical expressions for $S_o(A)$ and $k_{des}(A)$:

$$(4)$$

$$(5)$$

Thus, several physiochemical parameters were checked or optimized (i.e., $n_s^0 = 5 \times 10^{18}$ sites /m², $B = 0.05$, $C = 0.002 \text{ K}^{-1}$, $E_{ad} = 3.5 \text{ eV}$, and the activation energy (1 kcal/mol) and the steric factor (0.1 at $T \geq 925 \text{ K}$) for the ER reaction) to match the experimental $\gamma_O(T)$ curve for O over silica in the range 20° - 600°C; the authors also presented extrapolations of their results for higher temperatures (i.e., $T \leq 2000 \text{ K}$). The model II distinguishes adsorption, desorption, recombination reactions (ER and LH mechanisms) and dissociative adsorption for N/N₂ and O/O₂ systems on silica. Transition state theory (e.g., eq. (2) and (3)) and collision theory were used to derive the corresponding rate equations and a final expression of $\gamma_A(T)$. Some parameters were assumed (e.g., $n_s^0 = 2 \times 10^{18}$ sites /m², $E_{ad} = 2.6 \text{ eV}$ for N or O, $v_{||} = 62.6 \text{ cm}^{-1}$ for O and 55.6 cm^{-1} for N, $v_{\perp} = 417.0 \text{ cm}^{-1}$ for O or N,..) and other were adjusted to reproduce better the experimental $\gamma_O(T)$ and $\gamma_N(T)$ data (e.g., activation energies for ER and LH reactions, some steric factors,..); the authors also extrapolated their results until 2500 K.

Our calculated TST values agree with the low S_o values derived in both kinetic models. Moreover, its temperature dependence is much closer to model II shape, which is in between T1 and B1 curves for both systems.

In Figure 5 we show the calculated desorption rate constants for O and N over a first Si face of β -cristobalite (100) in front of the temperature for B1 and T1 minima. They are compared with the curves derived from both empirical models; in model I ³ it is assumed a value of 3.5 eV for the O adsorption energy, and in model II ⁶ is taken the same adsorption energy for O and N (2.6 eV), although the use a factor in eq. (3) (i.e., $P_{des} = 0.1$). The differences observed in the desorption rate constants are mainly produced because of the different DFT adsorption energies. Thus, there is better agreement for N adsorption, where our calculated adsorption energy for T1 site is close to those used in models I and II, but there are important differences for oxygen adsorption as we obtain much higher adsorption energies in both T1 and B1 sites. Therefore, our results show a clear different behavior for N and O. Nevertheless, as we pointed out in the introduction, there is a broad

range of E_{ad} derived from kinetic modeling on O and N recombination on silica-based surfaces. Thus, for instance, values such high as 5.95 eV have been used in another kinetic models for O and N recombination over RCG surfaces⁴⁵, which would be much closer to our current DFT results.

These high adsorption energies imply that the chemisorbed atoms will be desorbed only at relatively high temperatures ($T > 900$ K for N and $T > 1800$ K for O from Figure 5), so that these atoms will be held irreversibly on the surface and they will be removed only by atomic recombination (e.g., ER or LH processes) at lower temperatures. Experimental studies by using single-crystal adsorption calorimeter^{38,46} or thermal desorption spectroscopy⁴⁶ would be necessary to validate entirely our theoretical results. The calculated $S_{\text{o(A)}}$ and $k_{\text{des (A)}}$ for N and O would tend to increase the corresponding γ_{A} coefficients if the kinetic data⁶ for ER and LH were kept constant. However, a DFT study on the minimum energy paths and the transition states involved in ER and LH reactions (in progress in our group) will be necessary to obtain an accurate calculation of $\gamma_{\text{A}}(T)$ coefficients.

Finally, despite the assumptions made in the $S_{\text{o(A)}}$ and $k_{\text{des (A)}}$ calculations: TST equations, single-crystal, Si face, small effect of the coverage in DFT adsorption energies,..., we believe that our values are more suitable to be used in the mentioned kinetic models than the usual adjustable (semiempirical) parameters not derived from first principles, which differ considerably among the numerous empirical kinetic studies made up to date.

4. Summary and conclusions

In this work we have made a periodic DFT study (GGA/PW91) on the adsorption of atomic oxygen and nitrogen over β -cristobalite (100) considering the two lowest spin states of every system and the termination of the crystalline SiO_2 with a first face of Si or O.

Bulk calculations on different spatial symmetries of β -cristobalite show a good agreement with experimental and previous theoretical data, which gives additional reliability to the DFT method used in the work. Moreover, the slab model chosen to simulate the β -cristobalite (i.e., 6 layers relaxing 4 or 6) reproduces the main geometrical properties of experimental β -cristobalite and shows a good convergence on the adsorption properties for O and N.

The adsorption of O over β -cristobalite (100) indicates a strong chemisorption in two sites (on top Si and in a bridge) for a first Si layer, with an average adsorption energy of 5.89 eV (singlet state) or 4.87 eV (triplet state). For a slab terminated with an O layer the adsorption energy (bridge

3) is 4.10 eV (singlet state) or 3.67 eV (triplet state). The adsorption of N presents similar results. Thus, for a first Si layer we obtain an average adsorption energy of 4.12 eV (doublet state) or 1.80 eV (quartet state). For a slab ended with an O layer the adsorption energy in bridge 3 is 6.10 eV (doublet state) or 5.66 eV (quartet state). The values of the different adsorption energies, which depend on the adatom, the site and the spin state involved, can be qualitatively explained by analyzing the kind of bonds formed in each case.

The approach of either O or N on top oxygen of β -cristobalite (100) gives place to the abstraction reactions, which produce O₂ or NO molecules, respectively, without energy barrier.

Several diffusion transition states have also been characterized, which connect some of the adsorption minima with rather high energy barriers; this does not exclude the existence of much lower energy barriers in another directions of the cell (e.g., in the line between B1 and T1 minima).

Atomic sticking coefficients and desorption rate constants have been estimated within the temperature range 300 - 1900 K by means of the usual transition state equations and the standard approximations. The high adsorption energies found for O and N over silica imply that the atomic recombination processes (i.e., Eley-Rideal and Langmuir-Hinshelwood mechanisms) will have a more important role in the atomic detachment processes than the thermal desorption processes at temperatures lower than 1800 K for O and 900 K for N. Further experimental data should confirm these conclusions along with DFT calculations on these reactions, in progress in our research group.

Finally, the magnitude of the DFT adsorption energies also suggests that the published kinetic models of atomic O and N recombination on SiO₂ surfaces, which make use of low adsorption energies (e.g., 3.5 eV equal for O and N¹), should be revised, particularly for oxygen processes. It can be expected that the structural differences in silica based-materials (e.g., pyrex, cristobalite, RCG,..) will not give a large divergence in adsorption energies and hence that the present values could be still suitable for them.

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