



Hot atom chemistry: Oxygen at stepped platinum surfaces

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ABSTRACT

It is a paradigm in chemistry that chemical reactions are mainly governed by thermodynamics. Within this assumption, reaction rates can be derived from transition state theory which requires a quasi-equilibrium between reactants and activated transition state complexes that is achieved through friction. However, to reach thermal equilibrium through friction takes some time. Here we show, based on ab initio molecular dynamics simulations of the interaction of molecular oxygen with stepped Pt surfaces, that chemical reactions in heterogeneous catalysis can occur in a non-equilibrium fashion when the excess kinetic energy upon entering the potential well of a reaction intermediate is large enough.

1. Introduction

Our basic understanding of chemical reactions in the presence of a catalyst is based on thermodynamic concepts. Complex reactions can consist of several elementary reaction steps which are each characterized by a reactant and a product state that are typically separated by an activation barrier. Usually it is assumed that the redistribution of excess kinetic energy is much faster than the propagation from one reaction intermediate to the next [1]. Then chemical reactions occur at a characteristic reaction rate at a given temperature and chemical concentration that can be determined using transition state theory (TST) [2–5]. Its application demands a quasi-equilibrium between reactants and activated transition state complexes.

Reaching equilibrium has to be achieved through friction [4], i.e., through a strong coupling with the corresponding heat bath. This represents a crucial assumption underlying transition state theory. If there is only low-to-moderate coupling, transition state theory cannot be applied without refinement, as has already been discussed in the seminal work of Kramers [6]. Deviations from TST behavior have already been discussed for organic reaction intermediates [1]. Furthermore, so-called “hot atoms” dynamics have been invoked to explain experimental observations in the spatial distribution of dissociation products on surfaces [7,8]. On Al(111), according to scanning tunneling microscopy (STM) experiments, a small dosage of molecular oxygen exclusively leads to single oxygen atoms separated by an average distance of more than 80 Å [7]. Various mechanisms have been proposed to explain this surprising result. For example, subsurface migration of single oxygen atoms has

been invoked [9]. However, also a hot atom-like mechanism based on a cannonball abstraction process [10,11] has been proposed. First-principles based molecular dynamics simulations including spin selection rules [12,13] have been able to reproduce and explain the experimentally observed small sticking probability at low kinetic energies [14,15], but have not found any indications for the cannonball mechanism. On Pt(111), molecular chemisorbed O₂ molecules dissociate at higher temperatures with the oxygen atoms being preferentially two lattice sites apart from each other [8] which has also been explained by a hot atom mechanism and confirmed in kinetic Monte Carlo simulations [16]. A non-thermal, hot-molecule mechanism has also been proposed based on a combination of experiment and molecular dynamics simulations for the dissociative adsorption of methane on Ir(111) [17,18]. At low incident kinetic energy, methane molecules become trapped on Ir(111) in a physisorption well. However, according to molecular dynamics simulations, vibrationally pre-excited methane molecules can further react and adsorb dissociatively on Ir(111) before their vibrational and kinetic energy becomes accommodated [18]. Interestingly enough, in another computational study it was shown that most of the adsorption behavior at low energies can also be explained based on thermal rate constants which assumes accommodation prior to any further reaction [19]. Still, in the kinetic simulations, vibrationally pre-excitation has not been considered, but it has been argued that vibrational excitation of physisorbed molecules should not change the rate constants too dramatically.

This indicates that the unequivocal direct identification of hot atom dynamics in reactions on surfaces by a combination of experiment and

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theory is not easy to achieve. From an experimental point of view this is due to the fact that the lifetime of dynamical hot atom events is typically so short that these events can not be directly detected. As far as simulations are concerned, in recent years significant progress has been made by performing dynamical simulations that include the coupling either to a phonon bath [15,20–24] or to electron-hole pairs [25–30]. Such simulations have provided very valuable insights into hot atom dynamics in reactions at surfaces. Still it is fair to say that there is not yet a general understanding about the factors promoting hot atom reactions at surfaces.

In this study, I will demonstrate that hot atom dynamics plays a critical role in the interaction of O₂ molecules with stepped Pt surfaces. The adsorption and dissociation of oxygen on platinum surfaces are of significant technological importance, as they not only constitute crucial reaction steps in the car exhaust catalyst [31], but they are also relevant for the oxygen reduction reaction in fuel cells in aqueous environments [32–36]. Molecular oxygen can adsorb both molecularly and dissociatively on Pt(111) [8,37]. At low surface temperatures, however, oxygen does not directly dissociate on Pt(111), even if impinging with high kinetic energies [8,38,39]. Rather, it first adsorbs molecularly due to steric hindrance caused by the shape of the underlying potential energy surface, and only in a second step dissociates caused by thermal fluctuations, as demonstrated in tight-binding molecular dynamics studies [40,41].

Stepped surface are known to exhibit an enhanced catalytic activity [42–45] due to the presence of low-coordinated sites which typically interact strongly with adsorbates. In this context, also the interaction of oxygen with stepped surface has raised a lot of interest [46–52]. A joint experimental and theoretical study revealed that O₂ dissociation is strongly favored at the step sites [48]. DFT calculations found that the adsorption energies of oxygen atoms and molecules at Pt step sites are significantly enhanced compared to terrace sites [48,53,54]. However, interestingly enough the DFT calculations also showed that the enhanced O₂ dissociation is not caused by a lowering of the local dissociation barrier [48,53]. The exact O₂ dissociation mechanism at the step sites could not be revealed in these studies, but it was speculated that it still proceeds as a thermal equilibrium process rather than through a hot precursor [48]. Here I will provide evidence based on *ab initio* molecular dynamics simulations (AIMD) of O₂ adsorption on stepped Pt surfaces that it is indeed a hot atom or rather a hot precursor mechanism that contributes to the preferential O₂ dissociation on stepped Pt surfaces.

2. Computational details

In this work, the dynamics of oxygen adsorption on flat and stepped Pt surfaces has been addressed by performing *ab initio* molecular dynamics simulations on the basis of density functional theory (DFT). The whole adsorption process including dissociation events and the accommodation of the hot atoms has been treated in a fully consistent manner. The periodic DFT calculations have been performed using the Vienna *ab initio* simulation package (VASP) [55] in a spin-polarized fashion. The exchange-correlation effects have been described within the generalized gradient approximation (GGA) using the RPBE functional [56], as this functional yielded sticking probabilities of O₂/Pt(111) [57] in better agreement with the experiment than the PBE functional [58]. The one-electron valence states were expanded in plane waves with kinetic energies up to the cutoff energy of 400 eV, and the ionic cores were represented by projector augmented wave (PAW) potentials [59] as constructed by Kresse and Joubert [60]. The Pt(111) surface was modeled by a slab of five layers within a 3 × 3 geometry with the uppermost two layers free to move while the three bottom layers were kept fixed at the bulk geometry. For Pt(211) and Pt(533), 15-layer and 20-layer slabs, respectively, within a 1 × 3 geometry were used with the corresponding numbers of layers free to move. For all considered surfaces, the integration over the first Brillouin zone was replaced by the

summation over 3 × 3 × 1 special *k*-points. The (211) surface consists of (111) terraces that are three atom rows wide separated by (100)-like steps. (533) surfaces are rather similar, the (111) terraces are just four atoms wide. Note that it nowadays correspond to the state of the art to include dispersion effects in the DFT calculation of molecule-surface interactions [61,62]. However, it has recently been shown that dispersion corrections modify the surface reaction energy of O₂ dissociation from the molecular precursor state on Pt(111) only by about 0.1 eV [63]. Therefore dispersion corrections have not been considered in this study so that the computational setup is comparable to the one used in the previous DFT studies addressing O₂ adsorption on stepped Pt surfaces [48,53].

The AIMD simulations were performed using the Verlet algorithm with a time step of 1 fs. The trajectories were started 5 Å above the surface with random lateral position and orientation of the O₂ molecules without considering any zero-point vibrational energy in the initial conditions. This is motivated by the fact that the sum of all zero-point energies typically stays approximately constant along the reaction path for adsorption [64]. If not otherwise stated, the simulations were performed within the microcanonical ensemble. However, additional simulations were performed with the second Pt layer coupled to an Anderson thermostat [57,65,66] with a collision rate of 0.02 fs⁻¹.

Note that we do not take into account the possible electron transfer to electron-hole pairs. Its inclusion would lead to an additional energy dissipation channel and thus further energy losses. The importance of such electronically non-adiabatic effects on trapping processes is not fully clarified yet. However, according to a recent review [29] and explicit studies employing so-called electron friction approaches [25,26,67], non-adiabatic energy dissipation channels appear to have only small effects on calculated sticking probabilities. Experimentally, such non-adiabatic effects can be determined by measuring the so-called chemicurrent [68] whose magnitude scales with the interaction strength between adsorbate and surface [69]. The adsorption energy of the O₂ molecular precursor state at the step sites of Pt surfaces of about 0.9 eV according to previous calculations [48] and our own results (see Fig. 1) does not correspond to a particularly strong chemisorption. Therefore we did not take into account any energy losses due to electronically non-adiabatic processes in this particular computational study.

3. Results and discussion

In order to get a first impression of the interaction of O₂ with stepped platinum surfaces, we probe the potential energy surface of O₂/Pt(211) by determining so-called elbow plots [70] and comparing them to previous results for the O₂/Pt(111) system [57] (see Fig. 1). Such elbow plots correspond to two-dimensional cuts through the six-dimensional potential energy surfaces (PESs) as a function of the O₂ center of mass distance from the surface and the O-O distance with the remaining degrees of freedom kept fixed. In Fig. 1, so-called t-b-t geometries have been considered with the O₂ center of mass above a bridge site and the oxygen atoms oriented towards the adjacent top positions in a flat geometry, as illustrated in the insets of Fig. 1. On Pt(211), the O₂ center of mass is directly above the atoms at the upper side of the steps with the molecular axis being parallel to the steps.

The pronounced minima 2 Å above the surface in the O₂ t-b-t geometry with a slightly increased O-O bond length of about 1.8 Å correspond to chemisorbed superoxo-like (O₂⁻) molecular states, as derived from their magnetic moment in previous computational studies [71,72]. Note that the shape of the two PESs is rather similar, however, the depth of the molecular adsorption well differs significantly. Above the step sites, molecular adsorption is about 0.7 eV stronger, confirming the results of previous DFT studies [48,53]. The dissociation channel towards larger O-O distance visible in Fig. 1 does not correspond to the minimum energy path towards dissociation as in the determination of

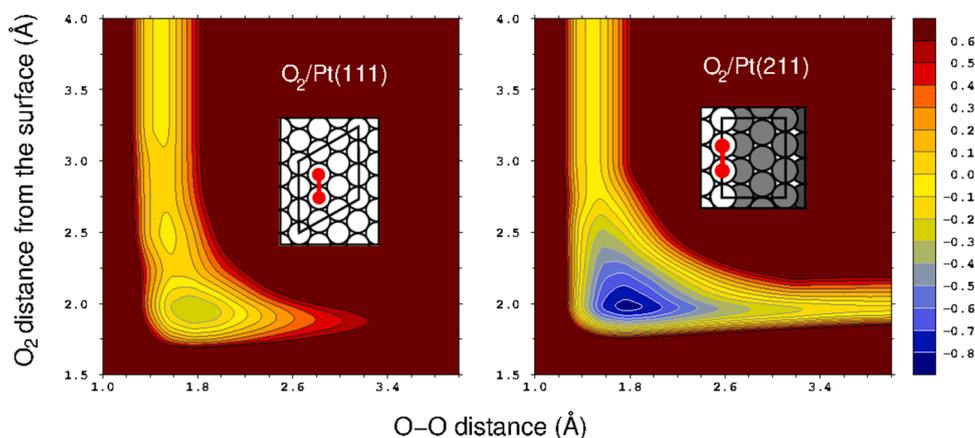


Fig. 1. Two-dimensional cuts through the six-dimensional potential energy surfaces of $O_2/Pt(111)$ and $O_2/Pt(211)$ as a function of the O-O distance and the O_2 center of mass distance from the surface in a t-b-t geometry (see text). The lateral position of the center of mass of the O_2 molecule and its orientation together with the surface unit cell are illustrated in the insets. On Pt(211), the O_2 center of mass is directly above the atoms at the upper side of the steps with the molecular axis being parallel to the steps. The contour spacing is 0.1 eV.

this two-dimensional cut through the multi-dimensional potential energy surface only the O_2 center of mass distance from the surface and the O-O distance were varied whereas in a true determination of the energy minimum path all relevant degrees of freedom need to be relaxed. Still, the configuration of the transition state towards dissociation on Pt(211), as illustrated in Ref. [53], is rather close to the t-b-t geometry used in the determination of the elbow plots. Hence, the calculated results presented in Fig. 1 confirm the previous findings that the barriers for O_2 dissociation taken as the difference between the energy of the transition state towards dissociative adsorption and the bottom of the molecular adsorption well are almost the same on the flat and the stepped Pt surface [48,53].

We now turn to the results of the AIMD simulations of O_2 molecules impinging on Pt(211) and Pt(533). For both surfaces, we have run more than 250 trajectories for each of the two initial kinetic energies $E_{kin} = 0.1$ eV and 0.8 eV with the Pt surface atoms initially at rest which corresponds to an initial surface temperature of $T_s = 0$ K in the microcanonical ensemble. This means that upon impinging on the surface, the

impact of the O_2 molecule on the surface will lead to an energy transfer and a heating up of the surface. Assuming a full transfer of the initial kinetic energy plus the gain from the adsorption energy of about 0.8 eV in the precursor state to the surface and considering the fact that there are 18 moving Pt atoms per surface unit cell of the (211) surface, a maximum temperature rise of about 350 K could be possible. However, as we will see below, within the first 2.5 ps of the AIMD runs, the Pt atoms gained a total kinetic energy of about 0.3 eV corresponding to a temperature rise of about 130 K for the (211) surface. For Pt(211), we have additionally run simulations with an initial surface temperature of $T_s = 140$ K in the microcanonical ensemble, i.e., without invoking any thermostat, and with the Anderson thermostat coupled to the second-layer Pt atoms. This temperature has been chosen as the STM experiments [48] were performed at this temperature. In the calculations within the microcanonical ensemble, there will again be a net energy transfer to the surface upon the O_2 adsorption whereas in the calculations with the Anderson thermostat, the hot spot created upon O_2 adsorption will successively be cooled down. Only the second layer had

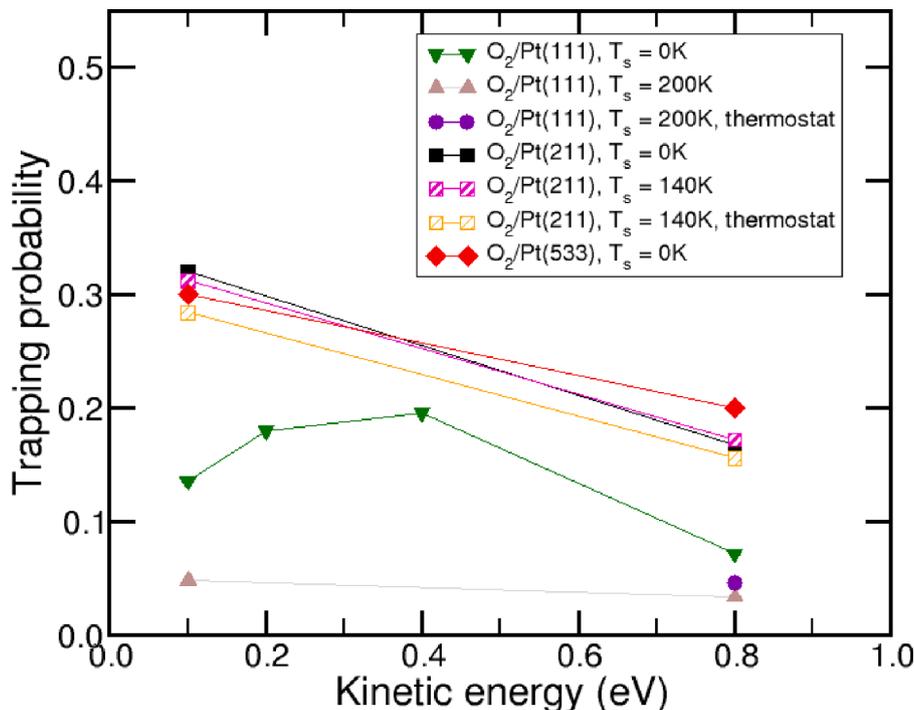


Fig. 2. Trapping probability of O_2 impinging on Pt(111) [57], Pt(211) and Pt(533) as a function of the kinetic energy for normal incidence. Computational results derived from AIMD simulations for the surface initially at rest ($T_s = 0$ K), at initial surface temperatures of $T_s = 200$ K and $T_s = 140$ K, respectively, within the microcanonical ensemble and invoking an Anderson thermostat for the second layer Pt atoms.

been coupled to the thermostat in order to avoid any direct influence of velocity changes due to the thermostat on the adsorption dynamics. The resulting trapping probabilities are plotted in Fig. 2 where we also include the results of AIMD simulations for $O_2/Pt(111)$ [57]. For Pt(111), the simulations at finite temperatures were performed at $T_s = 200$ K as corresponding molecular beam experiments were performed at this temperature [73]. The O_2 molecules were considered to be trapped when after at least 2.5 ps run time of the trajectories they had transferred their initial kinetic energy to their internal and the surface degrees of freedom.

First of all note that the calculated trapping probabilities with and without invoking the thermostat hardly differ. This suggests that the size of the surface unit cells, together with the relatively short run time of the AIMD simulations of less than 3 ps, is obviously sufficient to properly account for the energy dissipation in the surface slabs along the AIMD runs. The trapping probabilities at the stepped Pt surfaces are larger than on the flat Pt(111) surface which is in qualitative agreement with experimentally measured trapping probabilities for O_2 on Pt(533) [47] and Pt(553) [50], confirming the enhanced reactivity of the stepped Pt surfaces compared to Pt(111). Quantitatively, the AIMD results for Pt(533) are lower by almost a factor of two compared to the experiment. This might be a consequence of the fact that the RPBE functional is known to underestimate the interaction of molecules with surfaces, in particular when dispersion effects might play a role [63,74]. Note furthermore that apparently surface temperature effects play only a minor role, as far as the adsorption of O_2 on stepped Pt surfaces is concerned.

In order to better understand the energy dissipation of the O_2 molecule to the Pt substrate, in Fig. 3 the mean kinetic energies of the impinging O_2 molecule with an initial kinetic energy of 0.8 eV and the Pt substrate atoms of Pt(111), Pt(211) and Pt(533), respectively, are plotted along the run time averaged over all corresponding trapping events. The surface atoms were initially at rest corresponding to a surface temperatures of $T_s = 0$ K. Note that these simulations were performed on purpose in the absence of any thermostat because otherwise no reliable determination of the local energy redistribution upon the O_2

adsorption on the considered Pt surfaces would have been possible. The larger O_2 adsorption energies on Pt(211) and Pt(533) compared to Pt(111) are reflected in the fact that there is a larger energy transfer to the Pt atoms. Due to the stronger interaction, the O_2 molecules become more accelerated when impinging on the stepped surfaces and therefore also transfer more energy to the substrate. The energy distributions for Pt(211) and Pt(533) are rather similar. After about 1.5 ps, the mean kinetic energy of the surface atoms levels off at a value of about 0.3 eV. Considering the equipartition theorem which says that the mean kinetic and the mean potential energy should be the same, one can assume that the O_2 molecules have transferred about 0.6 eV to the stepped Pt surfaces. Still, their mean kinetic energy including vibrational and rotational energy and the motion parallel to the surface is about twice as large as on Pt(111), indicating that still a substantial amount of internal energy is associated with the trapped molecules.

Next, we consider the spatial distribution of the trapped O_2 molecules on Pt(211) and on Pt(533) at the end of the trajectories after at least 3 ps which is illustrated for Pt(211) in Fig. 4a for an initial O_2 kinetic energy of 0.1 eV and in Fig. 4b for an initial O_2 kinetic energy of 0.8 eV and for Pt(533) in Fig. 4c for an initial O_2 kinetic energy of 0.8 eV. On Pt(211), independent of their initial kinetic energy, all trapped molecules end up at the step sites. This illustrates that the dissipation to the substrate phonons is slow enough that the impinging molecules can still probe the three-atom wide terraces of Pt(211) and find the energetically most favorable adsorption sites, which is in agreement with experimental observations [48]. Note, however, that on Pt(533) with its four-atom wide terraces, after 3 ps there are still some trapped molecules located in the middle of the terraces, as is illustrated in Fig. 4c. Apparently, these terraces are already too wide to allow all impinging O_2 molecules to directly access the most favorable adsorption sites.

Interestingly enough, about three percent of all O_2 molecules impinging on Pt(211) and Pt(533) at both considered initial kinetic energies lead to dissociative adsorption. In contrast, on Pt(111) no such dissociative O_2 adsorption was found in AIMD simulations [57], in agreement with the experiment [38,39]. Figure 5a illustrates a dissociative adsorption event of an O_2 molecule impinging on Pt(211) with an

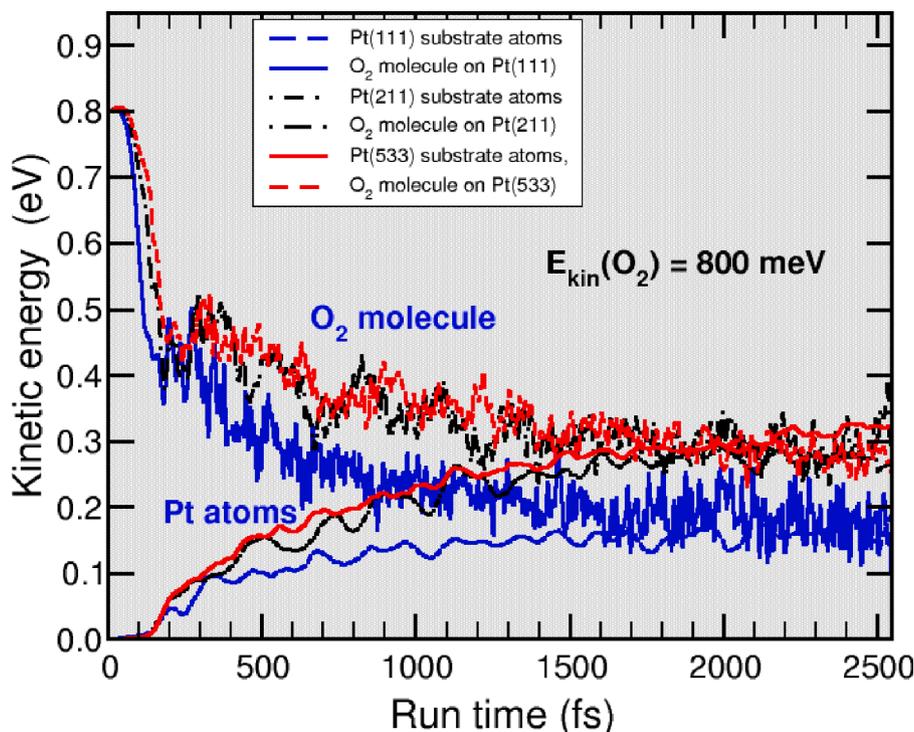


Fig. 3. Kinetic energy redistribution of the O_2 molecule and the Pt substrate atoms of Pt(111), Pt(211) and Pt(533) for an initial O_2 kinetic energy of 800 meV averaged over all adsorption events within the microcanonical ensemble for the Pt surface atoms initially at rest corresponding to a surface temperatures of $T_s = 0$ K.

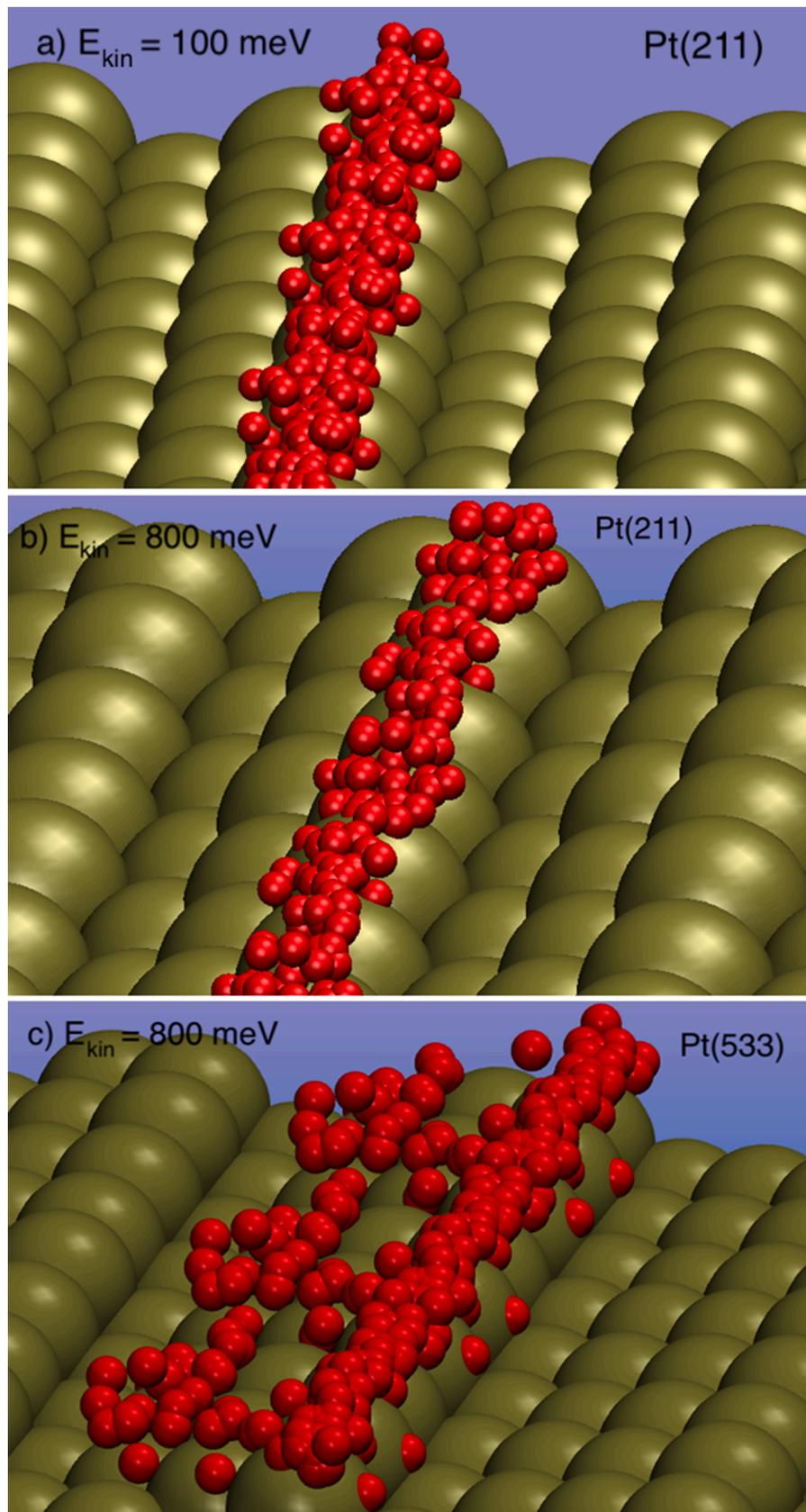


Fig. 4. Spatial distribution of O_2 adsorbed on a,b) Pt(211) and c) Pt(533) after impinging with random impact points within the surface unit cell with initial kinetic energies of the O_2 molecules of a) 100 meV and b,c) 800 meV. Note that the periodic images of the oxygen atoms are not plotted for the sake of clarity.

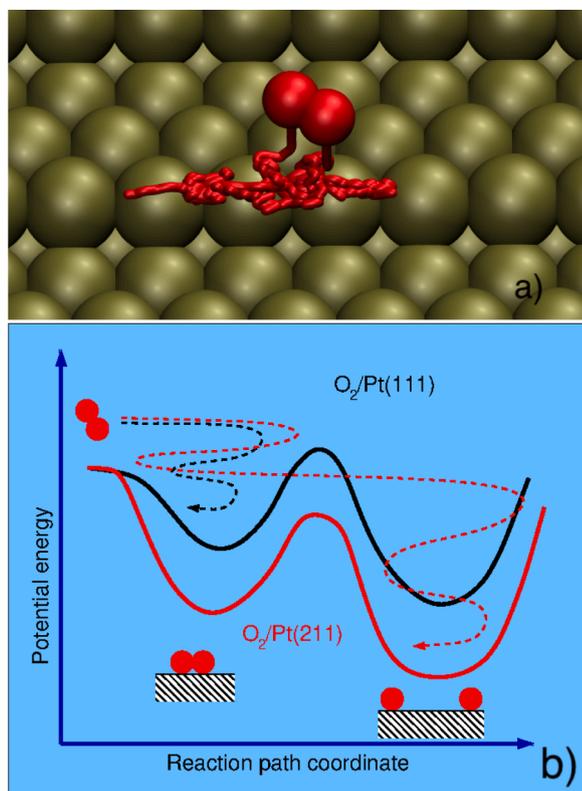


Fig. 5. Dissociative adsorption of O_2 on stepped Pt surfaces. a) Traces of an ab initio molecular dynamics trajectory of an O_2 molecule impinging on Pt(211) with an initial kinetic energy of 0.8 eV. The periodic images of the oxygen atoms are not plotted for the sake of clarity. b) Schematic drawing of the O_2 /Pt potential energy curves illustrating the hot atom mechanism.

initial kinetic energy of 0.8 eV, in particular the dynamical nature of the O_2 molecule trapped in the precursor state prior to dissociation. Upon hitting the Pt(211) surface close to the step edge, the O_2 molecule first reorients, the molecule bounces back and forth and starts to vibrate. Eventually, the molecule enters a configuration that is favorable for dissociation and the O-O bond breaks.

A schematic illustration of this process is provided in Fig. 5b using representative one-dimensional potential curves. Recall that the barrier for dissociation with respect to the molecular precursor state is of similar height on flat and stepped Pt surfaces [48], but the absolute energetic positions of the molecular precursor state and transition state towards dissociative adsorption are higher for Pt(111). Note furthermore that in principle a one-dimensional presentation of the potential energy surface is not sufficient to capture the details of the reaction dynamics. In Fig. 5b, there are two schematic trajectories of an O_2 molecule impinging on Pt(111) (black color) and on a stepped Pt surface such as Pt(211) (red color) included. Both particles are assumed to be scattered back from the activation barrier although their nominal energy is higher than the dissociation barrier. However, their particular configurations as far as, e.g., the molecular orientation or the lateral center-of-mass coordinates are concerned, do not correspond to the molecular configuration at the transition state so that these molecules are both initially scattered back upon the first encounter with the surface.

Still, upon impinging on the surface, the approaching O_2 molecule does not immediately equilibrate in the precursor well, this typically takes several bounces against the repulsive potential walls. With respect to the gas phase level, the absolute barrier for O_2 dissociation is higher on the flat Pt surface compared to the stepped Pt surfaces. Therefore, at the same kinetic energy the O_2 molecule will be much slower upon entering the transition state at Pt(111), and thus it is more likely that it will be redirected towards the molecular precursor state where it then

becomes trapped and eventually equilibrated.

On the stepped surfaces, the topology of the potential energy surface connecting the molecular precursor and the dissociated state might be rather similar. Still, in this region, the potential energy surface is lower in energy with respect to the O_2 molecule in the gas phase. Therefore it will be faster in this region which of course also means that the impact upon hitting potential walls might be larger. Yet, even if it rebounds upon the first impact, it might be redirected again towards the surface and keep enough kinetic energy to be able to finally cross the transition state region and become dissociated. So it is the incomplete equilibration in the region of the molecular precursor state which allows the molecules to remain “hot” and keep enough energy to overcome the dissociation barrier.

Note that the time scale of ab initio molecular dynamics simulations is still much too slow to really model equilibration events. Hence based on this study it cannot be excluded that also thermal equilibration events contribute considerably to the experimentally observed preferential dissociation of O_2 at Pt step sites. Still, the results of this AIMD study provide convincing evidence that a hot precursor mechanism can be operative in the dissociative adsorption of O_2 on stepped Pt surfaces.

4. Conclusions

In this work, I have presented ab initio molecular dynamics simulations of the interaction of O_2 molecules with stepped Pt surfaces. The Pt step sites correspond to active sites due to their lower coordination and attract the O_2 molecules upon impinging on the surface, as found both in experiments and in the AIMD simulations presented here. Interestingly enough, according to density functional theory calculations, the nominal dissociation barriers on Pt surfaces determined as the difference between the transition state towards dissociative adsorption and the bottom of the molecular adsorption well are rather similar on flat and stepped Pt surfaces. Still, in the AIMD simulations some direct O_2 dissociation events are found at the stepped Pt surfaces, whereas on Pt(111) no such event is found, even at kinetic energies that are higher than the barrier for dissociative adsorption of O_2 . The direct dissociative adsorption is caused by the overall more attractive O_2 potential energy surface at the stepped surfaces which can lead to an incomplete equilibration of the O_2 molecule upon entering the molecular precursor state so that the hot precursor molecule is still able to overcome the activation barrier for dissociative adsorption. The presence of this hot atom chemistry does, however, not preclude that there are also thermally activated O_2 dissociation events at the stepped surfaces.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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