



Interaction of oxygen with the Pt(1 1 1) surface in wide conditions range. A DFT-based thermodynamical simulation

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Abstract

We present the results of ab initio calculations of oxygen atomic adsorption in a wide range of coverage on Pt(1 1 1). At $\theta = 0.25$ ML, the O adsorption at fcc hollow site is clearly favoured over the hcp site. At $\theta = 0.5$ ML, the O adsorption energy decreases but the same site is favoured. When experimental or theoretical previously reported data are available, the calculated adsorption energies and site preferences are in good agreement. Among the various configurations and coverages investigated in the present work, no adsorption is stable beyond $\theta = 0.5$ ML, except by occupation of a subsurface tetrahedral site. In that case, a total O coverage of 0.75 ML could be achieved, which is only slightly less stable than the $\theta = 0.5$ ML configuration.

The use of thermodynamics permitted to explore the temperature–pressure stability domain corresponding to 0.25 ML, 0.5 ML and 0.75 ML. From this, we conclude that subsurface O species could be stable at temperatures lower than 700 K, with O₂ pressures of 1 bar or less.

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1. Introduction

The interaction of O₂ with Pt(1 1 1) has been explored for long by many investigators using many surface techniques. It is known that a molecular adsorption takes place at low exposure below

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120 K. Above this temperature, the molecule dissociates and an ordered (2×2) structure is formed with a 0.25 monolayer (ML) coverage (θ) where the O atoms occupy the fcc hollow sites [1–3]. The initial heat of adsorption was measured to be 1.76 eV with respect to $\frac{1}{2}\text{O}_2$ decreasing to ~ 0.88 eV and ~ 0.68 eV at coverages of 0.25 ML and 0.5 ML respectively [4]. These experimental results were confirmed by recent density functional theory (DFT) studies. Eichler et al. [5] calculated an adsorption energy of 0.83 eV in the fcc hollow site and 0.49 eV in the hcp site at an atomic O coverage of 0.5 ML. The same site-preference was reported by Sljivancanin and Hammer [6], with a dissociative adsorption energy of 0.7 eV at the fcc site at $\theta = 0.5$ ML.

Numerous experimental reports correspond also to harder O_2 exposure conditions on Pt(111). O_2 pressures up to 400 torr at 700 K led to low energy diffraction diagrams interpreted as the formation of $\text{PtO}_2(0001)$ precursors [7]. Although confusion with oxidation of low concentration impurities of Pt was possible [8,9], the formation of Pt surface oxide or subsurface oxide was largely invoked for various Pt surfaces [1,10,11].

Here we report the results of DFT simulations of dissociative adsorption of O_2 on Pt(111) leading to a wide range of atomic coverages (from 0.25 ML to 2 ML) and configurations. Our aim is to determine the stability range of the various phases including the subsurface oxygen in term of temperature and pressure in order to obtain a consistent diagram in relation with the experimental data. To our knowledge, the only phase diagram (temperature versus coverage) concerning this system was recently reported [12]. It was obtained from first-principle-based Monte Carlo simulations and is limited to 1 ML. Our aim is clearly different as the gas phase pressure is taken into account and our investigation extend to higher coverages. In this limited presentation, we could not pretend to an exhaustive description of the numerous configurations corresponding to the wide coverage range which are still under investigation. We will primarily try to locate the lowest coverage beyond which subsurface site occupation by oxygen become competitive over surface site population.

2. Theoretical method

The simulations were conducted using DACAPO [13]. This program is based on density functional theory (DFT). It uses a plane wave basis set and the Kohn–Sham one-electron equations are solved self-consistently, the ionic cores being represented by ultrasoft pseudopotentials.

For the results presented here, a slab formed by four or five Pt(111) layers was used with a (1×1) or (2×2) surface unit mesh with O atoms located on one side of the slab only. When only adsorbed O atoms were considered, most of the calculations were conducted with four Pt layers only, with relaxation of the two topmost Pt layers. Some limited cases computed with five Pt layers showed no important adsorption energy change. When subsurface oxygen was considered, for configurations showing stability with four Pt layers, the final computation was run with five Pt layers, the three topmost metal layers being free to relax. The slab is reproduced periodically in the perpendicular direction, the images being separated by vacuum equivalent to five interlayer Pt(111) spaces. The Pt–Pt distance corresponded to the equilibrium fcc parameter (4.00 Å) given by our computation for bulk Pt. The plane wave basis set was limited by a 400 eV energy cutoff. The surface irreducible Brillouin zone was sampled by 32/8 special k -points using a $(8 \times 8 \times 1)/(4 \times 4 \times 1)$ Monkhorst–Pack grid for the $(1 \times 1)/(2 \times 2)$ surface unit mesh respectively. The Perdew–Wang functional (PW91) was used in the generalised gradient approximation [14]. A Fermi broadening corresponding to $k_{\text{B}}T = 0.1$ eV was employed to help convergence (k_{B} is the Boltzmann constant). All the energies reported here were obtained after extrapolation to $T = 0$ K. For the O_2 molecule, the computation was performed with spin polarisation. For the O/Pt case, this revealed unimportant as already founded by [6]. The energy difference between our spin polarised and unpolarised calculations was in the 10^{-5} eV range i.e. largely in the errors bars of the DFT calculations. So the whole slab calculations were performed without spin polarisation. The energy gain (or O binding energy) corresponding to oxygen adsorption/absorption was calculated following:

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