



# Molecular oxygen adsorption on ferromagnetic platinum

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## ABSTRACT

Using density functional theory calculations, we found a change in the adsorption properties of oxygen due to the change in magnetic state of the Pt surface (paramagnetic to ferromagnetic). We note a superoxo-type  $O_2$  with lower binding energy but more elongated O–O bond on ferromagnetic Pt {modeled by Pt/M(001), M: Fe, Co}. Interestingly, an  $O_2$  spin moment direction of antiparallel with Pt is noted on Pt/Fe. This is due to the spin splitting of Pt d-states near the Fermi level shifting the spin-down states towards  $E_F$ . Monte Carlo simulations reveal that the reactivity properties of ferromagnetic Pt are retained beyond the room temperature.

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## 1. Introduction

The interaction of molecular oxygen with Pt is one of the best studied systems in surface science [1–6], often motivated by the outstanding industrial importance of the oxidation of Pt. Experimentally, molecular oxygen has been detected on low-index Pt surfaces  $\{(111), (110) \text{ and } (100)\}$  [7,8]. Although, the exact nature of the chemisorbed species cannot be determined, vibrational spectroscopy has suggested the existence of a peroxo-form ( $O_2^{2-}$ ) with O–O stretching frequency of 690–700  $cm^{-1}$  and superoxo-form ( $O_2^-$ ) with a stretching frequency of 840–890  $cm^{-1}$  [9–11]. Using vibrational frequency calculations based on density functional theory calculations (DFT), the superoxo-state is assigned to the most stable molecular oxygen adsorption configuration – top-bridge-top (*t-b-t*) [12,13]. It has been observed that the stability of the oxygen on Pt surface can be changed via the modification of surface electronic structure as a result of hetero-metal interaction or ligand effects attained in various Pt monolayer bimetallic structures (MBS) [14–16]. Generally, in the context of rectangular band model, the stability of oxygen is decreased due to the broadening and lowering of the Pt d-band as a result of a strong Pt and substrate interactions [15,17]. While the energetics of molecular oxygen adsorption on electronically modified Pt MBS have been investigated, the influence of the magnetic state of the metal surface on the geometric, electronic and magnetic structure of the adsorbate has not been explored. There have been reports on the facile oxygen dissociation on Pt catalysts on Co and Fe substrates based on half-cell experiments [18,19]. To some extent, such electrochemical systems render more complex reaction processes than gas-surface reactions, hence, the intrinsic role of the Fe and Co

substrates in altering Pt surface reactivity has not been systematically studied. Moreover, studies on magnetic phases of oxygen molecular assemblies on non-magnetic surfaces reveal interesting ferromagnetic or antiferromagnetic interactions depending on the coverage [20–22], but so far, the change in magnetic interactions due to the modification of the magnetic properties of the surface itself has not been investigated. These studies motivate this first description of the adsorption properties of  $O_2$  on ferromagnetic Pt versus the paramagnetic Pt.

## 2. Computational methods

The calculations performed are based on spin density functional theory (SDFT) [23,24] using Projector Augmented Wave (PAW) method [25] and plane-wave basis set, as implemented in Vienna *ab initio* Simulation Package (VASP) [26–29]. The ferromagnetic Pt is modeled by a Pt overlayer on magnetic substrate, M (M: Fe, Co). The M substrates are modeled by a five-layer bcc(001) slab in a  $(2 \times 3)$  super cell. Each slab is separated by  $\sim 12 \text{ \AA}$  of vacuum. The paramagnetic Pt (also denoted as pure Pt) is modeled by a four-layer fcc Pt(100)- $(1 \times 1)$  slab, which exhibits the same surface structure as that of the ferromagnetic Pt. The generalized gradient approximation (GGA) based on the Perdew, Burke and Ernzerhof (PBE) functional [30,31] is used for the exchange–correlation correction. Brillouin-zone integrations are performed on a grid of  $(4 \times 4 \times 1)$  Monkhorst–Pack *k* points with a smearing of Methfessel–Paxton method [32]. The optimized Pt/M surface is obtained by relaxing the Pt layer and that of the two top-most layers of the substrates using the conjugate-gradient method [33]. A plane-wave expansion with a cutoff of 400 eV is used throughout the calculations.

The temperature dependence of the magnetization of the Pt layer is determined using a combination of constrained DFT calculations [34] and Monte Carlo (MC) simulations. The inter-atomic

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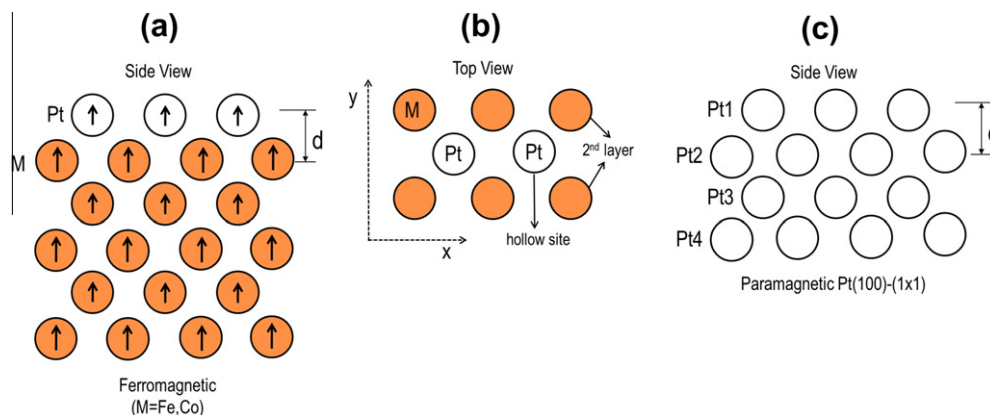
exchange parameters are obtained from a set of non-collinear magnetic configurations of two atomic layers of Pt–M and M–M. Such configurations are produced after rotating the first layer atomic moments and by fixing the local moment direction in non-equilibrium directions using a constraining field. The dependence of the energy difference between the new magnetic states and the ferromagnetic state on the orientation of spins is mapped onto Heisenberg model,  $H_{\text{eff}} = -\sum_{ij} J_{ij} \hat{e}_i \cdot \hat{e}_j$ , where the  $\hat{e}_i$  ( $\hat{e}_j$ ) is the vector representing the direction of local moments on the  $i^{\text{th}}$  ( $j^{\text{th}}$ ) atomic site and the  $J_{ij}$  is the exchange parameter between the  $i^{\text{th}}$  and  $j^{\text{th}}$  nearest neighboring sites. The estimated exchange parameters are then used in the Monte Carlo (MC) simulation to study the finite-temperature magnetic properties. For the MC simulation, the standard Metropolis algorithm is carried out within a system size of  $(L \times L \times n) = 20 \times 20 \times 6$ , where  $n$  is the number of atomic planes and  $L \times L$  gives the atomic sites in a plane. A total of  $\sim 1000$  MC steps are conducted, where, 1 MC step =  $L \times L \times n$  trials (spin flips). A two-dimensional periodic boundary conditions and free boundary condition perpendicular to the plane are adopted.

### 3. Results and discussions

We show in Figure 1 the atomic and magnetic structure of Pt/M and pure Pt. The optimized Pt layer distance ( $d$ ) from the M substrate is 1.62–1.63 Å. This is 0.30 Å shorter than that of paramagnetic Pt (1.93 Å). The lattice mismatch between the Pt layer and the substrates is very small (0.36% on Co and 0.49% on Fe) hence, the Pt layer is considered unstrained. This is consistent with experimental observations on layer-by-layer epitaxial growth of Pt on M [35,36]. An induced magnetic moment of 0.62  $\mu_B$  is noted on Pt (on Fe) and 0.43  $\mu_B$  is noted on Pt (on Co). The origin of magnetic property of an unfilled 5d-shell, which is nonmagnetic in pure metal, is usually understood in terms of strong mixing of 5d-states with M 3d-states, giving a spin-splitting of electronic states near the Fermi level ( $E_F$ ). We also observed the same phenomenon on pure Pt. The orbital-resolved local density of states (LDOS) for Pt and Pt/M are shown in Figure 2. We note that the spin-splitting changes the character of the d-orbitals. For instance, the spin-down  $d_{zz}$  state, which is filled in pure Pt is shifted towards the  $E_F$  in Pt/M (shown by the arrows in Figure 2b and c). The spin-up filled  $d_{xz}$  state in Pt/Fe is closer to  $E_F$  than in pure Pt. Since the interaction of Pt–M does not only involve spin-polarization of Pt, we checked the contribution of ligand effects to the Pt-d states using the d-band center, defined as average energy of the d-band. We note that in the non-spin-polarized case (NM), the d-band center of Pt on Fe,  $-2.56$  eV and Pt on Co,  $-2.41$  eV are much lower as compared to

that of pure Pt ( $-1.80$  eV). Upon inclusion of spin-polarization, the d-band center of the bimetallic systems ( $-2.42$  eV for Pt on Fe and  $-2.20$  eV for Pt on Co) are shifted a little higher than the NM counterparts but are still lower than that of pure Pt.

The most stable molecular  $O_2$  chemisorption on Pt(100)-(1 × 1) is on top-bridge-top ( $t$ - $b$ - $t$ ) (Figure 3) in agreement with previous theoretical studies [12,13]. The adsorption energy is  $-1.29$  eV with respect to gas phase  $O_2$ . This stable site is obtained by scanning the high symmetric sites for  $O_2$  adsorption as shown in Figure 4a. The top-hollow-top ( $t$ - $h$ - $t$ ) site also yields a molecularly adsorbed  $O_2$  with much less binding energy ( $-0.40$  eV), the rest of the sites render a dissociation of  $O_2$ . The vertically adsorbed  $O_2$  on bridge ( $b$ - $b$ ), hollow ( $h$ - $h$ ) and top ( $t$ - $t$ ) are barely stable and resemble that of gas phase. Here, we just focus on the most stable molecularly adsorbed  $O_2$  which is at  $t$ - $b$ - $t$ . The calculated O–O bond-length for  $t$ - $b$ - $t$  site,  $r$  is consistent with other theoretical results on Pt surfaces (1.36–1.37 Å) [8]. The calculated vibrational frequency is  $893$   $\text{cm}^{-1}$  and the magnetic moment is  $0.24 \mu_B$ . This confirms the superoxo-form of  $O_2$  on paramagnetic Pt(100)-(1 × 1) as in the case of other Pt facets. But what happens when  $O_2$  adsorbs on ferromagnetic Pt? We found that the most stable  $O_2$  configuration on Pt/M is also  $t$ - $b$ - $t$  owing to the same surface structure of the systems, with an adsorption energy of ( $-0.93$  eV {Pt/Co} and  $-0.87$  eV {Pt/Fe}). The other stable molecular  $O_2$  is also on  $t$ - $h$ - $t$  site with binding energies,  $-0.17$  eV (Pt/Co) and  $-0.14$  eV (Pt/Fe). On Pt/M, we note a significant increase in the distance of  $O_2$  from the surface ( $z$ ) (Figure 4c and d). Also, the adsorption energy is smaller, which can be attributed to the weaker interaction with Pt due to its lower d-band, in agreement with general trends on Pt MBS discussed previously [14–16]. However, the  $r$  is  $0.01$  Å greater than in paramagnetic Pt. This cannot be related to the same mechanism above, since, a lower Pt d-band should correspond to reduced electronic states at  $E_F$  ( $\text{DOS}_{E_F}$ ) as described in previous theoretical work on Pt [37]. In this case, the extent of the filling of anti-bonding states, which correlates to the O–O bond elongation, is strongly affected by the ( $\text{DOS}_{E_F}$ ). As we have seen earlier in Figure 2, spin-up (spin-down) components of  $d_{xz}$  ( $d_{zz}$ ) states, which are lower in energy in paramagnetic Pt, are shifted higher in energy in ferromagnetic Pt. In fact, Pt on Fe has a very sharp spin-down Pt  $d_{zz}$  peak right at  $E_F$ . These higher spin-down components of d-states in ferromagnetic Pt could explain the promotion of the elongation of O–O bond. We verify this conjecture in Figure 5a–c where  $O_2$ - $\pi^*$  and Pt-d states hybridization is depicted. Specifically, we show the extent of the filling of the antibonding states of  $O_2$  parallel to the surface ( $\pi_{\parallel}^*$ ) for each system (shown by the arrows) as a result of this hybridization. We note that  $\pi_{\parallel}^*$  states is filled on Pt/Fe, partially filled on Pt/Co and nearly empty



**Figure 1.** Schematic diagram of the (a) and (b) Pt/M and (c) Pt structures. The most stable site of Pt atom on M is shown in (b) and the side view of the reference system Pt(001)-(1 × 1) viewed along [010] direction is shown in (c). Local moment directions are shown in (a).

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