

Mechanism of associative oxygen desorption from Pt(111) surface

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Abstract. Mechanism of the associative desorption of oxygen from the Pt(111) surface has been studied on atomic level by means of DFT/GGA calculations and kinetic Monte Carlo simulations. It has been found that two oxygen adatoms can occur, with sufficient probability, in neighboring on-top sites, which is essential for formation and subsequent evaporation of the oxygen molecule. Monte Carlo simulations have demonstrated effectiveness of this channel for O₂ formation on Pt(111) and strongly support the suggested model of associative desorption from transition metal surfaces.

PACS. 68.43.Mn Adsorption/desorption kinetics – 68.43.-h Chemisorption/physisorption: adsorbates on surfaces – 68.35.Bs Structure of clean surfaces (reconstruction) – 71.15.-m Methods of electronic structure calculations

1 Introduction

Adsorption and desorption of oxygen on transition metal surfaces play an important role in many surface phenomena such as corrosion and various chemical reactions. In particular, oxygen adsorption is the limiting stage of the reaction of CO catalytic oxidation on Pt(111) surface, which, due to its practical importance, has been a focus of interest for several decades. Among various substrates, the (111) surfaces of fcc transition metals are the most suitable for experimental studies of kinetics of oxygen adsorption, structures of both molecular and atomic oxygen layers [1–10], in large part, due to close packed structures of these surfaces which provide their high stability with regard to possible adsorption-induced surface reconstruction [11–14].

At low temperatures (below 150 K [7]) oxygen on the Pt(111) surface adsorbs in the O₂ molecular form. The molecular adsorption can be considered as an intermediate stage (“intrinsic precursor state”) for subsequent dissociative chemisorption, which requires some activation energy [7, 15–19]. It is well established that from the Pt(111) surface oxygen desorbs in the molecular state [7]. Corresponding TPD (temperature programmed desorption) peaks appear at ~700 K for Pt(111) [6, 7, 20].

Associative desorption requires reunion of two atoms, which seems quite improbable both right on the surface and far from the surface. Indeed, should the two oxygen atoms on the surface occur sufficiently close to each other to form the molecular bond, they would immediately

dissociate back because of the influence of the substrate electrons. On the other hand, far from the surface, evaporated oxygen atoms hardly would find each other to form a molecule. Hence, there must be a narrow region near the surface where the association is possible.

To build-up an atomistic model of associative desorption, detailed first-principles calculations of energies of interactions between the atoms and surface as well as between the gas atoms are required. Such calculations for hydrogen on the Mo(110) surface [21] have revealed a narrow range of distances from the surface, about 0.5 Å, favorable for association of the hydrogen atoms. Results of Monte Carlo simulations of TPD spectra with energy parameters obtained by DFT calculations have been in agreement with experiment, thus confirming the validity of the suggested model.

The properties of chemisorbed oxygen layers on transition metal surfaces significantly differ from hydrogen adlayers, in particular, because of a strong repulsive lateral interaction between oxygen adatoms [22]. The lateral interaction can be considered as a superposition of a dipole-dipole and indirect interactions [23–25] and results in forming (2×2)O structure at saturating 0.25 coverage on Pt(111) [22]. The atomistic model of CO oxidation [13] suggests that formation of the CO₂ molecule is accomplished right on the surface and only with those oxygen adatoms which occupy hcp threefold hollow sites. It is therefore not clear, on the atomic point of view, how the reaction of formation of the oxygen molecule on the Pt(111) surface will go. In particular, the aim of the present study is to obtain a consistent picture of the associative oxygen desorption by using the methods

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(DFT repeat-slab calculations and Monte Carlo simulations) and models successfully applied previously to the H/Mo(110) [21] and (CO+O)/Pt(111) [13] systems.

1.1 Method of calculations and binding energies for O atoms on Pt(111)

The DFT semirelativistic calculations of total energies and related favorable structures, using the repeat-slab model to maintain periodicity in the direction normal to the surface, were carried out with ABINIT code [26], using Troullier-Martins (TM) norm-conserving pseudopotentials [27], $4 \times 4 \times 1$ Monkhorst-Pack [28] set of special k -points, and generalized gradient approximation (GGA) in Perdew-Burke-Ernzerhof form [29] for the exchange-correlation. The O atoms were adsorbed in various sites on one side of the slab. The positions of the oxygen atoms and substrate atoms in the topmost surface layers were optimized until the forces on atoms converged to less than 0.02 eV/\AA . The vacuum gap was about the thickness of the slab. The surface unit cell for the Pt(111), used in the calculations of oxygen desorption, and three considered configurations of oxygen molecules are shown in Figure 1.

Oxygen is known as a “difficult case” in pseudopotential calculations [13, 14, 30, 31] because of slow convergence of the total energy with regard to the number of plane waves included in the basis set. Thus, while the 1×10^{-3} Hartree (0.027 eV) convergence in bulk calculations with the TM potentials for Pt was readily achieved with energy cutoff 20 Hartree (40 Ry) (giving also the equilibrium lattice constant of 3.96 \AA , in reasonable agreement with 3.92 \AA experimental value), obtaining of well-converged values of total energy for oxygen molecule and for the O/Pt(111) adsorption system required a relatively high energy cutoff 36 Hartree. It should be noted that convergence of 0.01 \AA with regard to the bondlength in the oxygen molecule (1.20 \AA , consistent with experimental value 1.21 \AA [32]) was achieved already with 20 Hartree cutoff.

The binding energy E_b (positive) between an oxygen atom and a substrate can be defined as the difference of total energies of the system in initial and final states, i.e. of Pt(111) with adsorbed oxygen and of the separated substrate and (desorbed) oxygen atom:

$$-E_b = E_{\text{Pt+O}} - E_{\text{O}} - E_{\text{Pt}}, \quad (1)$$

where $E_{\text{Pt+O}}$ is the total energy of the system of 5 Pt layers and adsorbed atomic oxygen, E_{O} is the total energy of the oxygen atom, and E_{Pt} is the total energy of the substrate. To evaluate the binding energy, calculations of the total energies were performed for 5-layer slabs of Pt(111), covered with $(2 \times 2)\text{O}$ layer, and for a clean surface. Optimization of the surface and the next to the surface atomic layers resembles surface relaxation and therefore allows for determination of the energies of the substrates in the final states.

Estimation of the energy of O atoms is not a trivial task [13, 32] and deserves some comments. The problem with correct evaluation of the energy of oxygen atom

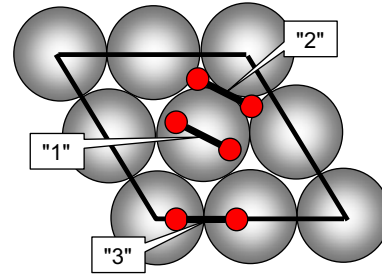


Fig. 1. The surface unit cell for the Pt(111), used in the calculations and three considered configurations of oxygen molecules: “1” – hollow-top-hollow’ “2” – hollow-bridge-hollow, and “3” – top-bridge-top.

as well as with related binding energy in O₂ molecule in plane-wave calculations occurs mainly because of a triplet ground state of the O atom. This feature requires spin-polarized calculations for oxygen atoms “in a big box”, which implies either ferromagnetic or antiferromagnetic state of the model crystal. Thus, without account for spin polarization, pseudopotential calculations give an unphysical value of the binding energy in O₂ molecule (about 9 eV). In contrast, while the energy of the O₂ molecule formed by two oxygen atoms with opposite initial spins is equal to that calculated for non-polarized molecule, step-by-step increase of the interatomic distance (Fig. 1) ends in two separate O atoms in triplet state and very reasonable esteem of the binding energy (5.33 eV , consistent with both experimental value 5.1256 eV and results of other calculations ($E_{\text{bind}} = 5.918\text{--}6.29 \text{ eV}$) [32]). (To avoid these problems, Kiejna and Nieminen [33] suggested evaluation of the O atom energy as one-half of the energy of O₂ molecule; alternatively, the adsorption energy can be estimated by calculations for the O layer “evaporated” to the middle of the vacuum gap [34]).

Oxygen adatoms on the Pt(111) surface tend to occupy fcc threefold hollow sites [12, 13]. Then, the adsorption energy for oxygen in these sites, neglecting lateral interactions, can be readily estimated using O atom energy determined in the course of the O₂ dissociation. For O in the fcc sites on Pt(111) thus derived binding energy is of 3.7 eV . Hence, while thermodesorption of oxygen atoms from Pt(111) seems, in principle, possible (if for some reason the oxygen atoms cannot unite), it definitely may be ruled out because of unrealistic temperatures required to break the strong adsorption bonding. In contrast, the energy required for an associative desorption decreases to some 2.1 eV (evaporation of two oxygen atoms minus the gain due to formation of the molecule), which is consistent with position of the peak in TPD spectra at approximately 700 K [6, 7].

Oxygen adsorption apparently removes the inward relaxation of the clean Pt(111) surface (about 0.5% [13]), approximately restoring the bulk interlayer spacing (2.26 \AA). The surface relaxation and binding energies are largely independent on the thickness of the substrate slab. This means that electronic structure of the Pt(111) surface, due to quite effective screening, can be well reproduced

already with an unrelaxed 3-layer slab, which was used for purposes of search of possible paths of the association of oxygen atoms. The choice of the 2×2 rhombic surface unit cell, shown in Figure 1, allows for a convenient description of probable ways of the reaction.

1.2 Results and discussion

It is reasonable to search for probable ways of the association starting from favorable positions and orientations of adsorbed oxygen molecules. There are several symmetric orientations of the O_2 molecular adsorption on the Pt(111) surface which can serve as possible precursor states for dissociative adsorption [15]. Following notations suggested by Eichler and Hafner [15], symmetric orientations of the molecules with regard to the surface cell, adopted in present work, can be described as hollow-top-hollow, hollow-bridge-hollow, and top-bridge-top (Fig. 1). These three configurations have been investigated with respect of dependencies of potential energies on distances between oxygen atoms d_{O-O} for several distances z from the surface ($z = 0$ corresponds to the plane passing through centers of the surface atoms). Potential energy plots, presented in Figure 2, were calculated with regard to the energy of the system for a free oxygen molecule sufficiently far from the surface (zero of the energy scale).

For configuration “1” (hollow-top-hollow), association of the atoms into a molecule is possible only when the atoms find each other at the distances from the surface more than $z = 2.0 \text{ \AA}$ (Fig. 2a). The optimal distance between oxygen atoms in this state is found to be of 1.4 \AA . This distance somewhat exceeds the bondlength in a free oxygen molecule, which can be explained by the influence of the surface onto the binding electrons. At lower z , repulsion between O atoms unavoidably will result in dissociation (see the curve for $z = 1.5 \text{ \AA}$ in Fig. 2a).

For configuration “2” (hollow-bridge-hollow), situation is quite similar (Fig. 2b). Equilibrium distance between oxygen atoms in the molecule at $z = 2.5 \text{ \AA}$ is of 1.28 \AA , and with decreasing distance from the surface, the molecule will dissociate with subsequent chemisorption of O atoms. As well as in configuration “1”, to form a molecule, oxygen atoms have to be moved away from the surface for nearly 2 \AA , which requires significant amount of energy, about 3.8 eV per atom (with regard to the energy of the system with oxygen atoms in fcc adsorption sites). Hence, configurations “1” and “2” hardly could serve as probable channels for the associative desorption of oxygen from the Pt(111) surface. Furthermore, formation of the molecule would require simultaneous excitations of oxygen atoms to appear sufficiently close to each other at the distance $z = 2 \text{ \AA}$ from the surface, which makes these ways of desorption unrealistic.

The interaction between oxygen atoms in configuration “3” (top-bridge-top) turns out to be significantly different (Fig. 2c). Indeed, attraction between the adatoms appears already for $z = 1.75 \text{ \AA}$ and, the most important, holds also for distances between oxygen atoms up to 2.19 \AA that is the distance between Pt atoms of the Pt(111) surface.

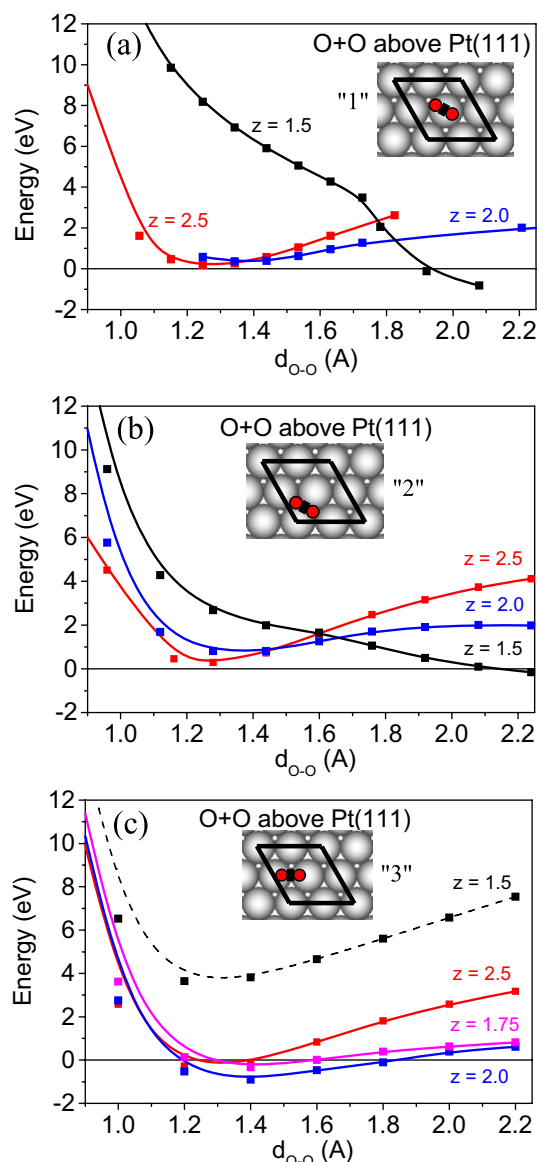


Fig. 2. Potential energy of oxygen molecule at various distances z from the Pt(111) surface: (a) for the hollow-top-hollow (“1”), (b) hollow-bridge-hollow (“2”), and (c) for the top-bridge-top (“3”) configurations. Zero on the energy scale corresponds to the energy of the system for a free oxygen molecule sufficiently far from the surface.

This configuration of oxygen molecule is found to be the most favorable (in agreement with results of calculations by Eichler and Hafner [15] and Gross et al. [17]). The distance from the surface for equilibrated molecule is 1.9 \AA , and the bondlength in the molecule is of 1.38 \AA .

It is worth noting that for oxygen molecules at 2.5 \AA from the surface, the dependence of the energy on the distance between oxygen atoms is about the same for all configurations. However, for lower z , the plots are remarkably different. In particular, for the molecule in configuration “3”, the $z = 2.0 \text{ \AA}$ distance is favorable (by 0.8 eV), and though decrease of z will cause increase of

total energy (which means repulsion from the surface), the molecule will not dissociate. This is evident from the increase of energy with increasing distance between O atoms at all z (Fig. 2c). This feature makes configuration “3” (top-bridge-top) the most probable for association of oxygen atoms, which is the limiting stage of the desorption process from the surface.

The most important feature of the plots, presented in Figure 2, is that they allow for a natural assumption of a “precursor state” for the association of oxygen atoms in molecule. Namely, on-top sites can be good candidates for such states of oxygen adatoms. It should be noted also that oxygen atoms can be equilibrated in on-top sites on Pt(111), which implies a metastable state of the O adatoms in these sites. Though the position of adsorbed oxygen atoms atop of Pt atoms is less favorable than in hollows and therefore at low temperatures all O atoms will occupy threefold fcc sites, at higher temperatures some of atoms can move to the on-top sites. The calculated barrier for diffusion step from fcc site to on-top site is of 1.36 eV, and the optimized length of the Pt–O bond in on-top configuration is of 1.9 Å, which is approximately the same as z for the equilibrated O₂ molecule in configuration “3”. Hence, the most favorable channel for O₂ formation on Pt(111) should be as follows. First, due to thermal excitations, some of O atoms get moved to on-top sites. Because of the nearly zero lateral interaction between the atoms in on-top sites they can occur in the nearest neighbor on-top sites. Second, should the atoms be slightly shifted from the on-top sites, they will approach each other due to lateral attraction, as evident from the potential plot for $z = 2.0$ Å in Figure 2c.

The course of formation of the molecule can be illustrated by contour maps of calculated distributions of the electronic density in the normal plane drawn through the oxygen atoms (Fig. 3). The distributions shown in Figure 3 have been obtained by means of the “cold” Broyden optimization (that is, oxygen atoms were allowed to move by the action of forces estimated from the gradients of the potential energy). Starting position (Fig. 3a) corresponds to oxygen atoms, slightly shifted from on-top sites. In the course of optimization, O atoms move towards each other until the molecule is formed (Fig. 3c). Desorption of the formed molecule requires some ~ 0.8 eV energy, and distributions of electron density, shown in Figures 3d–3f, were obtained by optimization of the bondlength d_{O-O} for fixed distances z from the surface.

The suggested way of association of oxygen atoms into O₂ molecule on Pt(111) might seem rather improbable. Indeed, there is a strong repulsion between adsorbed O atoms [22], which results in the formation of (2×2) structures at saturation coverage $\theta = 0.25$, while the model implies that two O adatoms occur in the neighboring on-top sites. Nonetheless, as we show by Monte Carlo simulations, in fact this channel of the net process of associative desorption is very realistic.

For modelling oxygen desorption from Pt(111), we used our set of advanced Monte Carlo programs, verified in CO/Pt(111) adsorption and structures formation [22] as

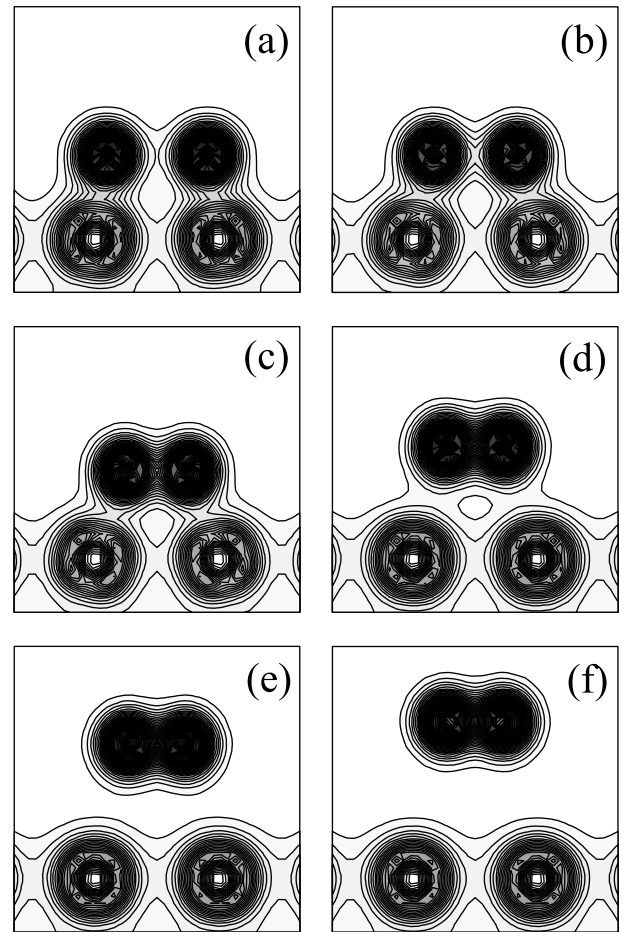


Fig. 3. Contour maps of distributions of electronic density as a function of distance between oxygen atoms in the top-bridge-top configuration on the Pt(111) surface, shown in the normal plane containing the oxygen atoms.

well as in simulations of kinetics of dissociative hydrogen adsorption on the W(110) and Mo(110) surfaces [18]. Details of the method, which explores the standard Metropolis algorithm for the lattice gas model [35,36] and includes account for long-range dipole-dipole and indirect interactions between adsorbed particles, were given elsewhere [19,22,37–39]. Below we describe features specific for the associative oxygen desorption.

The rearrangement of particles (“surface diffusion”) is performed by movements (“jumps”) of randomly chosen adatoms to neighboring sites. The probability of a jump, $\exp(-\Delta E/kT)$, depends on the difference of energies ΔE of lateral interaction with other adsorbed particles for the initial and final configurations and on the activation energy for diffusion. When the jump leads to a gain in energy ($\Delta E < 0$) or estimated probability exceeds a random number, the jump is accomplished. Otherwise the attempt of the jump is failed and the particle remains at the original site.

For the simulation of the suggested way of associative oxygen desorption, three types of adsorption sites have been included in the lattice, namely, threefold fcc,

threefold hcp, and on-top sites. These sites are distinct by binding energies, as estimated from DFT calculations. Specifically, difference in oxygen binding energies between hcp and fcc threefold hollow sites is of 0.52 eV and between on-top and fcc hollow site is of 1.36 eV. These energy barriers, together with lateral interaction, control distribution of oxygen atoms and relative occupation of the sites. Therefore they have been added to ΔE , which determines probability of a random jump to the neighboring site.

Modeling of the TPD spectra was conducted using a routine algorithm [18, 19, 37, 40–42] with a stepwise 5° increase of temperature. Actual rate of increasing temperature is simulated by adapting the number of diffusion attempts for oxygen atoms at each temperature step. Then, the rate of associative desorption is determined as the number of the O_2 molecules evaporated at given temperature per second. In the model, probability of desorption can be readily estimated if we assume that occurrence of two oxygen atoms in the nearest neighboring on-top sites is sufficient for desorption. Thus, the probability of desorption of a molecule per second can be presented as $W = \nu \exp(-E_{des}/kT)$ with the desorption energy E_{des} substituted by the energy required for excitation of an O atom to an on-top site, with additional requirement of existence of the previously excited atom in a neighboring on-top site.

TPD spectra and corresponding typical snapshots, obtained in the course of simulations of the oxygen thermodesorption from Pt(111), are shown in Figure 4. At temperatures below 600 K all oxygen atoms move over the threefold sites, while at higher temperature some of them appear in on-top sites. Occasionally, they can occur in the neighboring on-top sites and desorb from the surface. This mechanism is found to be surprisingly efficient, and, with calculated 1.36 eV energy of excitation of O atoms from fcc threefold to on-top sites, to adjust the temperature corresponding to the main peak in simulated spectra to experimental temperature 700 K [7], the frequency factor ν has to be taken about 10^9 s^{-1} . Alternatively, with $\nu = 10^{13} \text{ s}^{-1}$ (which can be attributed to typical oscillations of chemisorbed O atoms) the proper peak position was achieved with 2.0 eV activation energy. This value is consistent with 2.1 eV adsorption energy, estimated from binding energies between oxygen atoms in the molecule and between oxygen adatoms and Pt(111) surface (see Sect. 2). On the other hand, the net energy of evaporation can be estimated as a sum of excitations of two O atoms from fcc threefold sites to on-top sites, which leads to formation of the precursor state with energy that for 0.6 eV exceeds the energy of the system with evaporated oxygen molecule (see Fig. 2c). Again, in perfect agreement with evaluation from calculated binding energies, this gives $E_{des} = 2 \times 1.36 - 0.6 = 2.1 \text{ eV}$.

As follows from Monte Carlo simulations, the high-temperature shoulder on the main peak of TPD spectra for O/Pt(111) strongly depends on the strength of the lateral interaction between adatoms and related heights of barriers for surface diffusion. With increasing energy of the lateral repulsion between O adatoms, the probability

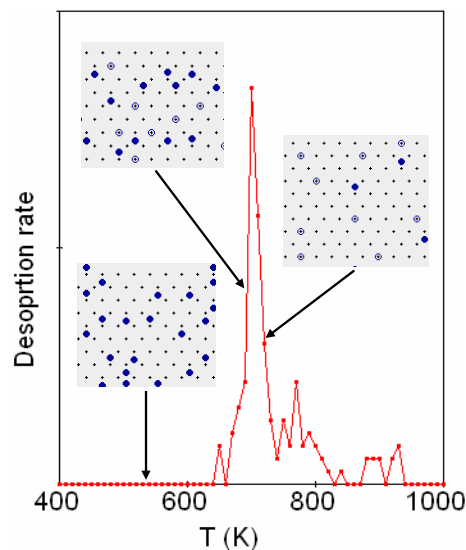


Fig. 4. TPD spectra and typical snapshots, obtained in the course of simulations of oxygen thermodesorption from Pt(111). Dots denote on-top sites on the surface, filled and open circles stand for O atoms in the threefold sites and on-top sites, respectively.

of the jump from on-top sites to fcc sites decreases, which can lead to decrease of the diffusion rate. In particular, the probability for two oxygen atoms to appear in neighboring on-top sites decreases, which results in the changing shape of the desorption peak.

2 Conclusion

We have suggested a model for the associative oxygen thermodesorption from Pt(111) implying that two oxygen adatoms can occur in neighboring on-top sites, which is an almost sufficient prerequisite for the formation and subsequent evaporation of oxygen molecules. Though this channel of thermodesorption may not be unique, it is nonetheless quite probable due to lateral attraction which appears between oxygen adatoms excited to the on-top sites. Kinetic Monte Carlo simulations support the effectiveness of the suggested mechanism of associative desorption of oxygen from transition metal surfaces.

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