

Waltzing with O₂

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Oxygen vacancies are perhaps the most common defects on the surfaces of transition metal oxides. They alter the adsorption and other chemical properties of the surfaces dramatically and play important roles in catalysis, photocatalysis, and weathering. On page 377 of this issue, Schaub *et al.* (1) reveal a surprising new mechanism for the migration of these vacancies.

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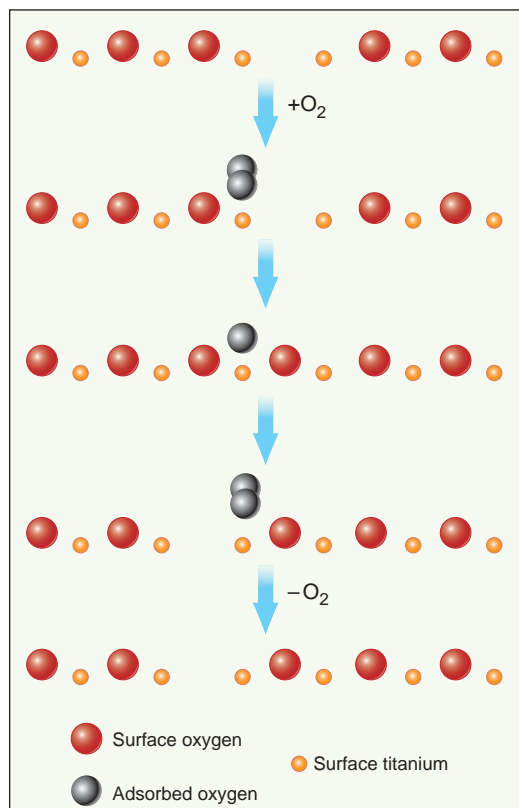
The authors use atomically resolved images of a well-ordered TiO₂ surface obtained with a scanning tunneling microscope (STM) to investigate oxygen vacancy migration. They provide compelling evidence that the migration of oxygen vacancies is catalyzed by transiently adsorbed molecular oxygen (O₂). Because of this catalytic effect, the new mechanism is likely to be dominant when O₂ is present.

Surface oxygen vacancies often participate as a reactant or product in oxidation reactions catalyzed by transition metal oxide surfaces. For example, when an adsorbed organic molecule is oxidized at an oxide surface, the oxidant is often a surface lattice oxygen atom, resulting in the creation of a surface oxygen vacancy (2). After this oxidation step, O₂ from the gas phase must react with the oxide surface to regenerate the surface oxygen. The initial step in this regeneration may be binding of an O₂ molecule at an oxygen vacancy site (3). Vacancies usually bind adsorbed molecules more strongly to an oxide surface (3–5) and can form particularly active sites for bond-breaking in adsorbed molecules (3, 5–7).

Oxygen vacancies are also involved in photocatalysis on semiconducting oxide surfaces (3, 4, 8). They are often critical for the creation of special charged sites that can be important in the separation or recombination of electron-hole pairs. The charges at oxygen vacancies, which can differ when bound by adsorbates, can change the local electronic structure of semiconductor oxide surfaces, which again can be important in electron-hole pair separation.

The nucleation and immobilization of metal nanoparticles also preferentially occur at oxygen vacancies (9–11). Oxygen vacancies are thought to alter the catalytic activity of the metal clusters (10, 11).

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Assisted migration. A fundamentally new mechanism for oxygen vacancy migration on oxide surfaces involves transiently adsorbed O₂ as a sort of catalyst, as revealed by fast STM imaging of TiO₂.

Oxide-supported transition metal nanoparticles are widely used as catalysts.

Schaub *et al.* were able to collect series of atomically resolved STM images of a cold TiO₂(110) surface with a repetition rate as quick as 1.1 s per image. They identify molecularly adsorbed O₂ as bright spots in their images, centered above five-coordinate Ti surface atoms. The number of adsorbed O₂ molecules increases with O₂ exposure at ~200 K. The O vacancies migrate only when such an O₂ species is nearby.

The authors propose that adsorbed O₂ diffuses across the surface to find a vacancy. It then dissociates to fill that vacancy, producing an O adatom on one of the two nearest Ti atoms. The O adatom quickly reacts with one of the two nearest surface lattice O atoms to regenerate an O₂ molecule and a new vacancy, often at a different location (see the figure).

The statistics of vacancy migration derived from the STM images are consistent with this mechanism: The abstracted O atom is selected from the three possible sites with

statistical probability. The process is very fast even at ~220 K. Sometimes, the authors identify another adsorbate, which they interpret as the transient intermediate structure in this vacancy migration mechanism.

The net effect of this atomic-scale waltz is vacancy diffusion that is much faster perpendicular to the rows of bridging oxygen atoms on this (110) surface than parallel to these rows. This directionality is rather surprising: Adsorbate diffusion by the usual site-to-site hopping mechanism on such “row/trough” surfaces proceeds much faster parallel to the rows (12). The simplest imaginable diffusion mechanism for oxygen vacancies is also parallel to the rows. This simple path is clearly much slower than the observed process if O₂ is present to catalyze the latter.

Schaub *et al.* made their measurements on one of the most thoroughly studied oxide surfaces, rutile TiO₂(110). This surface has received so much attention because TiO₂ is important both as a support for metal catalysts and as a photocatalyst and electrocatalyst in its own right. A large number of experiments have revealed the atomic details of its structure (3, 4, 13–15). Anyone currently studying—or planning to study—this and related surfaces needs to control the number and distribution of oxygen vacancies. The new results will therefore be of great practical importance.

The fundamentally new and unexpected mechanism for surface oxygen vacancy migration discovered by Schaub *et al.* probably operates on a wide range of other transition metal oxide surfaces. It will be particularly important under conditions where O₂ is present—for example, in oxidation catalysis and in weathering.

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