Dissociation of O_2 on the reduced SnO_2 (110) surface

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We report evidence from plane-wave (PW) pseudo-potential calculations, which suggests that neutral, molecular oxygen dissociates exothermically at bridging oxygen vacancies on the SnO_2 (110) surface, supporting recent experimental data.

Stannic oxide (SnO_2) is widely used industrially as a selective catalyst in oxidative dehydrogenation and is also a highly tuneable gas sensor, used in the detection of reducing gases. Although a wealth of experimental literature exists on SnO_2 reaction kinetics and profiles,[1,2] speculations on reaction mechanisms are a subject of contention. One such area of debate is the question of how oxygen gas effects the observed, substantial increase in surface conductivity. Of general interest is the need to establish how feasible homolysis of O_2 is at the surface. We have established previously that the adsorption energy of neutral oxygen at the surface is extremely small[3] (<0.02 eV). Here, we describe a theoretical study to elucidate the thermodynamic viability of the dissociation of O_2 with the reduced (110) SnO_2 surface. On a reduced surface, the bridging oxygen vacancies can facilitate the first step in the Mars and van Krevelen[4] reaction, which underpins its catalytic and sensing properties.

Experiment[1] and previous calculations (including atomistic[5–7] and PW studies[8–10]) have shown the (110) surface to be energetically the most stable surface under ambient conditions. To generate a model for the surface, we first performed a constant pressure relaxation of the bulk unit cell using the VASP[11–13] code. We used an energy cut-off of 495 eV, an ultrasoft pseudo-potential for the Sn and O ions and the Ceperley–Alder expansion for local exchange. The resulting relaxed lattice parameters of $a = b = 4.725$ and $c = 3.180$ Å, are in excellent agreement with the experimentally measured values of 4.737 and 3.186 Å, respectively, and reproduce the experimental c/a ratio of 0.673. We then constructed a cell to describe the (110) surface, containing three cell layers forming a slab, comprising a total of 72 ions. We selected a vacuum width of 5.0 Å having verified complete convergence of the surface energy at 4.51 Å. Upon relaxation of the surface, we obtained a surface energy of 1.19 J m^{-2} in close agreement with previous atomistic[5–7] and PW studies.[8–10]

We verified the quality of the oxygen pseudo-potential by calculating the spin-polarised, relaxed bond length and binding energy for the molecular oxygen triplet. The oxygen bond length of 1.225 Å compares well with the measured value of 1.216 Å.[14] The binding energy (BE) of oxygen is overestimated at 7.0 eV compared with the experimental value of 5.1 eV;[14] this is a generic feature of LDA based methods. Although we would expect gradient corrections to improve the agreement with experiment for the molecular binding energy, we in fact obtained considerably poorer lattice constants for SnO_2 using GGA pseudo-potentials. Therefore, for methodological consistency, we have used LDA pseudo-potentials throughout.

Fig. 1 shows a schematic of the dissociation process. Light spheres indicate oxygen, dark spheres represent tin and black spheres signify dissociated oxygen. Site A is a bridging oxygen, whilst Site B is a five coordinate tin site and C is the oxygen vacancy. The first step in this process is the formation of a bridging oxygen vacancy; the second is the dissociation of oxygen at the vacancy with encapsulation of an oxygen atom in the vacancy, and the adsorption of the monoatom at a neighbouring five-fold Sn site.

Table 1 summarises the total energy of formation for the configurations calculated using an identical cell geometry.

The energy of dissociation can be expressed as the difference between the undissociated and dissociated surfaces, where the initial configuration is simply one where oxygen is non-interacting with the defective surface, *i.e.* the energy of the isolated oxygen molecule plus the energy of the defect-containing surface. Thus, the dissociation of oxygen is exothermic, releasing a net energy of 0.59 eV. In considering the equilibrium between molecular and atomised oxygen, we note that the energy of adsorption of the monoatom to the five-fold Sn site is -1.25 eV, whilst the vacancy formation energy is $+2.84$ eV. (We have assumed the vacating oxygen atom combines with another gaseous oxygen monoatom to form paramagnetic molecular oxygen). The monoatom is adsorbed 2.02 Å above the five-fold tin site, and its spin is reduced to a singlet.

Using these calculations, we can consider the end-points of dissociation for two other reactions; first that where oxygen dissociates to occupy two adjacent bridging oxygen vacancies

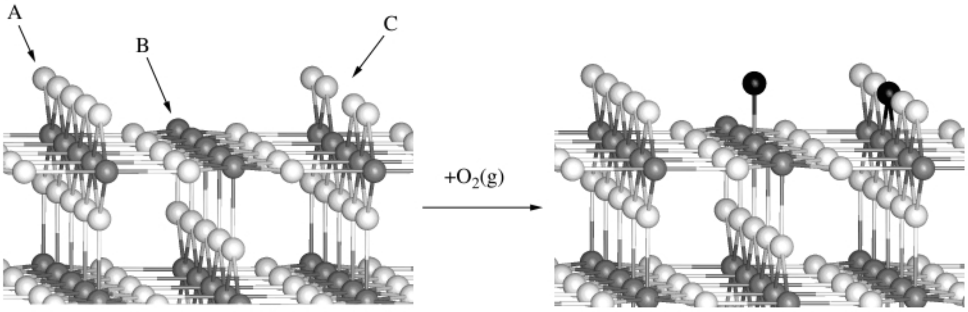

Fig. 1 Schematic oxygen dissociation process. The darker atoms in the final state come from the O_2 molecule: one atom fills the O vacancy (C), and the other is adsorbed on the five-coordinated Sn site (B).

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Table 1 Total energies of formation

Configuration	Energy/eV
SnO_2 perfect surface	-496.388
SnO_2 with bridging defect	-488.386
O_2 molecule	-10.332
O atom	-1.678
SnO_2 with bridging defect + dissociated O_2	-499.312

(A) and secondly, where two adjacent adatoms are formed (B) and compare with the main study here, where one bridging vacancy is occupied and one adatom is formed (C). Reactions A and C are exothermic; -5.68 and -0.59 eV, respectively, whereas reaction B is endothermic, $+4.48$ eV. Therefore, in the absence of specific activation barrier heights, we would expect reaction A to proceed more quickly than C and that reaction B will not occur at low temperatures.

The fact that the dissociation process is predicted to be exothermic for reaction C is our fundamental result, since this strongly supports the proposition that oxygen dissociates at bridging oxygen vacancies, filling the vacancy and producing an oxygen adatom. This evidence corroborates the recent postulate of Henderson and coworkers[15] who reported TPD (temperature programmed desorption) measurements with isotopically labelled oxygen. The authors suggested that below 600 K, oxygen on TiO_2 dissociates at bridging oxygen vacancy sites to fill oxygen vacancies and form adsorbed oxygen monoatoms at adjacent in-plane titanium sites on the TiO_2 (110) surface, a surface which is isostructural with the SnO_2 surface considered here. In addition, we have shown how two reactions (A and C) are concerted first steps in the generalised Mars and van Krevelen oxidative process.

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