On the switch between selective oxidation and selective hydrogenation of a terminal alkene on well-defined titania surfaces

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Stoichiometric, hydroxylated titania surfaces are effective for the partial oxidation of styrene to acetophenone. The initial product of reaction is styrene epoxide which undergoes isomerisation to acetophenone, the thermodynamically favoured product. The oxygen in the product derives exclusively from the water used for hydroxylation, and not from the titania lattice. Surface hydroxyl groups are the active sites for this 100% selective, partial oxidation. Controlled reduction of titania to TiO_x leads to the appearance of bandgap photoemission associated with the formation of Ti^{n+} ($n = 0$–3) at the surface. This results in complete suppression of all oxidation activity and a switch to selective hydrogenation: the reaction product is now ethylbenzene, again produced with 100% selectivity. The important implications of these findings for an understanding of the properties of metal/titania catalysts used for alkene conversion are discussed.

KEY WORDS: hydroxylated titania; styrene; selective oxidation; selective hydrogenation

1. Introduction

Heterogeneous epoxidation of alkenes by means of titania-based catalysts such as Au/TiO_2 [1,2] and TiO_2/SiO_2 [3–9] has attracted much recent interest due to the high selectivities that can be achieved. For example, Haruta *et al.* [1] reported $> 90\%$ selectivity in the epoxidation of propene using a catalyst containing 2–4 nm gold clusters supported on P25 titania. It is remarkable that in this case selective oxidation occurs only when *hydrogen* is co-fed with oxygen and propene, leading to the suggestion that the epoxidising agent could be a peroxo- or hydroperoxo-type species formed at the metal/titania interface [1]. With TiO_2/SiO_2 catalysts, hydroperoxides actually *are* used as the selective oxidant [3–9], and Thomas *et al.* [7] have used XANES and EXAFS to demonstrate that in Ti $\uparrow$ MCM-41 the active epoxidation site is a 4-coordinate Ti^{4+} species bound to three -OSi groups and one OH group, the OH oxygen being the oxidising species. On the other hand, titania-based catalysts are also effective for heterogenous reduction, both in solution [10] and with gaseous reactants [11]. Thus Yermakov *et al.* [11] showed that SiO_2-supported Ti metal is an efficient catalyst for the hydrogenation of benzene and cyclohexene, rationalising their findings in terms of Ti^{3+}-2H and Ti^{4+}-2H as the active sites.

Here we report on the reactive properties of *in situ* grown titania films whose surface oxidation state may be varied in a controlled way. The object was to produce nano-crystalline titania whose surface properties might be expected to mimic those of dispersed titania-based catalysts. The preparation, structure, composition and electronic properties of these titania films have been described in an earlier publication [12]. On these surfaces, we find that the surface chemistry of adsorbed styrene switches between selective oxidation and selective hydrogenation as the stoichiometry of the titania is varied in a controlled manner.

2. Experimental methods

Experiments were performed in a VG ADES 400 electron spectrometer system operated at a base pressure of 1×10^{-10} torr. The polycrystalline titanium sample ($10 \times 10 \times 0.5$ mm; Advent, 99.6%) was secured to the manipulator by spot welding and could be resistively heated to 1350 K and cooled to 100 K. Sulfur, carbon and phosphorus were removed by Ar^+ sputtering (15 μA/5 keV) at 900 K with occasional flashes to 1300 K to segregate sulfur from the bulk. XP spectra were obtained with MgKα radiation (1253.6 eV); a He I photon source was used for UPS measurements. Gas dosing was performed using a collimated source to enhance flux at the sample position. Styrene (99%, Aldrich) and de-ionised water were purified further by repeated freeze/pump/thaw cycles; Messer grade 99.998% oxygen was used for the oxidation procedures. Gas compositions within the UHV chamber were verified by mass spectrometry and quoted exposures, given in Langmuirs ($1\,L = 10^{-6}$ torr s^{-1}), are uncorrected for ion gauge sensitivity. For TPD/TPR measurement (15 K/s)

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the sample was positioned 2 cm from the quadrupole mass spectrometer (QMS) ioniser so that the signal arose almost entirely from the front face of the sample. Integrated product yields derived from the TPD/TPR data have been corrected to allow for mass discrimination effects in the QMS, total ionisation cross-sections, and the cracking patterns of relevant desorbing species.

3. Results and discussion

3.1. Temperature programmed reaction on stoichiometric TiO_2: Hydroxylation and oxygen isotope exchange

Figure 1 shows temperature programmed desorption traces for H_2O^{16} ($m/z = 17$) and H_2O^{18} ($m/z = 19$) from stoichiometric TiO_2^{18} following exposure to 0.03 L H_2O^{16} at 130 K. The TiO_2^{18} surface was produced by oxidation of polycrystalline Ti with O_2^{18}, as described previously [12]. It is apparent that no desorption of H_2O^{18} occurred and that there are two distinct peaks in the H_2O^{16} spectrum at 340 K and 490 K. These have been previously assigned, respectively, to desorption of molecularly adsorbed water and surface dehydroxylation [12] ($2OH_a \rightarrow H_2O + O_{surface}$). The key observation is the absence of oxygen exchange between lattice oxygen and the water produced at ~490 K by dehydroxylation. This observation stands in contrast to results obtained by Henderson *et al.* [13] on $TiO_2(110)$ for which it was found that dissociative water adsorption/desorption led to 100% incorporation of lattice oxygen into the desorbed water. This was attributed to dissociation of water molecules at vacancies in the bridging oxygen rows. However this should lead to only 50% incorporation of lattice oxygen in the desorbed water. The authors were therefore obliged to invoke high hydrogen adatom mobility in order to account for their result. In accord with this view, Brookes *et al.* [14] imaged bridging hydroxyl groups on water-treated $TiO_2(110)1 \times 1$ at 290 K. Whatever the origin of the difference in lattice oxygen lability, it seems clear that our titania surfaces must differ significantly from defective single crystal $TiO_2(110)1 \times 1$. In fact, STM images showed [12] that our polycrystalline oxide film consisted of ~60 nm crystallites within which ordered surface structures were not detectable: certainly, no {110} facets were found.

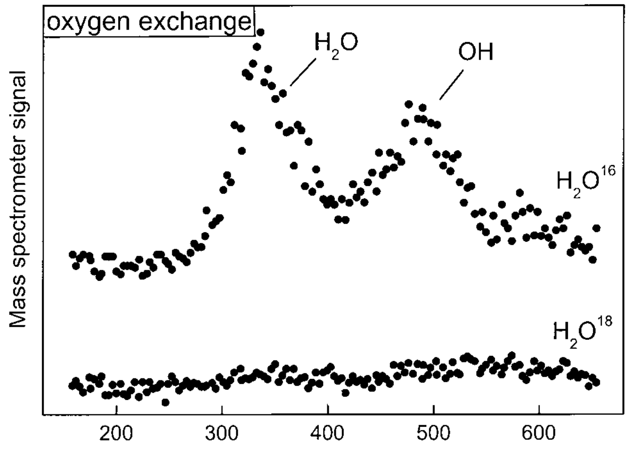

Figure 1. Oxygen exchange. Temperature programmed desorption traces for H_2O^{16} ($m/z = 17$) and H_2O^{18} ($m/z = 19$) from stoichiometric TiO_2^{18} following exposure to 0.03 L H_2O^{16} at 130 K.

3.2. Temperature programmed reaction with isotope tracing: The partial oxidation of styrene on hydroxylated, stoichiometric TiO_2

Figure 2 shows the results of an experiment in which the fully stoichiometric TiO_2^{18} surface was subjected to a 0.03 L exposure of a 1.75:1 mix of $H_2O^{16}:H_2O^{18}$ at 130 K, followed by flashing to 200 K in order to desorb any condensed CO and/or CO_2. The sample was then dosed with 0.01 L styrene at 130 K after which the temperature sweep was carried out. The products detected gave strong signals at $m/z = 43$ and 45. A close examination of reference mass spectra [15] of all possible products of reaction between styrene and hydroxyl enabled us to attribute unambiguously the $m/z = 43$ and 45 signals to the O^{16} and O^{18} isotopomers of the partial oxidation product acetophenone. For example, 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

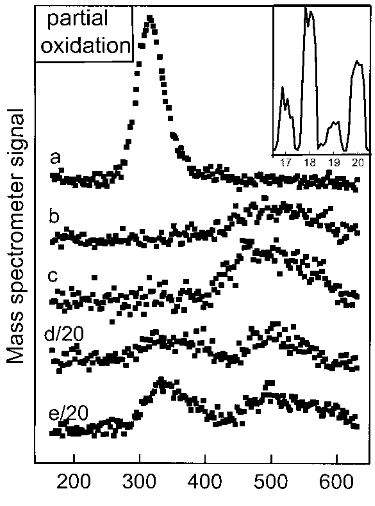

Figure 2. Alkene partial oxidation. TPR after exposure of stoichiometric TiO_2^{18} surface to 0.03 L of a 1.75:1 mix of $H_2O^{16}:H_2O^{18}$ at 130 K, then 0.01 L styrene at 130 K. Inset shows mass spectrum of water vapour used. Trace **a** shows desorption of unreacted styrene, **b** and **c** show the O^{18} and O^{16} isotopomers of acetophenone and **d** and **e** denote desorption of H_2O^{18} and H_2O^{16} respectively. The relative intensities of traces **b** and **c** are in quantitative accord with the isotopic composition of the initial water vapour.

hand, $m/z = 91$ is an intense peak in the mass spectra of the corresponding epoxide and aldehyde. Neither CO_2 nor any other product was detected: within our detection limits the process was 100% selective, with 55% of the initially adsorbed styrene undergoing conversion. Moreover, the relative yields of O^{16} and O^{18} acetophenone were in the ratio 1.72 : 1, which is very close to the oxygen isotope ratio in the originally adsorbed water (1.75 : 1). Among other things, this serves to confirm that the product contained only one oxygen atom. These measurements were performed repeatedly, and the ratios of the acetophenone isotopomer yields always coincided with the $H_2O^{16} : H_2O^{18}$ ratio in the water used for surface hydroxylation. Additional confirmation was provided by repeated control experiments in which 0.03 L of H_2O^{16} and 0.01 L styrene were allowed to react on TiO_2^{18}. In this case, only the $m/z = 43$ product was observed (O^{16} acetophenone) with no trace of the $m/z = 45$ product (O^{18} acetophenone).

We may therefore draw the following conclusions. First, that the oxygen involved in partial oxidation originates from the adsorbed water: lattice oxygen is not involved. Second, that the active oxidising agent is a chemisorbed hydroxyl group on the titania. Why do we obtain acetophenone as opposed to some other partial oxidation product? This issue is addressed below.

3.3. TPR: Isomerisation of styrene epoxide on TiO_2

It is well known that epoxides may be isomerised, homogeneously or heterogeneously, to yield the corresponding aldehydes or ketones [9,16,17]. Given the known epoxidising power of solids that contain the TiOx functionality, *e.g.*, Ti↑MCM-41 [7], we propose the following mechanism. The initial reaction results in styrene epoxidation surface by a surface hydroxyl group. Clearly, this is closely related to the findings of Thomas *et al.* who identified Ti-OH as the epoxidising site in Ti↑MCM-41 [7]. The resulting epoxide then undergoes isomerisation to acetophenone *via* a [1,2] hydride shift as shown in figure 3. This view is supported by an experiment whose results are shown in figure 4 in which *styrene epoxide* was dosed (0.03 L) onto a freshly prepared titania film at 130 K followed immediately by a TPR sweep. It can be seen that unreacted styrene epoxide ($m/z = 91$) desorbed at >300 K and that acetophenone ($m/z = 43$) was also formed, desorbing at >450 K. Furthermore, the shape and temperature span of this acetophenone desorption profile are very similar to those exhibited by acetophenone formed in the reaction of styrene with hydroxylated titania (figure 2). We therefore conclude that (i) the primary product of the styrene + Ti-OH reaction is indeed the epoxide, and (ii) desorption of the isomerised product is the rate determining step for appearance of gaseous acetophenone. The appearance of acetophenone as the gaseous isomerisation product is not unexpected. The enthalpies of formation of acetophenone and the corresponding aldehyde (benzaldehyde) are −90 kJ/mol and −52 kJ/mol respectively [18]. Therefore we observe the ketone, which is strongly thermodynamically favoured, rather than the kinetically favoured aldehyde.

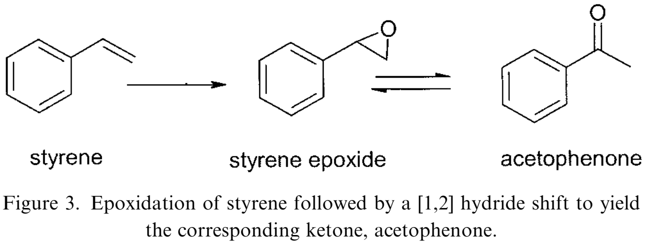

Figure 3. Epoxidation of styrene followed by a [1,2] hydride shift to yield the corresponding ketone, acetophenone.

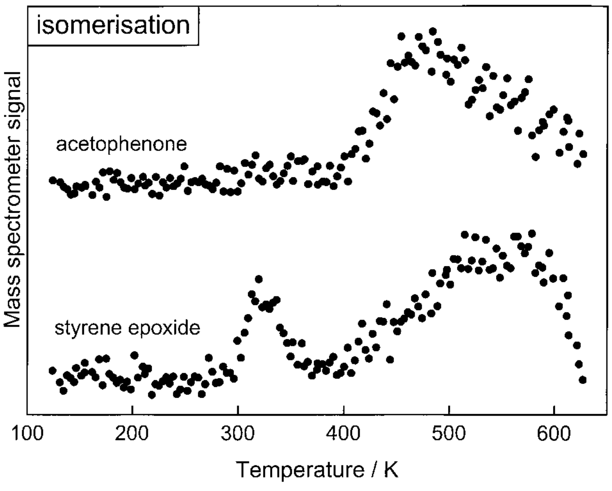

Figure 4. Epoxide isomerisation. TPR after exposure of stoichiometric TiO_2^{16} to 0.03 L of styrene epoxide ($m/z = 91$) showing conversion to O^{16} acetophenone ($m/z = 43$).

3.4. Titania valence band spectra as a function of state of oxidation

In an earlier paper [12] we showed that fully oxidised TiO_2 films are stable up to 473 K above which temperature diffusional mixing leads to the appearance of Ti^{3+}, Ti^{2+}, and Ti^0 sites at the surface, in addition to Ti^{4+}. This behaviour may be exploited to generate a series reduced titania surfaces with progressively lower oxygen content, suitable for reactive studies. Starting with the fully oxidised surface (designated ***A***), the following thermal treatments were therefore applied successively: one 600 K flash (***B***); three 600 K flashes (***B′***); 700 K for 30 s (***C***); 900 K/30 s (***D***). The He I UP spectra corresponding to surfaces ***A***, ***B***, ***C*** and ***D*** are illustrated in figure 5.

Surface ***A*** exhibits a valence band spectrum characteristic of fully stoichiometric TiO_2: no band gap emission is visible within the sampling depth of the measurement (~1.5 nm). After the first reducing treatment, the angle-resolved XP spectra (not shown) from surface ***B*** were unchanged. However, the onset of Ti 3d band gap

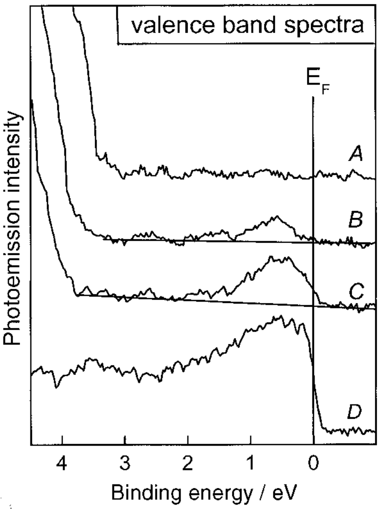

Figure 5. He I UP spectra showing development of band gap states with increasing degree of reduction of the titania film. Surface ***A***: stoichiometric TiO_2; surface ***B***: 600 K/flash; surface ***C***: 700 K/30 s; surface ***D***: 900 K/30 s.

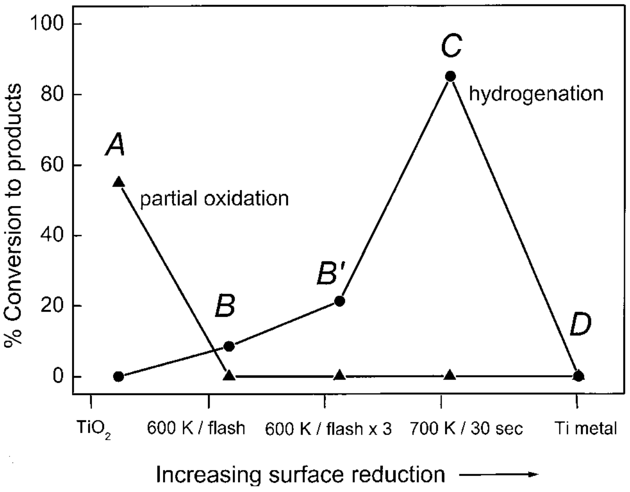

Figure 6. Switch from selective oxidation (acetophenone) to selective hydrogenation (ethylbenzene) as a function of surface oxidation state for surfaces ***A***, ***B***, ***B'***, ***C***, ***D*** (see text).

emission just below E_F is clearly apparent in figure 5. This is characteristic of occupied Ti 3d states resulting from reduction of Ti^{4+} and formation of non-stoichiometric TiO_x. The 700 K/30 s treatment (surface ***C***) did lead to changes in the XP spectra (not shown) which, at grazing photoelectron exit, showed Ti 2p core level emission characteristic of Ti^0, $Ti2^+$, Ti^{3+} and Ti^{4+}. In line with this, the UP spectrum showed increased intensity due to band gap states, compared to surface ***B*** (figure 5). As we shall see later, surface ***C*** is characterised by the highest hydrogenation activity. The 900 K/30 s treatment (surface ***D***) resulted in complete reduction to Ti^0, confirmed by grazing exit XPS.

3.5. The partial hydrogenation of styrene on hydroxylated TiO_x

Controlled reduction of the titania surface following the procedures described above was used to investigate the effect of surface oxidation state on reactive behaviour for each of the surfaces ***A***, ***B***, ***B'***, ***C*** and ***D***. The results are summarised in figure 6, which also shows the behaviour of the acetophenone yield. In each case, the surface was dosed with 0.03 L water followed by 0.01 L styrene. Except for the stoichiometric TiO_2 surface, subsequent TPR showed that no oxidation products of any kind were formed. Instead, the TiO_x surfaces (***B***, ***B'***, ***C***) induced partial hydrogenation of styrene to ethylbenzene, the product being readily identified by its characteristic fragmentation pattern $(m/z = 91)/(m/z = 106) = 7/2$ [15]. Surface ***C*** exhibited maximum hydrogenation activity and the relevant raw data are shown in figure 7. It can be seen that ethylbenzene evolution occurred at >340 K followed by desorption of a small amount of unreacted styrene at ~450 K. A broad water desorption feature centred at ~350 K is seen, and no CO_2. Note that the styrene desorption temperature is ~150 K higher than for stoichiometric TiO_2, signifying stronger adsorption of the reactant on the reduced TiO_x surface.

3.6. Mechanism of styrene hydrogenation by water

The preceding results may be rationalised as follows. Progressive thermal reduction of the initial TiO_2 film generates increasing amounts $Ti^{0/2+/3+}$ species at the surface. Upon exposure to water, these are re-oxidised, for example $Ti^{I}_{2}O + H_2O \rightarrow 2\,HTi^{III}O$. The resulting TiH species then becomes the active site for selective hydrogenation, in line with the proposal of Yermakov *et al.* [11]. Clearly, selective hydrogenation occurs within a certain surface oxidation state window: if the surface is fully oxidised (stoichiometric TiO_2), water adsorption does not result in Ti-H sites as all the tita-

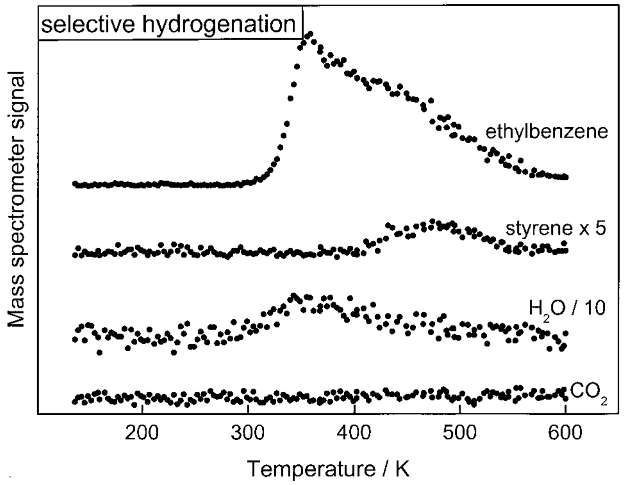

Figure 7. Selective hydrogenation. TPR showing formation of ethylbenzene ($m/z = 91/106 = 7/2$) after exposure of partly reduced surface ***C*** to 0.03 L H_2O^{16} and then 0.01 L styrene ($m/z = 78$) at 130 K.

nium atoms are in oxidation state 4+. With increasing reduction, Ti-H formation occurs and hydrogenation becomes possible. At the same time styrene adsorbs more strongly on the reduced surface than on stoichiometric TiO_2: this acts to improve activity by favouring hydrogenation over desorption. Surface ***C*** gives maximum hydrogenation activity because it contains enough reduced sites to dissociate all the water adsorbed, while the strongly adsorbed styrene molecule remains intact and thus available for hydrogenation. Increasing reduction leads to the presence of lower oxidation states of Ti, including Ti^0: these fragments adsorbed styrene [12], thus suppressing ethylbenzene formation.

3.7. *Implications for an understanding of the behaviour of metal/titania catalysts*

Thanks largely to the pioneering work of Haruta and his co-workers, there is much interest in the properties of Au/titania catalysts. Of these, perhaps the most interesting is the potential these materials offer as selective oxidation catalysts for terminal alkenes. In this application, depending on the conditions, the catalysts may *either epoxidise or hydrogenate* the C=C bond [1]. Whilst metal particle quantum size effects are undoubtedly of significance [19], relatively little attention has focused on the role of the titania phase. The present results suggest that the titania may itself play a central role in the surface chemistry of alkene conversion, especially when one recalls that a key requirement of "Haruta-type" catalysts is the co-feeding of oxygen *and* hydrogen in approximately equal amounts. Inevitably, therefore, large quantities of water are present in the reaction gas, and, according to our results, the titania surface will be extensively hydroxylated at reaction temperature ($\sim$500 K). Given our observation of a sharp switch in reactivity between partial oxidation and selective hydrogenation of the terminal olefin function in styrene, and that this molecule provides a good model for terminal alkene epoxidation [20], it appears that more explicit account should be taken of the oxidation state-dependent surface chemistry of titania itself.

Conclusions

(1) Stoichiometric, hydroxylated titania surfaces are effective for the partial oxidation of styrene to acetophenone. The initial product of reaction is styrene epoxide which undergoes isomerisation to acetophenone, the thermodynamically favoured product.

(2) The oxygen in the product derives exclusively from the water used for hydroxylation, and not from the titania lattice. Surface hydroxyl groups are the active sites for partial oxidation.

(3) Partial reduction of titania results in complete suppression of all oxidation activity. Instead, adsorbed water induces selective hydrogenation of styrene to ethylbenzene, with Ti-H being the likely active site.

(4) It seems highly likely that the behaviour reported here plays a significant role in determining the properties of metal/titania catalysts when the latter are used in applications involving co-feeding of hydrogen, oxygen and alkenes, under which reaction conditions water is necessarily present in the system.

Acknowledgments

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