

ReaxFF Grand Canonical Monte Carlo simulation of adsorption and dissociation of oxygen on platinum (111)

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ABSTRACT

Atomic-level Grand Canonical Monte Carlo (GCMC) simulations equipped with a reactive force field (ReaxFF) are used to study atomic oxygen adsorption on a Pt(111) surface. The off-lattice GCMC calculations presented here rely solely on the interatomic potential and do not necessitate the pre-computation of surface adlayer structures and their interpolation. As such, they provide a predictive description of adsorbate phases. In this study, validation is obtained with experimental evidence (steric heats of adsorption and isotherms) as well as DFT-based state diagrams available in the literature. The ReaxFF computed steric heats of adsorption agree well with experimental data, and this study clearly shows that indirect dissociative adsorption of O₂ on Pt(111) is an activated process at non-zero coverages, with an activation energy that monotonically increases with coverage. At a coverage of 0.25 ML, a highly ordered p(2×2) adlayer is found, in agreement with several low-energy electron diffraction observations. Isotherms obtained from the GCMC simulations compare qualitatively and quantitatively well with previous DFT-based state diagrams, but are in disagreement with the experimental data sets available. ReaxFF GCMC simulations at very high coverages show that O atoms prefer to bind in fcc hollow sites, at least up to 0.8 ML considered in the present work. At moderate coverages, little to no disorder appears in the Pt lattice. At high coverages, some Pt atoms markedly protrude out of the surface plane. This observation is in qualitative agreement with recent STM images of an oxygen covered Pt surface. The use of the GCMC technique based on a transferable potential is particularly valuable to produce more realistic systems (adsorbent and adsorbate) to be used in subsequent dynamical simulations (Molecular Dynamics) to address recombination reactions (via either Eley–Rideal or Langmuir–Hinshelwood mechanisms) on variously covered surfaces. By using GCMC and Molecular Dynamics simulations, the ReaxFF force field can be a valuable tool for understanding heterogeneous catalysis on a solid surface. Finally, the use of a reactive potential is a necessary requirement to investigate problems where dissociative adsorption occurs, as typical of many important catalytic processes.

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1. Introduction

The behavior of a solid catalyst may drastically change depending on the state of its surface. For example, the degree of surface coverage or oxidation may significantly reduce its catalytic performance, since the pure metal and its oxide typically show different reactive properties. Adsorbates may also induce significant surface restructuring, with a consequent change of the chemisorptive behavior of the catalyst. Therefore, it is particularly important to relate the surface coverage phases to the thermodynamic state of the surrounding gas, and their interactions with reactant and product molecules. This is essential to develop an understanding of surface reactivity.

The importance of platinum in surface science and catalysis has motivated numerous studies to characterize its interactions with oxygen. Despite this, several questions on the nature of the adsorbed

oxygen phases remain open. Although there is a reasonable understanding of O adlayers at $\theta \leq 0.25$ ML (1 ML is the surface density of top metal atoms, $\approx 1.51 \times 10^{19}$ atoms/m²), less is known on the exact nature of coverages above 0.25 ML. The progressive fading of the (2×2) low-energy electron diffraction (LEED) signal [1] has been interpreted by the formation of a honeycomb structure with atoms also occupying hcp sites [2], not supported by DFT calculations (e.g., Ref. [3]). Another possibility is that local restructuring in the form of Pt adatoms, induced by O atoms at coverages larger than 0.25, would disrupt the p(2×2) domains, thus attenuating the LEED signal [4]. More recently, STM imaging has revealed that atomic-scale protrusions begin to develop within p(2×1) domains at coverages as low as 0.4 at 450 K [5].

Knowledge of the surface state is crucial to understand recombination processes, occurring through an Eley–Rideal or a Langmuir–Hinshelwood mechanism. In this paper, we used all-atom ReaxFF Grand Canonical Monte Carlo (GCMC) simulations to study oxygen coverage on Pt(111) under various O₂ pressure and temperature conditions. GCMC is a simulation technique [6] designed to study adsorption. Because the sorptive substrate is modeled at the atomic level and binding sites are not

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pre-defined, the GCMC technique allows a more realistic description of the adsorbate, under a wide range of pressure and temperature conditions.

Previous numerical simulations have been restricted to kinetic Monte Carlo (kMC) techniques [7–10], which have provided numerous insights on the nature of O adlayers on Pt(111). Lattice-gas simulations do, however, assume a pre-specified list of transitions (and the associated probabilities or activation energies) and often a fixed substrate lattice. As such, they can be regarded as coarse-grained atomistic models. This somewhat restricts their applicability to problems characterized by a low surface coverage (<0.25 ML), as the assumption of a regular substrate lattice is likely to be less accurate at higher coverages [5].

In contrast to kMC schemes, our approach is to use a transferable classical interatomic potential within GCMC simulations, without relying on a pre-defined list of events. The force field parametrization used in this work could straight-forwardly be used in other Molecular Dynamics simulations. For example, one could perform a state-to-state classical trajectory study (similarly to Refs. [11,12]) of Eley–Rideal (E–R) O recombination on Pt(111), once the surface coverage has been determined using GCMC simulations.

Here, we briefly summarize the main experimental findings. LEED experiments have clearly indicated that oxygen atoms form a $p(2 \times 2)$ adlayer (shown in Fig. 1(a)) on a surface exposed to O_2 at ultra-high vacuum (UHV) conditions ($<10^{-6}$ Pa) and temperatures above ≈ 150 K [1,13–18].

The extremely rapid drop of the probability of O_2 dissociative chemisorption with increasing surface coverage [10,19,13,14] makes the adsorbing of higher concentrations of atomic oxygen impractical at typical O_2 fluxes (≈ 0.01 ML/s) used in UHV experiments [4]. More aggressive strategies must then be adopted to produce coverages above

1/4 ML. For example, by using NO_2 in UHV and heating the surface to 500 K to desorb NO, coverages up to 0.75 ML were obtained [15]. Ozone is an even stronger molecular oxidant than NO_2 and it has been used to produce oxygen coverages significantly larger than 0.25 ML [20]. More recently, large oxygen coverages have been obtained by Weaver et al. [4,21,5] using a partially dissociated O_2 beam.

Analysis of temperature programmed desorption (TPD) spectra has revealed a single broad peak at around 450 K for coverages up to 0.25 ML [4,21,14,15,13]. At larger coverages, two additional features appear in the TPD spectra, centered at around 560 K and 650 K. These, however, are poorly characterized. In fact, the LEED (2×2) pattern persists up to coverages of 0.5 ML [1], although faded. This appears to be consistent with an adlayer structure where O atoms occupy both fcc and hcp hollow sites, forming a honeycomb structure [2]. Such a picture was supported by a recent TPD study [2] using a combination of labeled O_2 molecules ($^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$).

At higher coverages $\theta > 0.25$ ML, oxygen atoms are more weakly bound to the Pt surface, and therefore they desorb associatively more readily than at lower coverages ($\theta \leq 0.25$ ML). Experimentally, the desorption energy Q^{st} has been estimated to be around 51 kcal/mol in the limit of zero coverage, dropping to 41 kcal/mol at $\theta = 0.25$ ML [15]. The study of Campbell et al. [13] reports $Q^{st} = 51$ kcal/mol at $\theta = 0$ ML and $Q^{st} = 42$ kcal/mol at $\theta = 0.25$ ML. A somewhat larger $Q^{st} = 55$ kcal/mol is measured from adsorption isotherms by Derry and Ross [19], although the scatter in the data masked the dependence of Q^{st} on θ . Markedly larger is the desorption energy from calorimetric measurements of Yeo et al. [10]: the initial desorption heat was found to be around 73 kcal/mol, which rapidly dropped to a saturation value around 36 kcal/mol at $\theta \geq 0.25$ ML. This implies a drop of around 150 kcal/(mol ML), i.e., almost a 4-fold increase compared to 40 kcal/(mol ML) deduced from the experimental evidence of Parker et al. [15] and the value of 30 kcal/(mol ML) used in the Monte Carlo simulations of Zhdanov and Kasemo [7]. Yeo et al. [10] suggest that the rapid decrease of Q^{st} with increasing θ is due to saturation of defect sites, such as steps.

The variation of Q^{st} with surface coverage provides information on the lateral interaction energy between oxygen atoms on the surface. All experimental studies (e.g., Ref. [15]) report that $\partial Q^{st}/\partial \theta < 0$ for $\theta < 0.25$ ML. This suggests that adsorbed oxygen atoms repel each other. The magnitude of such a repulsion has not been clearly determined though. The first nearest-neighbor (i.e., at one fcc separation a_{NN}) repulsion energy ϵ_1 (relative to two isolated adatoms O(s), see Fig. 1(b)) has been computed with ab initio calculations in various papers. Han et al. [22] report ≈ 0.9 kcal/mol, evaluated in the generalized gradient approximation (GGA) to density functional theory (DFT) with the Perdew–Wang exchange correlation functional, with a projector augmented wave (PAW) pseudopotentials method (as implemented in VASP). Tang and co-workers [23,24] state that $\epsilon_1 = 5.5$ kcal/mol, obtained with GGA–DFT equipped with the PW91 exchange correlation functional and ultrasoft pseudopotentials, using the DACAPO software. In Getman et al. [3], $\epsilon_1 = 4.7$ kcal/mol is obtained with DFT calculations with the supercell plane-wave basis approach contained in the VASP code. The PAW method and the PW91 electron exchange correlation functional were used. More recently, Wang [25] presents very similar computations to those of Getman et al. and finds $\epsilon_1 \approx 3$ kcal/mol.

The interaction energy ϵ_2 at $\sqrt{3}a_{NN}$ (i.e., second nearest-neighbor distance) is also repulsive: ≈ 0.3 kcal/mol (Han et al., [22]), ≈ 0.9 kcal/mol (Tang et al., [23]), ≈ 2.3 kcal/mol (Getman et al., [3]), 0.23 kcal/mol (Wang, [25]).

There is more controversy about the interaction energy ϵ_3 at two fcc separations $2a_{NN}$ (i.e., third nearest-neighbor distance), which is mainly attributed to lattice distortions induced by the adsorbed oxygen atoms [3,26,24]. The magnitude and sign of ϵ_3 should be responsible for the $p(2 \times 2)$ arrangement ($\theta = 0.25$ ML), which is indeed characterized by adsorbed O atoms spaced by 2 fcc separations (Fig. 1(b)). Some studies found that $\epsilon_3 > 0$, ranging from 0.1 kcal/mol [22] to 0.2 kcal/mol [3]. Yeo et al. report $\epsilon_3 \approx 5$ kcal/mol (although this value is deduced from the

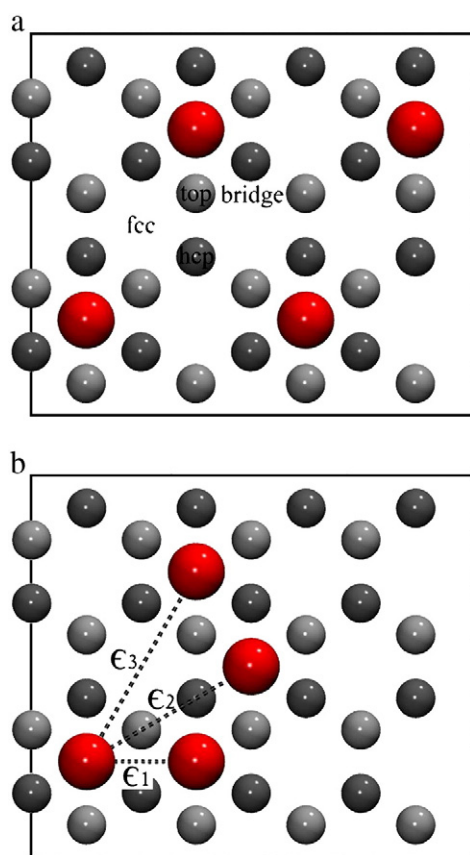


Fig. 1. (a) Oxygen adlayer on Pt(111). O atoms (in red) are arranged in a $p(2 \times 2)$ structure. The other most relevant adsorption sites are also indicated. (b) Geometry of 1st, 2nd, and 3rd fcc nearest O(s) on a Pt(111) surface. Light gray atoms occupy the top-most layer, whereas dark gray ones the underlying layer.

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