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Electronic Signatures of a Model Pollutant-Particle System: Chemisorbed Phenol on TiO₂(110)

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Abstract

Environmentally persistent free radicals (EPFRs) are a class of composite organic/metal oxide pollutants that have recently been discovered to form from a wide variety of substituted benzenes chemisorbed to commonly encountered oxides. Although a qualitative understanding of EPFR formation on particulate metal oxides has been achieved, a detailed understanding of the charge transfer mechanism that must accompany the creation of an unpaired radical electron is lacking. In this study, we perform photoelectron spectroscopy and electron energy loss spectroscopy on a well-defined model system – phenol chemisorbed on TiO₂(110) – to directly observe changes in the electronic structure of the oxide and chemisorbed phenol as a function of adsorption temperature. We show strong evidence that, upon exposure at high temperature, empty states in the TiO₂ are filled and the phenol HOMO is depopulated, as has been proposed in a conceptual model of EPFR formation. This experimental evidence of charge transfer provides a deeper understanding of the EPFR formation mechanism to guide future experimental and computational studies, as well as potential environmental remediation strategies.

Introduction

Radicals derived from many species of substituted benzenes are easily formed and stabilized through resonance with π orbitals in the aromatic ring^{1–3}. Recent studies have shown that such radicals may form from aromatic precursors chemisorbed to metal oxide particulate matter produced in combustion reactions and in soils contaminated by organic pollutants. The term “environmentally persistent free radical,” or EPFR, has been coined to refer to these composite organic/metal oxide pollutant particles. In addition to serving as precursors in the formation of toxic dioxins and furans^{4–9}, EPFRs have been observed via electron paramagnetic resonance (EPR) spectroscopy to have half-lives of hours or days under ambient conditions, and are detectable long after their formation when trapped in soils or sediments¹⁰ – long enough to present a significant danger in biological exposure^{11,12}. These

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species generate reactive oxygen species in aqueous solutions^{13,14}, and introducing them to living tissue can result in oxidative stress, cell death, and increased susceptibility to viral infection^{15–17}. An understanding of the formation mechanism of these EPFRs at the fundamental level is therefore of paramount importance in understanding their environmental toxicity and in guiding strategies for remediation. Employing a model system to gain insight, here we present surface science studies that directly mimic one of the basic aspects of EPFR formation – the chemisorption of phenol, an aromatic EPFR precursor, onto a well-defined rutile TiO₂(110) surface. Upon adsorption of phenol at elevated temperature on this model surface, we directly observe charge transferred into unfilled Ti 3*d* states and a shift to lower energy in the threshold of the system's optical absorption, which is consistent with the prevailing conceptual picture of EPFR formation involving an electron transfer from the organic precursor to the metal oxide.

In the inorganic fraction of combustion products and soils, SiO₂ tends to be the most common component^{4,5,18}, but is inert for EPFR formation. However, lab-created nanoparticles of commonly observed metal oxides such as CuO¹¹ and Fe₂O₃¹² supported on silica have been shown to form EPFRs after high-temperature exposure to precursors such as chlorinated benzenes and phenols, accompanied by indirect observations of the formal reduction of the metal oxide^{12,19,20}. EPR spectroscopy suggests that the radicals formed under moderate temperature conditions are either carbon- or oxygen-centered aromatic radicals with an intact phenyl ring^{11,12} (i.e. no further decomposition reaction occurs), which is supported by FT-IR studies¹⁹. Recently, we have also shown that EPFRs form on nanometer-sized rutile TiO₂ powder and, using electron energy loss spectroscopy (EELS), observed a lowering in energy of the π - π^* transitions in phenol chemisorbed on single-crystal TiO₂(110) under temperature conditions that result in radical formation in other systems²¹.

The functionalization of TiO₂ with organic molecules is itself of significant interest in the field of photovoltaics²² (PV). To overcome the wide band gap that prevents efficient photoabsorption, TiO₂ surfaces are functionalized with organic dyes that induce electronic states within the band gap and shift the onset of optical absorption. Thus for these and other reasons there has been considerable interest in the binding and photochemistry of substituted benzenes such as phenol, catechol, and nitroaromatics with easily prepared TiO₂ surfaces^{23–35}, as these can act as models for more complicated organic dyes.

However, these existing PV studies tend to focus on the electronic structure of the functionalized surface at or near room temperature. EPR spectroscopy indicates that phenol adsorption on TiO₂ powders at elevated temperature generates persistent phenoxyl radicals, and EELS indicates that the HOMO-LUMO gap of adsorbed phenol narrows with increasing adsorption temperature²¹. In order to better understand this, we will probe in more detail the electronic structure of this system under temperature conditions relevant for EPFR formation.

In this work, we perform photoemission and EELS measurements of phenol adsorbed at room temperature and at 220°C on single-crystal rutile TiO₂(110) as a model system for environmentally relevant species active for EPFR formation. Using resonant photoemission,

we are able to enhance the intensity of Ti 3d-derived electronic states, particularly the defect-induced state near the Fermi level. This state appears when excess electrons are trapped in the near-surface region through either the production of oxygen vacancies, Ti^{3+} interstitials, or by the transfer of charge from an adsorbate. As a complement to the photoemission measurements of occupied states, EELS measurements of low-energy electronic transitions let us probe the unoccupied states of the substrate and chemisorbed phenol as a function of temperature. The photoemission and EELS studies together demonstrate that the chemisorbed phenol-derived species formed after high-temperature adsorption is qualitatively different from that formed at room temperature. We show strong evidence that charge transfer from the chemisorbed species to the titania (“local reduction” of the titania) occurs after a high temperature phenol exposure, as conjectured by previous studies of particulate metal oxides. This observed signature lends support to the proposed mechanism by which EPFRs are formed on this model system, and may be consistent with other models of environmental EPFRs in general.

Methods

Photoemission measurements were performed at the 5m-TGM beamline at the Center for Advanced Microstructures and Devices (CAMD)³⁶, equipped with a 50mm hemispherical electron analyzer. All spectra, acquired in normal emission geometry, are normalized to a point on the background whose intensity solely derives from inelastic secondary electrons and not from any TiO_2 or adsorbate features. The clean $\text{TiO}_2(110)$ surface was prepared by cycles of 1.5 keV Ne^+ sputtering (30 min) and e-beam annealing to 700°C in 10^{-7} Torr O_2 (30 min) followed by cooling to room temperature in oxygen to prepare a surface free of oxygen vacancies. EELS measurements were performed in a separate UHV system consisting of a preparation chamber and analysis chamber separated by a gate valve. $\text{TiO}_2(110)$ was sputtered and annealed in oxygen as in the photoemission system, then transferred to the analysis side and probed using an LK2000 EELS spectrometer. All electronic EELS spectra were acquired using a primary beam energy of 30 eV in the specular geometry with an incident and exiting beam angle of 60° with respect to the surface normal. The energy resolution was approximately 30 meV as measured from the FWHM of the elastically scattered beam. All EELS spectra have been normalized to the elastic peak.

To dose phenol under various temperature and pressure conditions, solid phenol was loaded into a pyrex tube attached to a standard leak valve and purified by several freeze-pump-thaw cycles. To maintain consistency with the preparation conditions for EPFR-containing particulate matter prepared for chemical and biological research, we performed studies of high temperature adsorption using phenol at a pressure of 10^{-3} Torr, for a total dose of 10^6 L ($1 \text{ L} = 10^{-6} \text{ Torr}\cdot\text{s}$), accomplished by transferring the sample into a side chamber via load-lock. In the load-lock dosing setup, the sample was radiantly heated by a tungsten filament mounted near the sample stage, with temperatures measured by a type K thermocouple in contact with the sample mount. The load-lock was then pumped back to its base pressure before transferring the sample back into the main chamber. This load-lock dosing system was used for high temperature exposures in both the photoemission and EELS systems. At the photoemission beamline, dosing at room temperature and lower pressure (10^{-6} Torr or lower) was accomplished by opening the load-lock to the main chamber and dosing the

sample in the manipulator used for photoemission measurements. In the EELS system, lower pressure dosage was accomplished using a separate leak valve attached directly to the experimental chamber. To provide reference spectra of pure phenol for photoemission and EELS, we cooled the sample manipulator with liquid nitrogen and dosed enough phenol to form physisorbed multilayers (enough that no spectral features from TiO_2 are detectable), which we refer to as “phenol ice.”

Electronic structure calculations for an isolated phenol molecule were performed using the Gaussian09 software package using the B3LYP hybrid functional³⁷ and the 6-31G++ basis set. The density of states was obtained by convolving the calculated electronic states with a Gaussian function of FWHM 1.5 eV using GaussSum (see Fig. S1 in Supporting Information).

Results and Discussion

Figure 1a depicts normal emission photoemission spectra from phenol dosed at various conditions on the stoichiometric $\text{TiO}_2(110)$ surface. The spectra in Figure 1 were taken at room temperature using 40 eV photons after dosing under the conditions indicated, except for the “phenol ice” spectrum, which was taken with the sample held at -173°C . On the clean $\text{TiO}_2(110)$ surface, we see two prominent photoemission peaks centered around 5 and 8 eV, deriving from hybridized Ti 3d-O 2p π -bonding states and O 2p-Ti 3d σ -bonding states respectively. The intensity between 3 eV and the Fermi energy is nearly zero, indicating a nearly perfect, defect-free surface. The vertical dashed line labeled VBM indicates the position of the valence band maximum of the clean surface.

Upon deposition of 100 L phenol at room temperature, a significant shoulder on the upper end of the valence band appears, centered at approximately 3 eV, and significant intensity with some structure appears in the region from 9–15 eV. With reference to the difference spectra in Figure 1b), we assign the shoulder on the upper edge of the valence band to the phenol HOMO. As indicated by the vertical dashed line labeled HOMO, the onset of the HOMO lies approximately 1.1 eV above the TiO_2 valence band maximum. Exposure to 10^6 L phenol at 220°C results in a spectrum similar to the room temperature dose, but it is clear that the shoulder on the upper edge of the TiO_2 valence band at 3 eV has diminished, and subtle changes to the structure of the peaks between 6 and 10 eV have occurred. We observe a small amount of band bending after high-temperature adsorption – the 220°C dose bends the bands downward by 0.2 eV. (See Fig. S2 of the Supporting Information for analysis of the band bending taken from a core level peak.) The direction of band bending suggests charge donation from the adsorbed molecule to the surface after high temperature adsorption³⁸, although the magnitude of the charge transfer could be inferred to be small from the magnitude of the shift. (Per the description given by Zhang *et al*³⁸, adsorption of a charge donor causes a filled molecular orbital in the molecule to shift upward, interacting with unfilled states in the semiconductor to transfer an electron, which sets up an electric field at the surface whose effect is to shift the bands down.)

The difference spectra in Figure 1b were generated by correcting the spectra for the band bending noted above (the dosed spectra were shifted to align with the clean), then scaling

down the clean surface spectrum by a factor of 0.65 prior to subtraction to account for the attenuation of emission from the substrate due to the adsorbate. This presents a much clearer picture of the temperature-dependent changes in the adsorbate's molecular orbital structure. In the room temperature spectrum (black), the shoulder on the TiO_2 valence band is revealed as a distinct peak at 3 eV, very similar to that reported for catechol on rutile $\text{TiO}_2(110)$ though approximately 0.6 eV higher in binding energy^{24,25}. With reference to the spectrum of multi-layer physisorbed phenol at low temperature (pink) and the calculated molecular orbitals of an isolated phenol molecule (see also Fig. S1 of the Supporting Information), this is clearly the phenol HOMO. A second peak of equal intensity is revealed at 5 eV along with a higher-intensity peak at 7 eV. The structure between 8 and 12 eV remains unresolved, but the peaks at 13.7 and 17 eV are made more distinct, again similar to peaks observed for catechol/ $\text{TiO}_2(110)$ though higher in binding energy. With reference to the phenol ice spectrum and the calculation, we assign these high binding energy peaks as phenol σ orbitals.

Compared to the room temperature data, the high-temperature difference spectrum reveals substantially lower intensity in the phenol HOMO peak and in the 5 eV peak, a potential indication that these phenol-derived states have been depopulated. Hints of a new state at 4 eV are seen, although it is possible that this is also present in the room temperature spectrum but hidden due to strong overlap with the peaks on either side. States between 8.5 and 12.5 eV are more intense with respect to the room temperature spectrum, although still unresolved, and the two peaks at 13.7 and 17 eV are significantly reduced in intensity and broadened. The similarity of the difference spectra under both adsorption temperature conditions suggests that the species present after the high-temperature dose retains an intact phenyl ring and has not decomposed into smaller hydrocarbon fragments.

It is clear that the position of the phenol HOMO taken from the spectrum of phenol ice at -173°C is identical to that seen after chemisorption at both room temperature and 220°C (using the vertical dashed line as a guide to the eye), as are the phenol σ orbitals at binding energies above 13 eV and the weak feature at approximately 12 eV. These agree well with the electronic states of an isolated phenol molecule obtained from a DFT calculation (vertical bars in Fig. 1b and Fig. S1). We may tentatively say that the substantial changes in peaks below the HOMO (roughly from 4–10 eV binding energy) suggest that these are the molecular orbitals with significant hybridization to the $\text{TiO}_2(110)$ surface.

In Figure 2, we present spectra under the same conditions as Figure 1, but taken at a photon energy of 50 eV. At this photon energy, the intensity of Ti 3d-derived states is enhanced through resonance^{39,40}, which can give a clearer understanding of adsorption-induced changes Ti 3d-derived states in the substrate. Briefly, resonant photoemission exploits the constructive interference between two different excitation pathways to the same final state. In TiO_2 this selectively enhances the intensity of 3d-derived Ti peaks. At photon energies exceeding 47 eV, one produces excitations of the Ti 3p state and this excited electron rapidly decays, filling the 3p core hole and emitting a 3d electron. The interference of this resonant channel with the direct 3d emission process results in a roughly 5-fold enhanced sensitivity to these defect states. This particular resonance remains quite intense for a photon energy range of about 10 eV above the threshold⁴⁰. Thus in Figure 2 we present data

acquired at 50 eV to enhance Ti 3d-derived peaks, and in particular the peak at 0.8 eV binding energy that is not visible at photon energies below the resonance. These states are usually attributed to excess negative charge associated with surface oxygen vacancies and/or reduced interstitial Ti^{40,41}. This facilitates an understanding of which photoemission peaks are purely adsorbate-derived and which are Ti-derived.

The spectra we present in Figure 2 have a very different overall lineshape from the spectra in Figure 1 due to these resonant effects. The small defect-related peak at 0.8 eV is now present in the clean spectrum (blue) and appears with much higher intensity in the 220°C dose (red), but is absent after a room temperature dose (black). After both phenol doses, the additional peaks at binding energies 9.5 eV and higher are again apparent. It is evident again that dosing under either temperature condition contributes additional structure between approximately 6 and 10 eV. We observe band bending identical to that in Figure 1, so as in that figure, the difference spectra in Figure 2b are generated by first correcting for the band bending, then scaling down and subtracting the clean-surface spectrum.

The difference spectrum for the 100 L room temperature dose (Figure 2b, black) again shows the phenol HOMO at 3 eV as in the 40 eV data. The peak centered at approximately 5 eV (indicated by a dashed line), is now strongly enhanced in intensity with respect to the spectrum measured below the resonance threshold. Note also that the calculation for an isolated phenol molecule shown in Fig. 1 and the Supporting Information shows no occupied molecular orbital near this energy. The resonant enhancement of this 5 eV peak and the lack of close correspondence with an unperturbed state of phenol suggest that this state has some hybridization with Ti-derived states in the substrate. (The same observation applies to the high-temperature difference spectrum discussed in the next paragraph.) The remainder of the peaks at energies between 7 and 10 eV remain broad and unresolved, and the phenol-derived peaks at 13.7 and 17 eV are still apparent. Finally, we again note that the peak at 0.8 eV is reduced in intensity with respect to the clean surface. Having already corrected for attenuation after dosing, and having prepared a surface virtually free of oxygen vacancies before dosing, we attribute the change in this residual peak to the binding of phenol to surface sites near a reduced Ti interstitial, which is similar to the behavior observed for the adsorption of catechol on various titania surfaces^{24,25}.

The high-temperature difference spectrum at 50 eV (Figure 2b, red) is in some ways qualitatively similar to the corresponding difference at 40 eV (Figure 1b, red). As in the 40 eV spectra, the phenol HOMO here is vastly attenuated, the states between 8.5 and 12.5 eV are enhanced, and the higher binding energy peaks are attenuated. However, a significant and striking result that is not visible below the resonant threshold is demonstrated in greater detail in Figure 3, which directly compares the low binding energy region of the 50 eV difference spectra from the room temperature and 220°C phenol doses with no offsets added. It is obvious that phenol adsorbed at high temperature (open circles, red) enhances the intensity of the defect state with respect to that from a pristine TiO₂(110) surface, whereas phenol adsorbed at room temperature (open squares, black) suppresses it. Similarly, the phenol HOMO (here appearing as a shoulder at 3 eV on the side of the more intense peak at 5 eV) appears significantly attenuated after the high-temperature dose.

This strongly suggests that high temperature adsorption of phenol results in charge transfer from the adsorbed species to the electronic state of the TiO₂ that gives rise to the “defect” peak. Recall that, in studies of clean TiO₂(110), this peak is observed to grow as the density of both surface oxygen vacancies and reduced Ti interstitials increases⁴². Metal nanoparticle deposition on this surface has been observed to increase or suppress the intensity of this peak, depending on the tendency of the deposited metal to act as a charge donor or acceptor⁴³. However, one caveat should be noted here. Although the increase in intensity of the defect peak is a signature that charge is being transferred into the corresponding electronic state, which is consistent with our conceptual picture of the charge transfer involved in EPFR formation, it is also possible that the presence of surface –OH groups rather than solely the chemisorbed phenol contributes to the intensity of this peak⁴². However, preliminary vibrational EELS studies (see Supporting Information Fig. S3) suggest that surface –OH groups are not present after high temperature exposure. Further studies using scanning tunneling microscopy or vibrational spectroscopy would be useful to help determine the adsorption geometry of the phenol. Additionally, this evidence of charge transfer into the TiO₂ defect state should be taken into account in future attempts to model EPFR formation using density functional calculations.

Electron energy loss spectroscopy

EELS provides an extremely surface-sensitive probe of low-lying electronic transitions of well-defined surfaces, with virtually no contributions in the spectra from subsurface atoms. As we have already shown photoemission measurements of occupied electronic states in Figures 1–3, EELS measurements of transitions now permit us to infer details about the empty states of the system – the TiO₂ conduction band and phenol LUMOs. Figure 4 presents EELS spectra of clean and dosed TiO₂(110) from 0–9 eV loss energy, which encompasses the low-lying interband transitions in TiO₂ (band gap 3.2 eV) and the first few HOMO-LUMO transitions in molecular phenol^{44,45}.

Reading Figure 4 from bottom to top, we see that the major difference between oxygen-annealed (blue, “oTiO₂”) and UHV-annealed TiO₂(110) (green, “rTiO₂”) is the presence of an intense loss peak at 0.8 eV and a broad tail extending from that peak to the onset of interband transitions at 3.2 eV in the rTiO₂ spectrum. This arises from transitions from the defect-related Ti 3*d* occupied state to the conduction band, and is correlated with the presence of surface defects, exactly the same as the peak just below the Fermi level in photoemission that is shown in Figure 3. Note that this peak is absent in the EELS spectrum from oTiO₂, which is a strong indication that annealing in O₂ is sufficient to restore the vast majority of surface defects. The strong intensity of this defect-related peak compared to the interband transitions is again a signature of the extreme surface-sensitivity of EELS.

Multilayer phenol physisorbed on the UHV-annealed surface at –183°C (pink) shows two distinct loss peaks centered at 4.55 eV and 6.45 eV, with a weak shoulder at 5.8 eV. With reference to calculations and EELS data from molecular phenol presented in the literature, we can assign the latter two peaks and the weak shoulder as transitions between phenol molecular orbitals. The peaks at 4.55, 5.8, and 6.45 eV encompass a manifold of π - π^*

transitions dominated by excitations between the HOMO/HOMO-1 and LUMO/LUMO+1/LUMO+2 orbitals on the phenol⁴⁴.

The spectrum from phenol dosed at room temperature (black) contains peaks that almost perfectly align with the molecular orbital transitions from phenol ice (pink), but contains an extra and quite intense peak at with an onset at 2.1 eV that is not a feature from either the pure phenol or the clean TiO₂(110). The nearest analog in phenol seen either experimentally or theoretically is a dipole-forbidden singlet-triplet excitation⁴⁴, but it is implausible that this would give rise to such a strong EELS peak. We instead attribute this low-energy loss peak after a room temperature dose to excitations from the phenol HOMO to the TiO₂ conduction band. Note the 1.1 eV energy difference between the onset of this peak and the onset of interband transitions in clean oTiO₂ (indicated by the vertical dashed lines in Figure 4). This is identical to the energy difference between the TiO₂ valence band maximum and the onset of the phenol HOMO observed in photoemission shown in Figure 1. Thus, this new loss feature is indeed situated at exactly the right energy to result from a HOMO to conduction band transition. In effect, this demonstrates that functionalizing a stoichiometric TiO₂(110) surface with phenol does significantly shift the onset of optical absorption into the range of visible light.

By contrast, the spectrum from phenol dosed at 220°C (red) shows almost none of the distinct features visible in the spectrum from room temperature phenol (black). In light of the photoemission results presented above, we may attribute this to the depopulation of the highest occupied states of phenol after high-temperature chemisorption, which should correspondingly suppress the intensity of excitations from those states. As in the room temperature dosed spectrum, we see the onset of a transition at 2.1 eV (vertical dashed line) that likely results from a HOMO to conduction band excitation, but its intensity is now much lower, and at higher energies we see no distinct peaks but a broad continuum of losses. We note also that the low-energy intensity in this spectrum, below 2 eV, is substantially enhanced compared to all the other surface preparations shown here. The inset in Figure 4 shows the loss region from 0.5 – 2.1 eV, which encompasses the strong peak that comes from transitions from the TiO₂ defect state to the conduction band. The spectra in the inset are all shown at full scale and have no vertical offsets added. It is evident that the intensity of losses in this region is much higher for the rTiO₂ surface (green) than for the clean oTiO₂ (blue) or the room temperature and –183°C phenol (black, pink), but that the 220°C phenol dose (red) has a loss intensity higher even than the defect-rich rTiO₂ surface. This is again consistent with the photoemission data; as demonstrated in Figures 2 and 3, high-temperature chemisorption of phenol results in charge transfer into the Ti 3*d* state usually associated with oxygen vacancies, which should also result in the corresponding loss feature in EELS that we observe here. As the room temperature and low temperature dosed phenol also shows significant loss intensity in this region from some intrinsic loss process in the phenol, though lower than the rTiO₂ surface, it seems reasonable that the phenol dosed at 220°C should also show this contribution in addition to excitations from the formerly empty Ti 3*d* state, which would explain the enhanced intensity even with respect to the defect-rich rTiO₂.

Conclusions

We have studied the occupied electronic states of the phenol/TiO₂(110) system as a function of phenol dosing temperature, and correlated our photoemission studies with EELS measurements of the low-lying electronic excitations of the system in order to develop a picture of the low-lying unoccupied electronic structure as well. We find that after saturation doses of phenol at room temperature, the resulting photoemission spectrum exhibits features of intact chemisorbed phenol, similar to previous studies of aromatics on TiO₂, with the phenol HOMO located 1.1 eV above the top of the TiO₂ valence band. This is correlated exactly with EELS measurements, which show an excitation 1.1 eV below the onset of TiO₂ interband transitions after dosing phenol at room temperature, corresponding to an excitation from the phenol HOMO to TiO₂ conduction band. After dosing at 220°C, by contrast, we observe a significant attenuation of the phenol HOMO and phenol σ orbitals, accompanied by an enhancement of the Ti 3d-derived “defect” peak at 0.8 eV. We interpret this as a signal that charge is transferred from the phenol to the TiO₂ surface upon high temperature chemisorption, which is a direct observation of one step of the proposed mechanism for persistent free radical formation from a generic substituted benzene chemisorbed on a particulate metal oxide. In EELS, phenol exposure at 220° C shows low-energy losses reminiscent of the loss feature seen on a defect-rich TiO₂ surface, which corresponds to excitations from the defect-related state to the conduction band. This demonstration of charge transfer accompanying high-temperature chemisorption provides a direct confirmation of one feature of the prevailing schematic model of EPFR formation from an aromatic precursor, the transfer of an electron to from the organic species to the oxide. This should serve as a guide to future computational studies that attempt to model the radical formation.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.

(a) 40 eV valence band photoemission spectra of clean TiO₂ (blue, bottom), 100 L phenol dosed at room temperature (black, middle), and 10⁶ L phenol dosed at 220°C (red, top). (b) Difference spectra obtained from the data in (a), with a spectrum of multilayer physisorbed phenol on the sample at -173°C (pink, dashed curve) and the calculated occupied orbitals of a single phenol molecule (solid vertical bars) displayed for comparison. The procedure for generating difference spectra is described in the text. Spectra have been vertically offset for clarity. Vertical dashed lines are guides to the eye.

Figure 2.

(a) 50 eV valence band photoemission spectra of clean TiO_2 (blue, bottom), 100 L phenol dosed at room temperature (black, middle), and 10^6 L phenol dosed at 220°C (red, top). (b) Difference spectra obtained from the data in (a). The procedure for generating difference spectra is identical to that in Figure 1. All spectra have been vertically offset for clarity. Vertical dashed lines are guides to the eye.

Figure 3. Close-up of phenol HOMO/oxygen vacancy peak region of the difference spectra in Fig. 2. Here no vertical offset is added so that peak areas are more easily compared.

Figure 4.

EELS measurements of electronic losses of various preparations of $\text{TiO}_2(110)$ and phenol-dosed $\text{TiO}_2(110)$ surfaces. From bottom to top, we show oxygen-annealed $\text{TiO}_2(110)$ measured at -183°C (blue), UHV-annealed $\text{TiO}_2(110)$ measured at -183°C (green), 25 L phenol dosed and measured on UHV-annealed $\text{TiO}_2(110)$ at -183°C (pink), 10^6 L phenol dosed at 220°C on oxygen-annealed $\text{TiO}_2(110)$ measured at room temperature (red), and 100 L phenol dosed at room temperature on oxygen-annealed $\text{TiO}_2(110)$ measured at room temperature (black). Spectra are normalized to the elastic peak except for the second and third from the top, which have been scaled down by a factor of 0.5 as indicated in the figure. In the three topmost spectra, dots represent the measured data points, and the solid curves show the data smoothed by a binomial algorithm. The inset shows all spectra with their proper normalization and no vertical offsets added in the low-energy loss region from 0.5 – 2.1 eV, using the same color coding as the main figure, but only displaying the smoothed data.