The interaction of TiO$_2$ with molecular oxygen is an important factor in determining many fundamental reactions that take place on TiO$_2$-based materials$^{1-3}$ While adsorption of O$_2$ molecules is known to be mainly mediated by oxygen vacancies, the atomic structure and reactivity of adsorbed O$_2$ molecules on the reduced surface are still uncertain, particularly at saturation coverage. Results from recent temperature-programmed desorption (TPD) measurements$^{5,7}$ suggested that the full O$_2$ coverage on TiO$_2$(110) at low temperature ($\sim$120 K) would approximately be 3 times the surface vacancy population, and adsorbed O$_2$ molecules may exist in either weakly or strongly bound states associated with TPD features below 200 K and above 400 K, respectively. In addition, earlier experiments$^8$ identified the existence of two chemisorption states for molecular oxygen on TiO$_2$(110); that is, one can photo-oxidize coadsorbed CO and the other only undergoes fast photodesorption.

Most of the recent theoretical studies using density functional theory (DFT) have focused on understanding the nature of O$_2$ interaction with the reduced surface, by examining the adsorption and dissociation of a single oxygen molecule per vacancy or more.$^{9-11}$ In fact, on the basis of the unrestricted Hartree-Fock calculations, a structural model was proposed for adsorption of three O$_2$ molecules per vacancy, in which one O$_2$ molecule is located at the vacancy site while the others are at the sites atop adjacent Ti 5-fold-coordinated atoms, all in a perpendicular fashion.$^{12}$

In this paper, we propose a new adsorption model for molecular oxygen on reduced TiO$_2$(110), based on extensive first principles density functional calculations of the structure, bonding, and energetics of adsorbed oxygen species by changing the number of adsorbed O$_2$ molecules per vacancy. For the first time, as shown in Figure 1, our calculations predict formation of tetraoxygen (O$_4$) anchored at the vacancy site, which in turn allows adsorption of three O$_2$ molecules per vacancy in saturation coverage. The O$_2$ complex turns out to be substantially more stable than two gas-phase O$_2$ molecules in the triplet state, that is, one can photo-oxidize coadsorbed CO and the other only undergoes fast photodesorption.

Figure 1. Side (left panel) and top (right panel) views of lowest-energy configurations of O$_2$ at varying coverages: (a) $\theta = 1$, (b) $\theta = 2$, and (c) $\theta = 3$, where $\theta$ is defined as the number of adsorbed O$_2$ molecules per oxygen vacancy. Bond lengths of oxygen species are given in Å. The yellow, red, and gray balls represent adsorbed O, surface O, and Ti atoms, respectively.

Pack mesh of $k$ points. The nudged elastic band method (NEBM) was used to determine diffusion pathways and barriers. A reduced surface is generated by removing a bridging O atom from a 15-atomic layer ($2 \times 3$) slab that is separated from its periodic images by a vacuum space of 10 Å. For gas-phase O$_2$, we used the same size of periodic computation box, sufficiently large to avoid possible interactions with its replicas. Note that the ground state of the gas-phase O$_2$ molecule is the triplet state, which was used as the reference state for binding energy prediction of oxygen adsorbates on the reduced surface. Our previous studies$^{10}$ showed that the chosen conditions of spin-polarized DFT calculations are sufficient for describing the O$_2$–TiO$_2$(110) interaction.

For $\theta = 1$, that is, one O$_2$ adsorption per vacancy, the most favorable adsorption occurs when O$_2$ is positioned at the vacancy site in parallel fashion (Figure 1a). Electron delocalization from the vacancy site also renders stable adsorption sites for O$_2$ along neighboring Ti(5c) rows. The adsorbed O$_2$ may undergo migration along the Ti(5c) row, with a barrier of 0.54 eV, until reaching the lowest-energy configuration at the vacancy site by overcoming a barrier of 0.45 eV. The O$_2$ bond length of 1.48 Å, close to 1.46 Å for O$_2^{2-}$ (in H$_2$O$_4$), indicates that approximately two electrons transfer from the surface to the adsorbed (singlet state) O$_2$ (see Figure 2a). The O$_2^{2-}$ binding energy is predicted to be 2.72 eV, with respect to the gas-phase (triplet state) O$_2$.

When $\theta = 2$, as illustrated in Figure 1b, the most stable adsorption structure involves formation of a tetraoxygen (O$_4$) complex which is aligned between the O vacancy and an adjacent Ti(5c) atom. The O$_4$ binding energy is predicted to be 2.93 eV with respect to two gas-phase O$_2$ molecules in the triplet state. The O–O bond lengths in the O$_4$ complex are 1.50, 1.42, and 1.55 Å, between O1–O2, O2–O3, and O3–O4, respectively, where O1 is the O atom at the vacancy site, O2 the next nearest neighbor to the vacancy oxygen atom (O1), and O3 is between O2 and O4 (which is at the top site above the neighboring Ti(5c) atom). The atomic structure is similar to O$_4^{2-}$ (in H$_2$O$_4$), which gives 1.50 and 1.45...
transfer to the O4 complex from the vacancy site. We attribute the O3 bond lengths. This indicates that approximately two electrons also evidenced by recent experiments. While the shape of isolated Å, respectively, for the corresponding O1−. The authors acknowledge the Welch Foundation (F-1535) for their financial support of this work.

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