Adsorption, diffusion and dissociation of molecular oxygen at the defected rutile TiO_2 (110)-surface.

M. D. Rasmussen, L. M. Molina, and B. Hammer
Interdisciplinary Nanoscience Center (iNANO)
Department of Physics and Astronomy
University of Aarhus, DK-8000 Aarhus C, Denmark
Email: mdr@phys.au.dk

TiO_2 has in later years been termed a 'model system' for metal oxides. The material shows a range of fascinating phenomena, being photoactive, a good catalyst support and showing adsorbate induced diffusion of surface vacancies. Using first principles density functional theory, we have investigated the adsorption, diffusion and dissociation of O_2 on the (110)-surface of the rutile structure [1], this being the most stable surface of the most stable phase. Bridging oxygen vacancies are the most abundant surface defects. As electron donors capable of donating up to two electrons, they prove to be decisive in the surface oxygen chemistry through charge transfer to the adsorbate.

Vacancy-vacancy interactions are found to be large along the bridging oxygen rows, the vacancy creation energy declining by 1.0 eV when enlarging the distance between bridging oxygen vacancies from two lattice spacings to four lattices spacings. No similar interaction is seen between neighbouring rows. Even when vacancy coverage is low, the bridging vacancy creation energy is found to be 3.0 eV and relaxations around the vacancy are substantial and far reaching.

Adsorption of O_2 on the stoichiometric surface is energetically unstable, see figure. However, in the presence of a vacancy, adsorption potential energies become -2.3 eV in the vacancy and -1.7 eV on the titanium rows. Oxygen bond lengths extend upon adsorption, resulting in a 1.44 Å bond length for the molecule adsorbed in a vacancy and 1.40 Å on the row, indicating a doubly charged molecule. Barriers for dissociation and diffusion processes are in general high. Dissociation is slightly endothermic when charge is scarce in the system, however, if plenty of vacancies provide ample charge, it is strongly exothermic.

The key element of the O_2 reactivity on the surface is the charging of the adsorbate. When the adsorbate is located in the vacancy, two electrons are transferred from the vacancy to the adsorbate, causing the 1.44 bond length. When the adsorbate is on the row, slightly less charge is available, resulting in a somewhat smaller bond length. This charge transfer is not limited to adsorbates close to the vacancy but takes place even if the adsorbate is relocated several lattice spacings along the titanium row. Thus, the defects are the deciding factor in the oxygen chemistry of the surface; indeed the adsorption of O_2 is only possible on the reduced surface. We believe the underestimation of the band gab facilitates charge release from vacancies and have attempted modeling vacancies with smaller valence. This changes the surface oxygen chemistry radically.

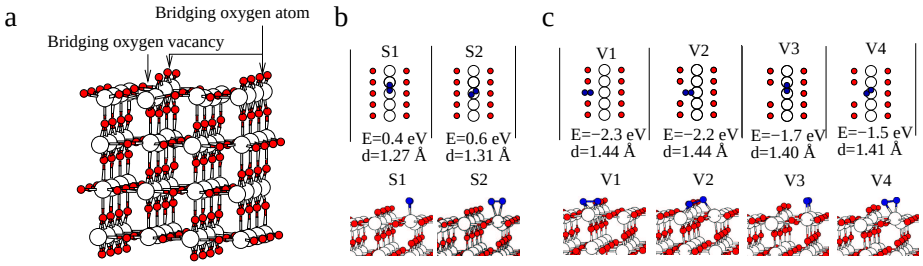

Figure 1: Ball-and-stick models of (a) the (110)-surface and most important adsorption sites on the (b) stoichiometric and (c) defected surface. E signifies O_2 adsorption potential energy, d bond lengths.

References

[1] M. D. Rasmussen, L. M. Molina, and B. Hammer, *Journal of Chemical Physics*, **120**, 988 (2004)

[2] R. Schaub, E. Wahlström, A. Rønnau, E. Lægsgaard, I. Stensgaard and F. Besenbacher, *Science*, **299**, 377 (2003)

[3] E. Wahlström, E. K. Vestergaard, R. Schaub, A. Rønnau, M. Vestergaard, E. Lægsgaard, I. Stensgaard and F. Besenbacher, *Science*, **303**, 511 (2004)