

COMMENTARY

Unraveling the complexity of oxygen reactions on Pt surfaces

Ana Gutiérrez-González^a and Rainer D. Beck^{a,1}

Platinum (Pt) is a key material in automotive catalytic converters used to clean up the exhaust of the combustion engine. Pt particles in a ceramic matrix serve as an oxidation catalyst to eliminate toxic carbon monoxide (CO) and unburned hydrocarbons (C_xH_y) from the engine's exhaust gases. For this process to work, air is added to the hot exhaust gas before it comes into contact with the catalyst surface where the oxygen molecules from the air stick and dissociate into oxygen atoms. The oxygen atoms adsorbed on the catalyst surface then react with CO and hydrocarbons and convert them into CO₂ and H₂O, which are released through the tailpipe into the atmosphere. This and other applications of Pt catalysts in the chemical industry have motivated extensive studies of oxygen adsorption on Pt surfaces, which have showed that O₂ sticking and dissociation on a Pt surface is far from a simple direct dissociation process first described by Langmuir 100 y ago (1, 2). In PNAS, Cao et al. (3) shed new light on the adsorption of oxygen by measuring O₂ sticking on a specially prepared (curved) single Pt crystal and by using a beam of rotationally aligned O₂ molecules incident on stepped single-crystal Pt surfaces (Fig. 1).

Previous experiments have shown that O₂ chemisorption on Pt is rather complex, proceeding via multiple channels occurring on both the step and terrace sites depending on the incident energy of the O₂ molecules (4–8). At low incident energy, the O₂ molecules are first trapped on the Pt surface in a weakly bound physisorbed state, where they can move along the surface and either desorb back into the gas phase or surmount an energetic barrier to reach one of several molecular chemisorption states (6). These chemisorbed states are precursors to the activated dissociation of O₂ into adsorbed O atoms, the active oxidizing species in the automotive exhaust catalytic converter. At higher impact energy, O₂ molecules in the gas phase can also directly enter the molecular chemisorption states without passing through the physisorbed precursor state.

Adding to the complexity is the fact that the probability for O₂ to dissociate is strongly influenced

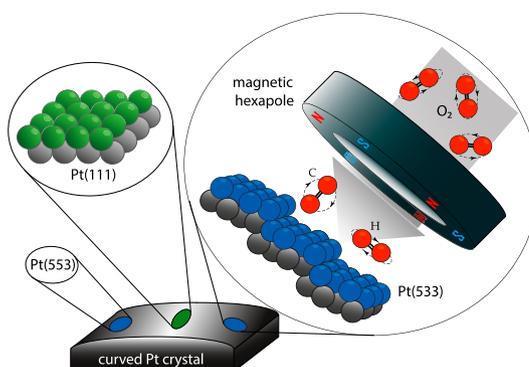


Fig. 1. Schematic representation of a curved platinum single crystal exposing a variable step density as function of position on the surface. The magnetic hexapole filter is used to align the rotation of incident O₂ molecules either in helicopter (H) or cartwheel (C) orientation.

by the adsorption site. Small Pt particles have flat areas of closely packed atoms (terraces) as well as a variety of lower coordination sites (like steps and kinks). Earlier experiments on model surfaces with different concentrations of terrace and step sites revealed the O₂ dissociation probability to be higher for a Pt surface containing steps than it is for the flat Pt(111) surface. However, the full details of the sticking process on the step and terrace sites as a function of incident energy could not be determined unambiguously by these conventional sticking measurements.

Recently, scientists from the Netherlands and Japan have combined their experimental expertise to obtain more detailed information about the role of steps and the molecular orientation in O₂ sticking and dissociation on Pt surfaces. In the Netherlands, Juurlink and colleagues (9) pioneered the use of curved single crystals for the systematic study of the role of steps in chemisorption reactions. On a curved single crystal, the density of steps changes linearly as a function of position on the crystal surface. Using spatially resolved sticking measurements, Juurlink and colleagues were able to disentangle the contribution of

^aLaboratoire de Chimie Physique Moléculaire, École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

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¹To whom correspondence may be addressed. Email: rainer.beck@epfl.ch.

the steps and terraces to the sticking process. In Japan, Kurahashi and colleagues (10, 11) developed a novel apparatus based on a magnetic hexapole field for selecting a single spin-rotational quantum state from a beam of O₂ molecules. This hexapole filter makes use of the fact that the electronic ground state of O₂ includes 2 unpaired electrons, giving them a spin magnetic moment, which makes it possible to manipulate the molecules with external magnetic fields. In passing through the hexapole filter, the O₂ molecules are rotationally state selected and can be aligned in space by a magnetic field. Kurahashi et al.'s apparatus used a magnetic hexapole to prepare the incident beam of O₂ molecules with well-defined orientation by switching the direction of the magnetic field before the O₂ molecules collide with a Pt surface (Fig. 1).

In PNAS, Cao et al. (3) report the first results of a collaborative effort focusing these 2 techniques on the details of O₂ sticking and dissociation on Pt surfaces. Cao et al. used a curved Pt single crystal to measure the sticking coefficient of O₂ as a function of step density and step type for different incident kinetic energies. Their results reveal how surface steps affect the sticking of O₂ on a Pt surface in different ways depending on the incident O₂ energy. Further details of the O₂ sticking process were uncovered using a beam of aligned O₂ molecules incident on the Pt surface. Combining their expertise, the collaborating researchers (3) explore the stereodynamics of O₂ sticking on stepped Pt surfaces. Here, the term stereodynamics refers to the study of the directional (steric) aspects of a chemical reaction, which requires the ability to control the relative orientation or alignment of the reaction partners. Stereodynamics experiments have a long history for unimolecular and bimolecular reactions in the gas phase (12). The stereodynamics of molecule/surface reactions have not yet been explored as extensively (13–15). The steric effects reported by Cao et al. (3) provide highly detailed information on the dynamical processes that are contributing to the sticking of O₂ molecules on a stepped Pt surface.

Remarkably, the results reveal that the dependence of the reaction probability on O₂ alignment is different on the Pt terraces and steps. On terrace sites, O₂ sticking has a strong preference for so-called helicopter alignment, where the O₂ molecules

rotate with their bond axis parallel to the plane of Pt surface. "Cartwheeling" O₂ molecules, with their bond axis rotating in a plane perpendicular to the surface, are less likely to stick on the terraces (Fig. 1). Cao et al. (3) conclude that O₂ incident on the terraces can directly enter the molecular chemisorbed state only if the incident O₂ alignment is favorable; that is, helicopter-like. In contrast, on the steps, at low incident energy, O₂ sticking is

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observed to be almost independent of alignment; that is, helicoptering and cartwheeling O₂ have the same sticking probability (this observation is consistent with the idea of trapping in a physisorbed state). The steps merely serve to deflect the direction of motion of incident O₂ molecules from perpendicular to parallel to the surface and thereby facilitate trapping in the physisorbed state, which is a precursor to molecular chemisorption of O₂. With increasing incident energy, the picture changes: On the terraces, the sticking probability increases and the alignment dependence decreases, while on the steps, a new alignment-dependent channel for sticking in the molecular chemisorbed state opens up, where O₂ molecules stick preferentially if their bond axis is aligned parallel to the step direction. Moreover, at high incident energy, sticking on the steps is also favored if the O₂ molecules are aligned in a helicopter-like rotation relative to the step facets.

The sticking measurements using a curved Pt single-crystal surface combined with information on the alignment dependence of O₂ sticking on steps and terraces yields a detailed picture of the different channels involved in O₂ adsorption on a stepped Pt surface. These new data are ideally suited for facilitating the development and testing of improved theoretical models for this and other chemical reactions at surfaces that are important for heterogeneous catalysis. Future advances in theory should lead to a predictive understanding of molecule/surface reactions, which will in turn be very valuable in the search for more efficient catalysts.

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