

Synthesis of Stilbene from Benzaldehyde by Reductive Coupling on TiO₂(001) Surfaces

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Abstract: Reductive coupling to form stilbene is the dominant reaction of benzaldehyde on TiO₂(001) single-crystal surfaces reduced by argon ion bombardment. Stilbene yields of 56% of the adsorbed benzaldehyde layer and selectivities up to 72% of the benzaldehyde reacted were obtained in temperature programmed desorption experiments under ultrahigh vacuum conditions. Reductive coupling requires a reduced surface. The stilbene yield decreased by an order of magnitude when the TiO₂(001) surface was oxidized by annealing at 850 K prior to benzaldehyde adsorption. The extent of surface reduction was determined from the populations of titanium cations in different oxidation states quantified by X-ray photoelectron spectroscopy. The activity of the surface for reductive coupling was found to track the extent of surface reduction as the latter was varied either by annealing or ion-bombardment procedures. However, in contrast to the mechanism commonly proposed for reductive coupling of aldehydes with titanium-based reagents in liquid–solid slurries, no Ti⁰ was observed by XPS even on the most active surfaces. The active site required for gas–solid reductive coupling is an ensemble of Ti cations in the +1, +2, and +3 oxidation states which collectively effect this four-electron reduction. These results demonstrate novel carbon–carbon bond formation on oxide surfaces in UHV and illustrate the application of surface analytical techniques to probe the sites of organic synthesis at the fluid–solid interface.

Introduction

The knowledge of surface chemistry derived from studies of reactions on well-defined surfaces holds the promise of providing clear linkages between homogeneous and heterogeneous catalysis of organic reactions. Strong cases have been made for the feasibility and importance of the connection of ultra-high-vacuum surface science to both fields. The parallels established between solid surfaces and organometallic complexes in solution—the “cluster-surface analogy” first suggested by Muetterties^{1,2}—have been primarily structural. Common ligands, e.g., carbonyls, alkoxides, alkenes, etc., often bind in a common fashion to metal complexes in solution and to metal surfaces with similar geometric arrangements of metal atoms.³ Looking toward heterogeneous catalysis, studies on metal single crystal surfaces have provided, in some cases, molecular-level insights into the “structure sensitivity” of catalytic reactions,^{4,5} as well as quantitative kinetics of elementary surface processes applicable to catalytic reaction cycles such as that for ammonia synthesis.^{6–9}

Two significant barriers exist, however, to the facile linkage of surface science results to either heterogeneous or homogeneous catalysis. The first of these is thermodynamic. Entropic considerations largely favor molecular disassembly processes, increasing the number of molecules by reaction under ultra-high-vacuum conditions. The direct study of important catalytic syntheses, especially those such as Fischer–Tropsch, hydroformylation, and olefin polymerization that involve formation of carbon–carbon bonds, is not generally feasible under the low-

pressure conditions at which most surface-sensitive, charged-particle spectroscopies can be applied. Typically one must either give up these spectroscopic tools in order to study catalytic reactions at relevant pressures or examine decomposition reactions in UHV and relate these to interesting synthetic processes by invoking microscopic reversibility. The barrier to extending the “cluster-surface analogy” beyond structure to explain and to predict the chemistry of solid surfaces and catalysts is more subtle. Well-defined metal surfaces, the traditional province of surface science studies, provide organic adsorbates with an extended array of zero-valent metal atoms with which they may coordinate and react. These arrays may provide possibilities for ligand coordination which mononuclear complexes in solution cannot, but more importantly, they remain essentially metallic. While structural analogies with oxidized metal centers in coordination complexes clearly exist,³ the dearth of analogous reactions between the two should not be surprising.

We have recently begun to address both of these barriers in studies of carbon–carbon bond formation under UHV conditions on well-defined metal oxide surfaces. Four different classes of C–C bond-forming reactions have been observed to date on single crystal surfaces of TiO₂; these exhibit different dependences on the coordination environment and oxidation state of surface cations, and it is possible to create and to destroy activity for each by variation of these surface characteristics. These reaction classes are (1) bimolecular coupling of carboxylates to form ketones,^{10,11} (2) aldol condensation of aldehydes,¹² (3) oligomerization and cyclization of alkynes,¹³ and (4) reductive coupling of carbonyl compounds to form olefins.^{14–16} These are superficially consistent

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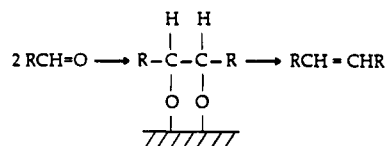
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with the two classes of C–C bond-forming reactions previously demonstrated in surface science studies on metals: cyclization of alkynes to thermodynamically favored aromatic products,^{17–20} and coupling of reagents containing “sacrificial substituents”. Examples of the latter include coupling of alkyl and phenyl ligands produced by dissociation of the weak C–I bond of the corresponding iodides on metal surfaces.^{21–23} The C–C bond-forming reactions observed on oxides are notable in two respects: first, their yields exceed more than one-half of the adsorbed molecules on properly prepared surfaces and, second, the substituents “sacrificed” need not be weakly bound in the reactant. Each of the carbon–oxygen double bonds broken in carbonyl reductive coupling has a dissociation energy of ca. 175 kcal/mol.²⁴

Of the four classes of C–C bond-forming reactions on TiO₂, the surface site requirements for ketonization and aldolization have been defined in previous studies.^{10–12,25,26} The reductive coupling of carbonyl compounds presents, we believe, important opportunities to demonstrate the direct application of surface science results to understanding and even inventing catalytic syntheses, as well as to demonstrate qualitative and quantitative analogies between the chemistry of surfaces and organometallic complexes. The possibility (and difficulty) of transforming reductive coupling from a stoichiometric surface reaction into a steady-state catalytic process has been considered in a previous communication.¹⁵ We report here a detailed examination of the reductive coupling of benzaldehyde to form stilbene on well-characterized surfaces of a TiO₂(rutile) single crystal in ultra-high vacuum. The focus of these studies is on the analogies which may be drawn with liquid-phase examples of reductive coupling with titanium-based reagents and on the new insights into the site requirements for this reaction which surface spectroscopic studies can provide.

Reductive coupling reactions of carbonyl compounds in the liquid phase typically fall into one of two classes. The first is coupling of two carbonyls to pinacols;²⁷ the second is that of carbonyl coupling to form olefins. The reductive coupling of aldehydes to form olefins was first observed using Ti halides in the presence of a reducing agent and is often referred to as the “McMurry reaction”. It was discovered independently, almost at the same time, by three different groups.^{28–30} This reaction is not limited to titanium: early transition metals, lanthanides, and actinides have been demonstrated to be active.³¹ In order to obtain electron-rich metal sites, the metal must be reduced by a strong reducing agent such as LiAlH₄, LiBH₄, Zn, Mg, or metal hydrides. The stoichiometric reductive coupling reaction utilizes 1 mol of reduced metallic reagent per mole of aldehyde or ketone coupled. According to McMurry, the carbonyl-coupling reaction takes place in two steps. The first is the reductive dimerization of the aldehyde (or ketone), forming a carbon–carbon bond. The product of this step is a 1,2-diolate or pinacolate intermediate.^{32,33}



The second step is the deoxygenation of the 1,2-diolate to form the olefin.^{32,33} The first step is essentially the pinacol reaction, known since 1859 to occur with reducing metals.³⁴ Evidence for the intermediacy of pinacولات in the reductive coupling with low-valent titanium species includes the isolation of pinacols in high yield when the reaction is carried out at 0 °C,³³ as well as the observation that deoxygenation of pinacols to olefins occurs with the same reagent at 60 °C.³³ It has also been demonstrated that deoxygenation can occur when the two oxygen atoms of the pinacolate intermediate are bound to different titanium sites; i.e., they need not necessarily be bonded in a five-member ring to a single titanium center. This was evidenced by the observation³³ that the deoxygenation of *cis*- and *trans*-camphanediols occurs at approximately the same rate (the oxygen atoms of the *trans*-camphanediols are too far apart and cannot be bonded to a common titanium atom).

As pointed out by Kahn and Rieke,³¹ the coupling of aldehydes and ketones in the liquid phase can be carried out homogeneously with organometallic titanium complexes, or heterogeneously with “slurries” of low-valent titanium derived from the reduction of TiCl₃ or TiCl₄. Those workers note, however, several points at which the mechanisms of the homogeneous and heterogeneous coupling reactions appear to differ, including the oxidation state of active titanium species.³¹ Thus such comparisons have provided limited insight into the identity of the active titanium species in the liquid–solid slurry reaction investigated extensively by McMurry and others.^{32,33} The nature of the titanium site has not been resolved for the heterogeneous reaction. It was originally proposed that Ti²⁺ is the active site.^{28,35} On the basis of evidence from electron spin resonance (ESR) it has been argued that Ti⁰ (titanium metal) is most likely the active site³⁶ and this has also been adopted by McMurry.³² Fürstner *et al.*³⁷ have recently summarized a number of inconsistencies regarding the nature of the low-valent titanium species required for this reaction. These previous studies have considered the batch, stoichiometric, liquid–solid, carbonyl coupling reaction. The recognition that this reaction can be carried out as a gas–solid reaction in UHV on TiO₂(001) makes it possible to determine the oxidation states of Ti cations on active surfaces directly with surface spectroscopic techniques such as X-ray photoelectron spectroscopy (XPS).

The activity of reduced TiO₂(001) single crystal surfaces for reduction and deoxygenation reactions of organic molecules has been demonstrated in previous studies.^{11,38,39} Methanol is reduced on this surface to give high yields of methane.³⁸ Formaldehyde can be reduced to methanol,³⁹ and formic acid and acrylic acid reduced to formaldehyde and acrolein, respectively.¹¹ Unlike reductive coupling of higher aldehydes, however, these examples do not increase the carbon number of the products relative to that of the reactants. The ability to manipulate (as well as to measure) the oxidation state of the surface is crucial to attempts to connect oxidation states to the sites required for these various reduction reactions. The near-surface region of the TiO₂(001) surface can be easily reduced by ion-bombardment.^{39–45} This procedure

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disorders the surface and preferentially removes oxygen, producing a surface containing Ti cations in the +4, +3, +2, and +1 oxidation states, as determined by XPS.^{39,45} No evidence for Ti⁰ has been obtained in studies of ion-bombarded TiO₂,³⁹⁻⁴⁵ yet such surfaces clearly exhibit activity for reductive coupling of carbonyl compounds.¹⁴⁻¹⁶ The extent of reduction of the TiO₂(001) surface can be varied both by changing the sputtering conditions and by annealing sputtered surfaces at different temperatures.⁴⁵ Annealing at modest temperatures causes oxygen migration from the bulk of the TiO₂ sample, and thus oxidation of the surface.^{10,11,39,40} Annealing at temperatures above 750 K is sufficient to restore the surface to an oxidized state and to generate well-ordered surface structures,^{10,46} as shown by low-energy electron diffraction (LEED).

This paper presents a study of the reductive carbonyl coupling on reduced TiO₂(001) surfaces in ultra-high vacuum, using temperature-programmed desorption (TPD) and XPS. Benzaldehyde was the probe reagent of choice, since, as shown by McMurry, aromatic aldehydes give higher yields of coupling products than their aliphatic counterparts,³³ and since the absence of α -hydrogens in this molecule precludes the aldol condensation reaction which competes with reductive coupling on titanium oxide surfaces.¹² Moreover, reductive coupling of benzaldehyde produces some of the highest molecular weight products yet synthesized in UHV surface science studies.

Experimental Section

The crystal preparation, crystal mounting, and argon ion bombardment conditions have been described elsewhere.^{10,39,45} Experiments were conducted in two UHV chambers. The first was a Physical Electronics Model 548 thin film analysis system, described previously^{10,39} and equipped with a single-pass cylindrical mirror analyzer for AES, four-grid LEED optics, and a quadrupole mass spectrometer for monitoring gaseous products. A cylindrical quartz envelope enclosed the ionizer of the probe of the mass spectrometer. The envelope had an aperture of smaller diameter than the front face of the single crystal. Thus, positioning the crystal in front of the aperture enabled the monitoring of gases coming from the crystal and discriminating against those coming from the sample mounting hardware. There were two additional openings, one at each side of the envelope, in order to facilitate pumping. The mass spectrometer was multiplexed with an IBM PC used for data acquisition during TPD experiments.

A typical TPD experiment was initiated by adsorption of benzaldehyde on the single crystal surface at room temperature. Benzaldehyde (Aldrich, spectra grade) was contained in a glass-metal sample tube attached to the dosing manifold and was purified with freeze-pump-thaw cycles until a reliable and reproducible fragmentation pattern was obtained with the mass spectrometer. Other reagents including stilbene, styrene, benzene, and toluene were employed in order to investigate their fragmentation patterns or desorption behavior. After dosing, the chamber was pumped down until a stable background pressure was reached, typically between 5×10^{-10} and 1×10^{-9} Torr. The envelope of the mass spectrometer was also degassed for a few minutes before the run was started. Heating was initiated (1.2 K/s) and the flux of molecules desorbed was monitored using the mass spectrometer. Up to 100 masses could be scanned at an interval of 3 to 4 s for the complete cycle. Sampling of a smaller number of mass fragments was also carried out to obtain higher resolution TPD spectra, with a proportionately shorter cycle time. To check for higher molecular weight products, especially in the case of benzaldehyde TPD, all masses up to 300 amu (the upper limit of the UTI 100 C mass spectrometer) were monitored in three identical runs.

Product identification in TPD experiments relied on matching major peaks at various mass-to-charge ratios with either pure component cracking

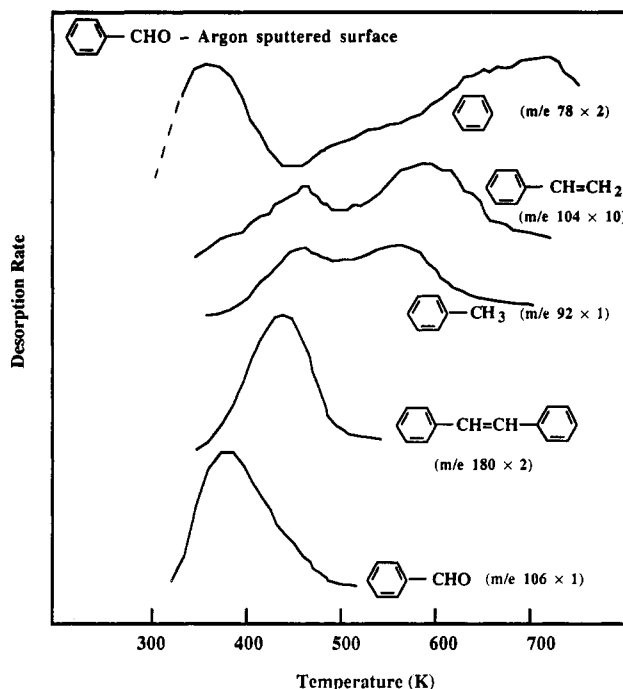


Figure 1. Temperature-programmed desorption spectrum following benzaldehyde adsorption on the reduced (ion bombarded) TiO₂(001) surface at 300 K.

patterns produced on the vacuum system or published cracking patterns.⁴⁷ After all major products were identified, contributions of high molecular weight products to low molecular weight products were removed using the pure component cracking pattern. Once peak areas representative of each separate product were established, relative molar yields were calculated by multiplying these areas by sensitivity factors which account for differences in ionization efficiency, mass spectrometer gain, mass fraction transmission, and cracking of different molecules.⁴⁸ The product selectivities reported below represent the fraction of the total product carbon contained in each product.

XPS experiments were conducted in a VG ESCALAB, described previously,^{39,49} equipped with an ultraviolet lamp, LEED optics, ion gun, electron gun, UTI mass spectrometer (also multiplexed with a personal computer and with its ionizer enclosed by a cylindrical quartz envelope), and a twin-anode X-ray source. All spectra were collected using the Al anode operated at 600 W (15 keV \times 40 mA). A typical XPS experiment was carried out as follows. After degassing the X-ray source (until a stable background pressure, typically about $(3-4) \times 10^{-10}$ Torr, was obtained) with the crystal facing away from the source, the crystal was exposed to the aldehyde following the same procedure as that described during TPD experiments (there were no differences in the fragmentation pattern or TPD results for benzaldehyde whether the X-ray source was on or off). Unless otherwise specified, all spectra were collected at saturation exposure (ca. 2-3 langmuirs based on measurement of the uncorrected chamber pressure during direct dosing, i.e., with the crystal in front of the doser). For all spectra C(1s), O(1s), and Ti(2p) regions were scanned. For experiments in which XPS spectra were collected as a function of temperature, the first set in the series was collected as described above; the sample was heated to the desired temperature and cooled to room temperature before collection of additional spectra.

Results

1. Temperature-Programmed Reaction of Benzaldehyde on the Reduced TiO₂(001) Surface. Temperature-programmed desorption of benzaldehyde from TiO₂ surfaces reduced by prior ion bombardment leads to products of the same, lower, and higher carbon numbers than the reactant. A set of TPD spectra following adsorption of benzaldehyde at room temperature on a reduced surface is shown in Figure 1. Benzene ($m/e = 78$) desorbs from

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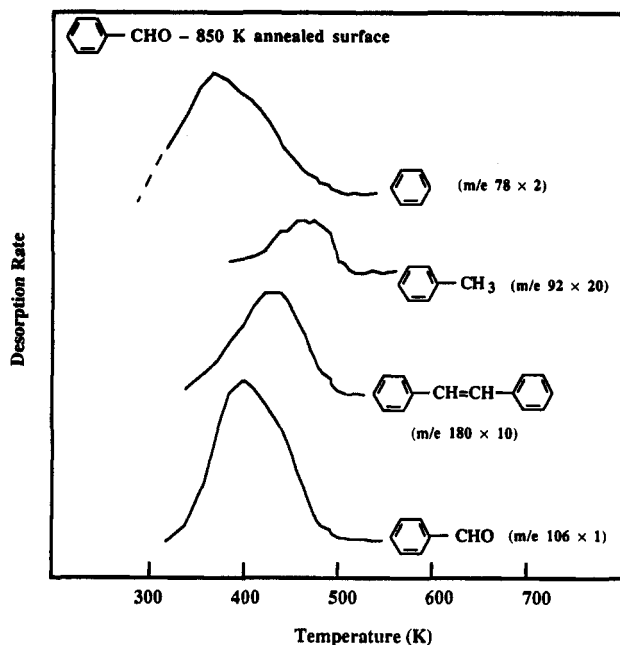
Table 1. Product Selectivity for C₆H₅CHO TPD on the Ar⁺-Bombarded TiO₂(001) Surface

product	peak temp (K)	selectivity (% of total C desorbed)
C ₆ H ₆	365	3
C ₆ H ₅ CHO	380	22
C ₆ H ₅ CH=CHC ₆ H ₅	440	56
C ₆ H ₅ CH ₃	460	5
C ₆ H ₅ CH=CH ₂	460	<1
C ₆ H ₅ CH ₃	560	7
C ₆ H ₅ CH=CH ₂	595	<1
C ₆ H ₆	650–720	1
unassigned products ^a		<5

^a See text.

two different states: a low-temperature peak at 365 K and a broad, flat state at 650–720 K. (The leading edge of the low-temperature benzene peak is obscured by a signal burst upon supplying power to the sample heater; this has been removed and the extrapolation to lower temperature is represented by a broken line in Figure 1.) Benzaldehyde ($m/e = 106$) desorbs at 380 K, while the expected carbonyl coupling product, stilbene ($m/e = 180$), desorbs at 440 K. Styrene ($m/e = 104$) and toluene ($m/e = 92$) both exhibit two desorption states at similar temperatures: styrene at 460 and 595 K, toluene at 460 and 560 K. While the diversity of products and desorption peaks is to be expected for a presumably non-uniform, sputtered surface, the selectivity to the reductive coupling product, stilbene, is quite remarkable. As shown by the complete distribution for volatile carbon-containing products in Table 1, more than half of the carbon contained in desorbing species was present as stilbene. Taking into account the unreacted benzaldehyde desorbed, the selectivity to stilbene among the products was 72%! The fractional yield of the only other product of increased carbon number, styrene, was less than 2%. Styrene has been reported as a product of reactions of stilbene on a number of metal oxides,³⁰ and we have previously suggested that high yields of styrene from benzaldehyde on TiO₂ powders arise from secondary reactions of the primary reductive coupling product, stilbene.¹⁵ The high ratio of stilbene to styrene in the present experiments on reduced TiO₂ single crystals in a UHV environment, where product readsorption and reaction are negligible, supports this hypothesis. Toluene, in contrast, is likely formed in parallel with stilbene; it represents the product of unimolecular reduction vs bimolecular reductive coupling to stilbene. Previous powder studies¹⁵ have shown that the unimolecular product is favored by the presence of titanium in its lowest oxidation states. The low selectivity to toluene on the reduced single crystal surface, where the fraction of Ti⁺ at the surface was ca. 12–18% of the total sampled by XPS as discussed below, provides additional support for this conclusion. Production of toluene from benzaldehyde requires deoxygenation and the addition of two hydrogen atoms. This hydrogen is likely liberated by decomposition processes which also result in surface carbon deposition (shown to occur using XPS). Previous XPS and TPD results for formaldehyde and carboxylic acids on reduced TiO₂(001) surfaces have shown similar reactant reduction and surface carbon deposition reactions.^{10,39}

No other major products were found although all masses up to $m/e = 300$ were checked. Both CO and CO₂ were detected in small quantities as gradually increasing signals above 800 K, as a result of the burnoff of deposited carbon, as previously observed.^{10,39} Products which were not detected (and the mass fragments characteristic of each) included benzyl alcohol ($m/e = 107, 108$), phenol ($m/e = 94$), biphenyl ($m/e = 154$), stilbene oxide ($m/e = 196$), and 1,2-diphenyl-1,2-ethanediol ($m/e = 214$). No mass fragments heavier than that of stilbene ($m/e = 180$) were detected. A number of small, high-temperature peaks

**Figure 2.** TPD spectrum following benzaldehyde adsorption on the oxidized (850 K annealed) TiO₂(001) surface at 300 K.**Table 2.** Product Selectivity for C₆H₅CHO TPD on the 850 K Annealed TiO₂(001) Surface

product	peak temp (K)	selectivity (%)
C ₆ H ₆	375	11
C ₆ H ₅ CHO	400	67
C ₆ H ₅ CH=CHC ₆ H ₅	440	20
C ₆ H ₅ CH ₃	470	2.3

between 550 and 750 K with masses up to $m/e = 152$ could not be assigned to any plausible product. As shown below, the C(1s) peak area in XPS remaining after heating the adsorbed layer to 525 K was only 14% of the total C(1s) area that can be attributed to volatile organic products following room temperature adsorption of benzaldehyde. Taking into account this value, the small magnitude of the unidentified peaks, and the quantitative yields of identified products evolved at temperatures greater than 525 K (toluene, styrene, and benzene), we conservatively estimate the selectivity to the unassigned products to be less than 5% (see Table 1).

2. Reactions of Benzaldehyde on the Oxidized (850 K Annealed) TiO₂(001) Surface. The reaction of benzaldehyde in TPD experiments exhibited important qualitative and quantitative differences on reduced and oxidized TiO₂ surfaces. A set of TPD spectra following benzaldehyde adsorption on the 850 K annealed surface is shown in Figure 2. Although the identity of the products was the same on both surfaces (except for the absence of styrene on the oxidized surface), the distribution of desorbing species was drastically different (Table 2). Benzene desorbed at 375 K, exhibiting only one desorption state (vs two on the reduced surface). This peak for benzene was limited by the kinetics of benzene desorption¹³ and, as its small intensity was quite insensitive to the state of the surface, we cannot rule out the adsorption of more volatile benzene impurities during benzaldehyde exposures. The higher temperature desorption state for toluene, like that of benzene, was suppressed on the 850 K annealed surface, as was all production of styrene. While benzaldehyde desorbed at 400 K, slightly higher than on the reduced surface (380 K), stilbene desorbed at the same temperature on both surfaces (440 K). The amount of stilbene produced, however, was much less than on the reduced surface, while the amount of unreacted benzaldehyde was greater. Toluene desorbed in a single peak at 470 K in smaller amounts than on the reduced surface. The stilbene/toluene ratio was higher on the annealed surface, consistent with the proposition

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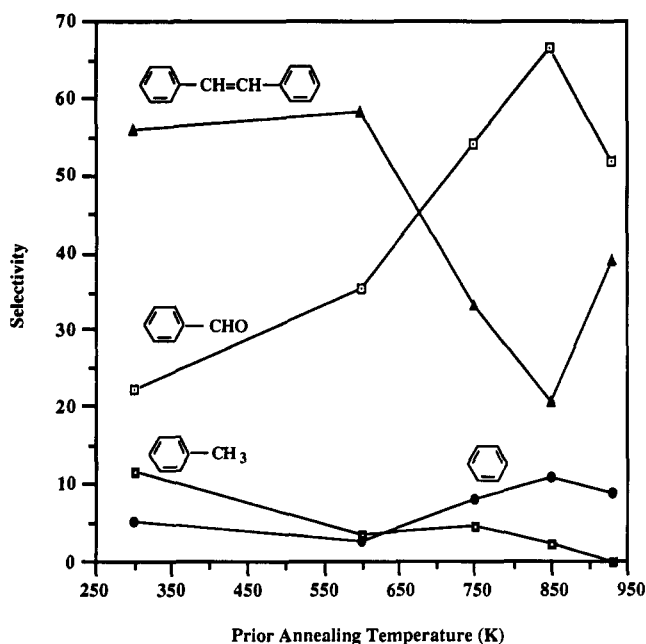


Figure 3. Selectivity of benzaldehyde temperature-programmed desorption/reaction as a function of the temperature at which the sputtered surface was annealed prior to adsorption of benzaldehyde at 300 K.

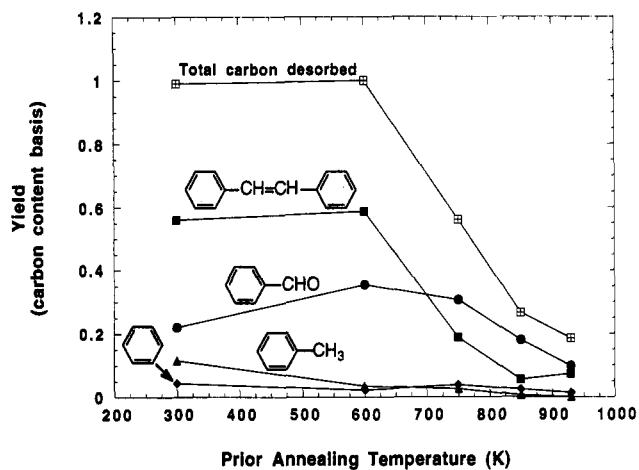


Figure 4. Yield of desorbing products from benzaldehyde as a function of the prior annealing temperature of the surface. The maximum value of the total yield of volatile species was obtained on reduced surfaces and is assigned a value of unity. Individual product yields are shown on the same scale.

that unimolecular reduction to toluene is favored on the more reduced surfaces. Detailed results of the variation in distribution of desorbing species as a function of prior annealing temperature are presented in Figure 3. Several trends are evident. As the surface becomes more oxidized, the production of toluene monotonically decreases, and is nonexistent on the most highly oxidized surface. Most striking, however, is the dependence of stilbene and benzaldehyde yields on the state of the surface. Since stilbene is produced by a reductive coupling, it is favored on reduced (ion bombarded and low temperature annealed) surfaces. Benzaldehyde desorption is favored by less reactive, oxidized surfaces. These contributions manifest themselves in an almost 10-fold decrease in the stilbene/benzaldehyde ratio, from 2.5 to 0.3 between the annealed, Ar^+ bombarded surface and the 850 K annealed surface, as noted previously.¹⁴ The apparent upturn in stilbene selectivity on the surface annealed at 930 K in Figure 3 is likely an artifact arising from the much lower coverages of all products and the correspondingly greater uncertainty in calculating selectivities on the fully oxidized surfaces.

Indeed, fractional yields and product selectivities from TPD experiments alone do not adequately convey the change in the pattern of reactivity of the surface upon annealing. Using the total C(1s) peak areas after adsorption of benzaldehyde at room temperature as an indicator of adsorbate coverage, it is clear that the 850 K annealed surface is significantly less active for adsorption and for reaction than the sputtered surface. As discussed below, the ratio of the C(1s) peak areas after benzaldehyde adsorption on the sputtered and 850 K annealed surfaces was 3.3:1. When combined with the decrease in the fractional conversion of benzaldehyde to stilbene on the annealed surface, this translates to a 10-fold decrease in the absolute yield of stilbene upon oxidizing the surface. The ratio of C(1s) areas following benzaldehyde adsorption on these two surfaces is quite consistent with the coverage change evident in Figure 4. This figure illustrates the total coverage and the yields of the various organic species desorbed after benzaldehyde adsorption vs the temperature to which the surface was previously annealed. Both the total coverage and the yield of stilbene exhibit precipitous drops for annealing between 600 and 850 K—precisely the region of temperature at which the most dramatic changes in the oxidation state of surface cations occur.^{10,39,45}

3. Kinetics of Stilbene Desorption from TiO_2 Surfaces. Although the yield of stilbene from benzaldehyde decreases by an order of magnitude between the reduced and oxidized surfaces, the stilbene peak temperature is unaffected. This suggests that the rate-determining step in the evolution of stilbene into the gas phase is not bimolecular reductive coupling, as this reaction might be expected to exhibit second-order kinetics which would be manifested in a strong coverage dependence of the peak temperature. In fact, as will be shown by XPS below, benzaldehyde oxidizes the reduced TiO_2 surface upon its adsorption at 300 K. If one applies the pinacolate mechanism proposed by McMurry, the deoxygenation of surface species (i.e., the oxidation of Ti suboxides) is the final step in the production of olefins in the reductive coupling of aldehydes. Therefore stilbene must be formed at the point at which the surface is oxidized. If the latter occurs at 300 K, the subsequent evolution of stilbene into the gas phase at 440 K would likely be limited by the kinetics of its desorption, rather than its formation. This was confirmed by experiments examining stilbene adsorption and desorption. Figure 5 compares the TPD spectra for stilbene following adsorption of benzaldehyde and *cis*-stilbene on sputtered TiO_2 surfaces. [The volatility of *cis*-stilbene (a liquid at room temperature) is greater than that of *trans*-stilbene (a solid at room temperature) and its transfer into the vacuum system is therefore much easier. Experiments with *trans*-stilbene were abandoned because of difficulties associated with its low volatility. The stilbene isomers produced by benzaldehyde coupling are not resolvable by mass spectrometry as employed in our TPD experiments, and no isomeric preference is implied by the comparison in Figure 5.] As shown in Figure 5, the peak temperatures for stilbene desorption were essentially the same (440 K) regardless of its source. No products other than stilbene itself were observed following stilbene adsorption on the reduced surface. These results indicate that the release of stilbene from the surface in the reductive coupling of benzaldehyde is limited by the kinetics of its desorption. If one assumes a typical preexponential factor for this process of 10^{13} s^{-1} , the activation energy calculated from the peak temperature for a heating rate of 1.2 K s^{-1} is 28.3 kcal/mol. The small differences in shape between the stilbene peaks in Figure 5 can be ascribed to the difference in the oxidation state of the surface from which the stilbene desorbs. Formation of stilbene from benzaldehyde oxidizes the surface; thus, if one begins with the surface reduced to the same extent, stilbene will desorb from a slightly more oxidized surface when it is produced from benzaldehyde than when it is simply adsorbed and desorbed.

4. Alteration of Ti(2p) Spectra by Reductive Coupling of Benzaldehyde. The extent of surface oxidation produced by

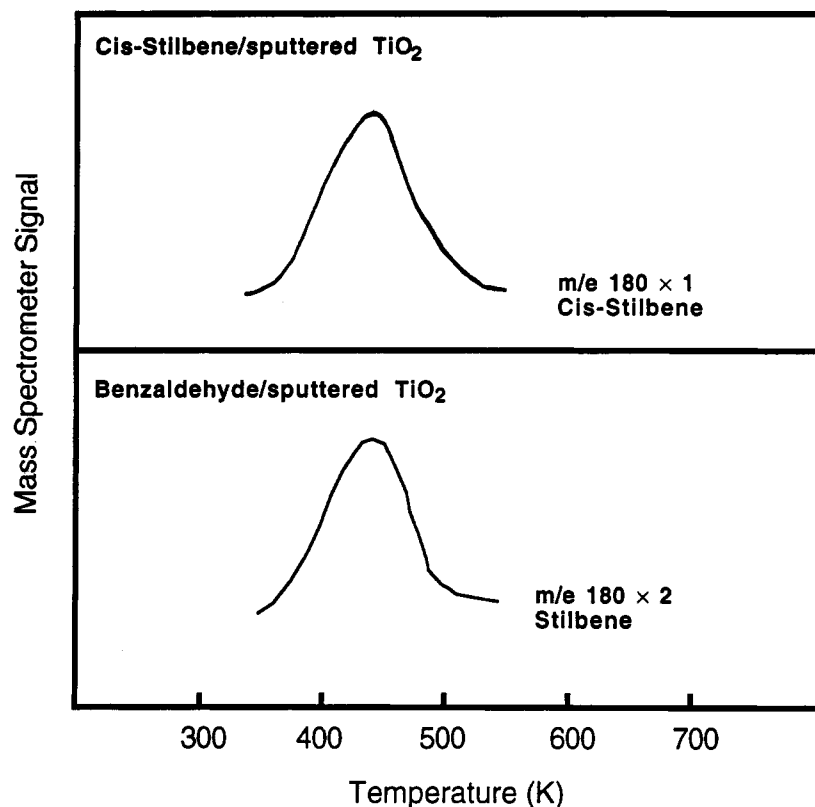


Figure 5. Comparison of TPD spectra for stilbene desorption following adsorption at 300 K on the reduced surface of benzaldehyde and *cis*-stilbene.

reductive coupling can be probed by XPS before and after adsorption or TPD. In principle one could extract such information from changes in the absolute intensity of the O(1s) lines of the oxide surface; however, such an analysis is complicated by other factors, such as attenuation of the signal from the solid by the organic overlayer adsorbed on it. The relative changes in population of titanium cations in different oxidation states provide a better measure of surface oxidation state, and do not require additional intensity calibrations or corrections. We have previously shown both the qualitative changes in the Ti(2p) envelope induced by adsorption of other oxygenates such as acetic acid¹⁰ and formaldehyde,³⁹ and the quantitative variation of cation populations with annealing temperature of the reduced TiO₂ surface.⁴⁵ We consider here the quantitative change in the oxidation state distribution of surface Ti cations produced by the adsorption and reaction of benzaldehyde.

Figure 6a presents the Ti(2p) region of the XPS spectrum of a TiO₂(001) single crystal sputtered with Ar ions for 1 h and the spectrum of the same surface after adsorption of benzaldehyde to saturation (curve b). Curve c depicts the spectrum of a fully oxidized surface, for comparison. Without deconvolution of the spectra, one can discern increases in the relative intensity of the spectrum of the reduced surface at ca. 459 and 465 eV following adsorption of benzaldehyde. These energies are characteristic of the Ti2p_{3/2} and Ti2p_{1/2} lines for Ti⁴⁺ species, respectively.^{39–45} An effect of benzaldehyde adsorption is also observed at the low binding energy side of the Ti(2p_{3/2}) envelope. There is a decrease of the relative intensity at ca. 455–456 eV, a region which contains contributions from Ti²⁺ and Ti⁺. Thus, benzaldehyde adsorption oxidizes the surface, increasing the population of oxidized species at the expense of more reduced ones. Changes in the distribution of titanium oxidation states comparable to that illustrated in Figure 6 can also be produced by adsorption of other carbonyl compounds^{16,39} as well as by annealing at modest temperatures (<500 K); changes of this magnitude can be quantified, as shown previously.⁴⁵ An analysis of the change in the XPS Ti(2p_{3/2}) core levels of Ti cations in each oxidation state following benzaldehyde adsorption is presented in Table 3. The Ti(2p_{3/2})

peak positions of the different oxidation states of Ti cations were presented previously.⁴⁵ Before benzaldehyde adsorption, the percentage of Ti⁴⁺ in the region sampled by XPS was 34%, while after adsorption it increased to 38%. This was accompanied by a simultaneous decrease of the percentage of Ti⁺ and Ti²⁺ cations from 22 and 12 to 20 and 10, respectively. A very small change in the population of Ti³⁺ cations was observed. This does not necessarily imply that Ti³⁺ cations are unaffected by benzaldehyde adsorption; in fact while part of the Ti³⁺ could be oxidized to Ti⁴⁺, part are restored by oxidation of Ti⁺ and Ti²⁺ cations.

From data such as those in Table 3, one can also calculate the extent of reduction and the oxygen deficit (relative to TiO₂) of the surface, as well as the changes produced by deoxygenation of adsorbates. If the extent of reduction is defined as the average valence difference relative to Ti⁴⁺, it can be computed from data such as that in Table 3 by

$$\xi_{\text{red}} = \sum_{n=0}^4 X_{\text{Ti}^{n+}}(4-n)$$

where $X_{\text{Ti}^{n+}}$ is the fraction of the Ti species in the $+n$ oxidation state. $\xi_{\text{red}} = 1$ corresponds to an average oxidation state of +3, $\xi > 1$ means that the average oxidation state in the near-surface region is less than +3. The value of ξ corresponding to the analysis of the freshly sputtered surface for the experiment in Table 3 is 1.12, and the value after adsorption of benzaldehyde is 1.02. If one assumes that the local stoichiometry associated with Ti cations in the +1, +2, +3, and +4 oxidation states corresponds to the stoichiometric compounds Ti₂O, TiO, Ti₂O₃, and TiO₂, respectively, one can compute the average O/Ti ratio for the XPS sampling region from the extent of reduction:

$$\text{O/Ti} = 2 - \xi_{\text{red}}/2$$

or

$$\Delta\text{O} = \frac{1}{2}\Delta\xi_{\text{red}}[\text{Ti}]$$

Thus the $\Delta\xi$ value of 0.1 between the two columns in Table 3

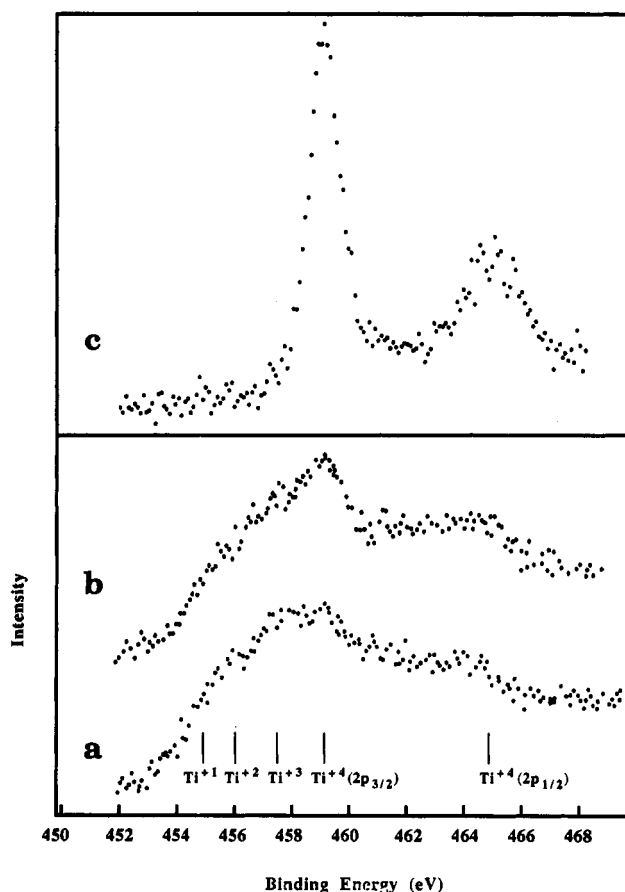


Figure 6. Ti(2p) X-ray photoelectron spectra: (a) spectrum of the TiO_2 (001) surface reduced by bombardment with 2 keV argon ions for 1 h; (b) surface in part a following adsorption of benzaldehyde at 300 K; (c) spectrum of a fully oxidized (850 K annealed) surface.

Table 3. Population of Ti Cations in Different Oxidation States for the Reduced TiO_2 (001) Single Crystal Surface before and after Benzaldehyde Adsorption at 300 K

Ti^{n+}	% of $\text{Ti}(2p_{3/2})$ envelope		% change
	before PhCHO	after PhCHO	
Ti^{1+}	12	10	-16
Ti^{2+}	22	20	-9
Ti^{3+}	32	32	0
Ti^{4+}	34	38	+12

corresponds to an average increase of 0.05 oxygen atoms per titanium *within the near surface region sampled by XPS*. However, since for a uniform solid the fraction of the XPS signal collected normal to the surface that originates from the topmost layer is only $(1 - e^{-a/\lambda})$ of the total,^{51,52} the change in oxygen concentration at the surface produced by benzaldehyde adsorption is substantially greater than 5% of a monolayer. Applying the values of the interlayer spacing, a , for TiO_2 of 1.5 Å (one-half the unit cell length in the [001] direction⁵³) and the mean free path, λ , of Al $K\alpha$ excited $\text{Ti}(2p)$ photoelectrons in TiO_2 (13 Å^{43,54}), one can estimate the fraction of the $\text{Ti}(2p)$ signal from the topmost layer to be 11% of the total, in good agreement with previous calculations.⁴² When the net increase in the oxygen concentration is normalized by this value, one obtains a value of 0.5 monolayer of oxygen atoms deposited by reaction of benzaldehyde. This is precisely the stoichiometric oxygen requirement to convert one

monolayer of Ti_2O_3 to TiO_2 . When combined with the conversion of benzaldehyde determined from TPD experiments, this value suggests that >0.6 monolayer of benzaldehyde is adsorbed initially, and 0.5 monolayer reacts with 72% selectivity to stilbene. Reductive coupling is clearly the dominant chemistry on these surfaces; it is not a trace reaction requiring specialized defect sites.

5. C(1s) Spectra of Benzaldehyde-Derived Layers on Reduced and Oxidized TiO_2 (001) Surfaces. It is fortunate that the chemistry of benzaldehyde on TiO_2 is relatively selective, even on the non-uniform, sputter-reduced surfaces, and that strong analogies exist between this chemistry and reductive coupling with other titanium-based reagents. The C(1s) spectra of the adsorbed layer in this case are unusually ineffective in resolving the identities of adsorbed species. Little insight can be extracted from the XPS data regarding the mechanism of reductive coupling, particularly the suggestion that surface pinacolates are important intermediates.

The TPD results for benzaldehyde on the reduced (001) surface showed that stilbene and unreacted benzaldehyde were the principal species desorbed. $\text{Ti}(2p)$ spectra before and after adsorption demonstrated that oxidation of the reduced surface occurs upon benzaldehyde adsorption at room temperature. Therefore one would expect that the adsorbed layer would consist primarily of adsorbed benzaldehyde and stilbene molecules following benzaldehyde adsorption on the reduced surface. These two molecules, unfortunately, exhibit virtually identical C(1s) spectra.

Figure 7 depicts the C(1s) spectra following adsorption of *cis*-stilbene and benzaldehyde on the reduced TiO_2 surface of benzaldehyde on the oxidized TiO_2 surface and of benzaldehyde adsorbed on the ZnO (001) surface,⁵⁵ all obtained with the same spectrometer. Benzaldehyde adsorbs molecularly on the ZnO -(0001) surface, producing XPS and UPS spectra in good agreement with gas-phase spectra for this molecule.⁵⁶ As shown above, benzaldehyde adsorbed on the oxidized TiO_2 (001) surface must be present mainly in molecular form; roughly two-thirds desorbs intact and one-third reacts. The C(1s) spectra for benzaldehyde on oxidized ZnO (0001) and TiO_2 (001) surfaces may therefore be taken as representative of the adsorbed molecule. Not surprisingly, the two spectra are quite similar. On the oxidized TiO_2 surface the C(1s) peak for benzaldehyde is centered at 284.8 eV with a fwhm of 2.1 eV. The C(1s) envelope exhibits a somewhat extended tail on the high binding energy side. This asymmetry can be assigned to contributions from the carbonyl group of benzaldehyde, which would be expected to account for 1/7 of the total C(1s) intensity and to exhibit a C(1s) binding energy ca. 2 eV greater than that of the ring carbons.⁵⁶ The spectrum for benzaldehyde on the ZnO (0001) surface is virtually identical in shape: a slightly asymmetric peak with a fwhm of 2.0 eV located at 285.6 eV. In both cases the peak widths are comparable to those obtained for other adsorbates containing only a single type of carbon.^{10,39,57} The C(1s) binding energy difference of 0.8 eV for benzaldehyde on the two different oxides is consistent with those observed in previous comparisons of a number of organic adsorbates on the TiO_2 (001) and ZnO (0001) surfaces,^{38,57} provided that one takes into account the systematic 0.5-eV shift of the C(1s) energies of aromatic compounds on the ZnO (0001) surface relative to the ZnO (0001) surface.⁵⁶

Turning now to the C(1s) spectrum for benzaldehyde on the reduced TiO_2 (001) surface, Figure 7c, one sees that it is quite similar to the spectrum on the oxidized surface. The peak position is the same, 284.8 eV, and the C(1s) envelope for the benzaldehyde layer on the sputtered surface is only slightly broadened (fwhm = 2.25 vs 2.1 eV) relative to that on the oxidized surface. This small extent of broadening could be accounted for by the greater

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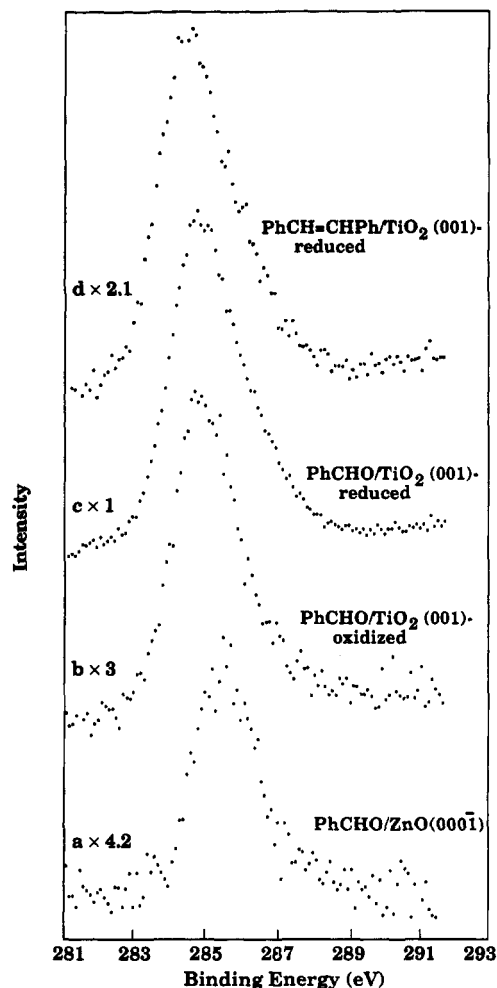


Figure 7. C(1s) X-ray photoelectron spectra for benzaldehyde and stilbene on oxide surfaces: (a) spectrum for benzaldehyde adsorbed on the ZnO(0001) surface;⁵⁵ (b) spectrum following benzaldehyde adsorption on the oxidized TiO₂(001) surface; (c) spectrum following benzaldehyde adsorption on the reduced TiO₂(001) surface; and (d) spectrum for *cis*-stilbene adsorbed on the reduced TiO₂(001) surface.

heterogeneity of this surface, without invoking adsorbed species other than benzaldehyde. The spectrum for the benzaldehyde-derived adlayer on the reduced surface is not incompatible, however, with the conclusion from the TPD and Ti(2p) spectra that stilbene is the majority species on this surface. As can be seen in Figure 7d, the C(1s) spectrum of *cis*-stilbene on the reduced surface (little adsorbs on the oxidized surface) is also nearly indistinguishable from those obtained following benzaldehyde adsorption on either TiO₂ surface. The peak position (284.6 eV) and fwhm (2.4 eV) for *cis*-stilbene are too near those of benzaldehyde to permit one to analyze the spectrum of the benzaldehyde-derived adlayer on the reduced surface in terms of distinguishable contributions from molecular benzaldehyde and stilbene species. Moreover, the qualitative shapes of the envelopes are quite similar for both molecules; the carbonyl group of benzaldehyde and the olefinic linkage of stilbene both contribute intensity on the high binding energy side of the principal ring peak in both cases.

The C(1s) spectra of Figure 7 are sufficient to rule out some potential surface intermediates, but not others. For example, formation of surface carboxylates from aldehydes on oxide surfaces can occur either by oxidation^{56,58,59} or by Cannizzaro-type disproportionation.⁴⁹ In the absence of gas-phase oxygen, we have not observed any evidence for aldehyde oxidation on any

of the TiO₂ single crystal or powder samples examined to date.^{12,15,39} XPS and TPD results for formaldehyde (which, like benzaldehyde, lacks α -hydrogens and is therefore incapable of aldol condensation) did indicate contributions from the Cannizzaro reaction to the product slate for this molecule on oxidized TiO₂(001) surfaces.³⁹ The data of Figure 7, however, are sufficient to exclude the Cannizzaro reaction of benzaldehyde on either reduced or oxidized TiO₂ surfaces. This reaction would produce equimolar amounts of benzyl oxide and benzoate intermediates (some of which might be expected to form molecular alcohol and acid products in TPD experiments, as do their aliphatic analogs³⁹). C(1s) spectra for the alkoxides would be expected to lie within the envelope for benzaldehyde and other adsorbed aromatics, but the carboxylate group of benzoates, like other carboxylates, should appear at ca. 289.5 eV,¹⁰ well separated from the core levels for the ring carbons.⁵⁶ There is no discernible intensity above the background in this region of the C(1s) spectra of Figure 7 and no detectable desorption of benzyl alcohol or benzoic acid in TPD experiments; thus neither aldehyde disproportionation nor oxidation occurs on these surfaces.

Just as benzyl oxide species, if they were formed, would be expected to be difficult to resolve from the benzaldehyde envelope, so too are the pinacolate intermediates (e.g., $-\text{O}-\text{C}(\text{Ph})(\text{H})\text{C}(\text{H})(\text{Ph})-\text{O}-$) postulated by McMurtry^{32,33} to be intermediates in the reductive coupling of carbonyl compounds beyond the reach of these XPS experiments. Aliphatic alkoxides on TiO₂ give rise to C(1s) features at 286.5–286.8 eV.^{38,57} While such contributions in the spectra of Figure 7 would be consistent with the peak broadening observed on the high binding energy side, contributions of alkoxide moieties would be virtually indistinguishable from similar contributions of the carbonyl groups of benzaldehyde molecules or the olefinic carbons of stilbene. As noted above, however, both the desorption-limited evolution of stilbene and the increase in the average oxidation state of titanium following benzaldehyde adsorption on the reduced surface at 300 K argue against the presence of a significant population of stable pinacolate intermediates at this temperature.

The C(1s) spectra of the benzaldehyde-derived adlayers on TiO₂ as a function of temperature provide further insights into the activity differences between reduced and oxidized surfaces and help verify the product calibrations for TPD experiments. The evolution with temperature of the C(1s) spectra following benzaldehyde adsorption on reduced and oxidized TiO₂(001) surfaces is shown side-by-side in Figure 8. The C(1s) peak areas vs adlayer annealing temperature are plotted in Figure 9. It is clear that on both surfaces the shape of the C(1s) envelope changes little between the adsorption of benzaldehyde at 300 K and temperatures up to ca. 550 K at which organic products are still seen in TPD. This is not surprising since, as shown above, the C(1s) line shapes of reactants, likely intermediates, and detected products are essentially indistinguishable. The spectra do change, however, once all aromatic products have desorbed, and only carbonaceous residues remain on the surface. On both surfaces spectra obtained after heating the adsorbed layer to 750 K can be described as small, symmetric peaks at ca. 284 eV, consistent with carbon deposited in the course of oxygenate decomposition.^{10,12} One of the striking aspects revealed by Figure 9 is that the amount of carbon deposited on the two surfaces is virtually the same. Thus the highly reactive, heterogeneous, reduced TiO₂(001) surface is no more prone to "coking" than its oxidized counterpart, an observation which bodes well for attempts to render carbonyl reductive coupling catalytic.¹⁵

As shown in Figure 9, the total C(1s) signal intensity after heating to 750 K was 9% of that following adsorption of benzaldehyde on the reduced TiO₂(001) surface. This suggests that the fractional yields of volatile products in Table 1 should be multiplied by a factor of 0.91 to account for the 9% of the adsorbed reactant decomposed to nonvolatile carbonaceous

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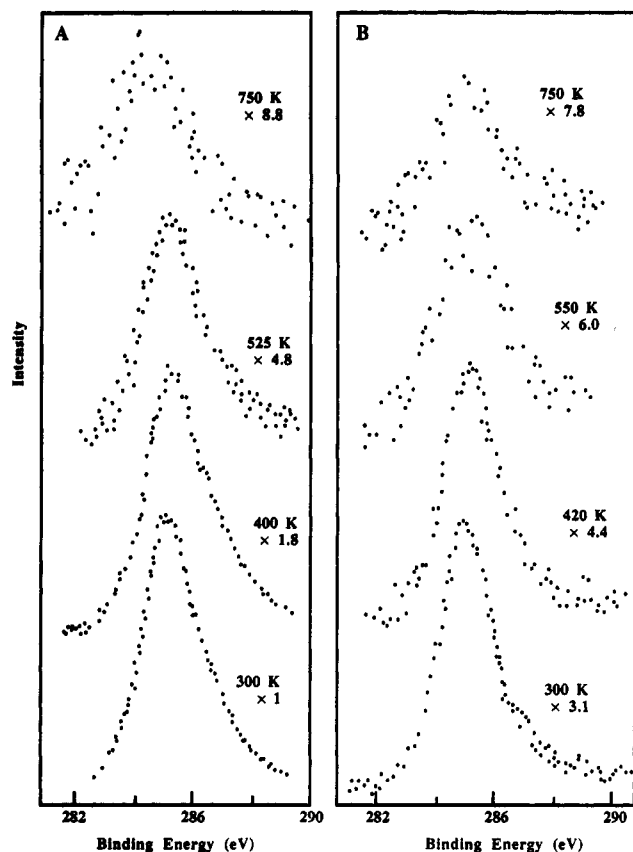


Figure 8. C(1s) X-ray photoelectron spectra following benzaldehyde adsorption at 300 K on TiO₂(001) surfaces and heating to the temperatures indicated: panel A, reduced surface; panel B, oxidized surface.

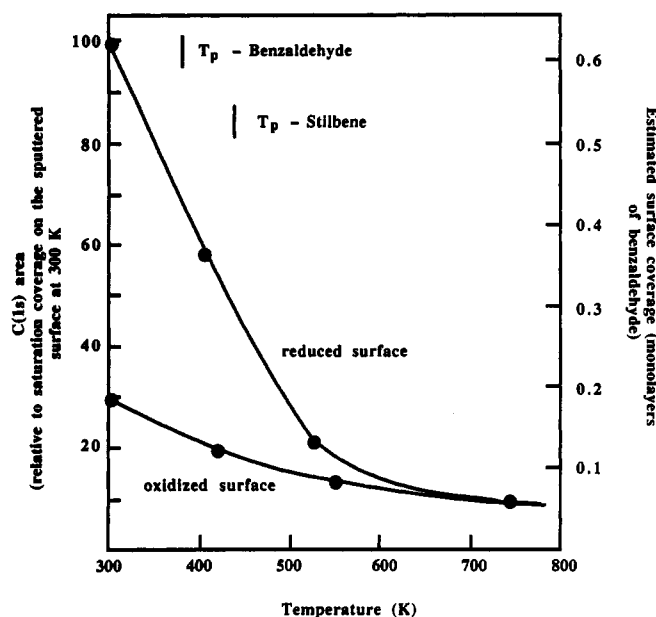


Figure 9. C(1s) area vs the temperature to which the benzaldehyde adlayer was heated for the reduced and oxidized TiO₂(001) surfaces. The locations of the benzaldehyde and stilbene desorption peaks in TPD experiments are indicated on the figure.

residues. The TPD results and the product calibrations in Table 1 further suggest that 12% of the benzaldehyde molecules initially adsorbed leave the surface as volatile hydrocarbon products between 525 and 740 K; the change in the C(1s) area between these two temperatures in Figure 9 is 13% of the initial value, supporting the TPD calibration. If one further normalizes these data by the amount of oxygen deposited on the surface, 0.5 monolayer based on the change of the distribution of Ti oxidation

states, one obtains the following accounting of the fate of benzaldehyde on the reduced surface: of 0.625 monolayer of benzaldehyde adsorbed, 0.125 monolayer desorbed intact, 0.32 monolayer converted to stilbene, 0.07 monolayer to toluene, 0.02 monolayer to benzene, 0.01 monolayer to styrene, 0.03 monolayer to unidentified organics, and 0.05 monolayer to carbonaceous deposits. Again, given the heterogeneity of this surface, the selectivity to reductive coupling vs "waste" products is remarkable.

One can now proceed to examine the trends in C(1s) areas on the well-oxidized surface. Utilizing the calibrations above, we estimate the initial saturation coverage of benzaldehyde at 300 K to be 0.2 monolayer, of which 0.09 monolayer desorbs intact, 0.03 monolayer forms stilbene, 0.015 monolayer forms benzene, and less than 0.01 monolayer forms toluene, and 0.05 monolayer remains on the surface as carbonaceous deposits. Once again the TPD and XPS results are in reasonable agreement; the TPD experiments indicate that all volatile organics are completely desorbed by 550 K, while XPS shows a net decrease in the C(1s) signal beyond this point of only 0.02 monolayer. Perhaps more important is the comparison one can draw between the reduced and oxidized surfaces. In both cases the amounts of unreacted benzaldehyde desorbed are approximately the same, ca. 0.1 monolayer, as are the amounts of nonvolatile carbon deposited, ca. 0.05 monolayer. The absolute yield of stilbene and all other volatile reaction products on the fully oxidized surface is only 0.05 monolayer. This may be taken as a reasonable estimate of the concentration of reduced defect sites on this surface. Because of the sampling depth of XPS discussed above, 5% of the topmost layer containing Ti cations in oxidation states below +4 would contribute only 0.5% of the total Ti(2p) signal, and it is not surprising that such low concentrations are essentially unresolvable. In contrast, upon reduction of the surface by ion bombardment, the yield of aromatic products of benzaldehyde reduction jumps by an order of magnitude, to nearly one-half monolayer, with two-thirds of the aromatic rings among these products contained in the stilbene desorbed.

Discussion

The synthesis of stilbene from benzaldehyde can be carried out on reduced surfaces of TiO₂ single crystals, even in ultrahigh vacuum. This reaction, which involves both the scission of two C=O bonds and the formation of higher molecular weight organic products, is surprisingly facile and selective. XPS results demonstrate that the oxygen removal step of the reductive coupling sequence occurs upon adsorption of benzaldehyde at 300 K; the evolution of stilbene at 440 K is limited by the kinetics of its desorption, rather than its formation, as demonstrated by TPD experiments. Reductive coupling of benzaldehyde to form stilbene requires the presence of titanium cations on the surface in oxidation states lower than +4, and activity for this reaction can be quenched by thermal treatment of reduced surfaces at temperatures sufficient to oxidize the surface by diffusion of oxygen atoms from the bulk lattice. However, in no case have we found evidence by XPS for the presence of Ti⁰ species on ion-bombarded TiO₂ surfaces active for stilbene synthesis. These reduced surfaces contain Ti cations in the +1, +2, +3, and +4 oxidation states. They produce stilbene yields as high as 56% of all benzaldehyde adsorbed and selectivities as high as 72% of the benzaldehyde reacted.

The coupling of carbonyl compounds and the synthesis of products containing multiple aromatic rings were unprecedented in the literature of either metal or metal oxide surface science prior to the initial report on reduced TiO₂ single crystals.¹⁴ Subsequently Bent and co-workers²³ have demonstrated that the Ullman coupling of phenyl iodides to form biphenyl occurs on copper surfaces in a UHV environment. These reactions are similar in that both involve C-C bond formation to produce a product with two aromatic rings. Both are rendered thermo-

dynamically favorable, even under UHV conditions by the deposition of "sacrificial substituents", either oxygen or iodine, on the active surface as a consequence of the coupling reaction. However, beyond these simple parallels, there is little reason to suggest that these reactions exhibit mechanistic similarities.

The reductive coupling of carbonyl compounds to form olefin products with twice the carbon number of the reactants can be accomplished on reduced titania surfaces for a number of reagents besides benzaldehyde. These include aliphatic and α,β -unsaturated aldehydes,¹⁴ cyclic ketones such as cyclohexanone and cyclohexenone,¹⁶ and benzoquinone.¹⁶ On reduced TiO_2 powders, we have shown that 1-phenylpropene can be synthesized by cross-coupling of benzaldehyde and acetaldehyde.¹⁵ While this list of examples of gas-solid carbonyl coupling reactions clearly falls short of the magnitude of that developed by McMurry for the liquid-solid reaction,^{32,33} it does suggest that this chemistry is generalizable to a broad range of synthetic and potentially catalytic coupling reactions.

The chemistry of benzaldehyde on reduced titania single crystal surfaces does exhibit several notable differences from that of its non-aromatic analogs. First, benzaldehyde exhibits the highest yield of reductive coupling products of any of the carbonyl compounds examined on TiO_2 surfaces. This observation is quite consistent with the behavior of these reagents in the liquid-solid reaction; the highest coupling yields are obtained for aromatic aldehydes and ketones.^{32,33,60} Second, the principal reaction competing with bimolecular reductive coupling of benzaldehyde to stilbene is the unimolecular reduction of benzaldehyde to toluene. Unimolecular reduction is also an important side reaction for the other aldehydes examined on reduced TiO_2 surfaces: formaldehyde is reduced to methanol,³⁹ acetaldehyde to ethanol,¹² and acrolein to allyl alcohol.⁶¹ In contrast to these non-aromatic aldehydes, however, benzaldehyde produced no detectable benzyl alcohol; instead, deeper reduction to toluene was observed. Indeed none of the products formed from benzaldehyde on reduced surfaces contained oxygen. While this product slate clearly reflects the activity of reduced titania for deoxygenation, consistent with its ability to reductively couple aldehydes to form olefins rather than pinacols, benzaldehyde was unique among the aldehydes and ketones examined in producing no alcohols.

None of the side products of benzaldehyde coupling to stilbene on the surfaces examined exceeded 12% of the adsorbed adlayer on a carbon basis, as illustrated in Figure 3. Given the inability of XPS to distinguish between the reactant in this case and the major product, the mechanisms (and adsorbed intermediates involved) for formation of toluene, styrene, and benzene are unclear. One can, however, extract some insights from the dependence of these on the characteristics of the titania surfaces, both single crystals and powders,¹⁵ on which they have been observed. As noted previously, toluene formation is favored by the most highly reduced surface sites; physical mixtures of TiO_2 and Ti powders produced much more toluene from benzaldehyde than did TiO_2 powders subjected to the same reduction and pretreatment procedures.¹⁵ The selectivity trends for toluene production on reduced TiO_2 single crystals support this conclusion. As demonstrated previously,⁴⁵ annealing the ion-bombarded TiO_2 (001) surface to ca. 600 K has the greatest effect on the population lowest oxidation state cations, i.e., Ti^+ sites. As shown in Figures 3 and 4, prior annealing of the reduced surface even at these low temperatures causes a more than 3-fold decrease in toluene production from benzaldehyde, while the stilbene yield actually increases slightly. These results suggest that unimolecular reduction and deoxygenation of benzaldehyde occurs on the sites with the highest affinity for oxygen, i.e., the most reduced sites. If one assumes that the reductive coupling mechanism proposed for the liquid-solid reaction also applies to the gas-solid reaction

on reduced titania, then stilbene would be produced by a two-step sequence of benzaldehyde association and pinacolate deoxygenation. Toluene production on more highly reduced sites could be accounted for by inversion of this sequence, i.e., initial deoxygenation of the aldehyde, precluding coupling.

The amounts of styrene and benzene produced from benzaldehyde were even smaller than that of toluene. Styrene production is notable, however, in that this reaction must also involve carbon-carbon bond formation. It is conceivable that styrene is produced by coupling of benzaldehyde with C_1 fragments from other reactions, e.g., scission of the acyl group from the ring to form benzene. Such "methylenation" reactions of aldehydes and ketones with organometallic titanium complexes are known.⁶² However, the absence of other C_1 products, including CO, argues against the presence of such intermediates on the surface. We have suggested previously that the much higher styrene/stilbene ratio observed in benzaldehyde TPD on reduced titania powders is due to the initial formation of stilbene by reductive coupling, followed by cracking of stilbene to styrene plus benzene upon subsequent encounters with other active surfaces before exiting the sample bed.¹⁵ On single crystals in ultrahigh vacuum, readsorption problems are avoided, and one would expect styrene production by this mechanism to be suppressed. This was indeed the case for the present results; the selectivity to styrene was less than 2%. This small amount may be attributed to retention and cracking of small amounts of stilbene on high binding energy sites on these non-uniform, reduced surfaces. Stilbene cracking to styrene would also account for a portion of the small amount of benzene produced, most likely that in the high-temperature peak. The offset between the styrene and benzene desorption temperatures suggests that stilbene cracking is not the rate-determining step for the latter. Deposition of surface phenyl groups by stilbene cracking, followed by decomposition and self-hydrogenation of these intermediates at elevated temperature, is a plausible explanation consistent with the high temperatures required for aromatic decomposition on oxide surfaces.⁵⁶

The key point of this work, however, is the insight it provides regarding the sites required for reductive coupling of aldehydes to form olefins with reduced titanium-based reagents. In the absence of Ti^0 species which could effect the four-electron reduction of two molecules of benzaldehyde to one of stilbene, reductive coupling *must* involve multiple titanium centers at the surface. These centers collectively must be capable of accommodating the two oxygen atoms deposited on the surface for each olefin molecule formed. These ensembles of titanium cations in lower oxidation states than +4 undergo a net 4-electron oxidation by this process. One would therefore expect the activity of reduced TiO_2 surfaces for reductive carbonyl coupling to reflect the capacity of these surfaces for oxidation. *That is, the reductive coupling activity should track the extent of reduction of the surface relative to stoichiometric TiO_2 .* Two such correlations appear in Figures 10 and 11, in which the stilbene yield from benzaldehyde and the extent of reduction, ξ_{red} , are shown as a function of surface treatment. Figure 10 illustrates the decline of both stilbene yield and ξ_{red} as a function of the temperature at which the surface was annealed prior to benzaldehyde TPD. Neither is strongly affected by annealing at temperatures up to 600 K. Below this temperature there is little oxygen diffusion from the bulk and little reoxidation of the surface by thermal treatment, as demonstrated previously.⁴⁵ Annealing at temperatures above 600 K does produce significant reoxidation of the surface; the extent of reduction decreases precipitously as the stoichiometry of the near-surface region sampled by XPS increases from ca. $\text{TiO}_{1.35}$ on the sputtered surface to near TiO_2 on surfaces annealed at 750–950 K.⁴⁵ The yield of the reductive coupling product also drops by an order of magnitude over the range of prior annealing temperatures from 600 to 850 K. The decline

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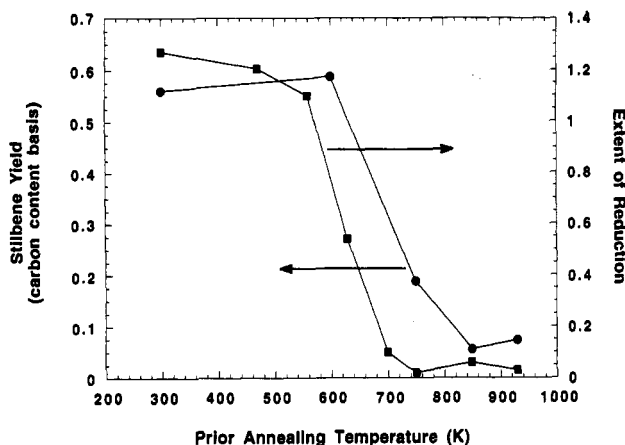


Figure 10. Stilbene yield and extent of surface reduction vs the temperature at which the reduced $\text{TiO}_2(001)$ surface was annealed. The stilbene yield values are scaled against the maximum total yield of desorbing carbon-containing species, as in Figure 4.

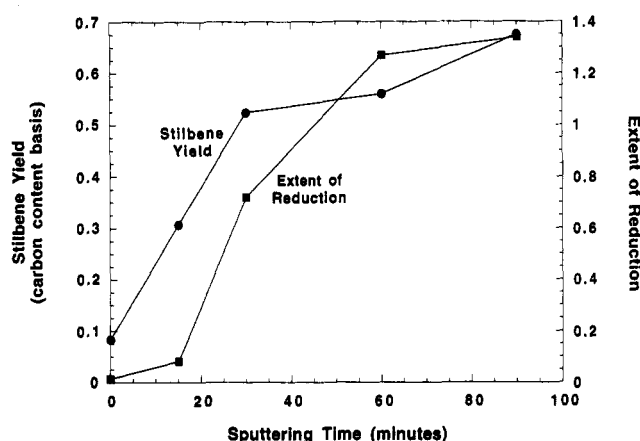


Figure 11. Stilbene yield and extent of surface reduction vs the period of sputtering an oxidized surface with 2 keV argon ions. Stilbene yields are presented on the same scale as in Figures 4 and 10.

in reductive coupling activity from TPD experiments is not quite as sharp as that of the extent of surface reduction, ξ_{red} , but it is clear that reductive coupling is quenched by oxidation of the surface upon annealing at modest temperatures. The same connection between reductive coupling activity and ξ_{red} is demonstrated by Figure 11 as a function of increasing surface reduction by sputtering. Both the stilbene yield and ξ_{red} rise monotonically with increasing sputtering time, reaching limiting values after 60–90 min of sputtering with 2 keV argon ions under the conditions employed. Both are affected most strongly by sputtering up to ca. 30 min, and the rise in reductive coupling actually leads the extent of reduction parameter, just as it lags it in the data of Figure 10. Both figures clearly demonstrate the strong, if imperfect, correlation of coupling activity with surface reduction.

It should be recognized that there is some variability inherent in the reduced, disordered surfaces of interest here, relative to ordered stoichiometric surfaces. Before each TPD experiment, for example, the surface must be prepared in the state desired. This involves sputtering to remove any carbon deposited by the previous experiment, annealing at 800–900 K for 1 h to fully oxidize the surface, sputtering at 300 K for 1 h to reduce the surface to a ξ_{red} level of ca. 1.2, and then annealing at the final "prior annealing temperature" shown in Figure 10 before cooling to 300 K for benzaldehyde adsorption and temperature-programmed desorption. The surfaces produced by moderate annealing are metastable and, below 750 K, disordered. Given the nature of these surfaces and their preparation, the absence of perfect overlap between coupling activity and the extent of

surface reduction is not surprising. It is significant, however, that the coupling activity is consistently somewhat higher than one might expect from the measured values of ξ_{red} , especially as the composition of the near-surface region approaches TiO_2 . As shown previously,⁴⁵ annealing the reduced $\text{TiO}_2(001)$ surface to progressively higher temperatures oxidizes the cations in the near surface region roughly in the sequence of their oxidation states. Thus Ti^+ species disappear from XPS spectra upon annealing to ca. 630 K, Ti^{2+} species disappear by 700 K, and the population of Ti^{3+} species plateaus by ca. 800 K.⁴⁵ The persistence of significant stilbene production from benzaldehyde after annealing the surface to 750 K provides evidence that the reductive coupling reaction can proceed even without the presence of measurable amounts of Ti^+ or Ti^{2+} ; even ensembles of Ti cations in the +3 state appear to be capable of carrying out this transformation. In this regard, the method of surface reduction employed in these experiments may enhance reductive coupling activity compared to alternatives which would produce more spatially uniform reduction of the solid. The damage to the near-surface region of the sample is greatest in the collision cascade region along the ion trajectory,^{63,64} thus one would expect the oxygen vacancies/reduced cations to be formed in clusters around these trajectories, rather than being uniformly distributed. Since data for both the liquid–solid and gas–solid reductive carbonyl coupling reactions point toward ensembles of reduced Ti centers as active sites for this reaction, clustering of these centers would clearly favor coupling activity.

It should also be recalled that ion bombardment reduces considerably more than one monolayer of the solid; the penetration depth for 2 keV argon ions in TiO_2 calculated by Schiøtt's method⁶⁵ is about 25 Å. Thus while reductive coupling requires titanium cations in lower oxidation states at the surface, it is not clear that all members of the ensemble which effects this four-electron reduction need be exposed in the topmost layer. Even if one assumes no long-range migration of the oxygen atoms abstracted from benzaldehyde at room temperature, subsurface oxygen vacancies/reduced titanium cations could still play a significant role in reductive coupling. For example, an active ensemble could consist of two Ti^{3+} cations at the surface and two more in the layer immediately below; the two oxygen atoms deposited by reductive coupling of a pair of aldehyde molecules could fill two vacancies between these layers, in the end bridging Ti^{4+} centers just as in the stoichiometric bulk. It is quite likely that even longer range transport of oxygen occurs to facilitate this reaction. Oxygen mobilities in reduced rutile are quite high, as demonstrated by the reoxidation of the surface by modest thermal treatment in vacuum, and oxygen diffusion is enhanced by the formation of layered shear structures known as Magneli phases which concentrate the reduced regions of the bulk.⁶⁶ Similar phenomena are exploited in commercially utilized selective oxidation catalysts. Keulks and co-workers^{67,68} have shown by isotopic labeling that oxygen from as many as 60 layers of bismuth molybdate catalysts used for propene oxidation and ammoxidation participates in the catalytic reaction. Oxygen transport in partially reduced molybdates is enhanced by the formation of crystallographic shear structures analogous to the Magneli phases of the TiO_2 rutile structure.^{69,70} Moreover, there are clear analogies between the chemistry of selective oxidation and reductive coupling. We have previously suggested a hypothetical catalytic cycle for reductive carbonyl coupling¹⁵ which is simply the cycle

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for oxidation via the Mars-van Krevelen mechanism⁷¹ followed by many oxidation catalysts,⁶⁹ but run in reverse.

The depiction above of the active site requirement and the role of the bulk oxide in reductive carbonyl coupling by gas-solid reactions with reduced titania shares many features with the liquid-solid reaction as it is typically described. Although they argue for the primary role of Ti^0 species, McMurry,³² Dams *et al.*,³⁶ and Kahn and Riecke³¹ all depict the pinacolate intermediate in reductive coupling as bridging two or more titanium atoms in a surface ensemble. Dams *et al.*³⁶ also describe a role for the subsurface region of the solid reagent. They depict a scheme in which surface titanium atoms are abstracted in the course of the reaction and leave the surface complexed with product molecules. Surface rearrangement exposes titanium atoms from the bulk, making them available for subsequent reaction events.³⁶ Whether one views the bulk solid as an oxygen sink, as we suggest for the gas-solid reaction, or as a titanium source, as suggested by Dams³⁶ for the liquid-solid reaction, the effect of the reductive coupling reaction is the same: the O/Ti ratio of the solid must increase.

Conclusions

Reductive coupling of benzaldehyde to form stilbene can be carried out at high yields, even in ultrahigh vacuum, on reduced TiO_2 surfaces containing Ti cations in the +1 through +4 states. Activity for this reaction tracks the extent of reduction of the near-surface region of the solid, as measured by XPS. The site required for the 4-electron reductive carbonyl coupling reaction

is an ensemble of Ti cations in the +1 to +3 states; both surface and subsurface cations may be part of these ensembles. This gas-solid reaction is strongly analogous to the liquid-solid "McMurry reaction" in which carbonyl compounds are reductively coupled to form olefins using reduced titanium reagents. The selectivities, temperatures, and ensemble site requirements for reductive coupling under the very different conditions of ultrahigh vacuum vs the liquid phase are in striking accord. The formation of pinacolate intermediates in the liquid-solid reaction is consistent with the alkoxide-forming tendencies of reduced TiO_2 surfaces toward carbonyl compounds, and the reaction mechanisms of reductive coupling in the liquid-solid and gas-solid examples appear to be analogous. The crucial difference between the present results and those obtained for the liquid-solid reaction is the complete absence of Ti^0 species on reduced titania surfaces that exhibit high activities for reductive carbonyl coupling. While this does not suggest that Ti^0 is not the principal form of the active reagent in the liquid-solid reaction, ensembles of titanium cations in the +1 to +3 states are clearly active for the gas-solid reaction. The novel demonstration that reductive carbonyl coupling can be carried out as a gas-solid reaction with reduced titania and that this reaction does not require complete reduction to the metal suggests that this chemistry might be performed by contact catalysis. We continue to pursue that goal.

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