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Characterization of TiO_2 surfaces active for novel organic syntheses

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Quantitative distributions were determined for the oxidation states of titanium cations on $TiO_2(001)$ surfaces reduced by argon ion bombardment and reoxidized by thermal treatment. Information about the inhomogeneity of these distributions within the near-surface region sampled by XPS was obtained by angle-resolved measurements in which the position of the analyzer axis was varied with respect to the surface normal. These experiments demonstrated that (1) sputtering with 2 keV ions produced a surface containing Ti cations in the 1+, 2+, 3+, and 4+, but not 0 oxidation states; (2) these were reoxidized in a roughly sequential fashion as the surface was annealed to 750 K, at which temperature reoxidation to Ti^{4+} was complete; and (3) the average oxidation state of the topmost layers of the ion-bombarded surface was slightly higher than that determined from XPS spectra collected normal to the surface. Since the surfaces reduced by argon ion bombardment are active for organic assembly processes, including reductive coupling of aldehydes to form symmetric olefins, these surface characterization results demonstrate that Ti^0 sites are *not* required to effect reductive coupling, in contrast to conclusions from previous slurry-phase studies. These observations enhance the possibility that reductive carbonyl coupling might be rendered catalytic, since a smaller cycle of oxidation states is required than previously recognized.

Keywords: titanium oxides; angle-resolved XPS; oxidation state distribution; coupling reactions

1. Introduction

One of the intriguing challenges in the study of surface chemistry under ultrahigh vacuum conditions is the direct examination of organic reactions with synthetic and potentially catalytic utility. Decomposition to lower molecular weight products is the norm for organic molecules on reactive surfaces because of the thermodynamic preference at low pressure for reactions which increase the

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number of molecules. Synthesis of products larger and more complex than the reactants by processes such as assembly of carbon–carbon bonds is much more difficult. One often has little choice but to study important catalytic assembly processes, e.g., olefin polymerization, carbonylation and hydroformylation, Fischer–Tropsch synthesis, etc., in reverse.

We have recently discovered several families of interesting organic syntheses which involve C–C bond formation, and which occur on metal oxide surfaces under UHV conditions. Two of these, ketonization of carboxylic acids and aldol condensation of aldehydes, occur on fully oxidized TiO_2 surfaces and exhibit different dependences on the local coordination environment of the Ti^{4+} cations exposed at those surfaces [1–4]. These reactions on single crystal oxide surfaces both have precedents as gas–solid catalytic reactions on high surface area oxides [5–7]. Other C–C bond forming reactions require reduced titania surfaces. Examples discovered in UHV include the reductive coupling of aldehydes and ketones to form symmetric olefins [8–11], cyclization of ethylene glycol to form benzene [12], and cyclotrimerization of alkynes to form alkyl benzenes [12]. The "precedents" that may be found for these reactions are typically liquid–solid *stoichiometric* processes [13–15]. The discovery that they can be carried out as gas–solid reactions, both on reduced TiO_2 single crystals in UHV and on partially reduced oxide powders at atmospheric pressure [9], holds the promise that they might emerge as new *catalytic* processes.

The ability to carry out these syntheses on (potentially) well-defined surfaces in UHV conveys a crucial advantage over previous slurry-phase studies with regard to understanding the mechanisms and site requirements. Attempts to determine the oxidation states of metal sites in liquid–solid reactions have relied almost exclusively on *indirect* measures, e.g., the stoichiometry of reduction reactions required to activate the solid phase [13,16] or the absence of a correlation between activity and the population of species in oxidation states observable by ESR [17]. The tools of modern surface science, in particular X-ray photoelectron spectroscopy (XPS), permit, in principle, the *direct* measurement of surface oxidation state throughout the course of in situ surface organic syntheses.

Our preliminary studies [8–12] have shown that the activity of reduced (by ion bombardment) titanium oxide surfaces for reductive coupling of carbonyl compounds and for cyclotrimerization of ethylene glycol and alkynes drops by an order of magnitude when these surfaces are oxidized by thermally driven diffusion of oxygen from the bulk. Because of the mobility of oxygen in this material, dramatic changes in both reactivity [8–12,18] and surface oxidation state [18,19] occur upon annealing at moderate temperatures (750 K and below). Two examples of the precipitous decrease of coupling activity with annealing are illustrated in fig. 1. The physical characteristics of the surface can be varied easily over a wide range; connection of these with performance in organic syntheses requires careful characterization.

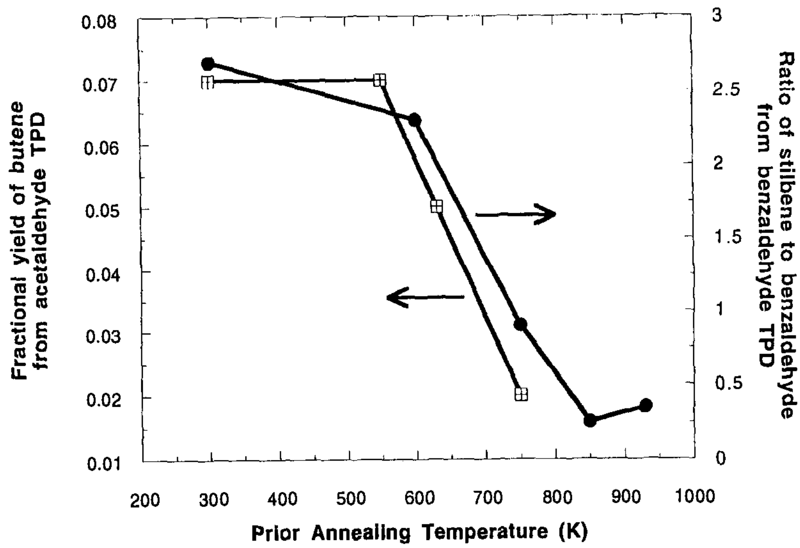

Fig. 1. Production of reductive coupling products vs. prior annealing temperature of the reduced $TiO_2(001)$ surface. (a) Stilbene from benzaldehyde [8]; (b) butene from acetaldehyde [11].

In order to provide evidence for the oxidation states of titanium present in reduced oxides proposed as potential catalysts for these reactions [9], we report here the characterization of reactive TiO_2 single crystal surfaces subjected to ion bombardment and annealing. The broad outlines of bombardment/annealing-induced changes in surface composition may be found in previous studies of TiO_2 [18–22], however resolution of several issues is important for understanding surface coupling reactions. First, many earlier studies of oxide single crystals were plagued by inaccuracies in temperature measurement, owing to difficulties in making direct contact between thermocouples and refractory oxide samples [23–25]. Contact of thermocouples with heated metallic portions of sample mounting hardware can lead to overestimation of actual surface temperatures by several hundred degrees. Since the oxidation state of TiO_2 surfaces is sensitive to surface temperature, and since temperature represents the principal means of control of surface state in these single crystal reactivity studies, it is important to establish a reliable temperature scale. Second, there exists a basic conflict regarding titanium oxidation state requirements for carbonyl coupling between the conclusions drawn from the indirect methods applied to liquid–solid slurry experiments and direct measurements in UHV. Several groups have suggested that Ti^0 centers, individually capable of undergoing a four-electron oxidation, are required for carbonyl coupling [13,17]. Neither we nor previous researchers have detected Ti^0 on ion-bombarded TiO_2 surfaces [18–22,26], yet these surfaces are highly active for carbonyl coupling [8–10]. This suggests that multiple surface cation sites collectively effect this four-electron reduction [9]; the populations of Ti cations in oxidation states actually present must be quantified in order to understand this process. This analysis also provides a basis for characterization of high surface area oxide materials that we have previously demonstrated to be active for reductive carbonyl coupling [9]. Third, because the reactive titania surfaces produced by ion bombardment and annealing are metastable, and because oxidation of these surfaces is typically performed by diffusion of oxygen from a near-stoichiometric bulk to a highly reduced surface, significant concentration gradients may exist within the sampling depth of XPS and other electron spectroscopies. We have therefore performed angle resolved XPS (ARXPS) measurements in order to assess the significance of such gradients and the confidence with which one may determine the oxidation state (or the absence of Ti^0) at the reactive gas–solid interface.

In order to determine the population of titanium cations in different oxidation states on both single crystals and powder, and the changes with various surface treatment processes, it is important to have reliable calibrations of XPS binding energies for the various oxidation states. However, as recently pointed out by Gonbeau et al. [26] "published values for the Ti(2p) peak of titanium oxides are relatively dispersed, except for TiO_2". Even for the Ti cations in the highest oxidation state, reported energies of the $2p_{3/2}$ line range from 458.5 eV [27,28] to 460.2 eV [29], with an average value of 459.0 ± 0.4 eV from more than 20 studies [18–22,26–28,30–47]. Even if there were absolute agreement regarding the energy differences between Ti^{4+} and lower oxidation states, the reported binding energies for these states would exhibit similar variations. However such agreement is, not surprisingly, lacking. In order to eliminate the scatter from different calibrations of absolute binding energies, it is useful to consider binding energy *differences* between Ti^{4+} and lower oxidation states, as has been done previously by Göpel et al. [21,47], Carley et al. [38], and Sayers and Armstrong [39]. Expanding the compilations of data from these sources, the average of value reported [18–22,26,28,32, 36–39,42,44,47] for the $2p_{3/2}$ line of Ti^{3+} species in titanium oxides is 1.7 ± 0.2 eV below that of Ti^{4+}. The relative position of the line for Ti^0 is also well defined, at 5.1 ± 0.2 eV below that for Ti^{4+} [21,27,34–39,46,47] with no separation reported of less than 4.7 eV. There is greater uncertainty regarding the position of the lines for Ti^{2+} and Ti^{1+} species. The average of positions reported [18–20,26,28,32,35–39, 47,48] for the $2p_{3/2}$ line for Ti^{2+} is 3.5 ± 0.4 eV below that for Ti^{4+}. Both we [18] and Göpel [21,47] have reported spectra for reduced titanium oxides exhibiting significant intensity at energies between those for the Ti^{2+} and Ti^0 states, and have assigned this to a Ti^{1+} state with a $2p_{3/2}$ binding energy 4.2 eV below that of Ti^{4+}.

There is a certain "time dependence" to these values which should also be noted. First, it has been argued that the binding energy values obtained for bulk suboxides such as Ti_2O_3 and TiO in pioneering work by Ramqvist et al. [35] and Franzen et al. [48] provide more reliable measures for Ti^{3+} and Ti^{2+} binding energies than do curve-fitted spectra of mixed oxides produced by reducing TiO_2 or oxidizing Ti metal. However, as pointed out by Beatham et al. [49], the prior treatment of suboxides is critical; air exposure will cause the surface to be more highly oxidized than the bulk, as is evident in some reported spectra of "authentic" suboxide samples [35,49], while in vacuo pretreatments may reduce the surface below the oxidation state of the bulk. Thus in spite of their fixed bulk stoichiometry, suboxide samples do not necessarily provide superior binding energy calibrations for lower oxidation states. Second, with the improvement of spectrometer resolution over the last two and one-half decades, reported line widths have decreased. With this evolution, one finds that the binding energy differences for the various oxidation states of titanium have tended toward the lower bounds of the ranges reported above. Our data [18] and the analysis of it are consistent with this trend.

The analysis of the population of Ti cations in different oxidation states below is therefore based on the following standards. The $2p_{3/2}$ line for Ti^{4+} species on fully oxidized TiO_2 surfaces is positioned at 459.3 eV [1,2,18,50–52] and may be used as a calibration value [47,50–52]. As noted previously, this places the O(1s) line at 530.6–530.7 eV [1] and the C(1s) line for residual carbon at 284.0–284.1 eV [1,52]. Upon partial reduction, the Ti^{4+} peak shifts to 459.0–459.1 eV [18]. This shift is quite consistent in size and magnitude with the work function and band bending differences between oxidized and partially reduced TiO_2 samples from both XPS and UPS studies [20,21,33,44,53,54], and it places the $2p_{3/2}$ line at the average value calculated above for various titanium oxide samples from the literature. Following the analysis of Rocker and Göpel [47] the $2p_{3/2}$ line for Ti^{3+} was located 1.6–1.7 eV below that for Ti^{4+}. The value for Ti^{2+} was 3.1–3.2 eV below that for Ti^{4+}. Ti^{1+} was positioned 4.2 eV below Ti^{4+}. Ti^{0}, if present, would be expected to be 5.1 eV below Ti^{4+}. These separations are in good agreement with our preliminary analysis [18] and with recent calibrations of relative binding energies for different oxidation states by Carley et al. [38] as well as those by Rocker and Göpel [47]. In analyzing the data reported below, the line widths of all $Ti_{2p_{3/2}}$ lines for different oxidation states were taken to be comparable, in accord with previous results from other laboratories [20,26,32,36,39,47], and the $2p_{1/2}$ line was located at 5.6–5.7 eV above the corresponding $2p_{3/2}$ line, as before [1,21,47].

2. Experimental

All experiments were performed in the VG Scientific ESCALAB system described previously [55]. This instrument was equipped with a mass spectrometer, twin anode X-ray source, ultraviolet lamp, electron and ion sources, LEED optics, and a hemispherical energy analyzer. The relative positions of the sample manipulator, X-ray and ion sources and the energy analyzer were as reported [56]. The base pressure in this instrument was 1×10^{10} Torr and was maintained by diffusion and sublimation pumping.

The (001)-oriented TiO_2 single crystal sample (10 mm × 9 mm × 1.5 mm) was prepared from a rutile boule (99.99%, Atomergic Chemetals Corp.) as described before [1,18]. In brief, it was aligned by the Laue method, cut, and mechanically polished to a mirror finish with 1 μm diamond paste. After installation in the vacuum chamber the single crystal was cleaned by repeated cycles of argon ion bombardment and annealing, as previously described [1,18].

The $TiO_2(001)$ single crystal was mounted using a sample holder made of tantalum foil (0.127 mm thick), spot-welded to 0.5 mm tantalum wires. The wires were spot-welded to two molybdenum rods of a rotatable sample manipulator. The sample temperature was monitored using a chromel–alumel thermocouple attached to the side of the crystal using high-temperature cement (Aremco Ultra-Temp 516). XPS and AES measurements showed that there was no migration of the cement during heat treatment.

A typical ion bombardment consisted of using a 2 keV Ar^+ beam, for a fixed time, with the angle of the incident beam at about 70° relative to the plane of the surface. Argon (Mathesson ultra pure) was introduced to the vacuum chamber through the gun and controlled manually by a variable leak valve. Two stage differential pumping was used in order to ensure low pressure inside the chamber. The pressure in the chamber was 3×10^{-7} Torr during ion bombardment. The emission current was adjusted to obtain a current of about 300 nA/cm^2 at the crystal.

X-ray photoelectron spectra of the Ti(2p) and O(1s) regions were obtained for the various sputtered and annealed surfaces created. The Al anode ($h\nu = 1486.6$ eV) was operated at 600 W in all cases. Angle-resolved spectra were obtained by collection of data with the sample rotated at different positions about the manipulator axis perpendicular to the axis of the analyzer entrance [58]. Data were obtained for photoelectron emergence angles from 90° (i.e., with the surface normal aligned with the analyzer axis) to ca. 40° (the angle of the extension of the analyzer axis with the surface plane). Spectra obtained at shallower emergence angles contain greater contributions from the topmost layers of the solid than do those collected normal to the surface.

3. Results

3.1. Ti(2p) CORE LEVELS OF THE $TiO_2(001)$ SURFACE AS FUNCTION OF SPUTTERING TIME

It has previously been shown [1,18–22,53,54,58,59] that TiO_2 single crystal surfaces and powders [39,60] are reduced by sputtering with argon ions. While well-annealed $TiO_2(001)$ single crystal surfaces contain Ti cations in only one oxidation state (4+), sputtered surfaces contain Ti cations in the 3+, 2+, and 1+ states in addition to the 4+ oxidation state [18]. The extent of reduction of the Ti cations, tracked by XPS of the $Ti(2p_{3/2})$ core levels, on the $TiO_2(001)$ surface as a function of sputtering time (keeping all other parameters fixed) is presented in fig. 2. In curve (a) the Ti(2p) region of a $TiO_2(001)$ single crystal, annealed to 750 K (i.e., fully oxidized [1]), is presented. Only one oxidation state is present, as evidenced by the narrow $Ti(2p_{3/2})$ peak at 459.3 eV with a small FWHM (1.2 eV). The $Ti(2p_{1/2})$ line for Ti^{4+} cations appears at 465.0 eV with a FWHM of 2.0 eV. Curve

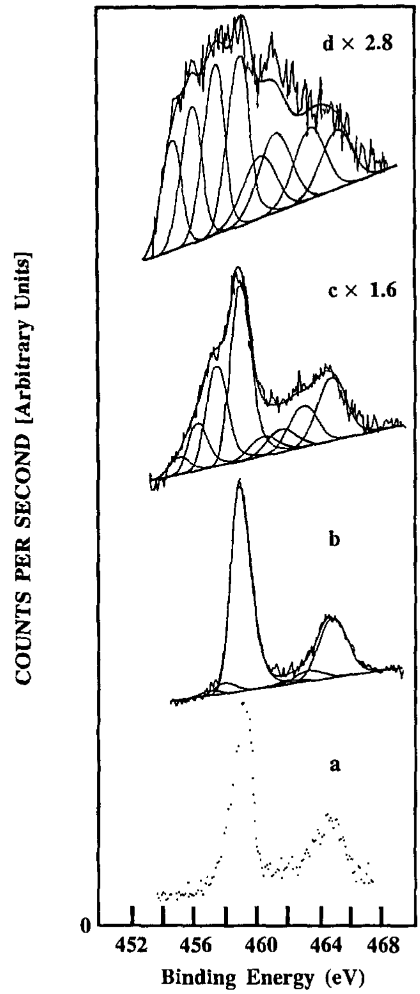

Fig. 2. Ti(2p) region of the TiO_2(001)-oriented single crystal as a function of sputtering time. (a) Not sputtered; (b) sputtered for 15 min; (c) sputtered for 30 min; (d) sputtered for 60 min. All spectra were obtained for emission along the surface normal ($\theta = 90°$).

(b) presents the Ti(2p) core levels of the same single crystal after sputtering for 15 min with 2 keV Ar^+ ions. A slightly broader peak at 459.2 eV with a FWHM of 1.54 eV is indicative of the presence of more than one oxidation state of titanium. Clearly, the principal contribution to the signal arises from Ti cations in the 4+ state, however two small peaks for Ti^{3+} and Ti^{2+} can be extracted by curve fitting on the low binding energy side of the Ti^{4+} peak. The presence of more than one oxidation state can also be seen from the $Ti(2p_{1/2})$ region where the peak at 465.0 eV has broadened to a FWHM of 2.3 eV. Curve (c) presents the Ti(2p) core levels of the TiO_2(001) single crystal sputtered for 30 min. A dramatic change is apparent in both the $Ti(2p_{3/2})$ and the $Ti(2p_{1/2})$ lines. The signal corresponding to Ti^{4+} cations shifted slightly to 459.0 eV; in addition two prominent shoulders are clearly seen at ca. 457 eV in the $Ti(2p_{3/2})$ region and at ca. 463 eV in the $Ti(2p_{1/2})$ region. Curve fitting indicated the presence of multiple Ti^{x+} species with $Ti(2p_{3/2})$ binding energies of 457.4, 455.9, and 454.8 eV, attributed to the 3+, 2+, and 1+ oxidation states, respectively. Curve (d) presents the $TiO_2(001)$ single crystal sputtered for 1 h. Clearly, much wider $Ti(2p_{3/2})$ and $Ti(2p_{1/2})$ peaks are present. The overlapping contributions from both Ti(2p) lines form a nearly continuous "peak" spanning the interval from about 454 to about 468 eV. By curve fitting, eight peaks were obtained, four in the $Ti(2p_{3/2})$ region and four in the $Ti(2p_{1/2})$ region. The $Ti(2p_{3/2})$ peaks correspond to Ti^{1+}, Ti^{2+}, Ti^{3+}, and Ti^{4+} states with binding energies of 454.8, 455.9, 457.4, and 459.0 eV, respectively. No evidence for Ti^0 was observed. As discussed above, the expected Ti^0 binding energy should lie about 5.1–5.2 eV below that of Ti^{4+}, i.e., below 454.0 eV; clearly no peak in this region can be fitted in fig. 2d.

Quantitative determination of the relative $Ti(2p_{3/2})$ peak areas of Ti cations as a function of sputtering time is presented in fig. 3. On the non-sputtered surface, all Ti cations are in the 4+ state. After 15 min of sputtering the concentration of Ti^{4+} cations decreased to 93.4% in favor of Ti^{3+} and Ti^{2+} states, which increased to 4.6 and 2.0% of the total, respectively. After 30 min the concentration of Ti^{4+} further decreased to 51.1%; those of reduced Ti^{3+} and Ti^{2+} cations increased to 30.3 and 13.6%, respectively. Small amounts (5.1%) of Ti^{1+} cations were also observed. After 1 h of sputtering the major species on the surface were Ti^{x+} cations with $0<x<4$. The population of Ti^{4+} cations decreased to 31% of the total. Additional sputtering produced only slight modification of the relative populations of Ti cations; the Ti^{4+} population decreased to about 24–25% after more than 2 h of

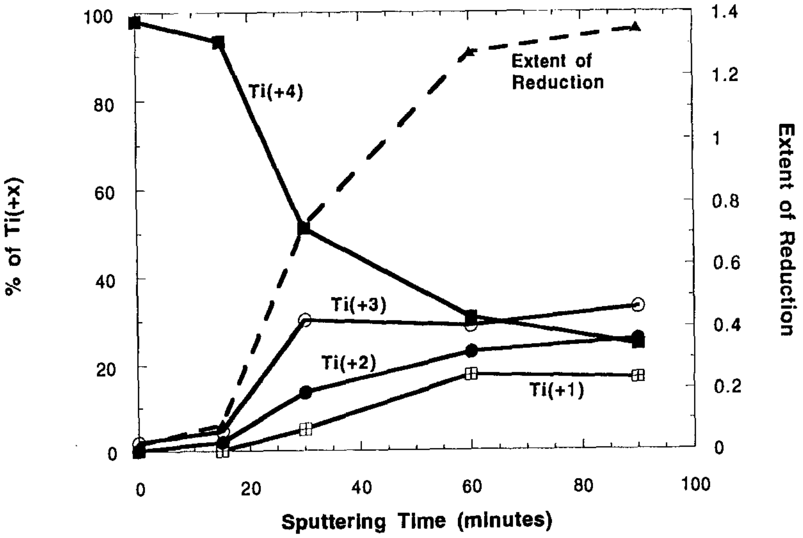

Fig. 3. Population of Ti cations in different oxidation states on the $TiO_2(001)$ single crystal surface as a function of sputtering time. Relative populations were determined from curve fits to the data shown in fig. 2.

sputtering (not shown). These data may be used to calculate a single parameter to characterize the average state of the surface. This is referred to in fig. 3 as the extent of reduction of the surface. This parameter is calculated by summation of the fraction of cations in each oxidation state, weighted by the difference in valence state relative to Ti(IV). Thus an extent of reduction of one indicates an average oxidation state of 3+, an extent of reduction greater than 1 indicates an average titanium oxidation state less than 3.

3.2. ANGLE RESOLVED X-RAY PHOTOELECTRON SPECTROSCOPY (ARXPS) OF THE SPUTTERED SURFACE

In order to probe further the different oxidation states on the sputtered $TiO_2(001)$ surface, angle-resolved XPS (ARXPS) data were obtained. Several workers have presented ARXPS of oxide surfaces and semiconductors in order to characterize the species at the outermost surfaces [60,61], the dispersion of metals in the case of metal-deposited-on-oxide catalysts [62], and the surface roughness of thin films [63]. In addition, ARXPS of TiO_2 single crystals has been reported for two different crystal planes, the (110) and (100) [22]. However, the authors of that work [22] performed relatively mild sputtering of their samples, and the only reduced state was Ti^{3+}. They also discussed the change in the area ratio of the Ti^{3+}/Ti^{4+} signals and that of the O(1s)/Ti(2p) signals as a function of the emergence angle of photoelectrons from the surface. Their results showed that the Ti^{3+}/Ti^{4+} signal ratio increased from the surface normal to about 60° from the normal, then it decreased at more grazing angles. Their explanation was as follows: since the relative intensity of the XPS signal at grazing angles emphasizes species present at the outermost surface, then Ti^{3+} and Ti^{4+} must not be homogeneously distributed in the near-surface region. However they did not observe any angular dependence of the O(1s)/Ti(2p) signal ratio. This might be because of the mild sputtering which produced a relatively small oxygen deficit, along with the relatively small difference in stoichiometry between the "limiting cases", Ti_2O_3 and TiO_2.

Fig. 4 presents the Ti(2p) core level regions of the sputtered $TiO_2(001)$ single crystal at two different analyzer positions. Fig. 4a is that of the crystal normal to the analyzer (photoelectron emergence angle, θ, = 90°), while fig. 4b is that of the crystal at $\theta = 40°$. Clear differences exist between the spectra collected at the two positions. At $\theta = 90°$ where sampling of the subsurface layers is maximized, the region below that of Ti^{4+} at 459.0 eV is emphasized. By curve fitting one can determine that Ti^{3+} has almost the same intensity as Ti^{4+}. Quantitative determination of the peak areas indicated that the ratio of the peak areas for Ti^{x+} $(0<x<4)$ to Ti^{4+} was 2.11. At $\theta = 40°$ (fig. 4b) there is some attenuation of the peaks for reduced Ti^{x+} species compared to that of Ti^{4+}; the ratio of peak areas for Ti^{x+}/Ti^{4+} decreased to 1.76. Since the relative intensities of the XPS lines for the species which are at the outermost surfaces increase at grazing angle (in this case at $\theta = 40°$), the results presented in fig. 4 indicate that the surface layer is less

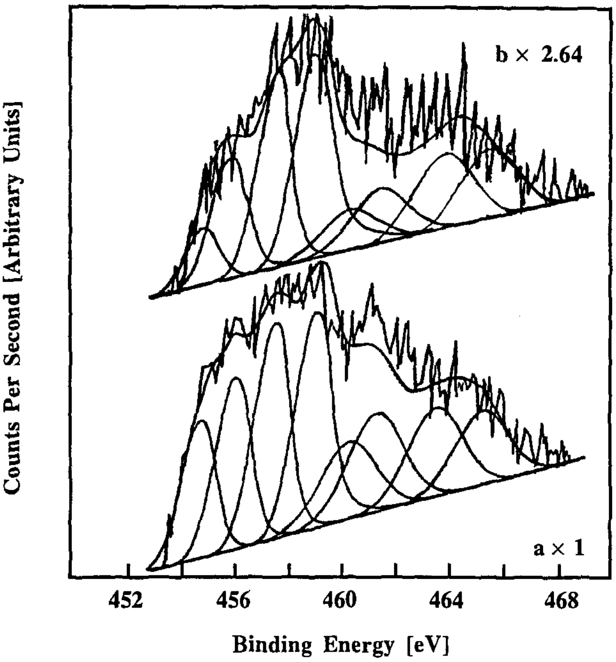

Fig. 4. ARXPS of the $TiO_2(001)$ surface after sputtering for 1 h. (a) Crystal at $\theta = 90°$; (b) crystal at $\theta = 40°$.

reduced than the region just below the surface. This reinforces the conclusion that Ti^0 species are absent at the outermost surfaces; if anything, the average oxidation state of the topmost layers is higher than the average sampled in XPS spectra collected along the surface normal. Fig. 5 presents the determination of the relative

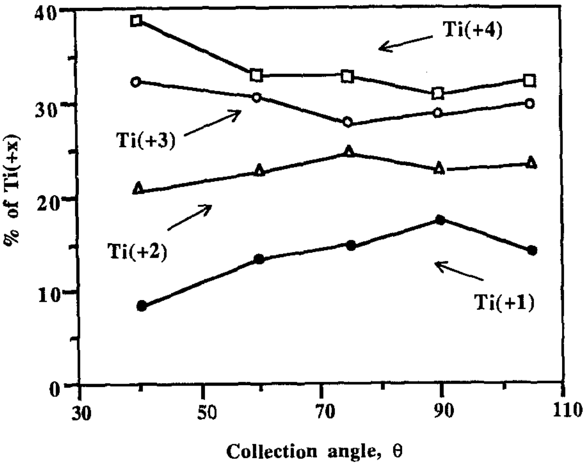

Fig. 5. Distribution of Ti^{x+}, $(0<x\leqslant 4)$, of the $TiO_2(001)$ surface, sputtered for 1 h, as a function of collection angle.

peak areas corresponding to the different oxidation states as a function of the collection angle. As shown, decreasing θ resulted in an increase of the fractions of Ti^{4+} and Ti^{3+} while those of Ti^{1+} and Ti^{2+} decreased, with the slope of the decrease of Ti^{1+} more pronounced than that of Ti^{2+}. The ratio Ti^{4+} to Ti^{x+} as a function of the collection angle is presented in fig. 6 in order to emphasize the direction of the gradient in the near-surface region. At $\theta = 90°$ the ratio is at its minimum, indicating that over-estimation of the relative abundance of reduced Ti^{x+} cations at the surface is usually made. At $\theta = 75°$ and $\theta = 105°$ the ratio is very close (0.475 versus 0.485) since at both positrons the surface normal is tilted at 15° from the analyzer axis; i.e., the crystal position is geometrically the same relative to the analyzer. (From this result one can also check the internal consistency of the values obtained by ARXPS.) A monotonic increase in the Ti^{4+}/Ti^{x+} ratio is observed with decreasing θ, reaching 0.68 at $\theta = 40°$. This again illustrates the enrichment in Ti^{4+} on the surface compared to the population obtained from the spectrum collected normal to the surface.

3.3. THE STATE OF THE SPUTTERED $TiO_2(001)$ SURFACE AS A FUNCTION OF ANNEALING TEMPERATURE

Heating the sputtered crystal to higher temperatures will result in oxidation of Ti cations by oxygen migration from the bulk to the surface. This has been studied in detail by XPS [1,18,19], by UPS [54,58,64], by AES [1,19,53,59] and by ELS [53,64]. The surface of the bombarded, reduced, $TiO_2(001)$ single crystal can be completely oxidized by annealing, in UHV, at 750 K for ca. 20 min [1,18]. How-

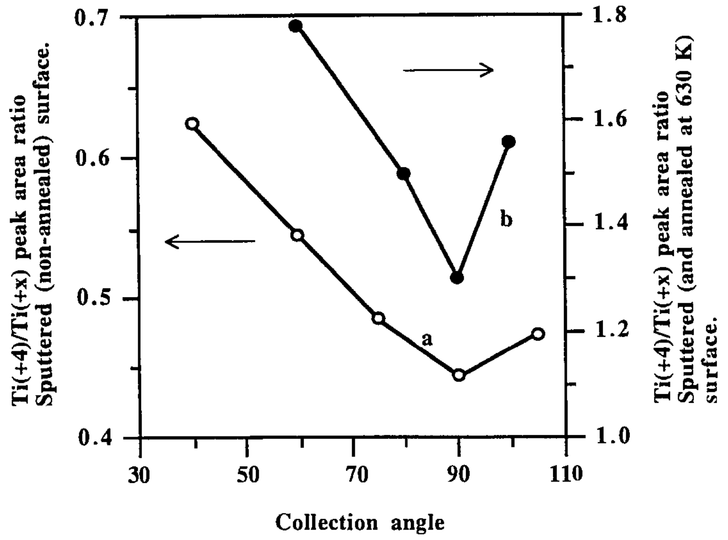

Fig. 6. Ti^{4+}/Ti^{x+} ratio, $(0<x<4)$, of the $TiO_2(001)$ surface, as a function of collection angle. (a) Surface sputtered for 1 h, (b) surface in (a) annealed at 630 K.

ever the relative populations of the different oxidation states of Ti cations during oxidation have not been followed quantitatively. It is important to determine the change in the cation oxidation states in order to account for the site requirements of chemical reactions occurring on these surfaces.

Fig. 7 presents the angular variation of the Ti(2p) region of the surface of a sputtered (for 1 h) $TiO_2(001)$ single crystal annealed at 630 K for 20 min. The changes in the relative intensities of individual peaks were less pronounced than in the case of similar experiments on the sputtered surface without annealing. However, several points can be obtained from these results and their comparison with those of the sputtered surface.

(1) Unlike the sputtered surface (fig. 4), Ti^{1+} cations are not present on the surface annealed at 630 K, indicating that the process of surface oxidation was already underway at this low temperature. This result is of importance for the study of the necessary active site for carbonyl coupling reactions, since the 630 K

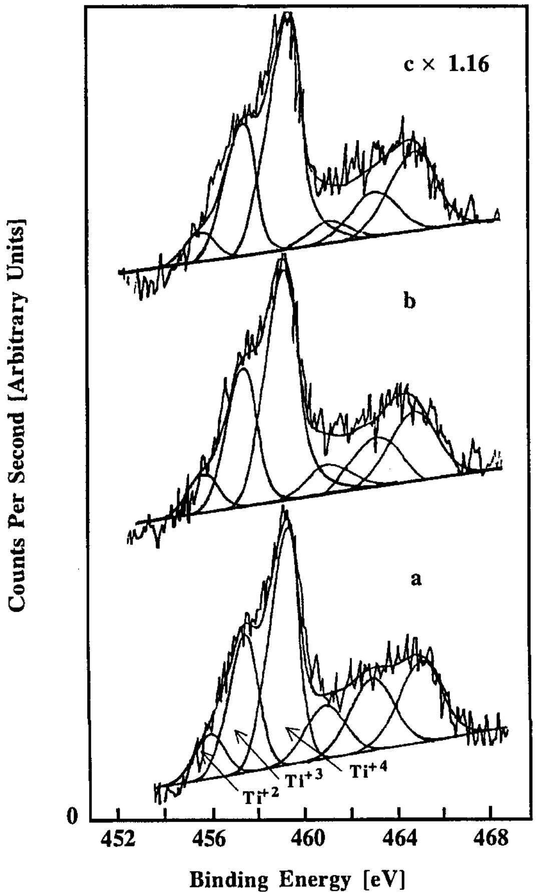

Fig. 7. Ti(2p) region of the $TiO_2(001)$ surface, sputtered for 1 h and annealed at 630 K for 20 min, as a function of collection angle. (a) $\theta = 90°$, (b) $\theta = 80°$, (c) $\theta = 60°$.

annealed surface still exhibits a significant level of activity for carbonyl coupling [8].

(2) The dominant contribution is from Ti^{4+}, unlike the case for the sputtered surface, where the Ti^{4+} and Ti^{3+} peaks were of similar intensity.

(3) The relative signal intensities for different Ti oxidation states on the 630 K annealed surface as a function of θ are presented in fig. 8. As for fig. 5 the maximum signal for reduced cations is obtained at $\theta = 90°$, however the angular variation is less pronounced in this case than for the sputtered surface prior to annealing. The trend in signal intensity versus angle is the same as that on the sputtered surface, however, and indicates that in both cases collection of spectra along the surface normal tends to underestimate the oxidation state of the surface.

Fig. 9 presents the distribution of Ti cations, as a function of prior annealing temperature of the sputtered surface. For all spectra the crystal was at the same position ($\theta = 90°$). All peaks were curve fitted using the same program, and with the same parameters. The following points can be drawn from this figure.

(1) The lower the oxidation state of Ti cations, the lower the temperature at which these disappear in favor of higher oxidation states. At about 630 K, Ti^{1+} cations were completely oxidized. At 700 K, Ti^{2+} were also completely oxidized, and only small amounts of Ti^{3+} were present; these latter cations were absent at 750 K. Qualitatively these results are similar to those previously presented [18].

(2) Up to 630 K the percentage of Ti^{3+} cations remains the same. This may represent a balance between the number of Ti^{3+} oxidized to Ti^{4+} with that of Ti cations in lower oxidation states than 3+ oxidized to Ti^{3+}. It does not imply that individual Ti^{3+} species are unaffected by annealing at this temperature.

(3) Annealing the crystal at temperatures higher than 750 K (up to 950 K) did not produce significant changes in oxidation state relative to the 750 K annealed surface. The Ti^{4+} cations were the only species present at 750 K and they represent

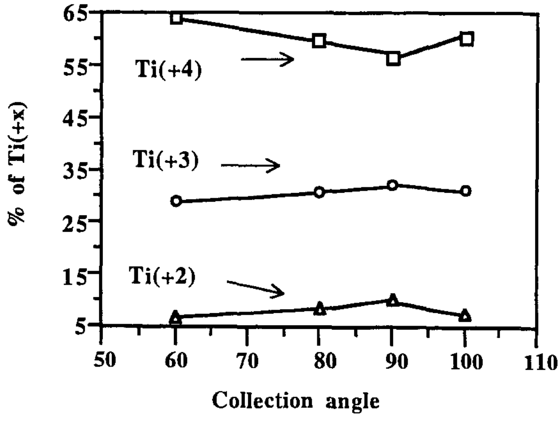

Fig. 8. Distribution of Ti^{x+}, ($0<x\leqslant4$), of the $TiO_2(001)$ single crystal, sputtered and annealed at 630 K for 20 min, as a function of collection angle.

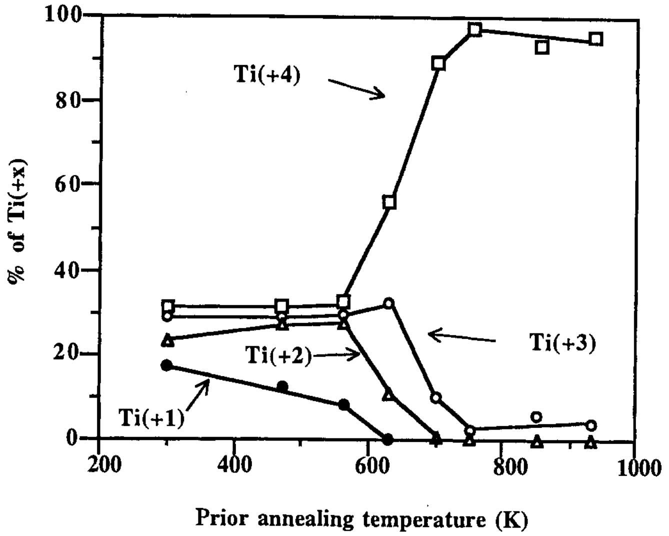

Fig. 9. Population of Ti^{x+}, ($0<x\leqslant4$), of the $TiO_2(001)$ samples after sputtering (at 300 K) and as a function of annealing temperature. XPS data collected along the surface normal ($\theta = 90°$).

more than 95% of all cations at 850 K and above. A very small amount of reduction occurs by annealing above 800 K, but the extent of thermal reduction at high temperature is minor compared to that obtained by sputtering the surface. Significant rearrangement of the stoichiometric TiO_2 surface does, however, occur in this temperature range [1,25].

4. Discussion

ARXPS data from the sputtered and annealed $TiO_2(001)$ surfaces support the following conclusions. (1) Reduced Ti cations are relatively less abundant at the outermost layers of sputtered surfaces than in the deeper regions within the XPS sampling depth. (2) The 630 K annealed surface is an intermediate surface between the sputtered and the fully oxidized surfaces. It does not contain Ti^{1+} species, and the Ti^{4+} cations represent about 50% of the overall Ti concentration. (3) Quantitative analysis of the Ti cation population as a function of progressive annealing demonstrated that the lower the oxidation state, the sooner it disappears during progressive annealing. Comparison of the reactivity data for reductive coupling reactions in fig. 1 with the oxidation state distribution in fig. 9 clearly establishes the connection between this chemistry and the presence of reduced sites on the surface.

The average oxidation state of Ti cations is somewhat higher at the outermost surfaces than in the subsurface region sampled by XPS. This suggests that slight overestimation of the extent of surface reduction can occur when measurements are done at 90° (collection along the surface normal, the usual sample position). While one would expect the near-surface region to be reduced, it is somewhat surprising to find that Ti cations at the outermost layers are less reduced on average. This implies that the gradient in Ti oxidation state (or oxygen concentration) is a non-monotonic function of depth below the surface. As one proceeds from surface to bulk of the sputtered sample, the average oxidation state of titanium at first decreases slightly and then increases to approach its value (4+) for bulk TiO_2. This does not necessarily imply that the thermodynamic activities of Ti and O species also exhibit a non-monotonic gradient. There is clearly a thermodynamic preference for maximizing the coordination number of surface atoms; this drives the reconstruction of the stoichiometric $TiO_2(001)$ surface to the stable $\{011\}$ and $\{114\}$-faceted configurations, for example.

The surface annealed at 630 K for 20 min showed even smaller variations in the concentration of Ti oxidation states as a function of collection angle than did the sputtered surface. Figs. 7 and 8, presenting the Ti(2p) regions and the populations of Ti cations, indicated a slight increase in the Ti^{4+} cation concentration at grazing angles. An additional important point which will be considered elsewhere is the absence of Ti^{1+} and the very small amounts of Ti^{2+} present. This surface is active for carbonyl coupling, even though it contains a much lower population of Ti cations in highly reduced states than the fully sputtered, un-annealed surface. Quantitative analysis indicated that the 630 K annealed surface contains Ti^{4+} at a level of ca. 60% with respect to the total titanium present. Further heating the surface decreases the Ti^{3+} to about 10% of the total Ti for the 700 K annealed surface, and all Ti^{2+} disappears by ca. 700 K. While the oxidation of TiO_2 single crystal surfaces was previously investigated by several authors [1,18,19], this is the first quantitative determination of the populations of Ti cations in different oxidation states as a function of the annealing temperature of the sample. This information is important in order to relate the chemistry of reduced titanium oxides, especially for novel organic coupling reactions of potential catalytic importance, to the titanium species actually present at the surface.

5. Conclusions

Titanium oxide surfaces active for reductive coupling of carbonyl compounds can be produced by ion bombardment of TiO_2. These surfaces contain no zero-valent titanium, but do contain Ti cations in oxidation states from 1+ to 4+. Angle resolved XPS experiments demonstrate that the surface layers of fully sputtered samples are slightly more oxidized than the average for the near surface region sampled by XPS along the surface normal. Thus, it is clear that reductive coupling of aldehydes to form olefins, which occurs on such surfaces, does not require Ti^0 sites individually capable of carrying out this four-electron reduction as suggested from previous indirect measurements carried out in liquid–solid slurries. Upon annealing, the near-surface region reduced by ion bombardment is reoxidized by oxygen diffusion from the bulk. The Ti cations are reduced in a roughly sequential fashion, with the lowest oxidation states disappearing at the lowest annealing temperatures. Upon annealing at 750 K, the TiO_2(001) surface returns to its fully oxidized state, and activity for reductive coupling and related reactions is lost. Quantification of surface oxidation states versus sample treatment procedures is essential for further understanding of the active site requirements of these interesting organic syntheses, and has a direct bearing on the potential for performing these catalytically.

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