Quenching of Electron Transfer Reactions through Coadsorption: A Study of Oxygen Photodesorption from TiO₂(110)

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Abstract

Using temperature programmed desorption (TPD) and photon stimulated desorption (PSD), we show that coadsorbates of varying binding energies on the rutile TiO₂(110) surface exert a commensurate inhibiting influence on the hole-mediated photodesorption of adsorbed O₂. A variety of coadsorbates (Ar, Kr, Xe, N₂, CO, CO₂, CH₄, N₂O, acetone, methanol or water) were shown to quench O₂ photoactivity, with the extent correlating with the coadsorbate's gas phase basicity, which in turn determines the strength of the coadsorbate-Ti⁴⁺ bond. Coadsorbed rare gases inhibited the photodesorption of O₂ by ~10-25%, whereas strongly bound species (water, methanol and acetone) nearly completely inhibited O₂ PSD. We suggest that coadsorption of these molecules inhibit the arrival probability of holes to the surface. Band bending effects, which vary with the extent of charge transfer between the coadsorbate and the TiO₂(110) surface, are not expected to be significant in the cases of the rare gases and physisorbed species. These results indicate that neutral coadsorbates can exert a significant influence on charge transfer events by altering the interfacial dipole in the vicinity of the target molecule.

Keywords

Photodesorption, $\text{TiO}_2(110)$, oxygen, photochemistry, coadsorption

1. Introduction

Through nearly three decades of fundamental science, the research groups of John Yates have repeatedly distinguished themselves as experts in the field of surface photochemistry. This leadership is prominently displayed in a number of review articles, (1-6) and in many detailed studies of the photodesorption of molecular oxygen from the rutile $\text{TiO}_2(110)$ surface. (7-16) Their efforts have contributed in making the O_2 - $\text{TiO}_2(110)$ system (17-22) one of the most fascinating examples of oxide surface chemistry (23-50) and photochemistry. (51-66)

The O_2 photon stimulated desorption (PSD) effect on $\text{TiO}_2(110)$ is observed for all coverages of chemisorbed O_2 , but is believed to result only from those molecules bound at Ti_{5c} sites. (63) O_2 PSD is not observed unless O_2 is adsorbed on the surface molecularly, which occurs for adsorption temperatures below 150 K. (36) Typically, O_2 PSD is assumed to be due the reaction of a photo-generated hole with a chemisorbed O_2^- , which neutralizes the anion and ejects O_2 from the surface, (7-10; 53; 56; 58; 64) although the pathway may also involve partial neutralization of an $(\text{O}_2)^{2-}$ species. (65) Sporleder and coworkers have shown that at least two hyper O_2 photodesorption states result, along with a thermalized channel, and that all three are wavelength insensitive for photons in excess of the bandgap. (55) UV irradiation also stimulates the dissociation of O_2 bound at V_O sites on $\text{TiO}_2(110)$. (56; 58; 63; 65) Like thermal dissociation, photo-induced dissociation of O_2 heals the vacancy and leaves a oxygen adatom on a nearby Ti_{5c} site. (63; 65) The carrier responsible for photodissociation is unclear, with indications being that either electrons (56; 58) or holes (63) may be responsible.

In this work, we endeavor to honor the memory and spirit of John Yates by extending his group's explorations of the effect of coadsorption on O_2 photochemistry on $\text{TiO}_2(110)$. Previous research has shown that the maximum amount of oxygen that can be chemisorbed on the reduced $\text{TiO}_2(110)$ surface, θ_{sat} , is approximately twice the vacancy concentration. (39) Because the surface coverage of the O_2 - Ti_{5c} species is always low (~ 5 -8% of available sites), the effect of coadsorption on O_2 PSD can be examined over a wide coverage range of the coadsorbate. Yates et al. used methanol co-adsorption as a potential hole scavenger and observed suppression of the O_2 PSD yield. (10) A band-bending model was later suggested to explain suppression of the O_2

electron-stimulated desorption by co-adsorbed methanol molecules. (67) Yet band-bending can not account for the ability of physisorbed species, such as Kr atoms, to also quench the O₂ PSD activity. (61) Therefore, the factors are unclear through which coadsorbates influence charge transfer reactions of a molecule like O₂ on TiO₂(110). Using a variety of species (Ar, Kr, Xe, N₂, CO, CO₂, CH₄, N₂O, acetone, methanol or water), we show that coadsorbates that interact with the TiO₂(110) surface as Lewis bases suppress the O₂ PSD signal. The selected coadsorbates range in binding strengths from weakly-bound physisorbed species to strongly chemisorbed molecules. The O₂ PSD suppression across this spectrum of coadsorbates is not attributed to band bending effects, as many species were incapable of donating significant charge into the TiO₂ surface. We propose that the inhibiting of the interfacial hole transfer from TiO₂ to chemisorbed O₂^{d-} anions is caused by a change in the surface dipole induced by even the weakest of coadsorbed molecules.

2. Materials and Methods

The experiments were performed in a UHV system that has been described previously. (57; 58; 61) The system consists of a closed-cycle helium cryostat, a molecular beam doser, a quadrupole mass spectrometer (QMS), a UV photon source, and surface diagnostic equipment. The typical base pressure was less than 1×10^{-10} Torr. A 10×10×1 mm rutile TiO₂(110) crystal (CrysTec GmbH) was mounted on a resistively-heated tantalum base plate. For temperature monitoring and control, a K-type thermocouple was spot-welded to the base plate. The minimum temperature was typically near 25 K. The TiO₂(110) surface was prepared by multiple cycles of sputtering with 2 keV Ne⁺ ions, followed by brief annealing in UHV at 950 K. The clean surface exhibited a sharp (1×1) low-energy electron diffraction pattern. (20) Depending on the level of reduction, the oxygen vacancy coverage, $\theta(V_O)$, on this surface varied between 5-8%, and could be measured using water TPD. (68; 69)

The TiO₂(110) sample was exposed to gases at the base temperature (unless otherwise noted) using a molecular beam, with typical fluxes of $\sim 1\text{-}3 \times 10^{14}$ molecules/cm²s at normal incidence to the surface. The molecular beam produced a film centered on the substrate having a diameter of 7.3 mm for the umbra and 7.9 mm for the penumbra. Oxygen dosing was performed with ultra-high purity gas (Air Liquid, 99.9995%), and the other gases were high purity grade (better than 99.9%). HPLC grade methanol and acetone (Aldrich) were used. The clean surface

was exposed to O₂ in excess of the amount needed to saturate the first layer at 25 K, and flashed to 100 K to remove physisorbed O₂. (31) Coadsorbates were then dosed at 25 K (except for water, methanol and acetone which were dosed at 80 K), followed by UV irradiation. Because the absolute first layer coverages (in molecules per cm²) were different for each coadsorbate, their coverages are expressed as the relative amounts required to saturate the first layer of the TiO₂(110) surface (based on TPD). A relative coverage term of ‘1 ML’ is used to indicate the first layer saturation coverage for each species. (Note: the ‘1 ML’ designation for each coadsorbate will translate into a different number of species per cm².)

Photon exposure was performed with a 100 W Hg lamp (Oriel #6281). The output of the lamp was focused onto a fiber optic cable that introduced the light into the UHV chamber, with the infrared portion of the output blocked using a water filter. The light was incident at 45° with respect to the surface normal. The distance of the fiber optic cable from the sample was chosen such that the illuminated spot was centered on, and somewhat larger than, the molecular beam spot on the sample. The entire UV portion of the lamp’s spectrum was used during photon irradiation. For the experiments reported here, all UV exposures were performed at the base temperature. During photon irradiation, the sample temperature increased by no more than 1 K. Typical photon fluxes were $\sim 3 \times 10^{15}$ photons/cm²s (for energies >3 eV) based on calibration with a silicon photodiode detector.

3. Results and Discussion

The influence of coadsorption on the photochemical properties of O₂ on TiO₂(110) is shown in Figure 1. The displayed PSD traces are from UV irradiation of chemisorbed O₂ on TiO₂(110) at 30 K. The black trace, from the clean surface, exhibited a prompt signal response on irradiation (time ‘0’) followed by an exponential-like decay as the surface became depleted of adsorbed O₂. Readsorption measurements indicate that roughly 40% of the chemisorbed O₂ can be photodesorbed, with the remainder experiencing photodissociation or persisting in molecular form despite irradiation. (58) Coadsorption of the same O₂-covered surface with ‘1 ML’ coverages of Kr (red), N₂ (green) and water (blue) resulted in varying levels of attenuation in the O₂ PSD signal. This effect was not due to chemical displacement of O₂ from either the surface or specific photo-active surface sites. In the case of Kr and N₂, coadsorption can be followed by removal of the coadsorbate with mild heating (<100 K) prior to UV irradiation, in which case the

O₂ PSD traces are identical to that for the clean surface (black trace). Therefore, it is the presence of the coadsorbate on the surface with O₂ that diminishes the O₂ PSD signal.

Figure 2 shows the total O₂ PSD yield as a function of coadsorbate coverage for a variety of coadsorbates, separated into three groups: rare gases (Ar, Kr and Xe; Figure 2a), physisorbed molecules (CH₄, N₂, N₂O, CO₂ and CO; Figure 2b) and chemisorbed molecules (H₂O, CH₃OH and C₃H₆O (acetone); Figure 2c). The extent to which these three groups of coadsorbates impact O₂ PSD, as gauged by their coverage dependences, is as follows.

The rare gases show a weak, but unmistakable attenuation effect on O₂ PSD. The total O₂ PSD signal decreased by 10-30% after the first layer on TiO₂(110) was fully occupied with the rare gas. Coverage-dependent effects on O₂ PSD are difficult to gauge for coverages below 50% saturation because these gases interact weakly with the TiO₂(110) surface (see Supplementary Material). These species likely diffuse too rapidly on the surface, providing transient interactions with O₂. However, it is clear from Figure 2a that the O₂ PSD yield was diminished as the rare gas coverage approached first layer saturation. Additional rare gas, forming a physisorption layer above the first layer, attenuated the O₂ PSD signal further, likely by causing collisions between the departing O₂ molecules and the second layer. (61)

Coadsorption of various physisorbed molecules (CH₄, N₂, N₂O, CO₂ and CO) with O₂ resulted in a near-linear attenuation of the O₂ PSD signal with coadsorbate coverage (Figure 2b). The magnitude of the O₂ PSD signal attenuation matched the strength of the coadsorbate – TiO₂(110) interaction (see below). As was the case for the rare gases, coverages of these molecules in excess of ‘1 ML’ continued to attenuate the O₂ PSD signal. Interestingly, coverages of these molecules above 2 ML did not fully quench O₂ PSD, suggesting that the second and higher layers may not uniformly cover the first layer.

The third category of coadsorbate comprises the most strongly bound molecules explored (water, methanol and acetone). As shown in Figure 2c, these exhibit the most pronounced impact on the O₂ PSD signal, attenuating the yield strongly with low coverages of the coadsorbate (<0.25 ML). For all three molecules, the O₂ PSD attenuation exhibited an exponential-like trend with increasing coadsorbate coverage. Acetone was particularly effective at suppressing the O₂ PSD signal, attenuating it to near zero with 75% of its first layer saturation coverage.

Band bending effects have previously been offered as an explanation for the influence of a coadsorbate on the stimulated desorption of O₂ from TiO₂(110). (5; 16; 67; 70) Band bending

results from formation of accumulation/depletion zones in a semiconductor surface region due to the shifting of charge at the interface. Surface defect chemistry (formation or reactivity) is a major source of band bending. Chemisorption of molecules at non-defect sites can also cause band bending when there is significant charge transfer between the adsorbate (as a donor or acceptor) and the semiconductor. The surface chemistry of chromyl chloride (CrO_2Cl_2) is illustrative. (71) Adsorption of this molecule on the clean $\text{TiO}_2(110)$ surface at 300 K causes upward band bending of ~ 0.3 eV. As the adlayer decomposes on heating (by breaking O-Cr bonds and depositing CrCl_2 on the surface), the bands bend downward by 0.6 eV. These band bending effects are linked directly to charge transferred between the adlayer and the surface during adsorption and thermal decomposition.

The impact of such band bending events on surface photochemistry is well-known. (5) Bands do not bend without significant charge transfer. For example, covalently anchored fullerenes bend the bands of a semiconducting diamond (100) surface, but physisorbed fullerenes do not. (72) Similarly, pyridine or acetone chemisorption on $\text{ZnO}(1\bar{1}00)$ both result in weak band bending (<0.1 eV), but physisorbed layers of these do not. (73) In these examples, interfacial dipole changes can result from adsorption (as revealed by work function changes) without significant charge transfer at the interface. The ability of physisorbed molecules and rare gases to alter the photochemical efficiency of O_2 PSD on $\text{TiO}_2(110)$ suggests that adlayers incapable of donating (or extracting) charge can play a role in influencing surface photochemistry. Figure 3 shows that the magnitude of the coadsorption effect on O_2 PSD scales with the gas phase basicity of the coadsorbate. (74) This is illustrated at two different coadsorbate coverages: at 50% saturation (top) and at saturation (bottom). In both cases, the extent to which the coadsorbate diminishes the O_2 PSD signal correlates remarkably well with the gas phase basicity. The three classes of species shown in Figure 2 are clustered into three regions of these plots, matching their relative basicity. These correlations suggest that the Lewis basicity of a coadsorbate somehow correlates with its ability to suppress the O_2 PSD signal.

TiO_2 surfaces are generally considered amphoteric, but the salient character is acidic because of the Ti^{4+} sites and weak basicity. (75) Data in Figure 4 shows that the binding energy of each coadsorbate, as derived from TPD (see Supplemental Material) using the Redhead equation, (76) systematically correlates with the coadsorbate's gas phase basicity. This is because the binding of the species predominately involves varying degree of electrostatic

interaction with Ti^{4+} sites on the surface. This indicates that the coadsorbates explored in Figures 2 and 3 interact with the Ti^{4+} sites by exploiting the basicity of the coadsorbate. This is the case even for the rare gases and the physisorbed molecules, where charge transfer is highly unlikely.

We suggest that the influence on O_2 PSD arises from the change in the interfacial dipole by the coadsorbate. This is schematically illustrated in Figure 5. The coadsorbed layers resulting from the species in Figures 2 and 3 should result in a net work function decrease (left) as each species orients with its negative poles toward the surface, as would be expected for most of the molecules explored here. We propose that the interfacial dipole established by these coadsorbed layers suppresses positive charge (holes) from being passed into the interfacial layer where O_2 can be neutralized and desorbed. In contrast, coadsorbate layers with the positive pole toward the surface (right side) should enhance O_2 stimulated desorption, as has been observed for O_2 coadsorbed with Cl. (67; 77)

The interesting exception is the rare gases. In their case, two factors are important: the polarizability which dictates the extent to which they can participate in electrostatic-like interactions, and their size, which influences the packing within the $\text{TiO}_2(110)$ troughs. The polarizability follows the trend: $\text{Xe} > \text{Kr} > \text{Ar}$, which is also the trend in size. The data in Figure 2 suggests that Kr is more efficient than Xe at suppressing O_2 PSD. Although the margin of difference is not substantial, a possible explanation for the higher impact of Kr may rest in its van der Waals diameter (~ 4.0 Å) being more compatible with approach to O_2 bound at the Ti^{4+} sites than that of Xe (~ 4.3 Å).

For the model proposed here, the work function change produced by an adsorbate layer is a key diagnostic. Although such measurements were not possible for this study, we rely on Hugenschmidt and coworkers (78) to illustrate this point. Figure 6 shows the work function change for water on $\text{TiO}_2(110)$ (triangles) for coverage up to 2 ML from the work of these authors. Similarly, we plot the change in the O_2 PSD signal (circles) as a function of water coverage. The two y-axes are conveniently scaled to illustrate that both metrics exhibit the same coverage dependence for water. In other words, the trend in the magnitude (and direction) of the interfacial dipole for adsorbed water mirrors the impact this molecule has on the PSD rate of O_2 . (Unfortunately, we are not aware of any other careful coverage-dependent work function studies on the other coadsorbed used in this study.)

As final confirmation on the importance of the interfacial dipole, Figure 7 explores the influence of hydroxylation on the O₂ PSD rate. Numerous groups have shown that water molecules dissociate at oxygen vacancy sites on TiO₂(110) to generate two bridging hydroxyls. Vacancy-hydroxylated surfaces can easily be prepared on TiO₂(110) without the presence of molecular water. (35) It has been shown that water dissociation at vacancy sites is primarily an acid-base reaction, with little or no charge transfer resulting from the associated Ti³⁺ cations and the water fragments. (35; 79-81) However, the data of Figure 7 shows that the O₂ PSD rate is suppressed by ~40% when the surface is hydroxylated to just a ~0.1 ML coverage. (The temperature of the coadsorbed system in these measurements is critical as O₂ and OH_{br} react above 200 K. (35)) As with the other species explored in Figure 2, hydroxylation decreases the surface work function (by ~0.3 eV) through formation of an interfacial layer that is oriented with its (net) negative pole toward the surface. (78; 82)

Coadsorbate-induced enhancements of PSD rates have been observed on metal surfaces. For example, photodesorption studies of simple molecules on metal surfaces (70; 83-86) reveal that coadsorption significantly impacts PSD rates (by as much as four orders of magnitude). Clearly, there is not occasion for band bending in the electronic structures of metal surfaces, but changes in local electron density and electrostatics from adsorption events are well-known. The enhanced PSD signals for molecules such as NO or O₂ in these cases have been attributed to such local effects on these metal surfaces. This is not to say that changes in band bending do not exist on TiO₂(110) as a result of adsorption or that that such phenomena do not contribute to photochemical events. There is ample evidence in the photoelectrochemical literature to justify such claims. However, this study shows that the local electrostatic effects of coadsorption can have a significant impact on photochemical events on TiO₂(110).

4. Conclusions

We have investigated the influence of a variety of coadsorbates on the hole-mediated photon-stimulated desorption of O₂ on TiO₂(110). The coadsorbate-substrate interactions range from weakly-bound rare gas atoms to more strongly-bound chemisorbed species. The coadsorbates suppress the O₂ PSD, with the degree of suppression correlates with the coadsorbate's gas phase basicity, which in turn determines the strength of the coadsorbate-Ti⁴⁺ bond. The results indicate that adsorbate-induced changes in the work function, which can occur even in the absence of

charge transfer between the coadsorbates and the substrate, affect the ability of holes to reach the adsorbed O₂. The coadsorbates studied here reduce the work function, and thus reduce the probability of holes reaching the surface. These results show that local changes in the electrostatic potential need to be considered along with the effects of band-bending in understanding photochemical events on semiconductor surfaces.

Acknowledgements

This work was supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences & Biosciences. The work was performed using EMSL, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory (PNNL). PNNL is a multiprogram national laboratory operated for DOE by Battelle under Contract DE-AC05-76RL01830.

Figures

Figure 1

O₂ PSD at 30 K versus time for $\theta(\text{O}_2) = \theta_{\text{sat}}$ and 0 or 1 ML of various co-adsorbed molecules. O₂ was dosed on annealed TiO₂(110) at 30 K, then the sample was annealed at 100K and co-adsorbates were dosed at 30 K (Kr and N₂) or 80 K (H₂O).

Figure 2

Integrated O₂ PSD signal versus coverage of coadsorbed molecules. (a) Ar, Kr, Xe and N₂; (b) CO₂, CH₄, N₂O and CO; and (c) H₂O, acetone and methanol plots.

$$\theta(\text{O}_2) = \theta_{\text{sat}}.$$

Figure 3

Integrated O₂ PSD signal for 0.5 and 1 ML of co-adsorbed molecules versus the basicity of these molecules. The basicity data are taken from (74).

Figure 4

Maximal binding energy of co-adsorbed molecules on $\text{TiO}_2(110)$ versus the basicity of these molecules. The maximal binding energies are calculated from the high-temperature edge of the TPD spectra using Redhead analysis. (76) The basicity data are taken from (74).

Figure 5

Change in interfacial dipole as result of a coadsorption

Figure 6

Integrated O₂ PSD signal (red circles) and change in work function, $\Delta\Phi$, (blue triangles) versus coverage of coadsorbed H₂O molecules. The axes for work function data, taken from the Hugenschmidt and co-authors, (78) and O₂ PSD yield data are scaled for illustration.

Figure 7

O₂ PSD versus time for O₂ dosed on annealed (black trace) or hydroxylated (red trace) TiO₂(110). $\theta(\text{O}_2) = \theta_{\text{sat}}$. O₂ was dosed on annealed or hydroxylated TiO₂(110) at 30 K, then the sample was annealed @ 100K prior to the PSD.

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TOC Graphic

Quenching of Electron Transfer Reactions through Coadsorption:

A Study of Oxygen Photodesorption from $\text{TiO}_2(110)$

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