

# First Principles Calculations of Oxygen Adsorption on a Stepped Pt(211) Surface

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Atom adsorption in the vicinity of surface defects such as steps and kinks affects strongly the catalytic processes occurring at transition metal electrodes used in oxygen sensors. Above 300 K, oxygen molecules are dissociated on platinum surfaces and diffusion of the adsorbed oxygen atoms can be important for the response speed of the sensor. It is not understood why the atomistic diffusion barrier on Pt(111) surface determined by scanning tunneling microscopy (STM) [1] is incompatible with the macroscopic diffusion barrier measured by field emission microscopy (FEM) [2], although it may be attributed to the diffusion and adsorption behavior near steps on vicinal surfaces. In this paper, oxygen adsorption on a stepped Pt(211) surface is investigated using first principles calculations based on density functional theory. The Pt(211) surface is composed of Pt(111) terraces and Pt(100) step-surfaces as shown in Fig. 1.

Calculations of the ground states are carried out using the VASP code with the PBE-GGA exchange-correlation functional and the PAW method [3]. We use a Pt(211) slab model of 9 layers with a  $(4 \times 2)$  surface unit cell, where one layer is defined as a block composed of three atomic layers exposed to vacuum (Fig. 1). As reference states, oxygen adsorption on flat Pt(111) and Pt(100) surfaces is also examined using slab models of 9 atomic layers with  $(4 \times 4)$  and  $(3 \times 3)$  surface unit cells, respectively. These are similar in size to the Pt(211) model. Lengths of the vacuum regions are taken as 18-20 Å. In all calculations, platinum atoms in the three surface layers on the adsorbing side are freely relaxed and the remainder held fixed.

The adsorption energy with respect to the energy of a free oxygen atom ( $E_{ad}$ ) on the Pt(111) surface is most stable with  $E_{ad} = -4.63$  eV at the fcc-hollow site. In contrast, the bridge site on the Pt(111) surface is unstable and energetically higher by  $\sim 0.5$  eV than the fcc-hollow site [4];  $E_{ad}$  on the Pt(100) surface has the lowest value of  $-4.71$  eV at the bridge site.

Ground-state calculations on the Pt(211) surface are started from 18 possible sites and result in 7 stable states which are labeled in Fig. 1(a). The obtained  $E_{ad}$  are plotted in Fig. 2 as a function of distance along  $[\bar{1}11]$ . Figure 2 also shows the relative adsorption energy, which is defined as the difference between  $E_{ad}$  on the Pt(211) surface and  $E_{ad}$  of the corresponding adsorption site on the corresponding flat surface. For example,  $E_{ad}$  of a hcp-hollow site on the Pt(211) surface subtracted by  $E_{ad}$  of the hcp-hollow site on the Pt(111) surface gives the relative adsorption energy of the hcp-hollow site. Energies for the edge sites (top and bridge) are compared to those on the Pt(100) surface. From the relative  $E_{ad}$ , it is found that, while adsorption sites around the edge are stabilized by over 0.1 eV, those near the bottom of the step tend to become less stable relative to the flat surfaces.

Finally, we consider effects of oxygen adsorption on the Pt(211) surface on diffusion. If we suppose that diffusion perpendicular to the edge occurs along the path  $3 \rightarrow 4 \rightarrow 5 \rightarrow 6 \rightarrow 7 \rightarrow 1 \rightarrow 3$ , the diffusion barrier of oxygen atoms,  $E_{diff}$ , should be larger than 0.9 eV as obtained from Fig. 2(a). This value is much higher than that calculated

for the Pt(111) surface  $E_{\text{diff}} \sim 0.5$  eV [4]. The experimental macroscopic  $E_{\text{diff}}$  is 1.2 - 1.5 eV [1] and the value by STM is  $0.43 \pm 0.04$  eV on the Pt(111) surface [2]. Our result is near to the macroscopic  $E_{\text{diff}}$  deduced from FEM, suggesting that the FEM measured the diffusion of oxygen atoms at a step.

## References

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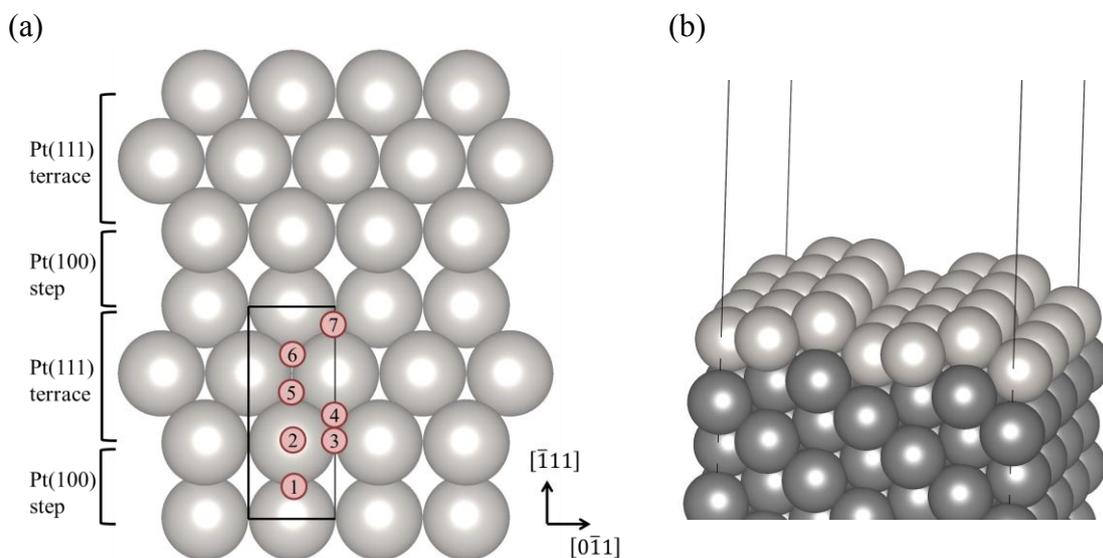


FIG. 1. (a) Top view and (b) side view of the stepped Pt(211) surface. In (a), the red circles labeled with numbers show the stable adsorption sites for an oxygen atom.

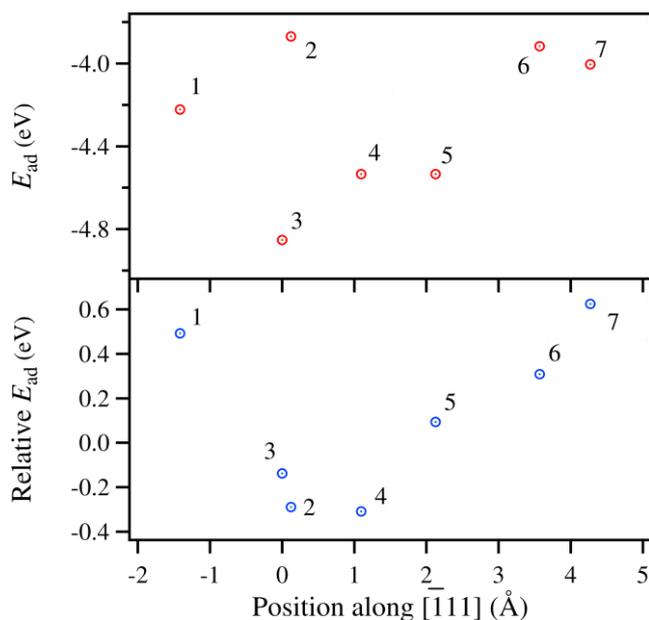


FIG. 2. Adsorption energy,  $E_{\text{ad}}$ , (top) and relative adsorption energy (bottom) of an oxygen atom on the Pt(211) surface.