

Pt(111) surface oxidation—from surface science to electrochemical surface science—a theoretical multiscale approach

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The widespread use of platinum in heterogeneous and electrocatalysis makes single crystal Pt surfaces the object of extensive study in (electrochemical) surface science. Because many catalytic reactions, e.g. catalytic exhaust purification in automobiles or the oxygen reduction reaction (ORR) in polymer electrolyte membrane fuel cells, are carried out in oxygen-rich environments, detailed knowledge of the structure and degree of oxidation of platinum surfaces under operando conditions is essential for understanding and regulating catalytic performance. However, because of the limited spatial, time, and energy resolution of currently available experimental techniques, such an understanding cannot yet be achieved solely on the basis of experiments – even in the case of the thermodynamically most stable and most widely studied Pt(111) surface.

In order to overcome these limitations, a theoretical multiscale approach has been developed and employed to investigate Pt(111) surface oxidation under ultra-high-vacuum, near-ambient-pressure, and electrochemical conditions. Since ReaxFF offers a computational speedup and a time- and length-scale extension compared with density functional theory calculations while retaining similar chemical accuracy, a reactive force field for Pt/O was parameterized [1] and used as the core of this multiscale approach. A study on the thermodynamics and kinetics of Pt(111) oxidation for coverages up to one atomic monolayer revealed four regimes of thermodynamically stable surface configurations, which are characterized by pure oxygen adsorption, high- and low-coverage oxygen induced platinum surface buckling, and subsurface oxygen, respectively. The obtained structures and corresponding simulated temperature programmed desorption (TPD) spectra compare favorably with and complement published scanning tunneling microscopy and TPD experiments [2]. To investigate structures with oxygen coverages exceeding one atomic monolayer, grand canonical Monte Carlo simulations were employed in a search for stable amorphous surface oxide structures. The structures identified using this procedure and the conditions (temperature and pressure) under which they were predicted to exist explain recent experimental observations and provide additional insight into the roles of platinum surface buckling and subsurface oxygen absorption for the surface oxidation process [3]. Finally, evaluating the stability of these stable amorphous surface oxide structures under electrochemical conditions predicts the potential range in which the electrocatalytic ORR occurs [4].

These surface-oxide and surface-oxide-precursor structures are expected to strongly impact the (electro)catalytic properties of partially oxidized Pt(111) surfaces since their catalytic properties may differ dramatically from those of bare platinum.

[1] Fantauzzi, D. *et al.* PCCP **2014**, 16 (42), 23118.

[2] Fantauzzi, D. *et al.* ChemPhysChem **2015**, 16 (13), 2797.

[3] Fantauzzi, D. *et al.* Angew. Chem. Int. Ed. **2017**, 56 (10), 2594.

[4] Fantauzzi, D. *et al.* in preparation.