

Surface Composition, Morphology, and Catalytic Activity of Model Polycrystalline Titania Surfaces

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XPS, UPS, STM, and TPR were used to characterize the oxidation state, morphology, and catalytic behavior of polycrystalline titania films grown by in situ oxidation of Ti metal. Depending on the conditions, either fully oxidized films (~ 6 Å, stoichiometric TiO_2 , stable to ~ 473 K) or partially reduced oxide films could be produced. The morphology of these films could also be varied by varying the pretreatment of the metal substrate: either coarse-grained or nanocrystalline material could be produced. Styrene adsorbs and desorbs reversibly from the fully oxidized titania surface in the absence of water. The hydroxylated, fully oxidized surface converts styrene to acetophenone, a partial oxidation product, with 100% selectivity. The water treated, partially reduced surface converts styrene to ethylbenzene, a partial hydrogenation product, with 100% selectivity. Reaction selectivity and the switch in selectivity are determined by the oxidation state of the surface and do not depend on its morphology. The relevance of these findings to an understanding of the properties of metal/titania catalysts is discussed.

Introduction

The most widely used industrial catalysts consist of oxide-supported metal particles. Over decades, many studies have been carried out in order to understand such materials in detail by making use of model systems composed of metal particles supported on single-crystal oxide surfaces.^{1–3} Titania/metal particle systems have attracted considerable interest because they can manifest the so-called strong metal–support interaction. Au/titania is especially topical, largely due to reports by Haruta and co-workers concerning its remarkable catalytic properties, especially in partial oxidation reactions.⁴ Depending on the conditions, the catalytic behavior of such systems toward alkenes can switch from partial oxidation to hydrogenation. For example it has been demonstrated⁴ that catalysts with gold clusters in the size range 2–4 nm will epoxidize propene with 90% selectivity and 1–2% conversion at temperatures of 303–393 K. However, if the only parameter altered is the gold loading being lowered so that the average cluster size is 2 nm or less, the catalyst switches from production of propene epoxide to propane. A number of single-crystal model studies have focused on the (110) face of titania,^{5–7} and the application of a variety of techniques has provided important insight into the nature of metal/titania interactions. In a related area, much work has been carried out on the oxidation of titanium metal by water, dioxygen, or atomic oxygen whose activity increases in the order listed.^{8–11}

Here we describe the synthesis and characterization (XPS/UPS/STM/TPR) of polycrystalline titania surfaces produced by in situ oxidation of Ti metal. These are intended to provide more realistic model surfaces of relevance to metal particle/titania catalysis.^{4,12} It is shown that different surface morphologies are obtainable, and most importantly, that the pure TiO_2 surface is itself an effective catalyst for styrene partial oxidation with water as the oxidant. Moreover, partial reduction of the titania surface

leads to a switch in reactivity from partial oxidation to partial hydrogenation. The implications of these findings for a more complete understanding of the behavior of metal supported titania catalysts are discussed.

Experimental Methods

Experiments were performed in a VG ADES 400 electron spectrometer system operated at a base pressure of 1×10^{-10} Torr. The $10 \times 10 \times 0.5$ mm polycrystalline titanium sample (Advent, 99.6%) was secured to the xyz manipulator by spot welding to Ta strips. It could be resistively heated to 1350 K and cooled to 100 K. The principal impurities, sulfur, carbon, and phosphorus, were removed by sputtering ($15 \mu\text{A}/5 \text{ keV}/900 \text{ K}$) with occasional flashes to 1300 K in order to segregate sulfur from the bulk. XP spectra were obtained with Mg K α radiation and UPS experiments were performed using a He I photon source. Gas exposure was carried out with a tube doser to enhance the flux at the sample position. Styrene (Aldrich, 99%) and deionized water were purified by repeated freeze/pump/thaw cycles, and Messer grade 4.8 oxygen was used for the oxidation procedures. Gas purities were monitored by mass spectrometry and quoted exposures are in langmuirs ($1 \text{ langmuir} = 10^{-6} \text{ Torr s}^{-1}$), uncorrected for ion gauge sensitivity. After sample preparation in UHV, STM data were acquired under ambient laboratory conditions using a Zeiss-Beetle SPM operating in the STM mode with using chemically etched W tips. For TPD/TPR measurement (15 K/s) the sample was positioned 2 cm from the collimated quadrupole mass spectrometer (QMS) ionizer so that the signal arose almost entirely from the front face. Integrated product yields derived from the TPD/TPR data were corrected to allow for mass discrimination effects in the QMS, ionization cross-sections, and the cracking patterns of relevant desorbing species. This allowed us to compare values for the activity and selectivity of the surface toward the various reactions discussed.

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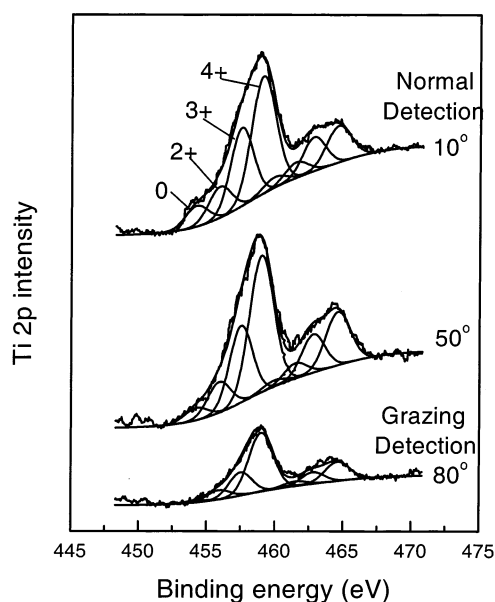


Figure 1. Angle-resolved Ti 2p XP spectra for a 36 000 langmuir O_2 /470 K treated polycrystalline Ti. Fitting shown for 4⁺, 3⁺, 2⁺, and 0 components.

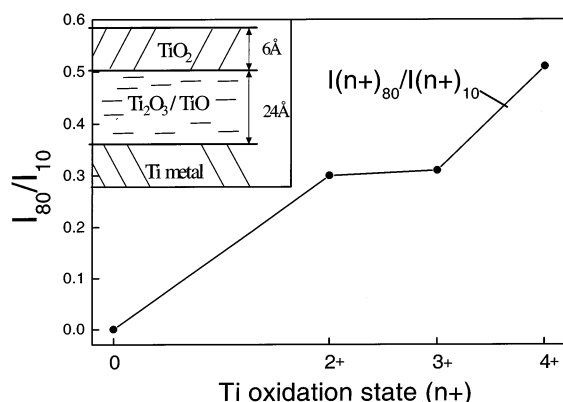


Figure 2. Dependence of grazing/near-normal Ti 2p intensity ratio for the various oxidation states present in a fully oxidized film.

Results and Discussion

Preparation, Composition, Stability, and Adsorption Properties of the Oxide Film. Oxidation of the Ti sample was achieved by dosing 36 000 langmuirs of oxygen at 473 K followed by cooling in a flow of oxygen to prevent subsequent surface reduction by diffusion of oxygen to the bulk. Figure 1 shows three Ti 2p spectra of the resulting oxide layer (henceforth referred to as “fully oxidized”) taken at different detection angles and fitted with four doublets corresponding to Ti oxidation states 0, 2⁺, 3⁺ and 4⁺; the binding energies (BEs) and fwhms correspond to literature values.¹¹ When the integrated intensities of each doublet are corrected for the different densities of the oxides and their ratios compared as a function of detection angle, it is clear that the attenuation of the various oxidation components with the increasingly grazing photoelectron exit is not constant but increases in the order: O > 2⁺/3⁺ > 4⁺. This is illustrated in Figure 2, which shows how the intensity ratios vary with oxidation state ($I_{80^\circ} =$ grazing and $I_{10^\circ} =$ normal detector angle). This demonstrates that the oxide can be characterized by a composition gradient in which the oxidation state of Ti increases toward the surface. This result is in line with other studies of oxidation of polycrystalline titanium.^{8–11} A more rigorous analysis of the type used by McCafferty et

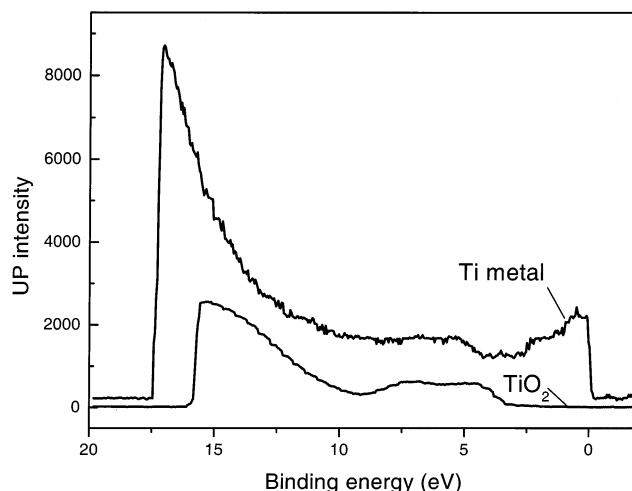


Figure 3. He I UPS spectra of the oxide overlayer and of clean titanium metal.

al.¹¹ that takes into account oxide densities, photoelectron inelastic mean free paths, photoionization cross sections, and the spectrometer function was performed on these data. The results (see inset to Figure 2) are consistent with a ~ 24 Å layer of lower oxides capped by a ~ 6 Å layer of fully stoichiometric TiO_2 . The Ti_2O_3 and TiO components were as a mixed layer, as both oxidation states exhibit the same attenuation with increasing grazing detection angle, as is apparent from Figure 2. Further evidence for the surface termination by a layer of TiO_2 will be presented below with the UPS results. It is well-known that TiO_2 grown below 573 K is amorphous in structure,^{13–15} and as our substrate temperature never exceeded 473 K during oxidation, we expect our films to also be of an amorphous nature.

XPS analysis of these oxide layers revealed that they are thermally stable up to 423 K, beyond which temperature partial decomposition occurred. For example, 2 min of annealing at 473 K resulted in broadening of the low binding energy side of the Ti^{4+} component in the 80° spectrum (not shown), indicating the presence of Ti^{3+} at the surface presumably resulting from diffusion of surface oxygen to the bulk.

He I UPS spectra of the initial oxide film (Figure 3) show a 3.5 eV shift in the low-energy photoelectron cutoff relative to titanium metal. This confirms that the surface is indeed composed of TiO_2 with its characteristic band gap of ~ 3.5 eV and the spectral contour is in good agreement with the literature.¹⁶

When the TiO_2 surface was cooled to 100 K and then dosed with 3 langmuirs of styrene, a C 1s peak was observed at 284.9 eV (Figure 4, trace b). By comparison with the reported BE for benzene adsorbed on $TiO_2(110)1 \times 1$,¹⁷ we assign this emission to intact adsorbed styrene molecules on the TiO_2 surface. Subsequent annealing (215 K/1 min) attenuated this signal while a 275 K/1 min anneal completely quenched it (Figure 4, trace a), corresponding to complete desorption of styrene. This is in contrast to the behavior observed upon adsorption of 2 langmuirs of styrene on the titanium metal surface at 300 K (Figure 4, trace d), which gives rise to a C 1s peak at 282.6 eV. A higher styrene exposure (12 langmuirs) resulted in broader C 1s emission (Figure 4, trace c) that can be fitted with two components: one at 282.6 eV assigned to a titanium carbide-like species,¹⁸ and the other at 284.9 eV corresponding to intact styrene molecules. These results imply that at low coverages styrene undergoes extensive dissociation on the reactive metal surface; the resulting titanium carbide-like film then accom-

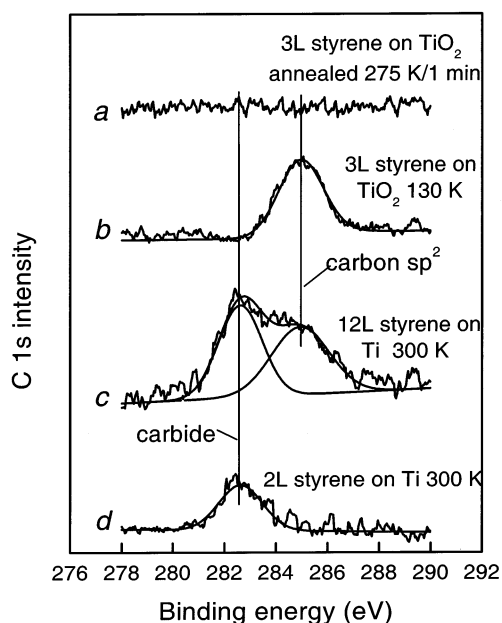


Figure 4. C 1s XP spectra after 2 and 12 langmuir styrene doses on titanium metal compared to spectrum obtained after a 3 langmuir dose on a fully oxidized titania film at 130 K.

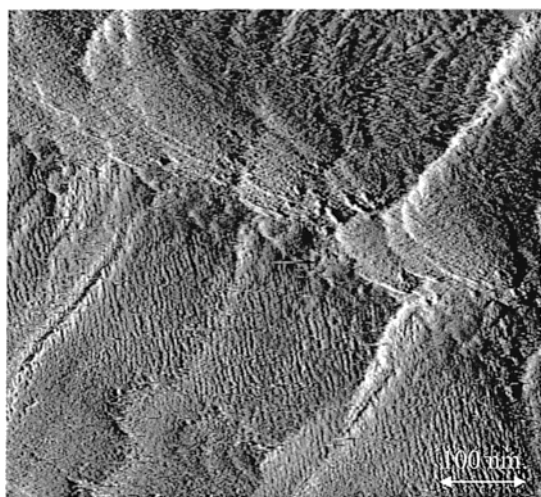


Figure 5. STM image of titania film prepared on Ti sputtered and annealed at temperatures below 1073 K. Image size 630 nm \times 630 nm.

modates further styrene without dissociation. Annealing the high-coverage surface to 400 K removed the 284.9 eV (molecular styrene) peak, leaving just the carbide signal, which persisted to >600 K and could only be removed by sputtering.

STM Results: Morphology of the TiO_2 Film. The UHV-prepared titania samples were examined by ex situ STM in constant current mode (tip voltage +0.7V, tunneling current 0.4 nA). It was found that the method of pretreatment of the titanium substrate prior to oxidation dramatically affected the morphology of the resulting oxide layer. As may be seen in Figures 5 and 6, argon ion sputtering of the titanium foil at temperatures below 1073 K produced, after oxidation, an oxide film with a generally flat and featureless morphology. On the other hand, oxidizing the Ti substrate after pretreating it by repeated flashing to 1373 K resulted in formation of distinct oxide grains with average dimensions of ~ 60 nm. This morphology was characteristic of all the areas examined (>10) of each sample studied by STM. The average height of the titania grains was 5 nm. Earlier STM and TEM work on polycrystalline TiO_2 involved titania thin

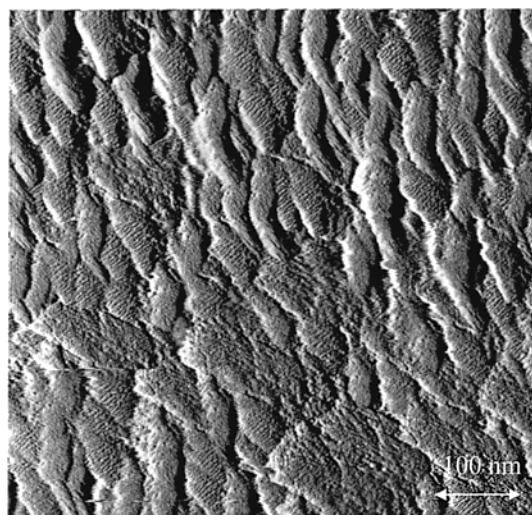


Figure 6. STM image of titania film prepared on substrate pretreated by repeated flashing to 1373 K during sputtering. Image size 630 nm \times 630 nm.

films grown by a variety of methods including precipitation of titania from solution,^{19,20} ionized cluster beam deposition,²¹ and oxidation of polycrystalline titanium foils.^{22,23} Radegran et al.²³ using TEM reported that oxidation of electropolished Ti foil at low temperature (370–420 K) resulted in thin, amorphous, morphologically homogeneous titania overlayers, whereas higher oxidation temperatures (570–720 K) gave thicker, rougher films exhibiting nanocrystallites of titania. The same authors also found that oxidation of glow-discharge-treated Ti foil exhibited a much larger corrugation than an oxide overlayer produced by oxidation of an electropolished Ti surface.²² These findings are consistent with ours in that they indicate a correlation between the morphology of the initial metal surface and that of the resulting oxide. However, our results also show clearly that the morphology of the oxide film is controlled principally by substrate pretreatment rather than oxidation temperature. That is, the image in Figure 5 reflects the morphology of the underlying metal surface after Ar^+ sputtering and low-temperature annealing, while the finer-grained morphology corresponding to ~ 80 nm oxide particles (Figure 6) is due to a different grain structure in the Ti substrate, induced by flashing to 1373 K prior to oxidation at 473 K.

Selective Oxidation and Selective Hydrogenation of Styrene by Water. Figure 7 shows TPR data resulting from the reaction between adsorbed styrene (0.01 langmuir) and a TiO_2 film predosed with 0.03 langmuir of water. The desorption products consist of unreacted styrene, water, and acetophenone (~ 480 K, resulting from partial oxidation of styrene). Acetophenone was detected at $m/z = 43$, which unambiguously distinguishes it from styrene and styrene epoxide. Thus the most characteristic feature of the mass spectrum of O^{16} acetophenone is an intense peak at $m/z = 43$ with zero intensity at $m/z = 91$. On the other hand $m/z = 91$ is an intense peak in the mass spectra of the corresponding epoxide and aldehyde. Strong confirmation of this assignment of the $m/z = 43$ signal to acetophenone is provided by both ^{18}O tracing experiments and styrene epoxide isomerization experiments described in detail elsewhere.²⁴ The water desorption shows two distinct peaks at 340 and 490 K. Based on both experimental and theoretical studies of water adsorbed on TiO_2 (110),^{25–30} we may confidently ascribe the 340 K peak to desorption of molecularly adsorbed water with the 490 K peak arising from dehydration of hydroxylated titania. These results strongly suggest that it is

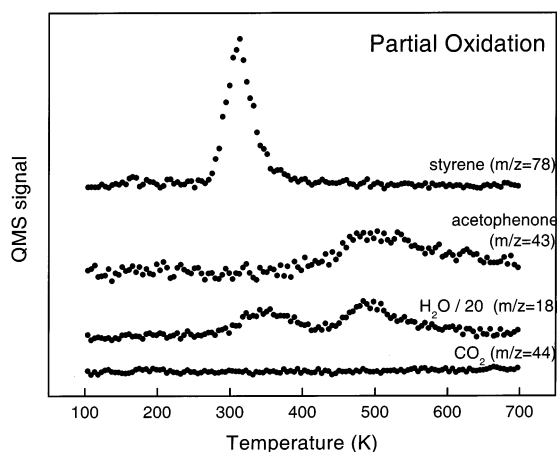


Figure 7. Selective oxidation. TPR spectra after adsorption at 130 K of 0.03 langmuir of water and 0.01 langmuir of styrene dosed on a fully oxidized titania film.

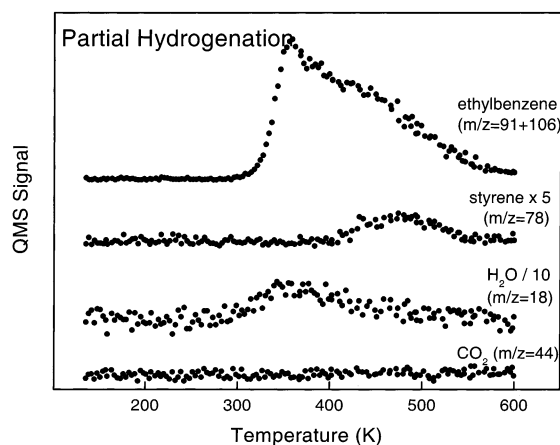


Figure 8. Selective hydrogenation. TPR spectra after adsorption at 130 K of 0.03 langmuir of water and 0.01 langmuir of styrene dosed on a partially reduced titania film.

the *hydroxylated* TiO_2 surface that is chemically active toward the alkene. Although no O 1s emission from surface OH groups could be detected in XPS due to the large contribution arising from lattice oxygen in the TiO_2 substrate, ^{18}O tracing studies show²⁴ that it is the oxygen atom from the water molecule that is incorporated into the acetophenone product. A possible implication is that OH is the chemically active surface species.

Figure 8 shows the corresponding behavior for a partially reduced titania surface produced by annealing the freshly prepared oxide film (673 K/30 s) before dosing the same amounts of water and styrene as before. A remarkable switch in chemistry occurs. In this case, the only product is ethylbenzene (resulting from partial hydrogenation of styrene) desorbing at ~350 K. This product is identified by its characteristic $m/z = 91$ and $m/z = 106$ peaks displaying intensities in the ratio 6:1.³¹ Exactly the same chemistry was exhibited by both types of samples as distinguished by STM. In other words, both reaction selectivity and the switch in selectivity are dependent on the oxidation state of the surface and independent of its morphology. Both the partial oxidation and hydrogenation reactions discussed proceed with 100% selectivity, as no CO_2 is detected. The relative product yields are 55% in the case of partial oxidation and 85% for hydrogenation.

These findings are reminiscent of the behavior of Au/titania catalysts used in the catalytic conversion of propene in the presence of hydrogen and oxygen.⁴ Here too, a switch in behavior between partial oxidation and hydrogenation of the

olefinic function is observed as a function of Au particle size. The Au/titania system is still very much the subject of active debate, not the least in regard to the role of hydrogen, without which partial oxidation does not occur. Our results show that the reactivity of the titania itself should not be overlooked, especially when the ambient gas contains water, as it certainly does in the case of hydrogen + oxygen + propene mixtures undergoing catalytic reaction over Au/ TiO_2 . It is highly likely that with such systems in situ water production generates a hydroxylated titania surface. For example, in the case of partially reduced titania, oxygen vacancies and the associated Ti^{3+} species at the metal/oxide interface could react with water to produce $\text{OH}^-(\text{Ti}^{4+}) + \text{H}_2(\text{Au})$, the hydrogen adatoms subsequently reacting with Au-adsorbed alkene molecules. Equally, one may write a speculative mechanism to account for partial oxidation by OH on fully oxidized titania/Au. The important point is that bifunctional catalytic behavior could occur, dominated by phenomena at the metal/titania boundary, and therefore strongly dependent on metal particle size.

Summary

1. Fully stoichiometric TiO_2 films $\sim 6 \text{ \AA}$ thick stable up to 473 K can be grown on polycrystalline Ti.
2. The oxide film morphology is dependent on the thermal history of the metal prior to oxidation.
3. Water treated titania surfaces exhibit very different reactive behavior toward adsorbed styrene, depending on their state of oxidation. The fully oxidized, stoichiometric TiO_2 surface induces partial oxidation of styrene to acetophenone. Partially reduced titania is active for production of ethylbenzene, a selective hydrogenation product.
4. Reaction selectivity and the switch in selectivity are determined by the oxidation state of the surface and do not depend on its morphology.
5. These findings are likely to be of relevance to a fuller understanding of the properties of metal/titania catalyst, especially Au/titania catalysts.

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