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McMurry Chemistry on TiO_2(110): Reductive C=C Coupling of Benzaldehyde Driven by Titanium Interstitials

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Abstract: Selective reductive coupling of benzaldehyde to stilbene is driven by subsurface Ti interstitials on vacuum-reduced TiO_2(110). A combination of temperature-programmed reaction spectroscopy and scanning tunneling microscopy (STM) provides chemical and structural information which together reveal the dependence of this surface reaction on bulk titanium interstitials. Benzaldehyde reductively couples to stilbene with 100% selectivity and conversions of up to 28% of the adsorbed monolayer in temperature programmed reaction experiments. The activity for coupling was sustained for at least 20 reaction cycles, which indicates that there is a reservoir of Ti interstitials available for reaction and that surface O vacancies alone do not account for the coupling. Reactivity was unchanged after predosing with water so as to fill surface oxygen vacancies, which are not solely responsible for the coupling reaction. The reaction is nearly quenched if O_2 is adsorbed first—a procedure that both fills defects and reacts with Ti interstitials as they migrate to the surface. New titania islands form after reductive coupling of benzaldehyde, based on scanning tunneling microscope images obtained after exposure of TiO_2(110) to benzaldehyde followed by annealing, providing direct evidence for migration of subsurface Ti interstitials to create reactive sites. The reliance of the benzaldehyde coupling on subsurface defects, and not surface vacancies, over reduced TiO_2(110), may be general for other reductive processes induced by reducible oxides. The possible role of subsurface, reduced Ti interstitials has broad significance in modeling oxide-based catalysis with reduced crystals.

Introduction

Determining the relationship between surface reactivity and defects is key to understanding the reactivity of reducible metal oxides. It is generally accepted that surface point defects, especially bridging oxygen vacancies, play a significant role in the reactivity of reduced TiO_2(110).[1,2] There is also, however, the possibility that subsurface defects, such as Ti interstitials and bulk oxygen vacancies known to contribute to bulk conductivity,[3] affect surface reactivity. For example, Ti interstitials are thought to be necessary for surface reoxidation at elevated temperatures,[4−9] and recent STM evidence has emerged showing that oxygen interacts with subsurface interstitials even at room temperature.[10] Furthermore, a recent paper on the adsorption of catechol on TiO_2(110) noted the independence of catechol adsorption on surface hydroxylation, suggesting that surface vacancies do not play a role in its adsorption.[11] We recently reported evidence for the participation of Ti interstitials in the coupling of acrolein to form 1,3-cyclohexadiene over the reduced (1 × 1) TiO_2(110) surface, also noting that surface hydroxylation did not affect the coupling reaction.[12] Importantly, interstitials were proposed to play a role in formic acid decomposition on the highly reduced (1 × 2) reconstructed TiO_2(110) surface, giving rise to the formation of new (1 × 1) islands.[8] The (1 × 2) surface is in a substantially reduced state, presumably Ti_2O_3,[8] which has been shown by the same authors to reconstruct back to the (1 × 1) surface in the presence of oxygen.[4] Thus, it is somewhat surprising that the less-reduced (1 × 1) TiO_2(110) surface is capable of undergoing similar terrace regrowth in the presence of organic species, as will be demonstrated here.

Herein, we establish that the reductive coupling of benzaldehyde is induced by Ti interstitials on the surface of TiO_2(110) using a combination of temperature programmed reaction

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spectroscopy and scanning tunneling microscopy (STM). We examined benzaldehyde because of its selectivity toward coupling over reduced $TiO_2(110)$ and for its widespread use as a solvent and as a flavor additive. Furthermore, we investigated the effects of oxygen and water on reactivity, as these components are important to, for example, environmental chemistry and industrial catalysis. Reductive coupling of aldehydes to olefins is an important catalytic process driven by Ti cations in solution[13,14] and on highly defective $TiO_2(001)$ created by Ar^+ sputtering.[15−20] Aldehydes, including benzaldehyde, are known to reductively couple over highly reduced rutile $TiO_2(001)$, created by Ar^+ bombardment;[15−17,19,20] however, the selectivity for coupling is generally low. Both the conversion and the yield of stilbene depended on the presence of reduced titanium centers; however, the surface was not structurally characterized and was very heterogeneous.[17,20] On the other hand, the yields of olefins from coupling formaldehyde and acetaldehyde on the more homogeneous annealed $TiO_2(110)$ surface are on the order of only a few percent.[21,22] Titanium dioxide was chosen as a model oxide in this study for several reasons. First, titanium dioxide is used in several applications such as solar cells, air purification, self-cleaning coatings, wastewater treatment, and in heterogeneous catalysis.[1,23−25] As a common component in paints and coatings, rutile TiO_2, in particular the most stable face, (110), serves as a well characterized and understood model for these experiments.[1] In fact, the (110) surface comprises ∼60% of the exposed faces in rutile powders, while ∼20% is made up of the (101) face, and the remaining ∼20% is the (100) face.[26] Rutile $TiO_2(110)$ is widely studied as a model for oxide surfaces because it can be studied using modern surface science techniques. For example, several detailed investigations have been reported on the interaction of both water and oxygen with this surface.[1,4,5,10,27−35] Notably, the $TiO_2(110)$ substrate is generally reduced by sputtering and heating in vacuum in order to render it sufficiently conducting for imaging and study with electron-based spectroscopies. Protocols have been developed to heal surface O vacancies, which generally represent $\leq 10\%$ of the surface sites; however, the degree of bulk reduction depends on the temperature used for annealing in vacuum and the number of preparation cycles of the crystal. The fact that TiO_2 prepared for surface science studies is bulk reduced necessitates the consideration of how subsurface and bulk defects affect chemical behavior.

In this work, we observe the selective coupling of benzaldehyde to form stilbene over the vacuum-annealed $TiO_2(110)$ surface with significant conversions of up to 28% and with 100% selectivity. The high selectivity and significant activity makes this an ideal system for imaging changes in the surface due to reaction. STM experiments show the formation of new titanium dioxide islands following benzaldehyde coupling to stilbene. By annealing to 900 K, we observed well-ordered $TiO_2(110)$ islands, providing direct evidence for Ti migration from the subsurface region to promote benzaldehyde reduction and formation of new titania seeds. These results are significant because they show new reactive centers are created on well-defined oxides; thus, interstitials may play a broad role in determining both thermal and photochemical activity.

Experimental Details

Temperature programmed reaction spectroscopy experiments were performed in a stainless steel ultrahigh vacuum (UHV) chamber with a base pressure of $\sim 1 \times 10^{-10}$ torr, outfitted as described previously[12] with Auger electron spectroscopy (AES), low energy electron diffraction optics (LEED), an Ar^+ gun for sputter-cleaning the surface, and a quadrupole mass spectrometer used for product identification in temperature programmed reaction studies. The $TiO_2(110)$ crystal (Atomergic Chemetals Corp.) was clamped to a tantalum back-plate in a manner described previously[12] and prepared with multiple (27) cycles of Ar^+ sputtering at room temperature (1 kV, 2 μA, 20 min), followed by annealing at 850 K for 5 min, prior to temperature programmed reaction experiments. This procedure was repeated until no impurities were detectable in AES. Finally, the crystal was heated to 900 K for 5 min, resulting in a sharp (1 × 1) LEED pattern. This preparation procedure led to a crystal with ∼10% surface defect sites, determined by integration of the 490 K peak in the desorption spectrum of water, attributed in the literature to the disproportionation of hydroxyl groups bridge-bonded to oxygen vacancy sites.[27,28]

Benzaldehyde (C_7H_6O, Aldrich, 99.5+%) and distilled water were further purified using several freeze−pump−thaw cycles. Dioxygen (Specialty Gases, 99.9+%) was used as received. Doses are given in Langmuir for all reactants, corrected for the dosing enhancement resulting from directional dosing as compared to background dosing but uncorrected for ion gauge sensitivity. Previous studies of H_2O estimate the coverage of the first layer to be in the range of $5.2-6.5 \times 10^{14}$ molecules/cm^2.[27,28] Saturation of this first layer of water corresponds to a dose of ∼1.2 L.

All temperature programmed reaction experiments were performed using a linear heating rate of 3.5 K/s while recording intensity data for several masses in a single experiment. The crystal was biased at −70 V to repel electrons emitted by the filament of the mass spectrometer. The selectivities for reactions were calculated using a method described in detail elsewhere.[36,37]

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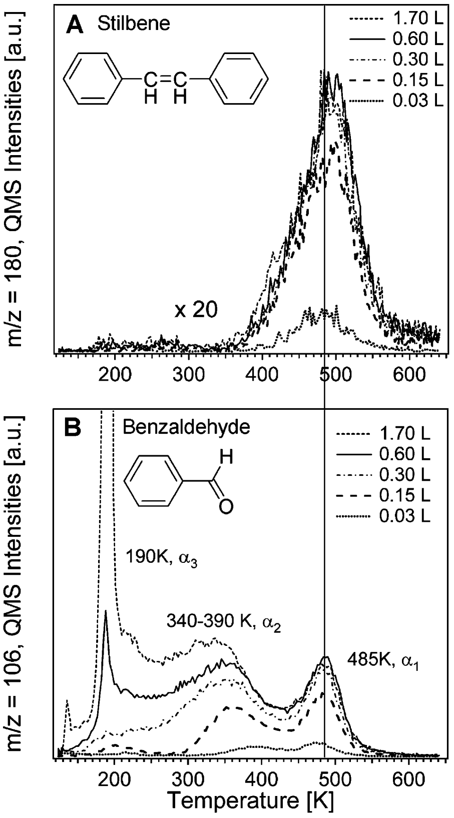

Figure 1. Temperature programmed reaction spectra as a function of benzaldehyde exposure on vacuum-annealed $TiO_2(110)$ at 120 K: (A) Stilbene evolution ($m/z = 180$, parent ion) and (b) benzaldehyde desorption ($m/z = 106$, parent ion). The heating rate for these experiments was 3.5 K/s.

Scanning tunneling microscopy (STM) experiments were performed at room temperature on a variable temperature Omicron STM (VT AFM model) in a chamber with a base pressure of $\sim 3 \times 10^{-11}$ torr. Benzaldehyde was dosed through a leak valve coupled to a directional doser which was positioned ~4 cm in front of the sample. The total coverage for these experiments was determined to be ~0.3 ML (relative to the concentration of 5-fold coordinated titanium ions on the surface, $5.2 \times 10^{14}/\text{cm}^2$) by counting the molecules on the surface. The STM sample was prepared in the same manner as above, with multiple cycles (28) of sputtering and annealing, until reduced to a blue color. We confirmed reactivity using a mass spectrometer (Pfeiffer Prisma 200) in the STM chamber. Sample heating was accomplished using a doped silicon wafer mounted directly beneath the sample, and a temperature calibration was separately performed using a type K thermocouple glued into a second sample with UHV-compatible ceramic glue (Aremco, Ceramabond 503). Finally, the chamber also contained an AES (Omicron) with which we checked sample cleanliness before and after reaction.

Results and Discussion

Reductive coupling of benzaldehyde to stilbene competes with molecular desorption in temperature programmed reaction experiments performed following exposure of the vacuum-annealed $TiO_2(110)$ surface to benzaldehyde at 120 K (Figure 1). For a dose of ~0.30 L benzaldehyde, 28% of the benzaldehyde is converted to stilbene, which evolves at 495 K (Figure 1A). Stilbene (parent ion $m/z = 180$ amu) was identified by comparison of the fragmentation pattern of the evolving species to that given in the NIST database. There is no residual carbon detected after temperature programmed reaction using Auger electron spectroscopy. Some hydrogen ($m/z = 2$) is observed to desorb from the crystal at ~200 K; however, this does not require exposure to benzaldehyde, and no additional hydrogen evolves, suggesting that hydrogen can trap in the crystal when sputtering to clean the surface, as discussed in the literature.[18,38] No other gaseous products were detected in a scan of all masses up to 200 amu.

Benzaldehyde ($m/z = 106$) desorbs in three features (Figure 1B): (1) a high temperature peak at ~485 K (α_1); (2) a strongly coverage dependent state that shifts from 390 K following a dose of 0.03 L benzaldehyde to 340 K for doses of 0.30 L and above (α_2); and (3) a low temperature multilayer peak at 190 K (α_3). The α_3 peak is attributed to sublimation of condensed benzaldehyde, since it grows indefinitely with benzaldehyde exposure. The α_2 peak is attributed to molecular benzaldehyde, most likely on the 5-coordinate Ti sites.

Stilbene formation immediately follows the α_1 benzaldehyde peak at all benzaldehyde doses (Figure 1). The stilbene and the α_1 peak populate proportionally for benzaldehyde doses less than saturation. The α_1 benzaldehyde peak is visible for all benzaldehyde doses and it does not shift significantly with exposure up to a saturation exposure of ~0.30 L benzaldehyde (Figure 1B). The activation energy for evolution of these species was estimated to be 126 ± 4 kJ/mol assuming a prefactor of $10^{13}\ \text{s}^{-1}$ and first order kinetics.[39] The evolution of benzaldehyde at 485 K suggests that oxygen remains bound in the molecule up to this temperature and that desorption competes with loss of oxygen to form the C−C coupling product in this temperature regime.

The α_2 peak is populated nearly simultaneously with the high temperature peak at ~390 K at the lowest coverage investigated. The fact that both the α_2 and α_1 peaks are observed at low benzaldehyde exposure and that they both thereafter increase in intensity with increasing exposure suggests that a fraction of the benzaldehyde that is bound in the α_2 state converts to the α_1 state during heating. Furthermore, both peaks saturate by ~0.30 L exposure to benzaldehyde.

The α_2 peak shifts from 390 to 340 K for benzaldehyde exposures of 0.03 and 0.30 L, respectively. This shift is attributed to repulsive interactions at higher coverage, similar to that of both acetone and water on TiO_2.[27,28,40] We roughly estimate the activation energy of desorption for this state to be in the range of 87 − 100 kJ/mol, again assuming a prefactor of $10^{13}\ \text{s}^{-1}$. The desorption energy extrapolated to zero coverage is, thus, 97 ± 4 kJ/mol. Our estimate does not account for coverage dependence in the pre-exponential factor. We tentatively assign the α_2-state to benzaldehyde adsorbed on Ti^{4+} sites based on comparison to previous studies of benzene, pyridine, 2,6-dimethylpyridine, *m*-xylene,[41] and benzoic acid.[42]

Previously, the activity for stilbene formation via reductive coupling of two benzaldehyde molecules on the Ar^+-bombarded and annealed (001) surfaces of TiO_2 was shown to correlate with the population of reduced titanium sites on the surface.[17] A mixture of Ti^{4+}, Ti^{3+}, Ti^{2+} and Ti^+ oxidation states was detected on the more active Ar^+-bombarded (001) surface, while

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predominantly Ti^{4+} was observed on the annealed substrate.[17] On both the bombarded and annealed (001) surfaces, stilbene is evolved in a broad peak from $\sim$350 K to $\sim$500 K, peaking at $\sim$440 K. Stilbene yields were 56% and 20% of the adsorbed benzaldehyde layer on the bombarded and annealed (001) surfaces, respectively, compared to a conversion of 28% herein on $TiO_2(110)$. Selectivity for stilbene was 72% on the bombarded (001) substrate, versus 60% on the annealed (001) substrate, compared to 100% selectivity for coupling on the (110) surface observed here. Whereas only stilbene is produced in our studies, the following products are produced on the bombarded (001) surface at the given temperatures and selectivities: benzene (365 K, $\sim$4%; 650−720 K, $\sim$1%), toluene (460 K, $\sim$6%; 560 K, $\sim$9%), styrene (460 K, $\sim$1%; 595 K, $\sim$1%), and some unassigned products ($\sim$6%). Residual surface carbon was also formed during reaction on the sputtered (001) surface, whereas no residual C was detected using Auger electron spectroscopy in our study of the (110) substrate. Additionally, benzene and toluene are produced on the annealed (001) surface at 375 K (selectivity $\sim$33%) and 470 K (selectivity $\sim$7%), respectively.

We observed an increase in activity with increased bulk reduction of $TiO_2(110)$. For example, the sample which converted 28% of the benzaldehyde to stilbene, (Figure 1), underwent 28 cycles of sputtering and annealing, while a sample which was only subjected to 4 cycles converted just 8% of the benzaldehyde. Repeated sputtering and annealing of titanium dioxide in vacuum gives rise to a blue tint as oxygen is removed from the crystal, and Ti^{3+} defects in the bulk are created, introducing color centers into the originally transparent substrate.[43] The notable difference between the bulk reduced rutile $TiO_2(110)$ substrate and the (001) surface is that the selectivity remains high for all preparations studied, yielding only stilbene and no other products.

As pointed out previously,[17] the reductive coupling of aldehydes to form olefins on reduced TiO_2 is analogous to the liquid-phase *McMurry* reaction which uses titanium halides as catalysts. In solution, the aldehydes are proposed to first reductively dimerize to form a pinacolate intermediate, followed by concerted elimination of both oxygen atoms to form an olefin.[13,14] In the liquid phase the pinacolate intermediate was identified via isolation of the pinacol at 0 °C, as well as via reaction of pinacols to form olefins at 60 °C.[13] There remains controversy about which titanium oxidation state is necessary for the liquid-phase McMurry reaction—both Ti^{2+} and Ti^0 have been proposed as reaction centers.[14,44] Notably, the reduction of benzaldehyde to stilbene is a 4 electron process. In the work by Idriss et al. on $TiO_2(001)$ surface,[17] no Ti^0 was detected using X-ray photoelectron spectroscopy, and reduction via an ensemble of cations in the +1 to +3 state is invoked.

We demonstrate here that surface oxygen vacancies are not solely responsible for the reductive coupling of benzaldehyde by repeated temperature programmed reaction studies of benzaldehyde without intervening surface treatment. The yield of stilbene from benzaldehyde reaction was the same in 20 consecutive temperature programmed reaction cycles in which the crystal was only heated to 650 K in between experiments. If surface oxygen vacancies were the only reactive site, the coupling should only occur on the freshly prepared surface, since annealing to 850 K is reportedly required for the production of oxygen vacancies after filling such sites with oxygen or hydroxyl groups.[27−29] Therefore, the coupling cannot be explained by a simple filling of surface oxygen vacancies by loss of oxygen from benzaldehyde.

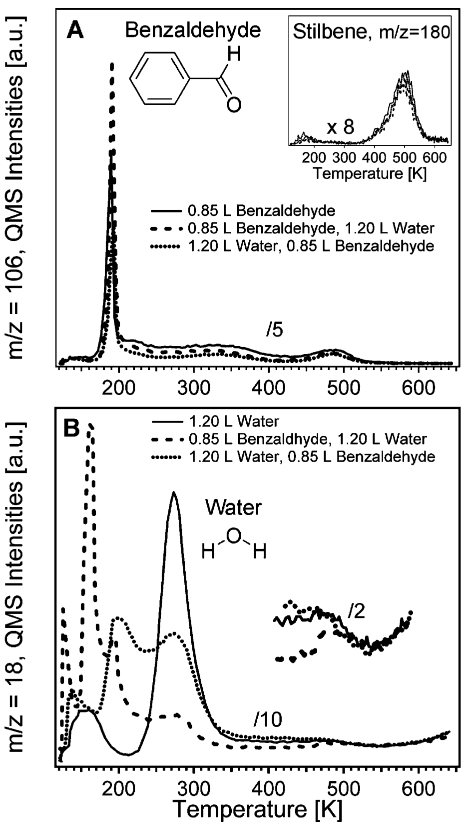

Figure 2. (A) Effect of the adsorption of water at 120 K on the temperature programmed reaction spectrum of benzaldehyde. (B) Corresponding effect on the desorption spectrum of water itself. The heating rate was 3.5 K/s.

We attribute the sustained activity for the reductive coupling of benzaldehyde to stilbene to the migration of Ti interstitials to the surface. The migration of titanium interstitials is known to promote surface regrowth under both reducing and oxidizing conditions at elevated temperatures,[4−6] and has recently been observed to occur at temperatures as low as $\sim$300−450 K with scanning tunneling microscopy (STM).[10] Furthermore, on the (1 × 2) surface reconstruction of rutile TiO_2, formic acid has been observed to cause the growth of new (1 × 1) islands at temperatures of >$\sim$400 K, reportedly via interaction of formate with interstitial Ti ions as mentioned above.[8] With this in mind, conversion of the α_2-benzaldehyde to a state, possibly a pinacolate-like intermediate, that leads to competing desorption in the α_1-state and oxygen loss could occur as the result of the migration of such defects to the surface during heating.

Water has no measurable effect on the yield of stilbene from coupling of benzaldehyde (Figure 2A inset)—added evidence that oxygen vacancies are not the primary reaction center. No new products were observed in the presence of water. There are no reports of water reaction with interstitials on $TiO_2(110)$—it only dissociates at surface vacancies as mentioned above.[39] It is reported, however, that formaldehyde, which couples over both the argon-bombarded and vacuum-annealed $TiO_2(110)$ surfaces to form ethylene,[21] does not couple following a dose of 2 L of water. The authors of this work claimed that coupling occurred via interaction with surface vacancies only, and that

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dosing water (therefore filling these vacancies with hydroxyl groups) quenched reactivity. It is also possible that water displaces formaldehyde, as it does in the case of styrene,[36] for example, thus preventing it from reacting. The observed difference between the reactivity of benzaldehyde and formaldehyde points to stronger binding to the surface in the case of benzaldehyde. We have observed a similar result in a study of acrolein and water on reduced $TiO_2(110)$, that is, water had no effect on the coupling reaction.[12]

We did, however, observe changes in the desorption spectra of both benzaldehyde and water when both species were adsorbed. First, the integrated desorption of benzaldehyde in Figure 2A decreases by ~45% (relative to that of benzaldehyde desorption alone for the same dose) when water is dosed on the surface before benzaldehyde adsorption (dotted trace). No significant change in integration is observed when water is dosed after benzaldehyde adsorption, although multilayer desorption increases. Furthermore, the solid trace of $m/z = 106$ for benzaldehyde alone is twice as intense in the α_2 peak than when water is dosed before benzaldehyde (dotted trace), and ~30% more intense than when water is dosed after benzaldehyde (hatched trace). This is likely the result of a competition between water and benzaldehyde for Ti^{4+} sites. Figure 2B shows the corresponding water desorption traces. The integrated desorption of water remains approximately the same relative to that of water alone (solid trace) when water is adsorbed before benzaldehyde (dotted trace), but decreases by ~25% when benzaldehyde is adsorbed before water (hatched trace). The peak at ~270 K, previously assigned to the adsorption of water at 5-fold Ti^{4+} sites,[27,28] is observed to decrease by a factor of 6 when benzaldehyde is adsorbed before water (hatched trace). This peak decreases by a factor of 2 when benzaldehyde is adsorbed after water (dotted trace). Our assignment of the α_2 peak to binding at 5-fold coordinated Ti^{4+} sites is thus supported by these observations. It is clear that benzaldehyde competes for Ti^{4+} sites, and water is displaced into second and multilayer desorption states, at ~200 and 160 K, respectively. Finally, we observed hydroxyl recombination at ~490 K in the desorption spectra of water whether benzaldehyde was present or not (Figure 2B inset). Thus, displacement of hydroxyls by benzaldehyde is ruled out.

We investigated the effect of exposing the surface to O_2 as a means of further investigating the role of defects in reductive coupling. While exposure of $TiO_2(110)$ to O_2 certainly heals surface vacancies, the interaction of O_2 with $TiO_2(110)$ is rather complex. Oxygen requires the presence of defect sites to bind at 120 K, adsorbing molecularly on the 850 K annealed surface.[29] Exposure of O_2 to the surface above 150 K leads to dissociation at oxygen vacancies. One of these O atoms is thought to fill a vacancy, while the other is present as an adatom.[29] Evidence for oxygen adatoms on the surface at temperatures up to 600 K is given in water desorption studies.[31] More recently, STM shows that O_2 can also dissociate in 5c-Ti troughs at room temperature in addition to the vacancies giving rise to new TiO_2 terraces upon heating.[10] This leads to an overall surface roughening which can be detected in the thermal desorption spectra of water.[30]

Exposure of the vacuum-reduced $TiO_2(110)$ surface to O_2 (800 L) at 120 K nearly quenches the yield of stilbene (Figure 3 inset). Exposure to O_2 also significantly decreases the α_1 benzaldehyde peak, such that only a broad tail remains (Figure 3). No O_2 desorption was detected in our experiments, nor were any other products detected. The α_2 benzaldehyde peak increases in intensity when benzaldehyde is dosed following O_2, though the total integration is approximately equal in both cases. These data indicate that the conversion of the α_2 peak to α_1 and the coupling product is inhibited by oxygen, likely because subsurface defects react preferentially with O on the surface. Importantly, the activity of the surface toward benzaldehyde coupling was completely restored after heating to 650 K during temperature programmed reaction of benzaldehyde on the surface first exposed to O_2. In contrast, heating to 850 K is required to recreate sites, presumably surface O vacancies, that are necessary to adsorb O_2.[29]

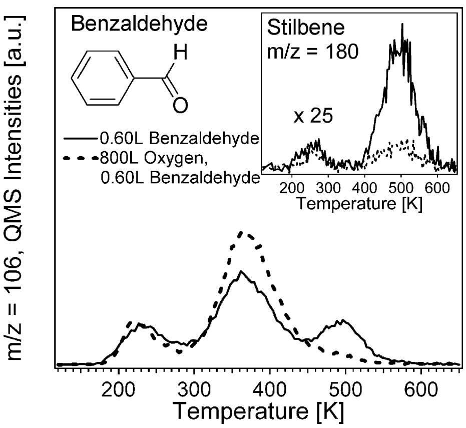

Figure 3. Temperature programmed reaction spectra following benzaldehyde (0.6 L) adsorption on $TiO_2(110)$ first exposed to 800 L of O_2 at 120 K: The solid trace is benzaldehyde alone and the dotted trace shows the effect of O_2. Stilbene evolution is shown in the inset. The heating rate was constant and 3.5 K/s.

Scanning tunneling microscopy experiments provide strong evidence for the involvement of titanium interstitials in the removal of oxygen from benzaldehyde and the subsequent formation of stilbene (Figure 4). First of all, it is important to note that multiple terraces with widths on the order of tens of nanometers and heights of 3.2 ± 0.4 Å are characteristic of surfaces prepared using our methodology (Figure 4A).[1] Larger terraces can be obtained using higher annealing temperatures; however, such a procedure can lead to even higher degrees of bulk reduction, and also strands of (1×2) reconstruction.[45] At higher magnification, rows of titanium atoms (bright) and rows of oxygen atoms (dark) with a spacing of ~0.65 nm between two titanium rows are clearly resolved (Figure 4b). The additional bright features between Ti rows at higher magnification have been variously attributed to bridging O vacancies and OH-species derived from ambient water.[1,10] As the presence of hydroxyls and vacancies does not affect the reactivity observed here, we did not attempt to distinguish these features.

There is clear evidence for growth of new TiO_2 islands after reductive coupling of benzaldehyde (Figure 4C and D). Benzaldehyde was first exposed to the surface shown in Figure 4A and B followed by annealing to 900 K, which is significantly above the evolution temperatures of both benzaldehyde and stilbene, and then cooled to room temperature for imaging (Figure 4C and D). The new features are apparent on the surface in a density of approximately 4 features per 100 nm^2, the average height of which measured to be 3.4 ± 0.9 Å. This height is close to that of the average measured terrace height of the clean surface, suggesting that they are in fact new small titania terraces. Feature width was on average 1.6 ± 0.2 nm. In some

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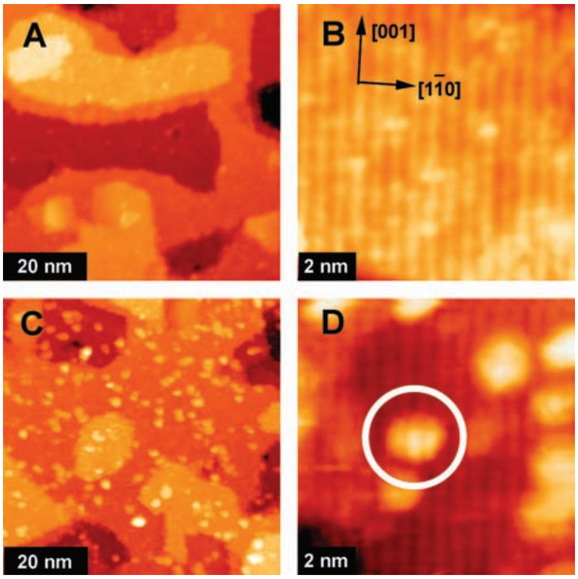

Figure 4. (A) STM image of a reduced (1 × 1) TiO_2(110) substrate, 65 nm × 65 nm. (B) Higher resolution image of the same surface in (A), 10 nm × 10 nm. (C) Same surface after deposition of a total of 0.3 ML benzaldehyde at room temperature, followed by annealing to 900 K (65 nm × 65 nm). (D) Same surface as (C), 10 nm × 10 nm. The new circled terrace exhibits the same row structure as the underlying terrace. Images were acquired with a bias of +2 V, and tunneling currents of 0.1−0.2 nA, in constant current mode.

cases it was possible to clearly image rows on the features resembling that of the underlying row structure of the larger terraces, as illustrated by the circled feature in Figure 4B. In fact, upon closer examination, these rows appear shifted by ~1/2 of a unit cell relative to the underlying lattice, which is consistent with what one would expect upon formation of a new terrace.[46]

Further support for the involvement of interstitials in the reaction studied here can be found in the literature. First, early work on titanium dioxide demonstrated the mobility of interstitial Ti through the ⟨001⟩ and ⟨110⟩ channels.[47] More recently, extensive studies of the interaction of titania with oxygen point to the involvement of interstitials in the reoxidation of the surface at temperatures in the range of 400−1000 K.[4,5,7] Titanium diffusion into the bulk starting at ~400 K was also demonstrated in studies of sputter reduced surfaces by Henderson, who employed isotopic labeling and static secondary ion mass spectrometry.[9] From these studies it is clear that interstitials move both into and out of the bulk. Wendt et al. recently observed a dissociation channel for oxygen at room temperature, attributed to the presence of near subsurface Ti interstitials.[10] The authors of this work also heated a surface exposed to oxygen at 120 K up to 443 K, and noted the formation of new titania islands which measured on average ~3.2 Å in height, in good agreement with the height of 3.4 ± 0.9 Å observed here.

Extending the idea of reaction of bulk interstitials with pure O_2 to other oxygen containing molecules, Bennett et al. reported an interesting study of the interaction of formic acid with the cross-linked (1 × 2) reconstructed surface of TiO_2(110).[8] Here, the surface is already in a strongly reduced state, presumably of Ti_2O_3 stoichiometry. They observed using STM, that upon dosing the surface with formic acid at room temperature, then annealing to 570 K and imaging at this temperature, new (1 × 1) islands formed, embedded within the (1 × 2) terraces. By analogy to their previous observations of the reoxidation of the (1 × 2) surface upon annealing in O_2,[4] this group claims that interstitials are likely involved in the growth of new (1 × 1) terraces observed. Our observations of similar island growth on the nearly pristine (110) surface unequivocally demonstrate the involvement of interstitials in the reaction of benzaldehyde on TiO_2.

Conclusions

We find here that bulk species dictate the surface reactivity of benzaldehyde over vacuum reduced TiO_2(110). Benzaldehyde couples with complete selectively over the surface, losing oxygen to form stilbene, which evolves at 495 K. We combine reactivity measurements with STM imaging to clearly establish that the reductive coupling is driven by Ti interstitials that migrate from the subsurface region, leading to growth of new TiO_2 islands upon reductive coupling. Nearly coincident with the evolution of stilbene, benzaldehyde evolves from the surface in a high temperature state at 485 K. This suggests that a common linkage, possibly a stable reaction intermediate, exists between this benzaldehyde desorption state and the C−C coupling pathway. In addition, benzaldehyde desorbs at 190 K from a multilayer state and from a coverage-dependent state from 340 to 390 K, corresponding to bonding at 5-fold coordinated Ti^{4+} ions. Strong destabilizing lateral intermolecular interactions likely lead to this significant low-temperature shift. Oxygen preadsorption at 120 K leads to a significant quenching of the coupling reaction, supporting our claim for the involvement of subsurface reduced sites such as Ti interstitials. Preadsorption of water surprisingly did not reduce the coupling activity measurably, thus the blockage of surface defects, namely vacancies, did not affect reactivity at all. Further proof for involvement of interstitials comes from STM evidence for new terrace growth following exposure to benzaldehyde and annealing to 900 K.

Our results demonstrate a complex interplay between mobile reduced Ti interstitials, water, oxygen, and adsorbed aldehydes on TiO_2(110). The McMurry-type coupling known to occur since the early 1970s,[33,34] which was found to hold true for strongly reduced TiO_2(001) surfaces,[21−23] also occurs on less reduced (110) substrates. We attribute the coupling to reaction with reduced titanium interstitials which migrate to the surface from the bulk. Thus, the subsurface region acts as a reservoir of reduced point defects, which are created by the bulk-assisted healing of sputtered and vacuum annealed surfaces. We show that these Ti interstitials play an important role in the reductive coupling of benzaldehyde, and propose that they may also be responsible in reduction reactions of other molecules on titania surfaces.

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