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The partial oxidation of isobutene and propene on $TiO_2(110)$

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Abstract

General techniques for the partial oxidation of alkenes by molecular oxygen are a goal for surface science and catalysis research as they may lead to more efficient and environmentally friendly industrial processes. To better understand the thermal surface chemistry of metal oxides toward alkene partial oxidation, the interactions of isobutene and propene on $TiO_2(110)$ were studied using temperature-programmed desorption (TPD). Isobutene was found to adsorb and desorb molecularly below 250 K on the clean surface. With exposure to oxygen (>1000 L) and unknown quantities of water (<10 L), isobutene monolayers on $TiO_2(110)$ react to form products that include methacrolein and isobutanal, as well as a third product that has a C_4H_8O stoichiometry. We tentatively assign this species to 2,2-dimethyloxirane (isobutene oxide). Structural conservation within this family of products points to a common surface intermediate that we propose results from the addition of O from a hydrogen peroxo (HOO) species to the C=C bond of isobutene. This hydrogen peroxo (HOO) species forms from the reaction of physisorbed water and oxygen, assisted by partial charge transfer from the $TiO_2(110)$ substrate. Initial studies reveal a similar reaction pathway for the partial oxidation of propene on $TiO_2(110)$, yielding acetone and propanal. This work suggests that TiO_2 surface sites on supported Au/TiO_2 catalysts are active for partial oxidation of alkenes.

Keywords: $TiO_2(110)$; Partial oxidation; Temperature-programmed desorption; Isobutene; Propene

1. Introduction

The selective partial oxidation of hydrocarbons by molecular oxygen is a continuing goal of heterogeneous catalysis research [1–5]. The carbonyls, epoxides, and alcohols produced through this chemistry are important intermediates in the production of both fine and commodity chemicals. Modern industrial processes achieve these reactions through the use of expensive and often toxic reagents, such as peroxides, mineral acids, peracids, and reducible metal oxides. Metal/metal oxide systems hold promise for the direct partial oxidation of hydrocarbons by oxygen, whereby oxygen-containing surface species or photogenerated peroxides may serve as oxidants. The discovery of new reaction mechanisms exploiting controllable surface properties may result in the development of new industrial processes that improve production efficiency and replace dangerous chemical reagents with more benign substances.

Titanium dioxide is a promising material, both as an active center and a support, for selective oxidation of alkenes. For example, various TiO_2-containing catalysts have been explored for the selective oxidation of alkenes to epoxides [6–20]. Mixed TiO_2–SiO_2 catalysts [7–14,18–20] have shown promise for alkene oxidation. In these catalysts, the active Ti^{4+} centers are isolated cations on the SiO_2 support that have tetrahedral coordination. Clusters of TiO_2, having octahedral Ti^{4+}, are less active than the isolated Ti^{4+} sites. Additionally, mechanical mixtures of TiO_2 and V_2O_5 in which TiO_2 is the major component selectively oxidize propene to its epoxide [21]. Nanoparticles of Au supported on TiO_2 have also shown activity for the selective epoxidation of alkenes [6,7,10,15–17,22]. Significantly, it has been found that other oxides (e.g., Al_2O_3, SiO_2, Fe_2O_3, Co_3O_4, ZnO, and ZrO_2) cannot be used interchangeably with TiO_2, further demonstrating the unique chemistry of TiO_2 in stabilizing Au particles and/or participating in the oxidation reaction. TiO_2 by itself has also been shown to catalyze

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the epoxidation of styrene [23,24]. Those studies found that surface hydroxylation was required to oxidize styrene and that lattice oxygen was not incorporated into the reaction product. In addition, the TiO_2 surface was shown to switch between selective oxidation and hydrogenation with surface reduction.

There has been considerable interest in and speculation on the mechanistic details of selective alkene epoxidation by O_2 over supported Au/TiO_2 catalysts. The need for H_2 in the reactant stream has lead several groups to speculate that a hydrogen peroxo (HOO) species is the active oxidant. It is believed that the Au nanoparticles catalyze the formation of this HOO species, which then diffuses onto the support and oxidizes the alkene there. This conclusion is consistent with results from studies in which hydrogen peroxide (H_2O_2) selectively oxidized alkenes on TiO_2-based catalysts without Au present [8, 18–20]. Two groups have provided evidence for the role of an HOO species in partial oxidation of alkenes using H_2 and O_2 over Au/TiO_2 catalysts. Based on H/D studies, Stangland et al. [15] observed a kinetic isotope effect that was consistent with the involvement of HOO. More recently, Sivadinarayana et al. [22] used inelastic neutron scattering to detect an HOO species on Au/TiO_2 after exposure to $H_2 + O_2$.

As yet there has been little work probing the mechanism of alkene partial oxidation on a model TiO_2 surface. Model systems, such as the rutile $TiO_2(110)$ surface, help provide insight into the molecular-level details of such surface reactions [25]. The $TiO_2(110)$ surface has become the prototypical titania single-crystal surface for the study of fundamental reaction processes on oxides. In this work, we report on the partial oxidation of isobutene and propene on $TiO_2(110)$. Partial oxidation products are formed when high exposures of O_2 impinge on the adsorbed alkenes at 95 K. Low exposures of O_2 ($\lesssim$100 L) or preadsorbed O_x ($x = 1$ or 2) were insufficient to initiate partial oxidation. This suggests that the rate-limiting step involves a low-probability reaction event between a physisorbed O_2 species and the alkene. Although water is a byproduct of the reaction, we also show that it is involved in the initial step in the partial oxidation reaction. These results provide evidence for the partial oxidation of alkenes on TiO_2-supported Au catalysts occurring on the support. The active oxidant may be an HOO species, in this case formed from the reaction of O_2 and water initiated by charge transfer from the reduced TiO_2 surface.

2. Experimental

All experiments were completed in a two-level UHV chamber with a base pressure of 2×10^{-10} Torr. A detailed description of the apparatus can be found elsewhere [26]. Briefly, the upper level of the system was equipped for TPD, Auger electron spectroscopy (AES), rear-view low-energy electron diffraction (LEED), secondary ion mass spectrometry (SIMS), and oxygen plasma treatment. The lower level of the chamber was outfitted with apparatus for high-resolution electron energy loss spectroscopy (HREELS). The chamber was also equipped with a fiber optic feed through attached to a 100 W Hg arc lamp (Oriel) that allows focused UV irradiation of sample surfaces. TPD spectra were collected using a quadrupole mass spectrometer (QMS, Extrel) multiplexed to digitally record information on up to 10 masses simultaneously. Ramp rates were set to 2 K/s for thermal scans over the range of 95–800 K.

The $TiO_2(110)$ sample was heated via contact to a resistively heated tantalum plate and cooled by thermal contact to a liquid nitrogen (LN2) reservoir. The $TiO_2(110)$ crystal was bulk reduced by annealing in vacuum at 850 K to a blue color. As a result of bulk reduction, an accompanying level of surface reduction resulted that was reflected by a surface oxygen vacancy concentration of about 7%. A type K thermocouple was attached to the crystal with ceramic glue (Ceramabond 503). After initial sputtering (Ar^+, 3 and 0.5 keV), a clean surface was maintained by annealing cycles at 850 K. AES was used to confirm surface cleanliness.

Isobutene and propene (Aldrich, research grade) were used as delivered. These gases were dosed through a micron-sized pinhole and down a directional doser that terminated 2 mm from the sample surface. Dosing was initiated by the introduction of a fixed pressure of gas into a reservoir behind the pinhole. A high length-to-diameter ratio tube within the chamber, provided a pseudo molecular beam of gas directed at the $TiO_2(110)$ crystal. Dosing was terminated by evacuating the gas reservoir behind the pinhole. Isobutene was dosed with the crystal held at 140 K, unless otherwise noted, to prepare adsorbed layers free of multilayer isobutene. Only first-layer propene could be formed from adsorption at the base temperature (95 K) of this system.

Oxygen (Scott Specialty Gases, zero grade) was dosed by backfilling either through a leak valve or through the aforementioned pinhole doser. In both cases, a LN2 cold trap was used to remove condensable impurities (e.g., water) from the O_2 gas line. Gas exposures by backfilling were monitored with an ion gauge, whereas gas exposures through the pinhole were obtained from calibrating the conductance through the pinhole doser. Coverages are expressed as monolayers (ML), with 1 ML equivalent to the areal density of Ti^{4+} cation sites on the ideal $TiO_2(110)$ surface (5.2×10^{14} molecules/cm^2).

3. Results

3.1. Isobutene

Fig. 1 shows mass 56 TPD traces from various exposures of isobutene on the clean $TiO_2(110)$ surface dosed at 140 K. In these TPD experiments there was no indication of decomposition of isobutene on the surface, and there also was no evidence of carbon left on the surface after TPD based on AES. Low coverages of isobutene desorbed in a peak at about 210 K that shifted to 190 K as the first layer saturated. This behavior reflects a small degree of repulsive interactions between adjacent molecules as the coverage increased. A high-temperature tail (>230 K) was observed.

The highest isobutene exposure shown in Fig. 1 (dashed line) was performed with the crystal held at 95 K. This TPD spectrum shows that the multilayer feature desorbed from the surface at 115 K. The leading edge of the multilayer state had its

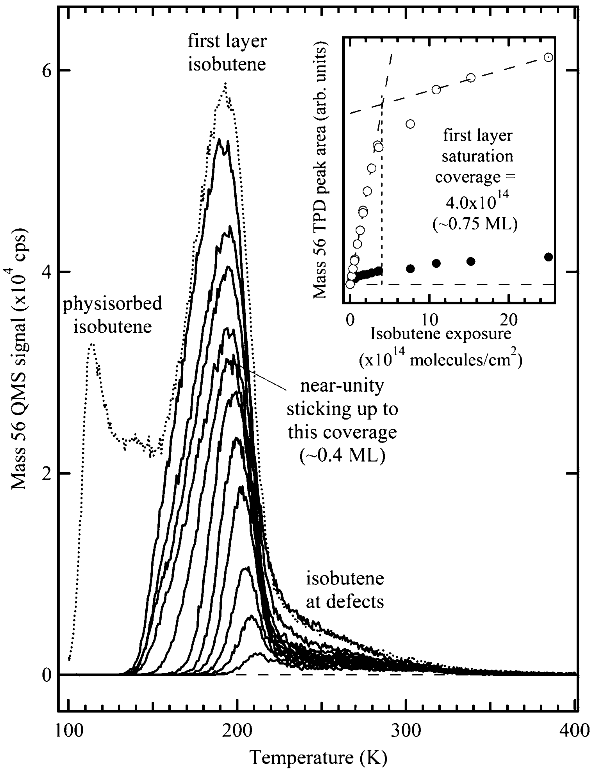

Fig. 1. Mass 56 TPD spectra from various exposures of isobutene at 140 K on clean $TiO_2(110)$. The dashed trace is for a saturation exposure at 95 K. The inset shows TPD peak area data versus isobutene exposure for the entire desorption profile (○) and for the high temperature tail (●).

onset at the base temperature of the apparatus (95 K). Because of this, isobutene molecules located in the multilayer desorb from the surface at 95 K. The multilayer state could be excluded by dosing isobutene with the crystal held at 140 K. In this way, a saturated first layer could be prepared without the presence of multilayer isobutene.

The inset to Fig. 1 shows the TPD uptake behavior of isobutene by the surface at 140 K as a function of exposure. The uptake was linear in the exposure range between 0 and $\sim 2 \times 10^{14}$ molecules/cm^2 (~0.4 ML). The signal continued to rise with exposure beyond this linear region, because adsorption took place on clean regions of the surface outside the spot on the crystal defined by the doser tube [27]. This effect is essentially an experimental artifact from overexposing the region on the crystal defined by the inner diameter of the doser tube. Uptake from this effect is evident by the slower growth in the TPD feature in the high-exposure regime. Intersection of the two uptake curves provides an approximation of the saturation uptake of isobutene on $TiO_2(110)$ at 140 K based on TPD. The peak area of the tail (filled circles in the inset of Fig. 1) increased slowly with additional exposure, but the majority of this signal resulted from the pumping tail of the main isobutene TPD feature. Extrapolation of the uptake trend of this tail feature back to the total uptake data (empty circles) provides an approximate coverage of this tail of ~0.03 ML. This coverage corresponds to about half of the surface oxygen vacancy sites for this crystal (~0.07 ML based on water TPD [28]).

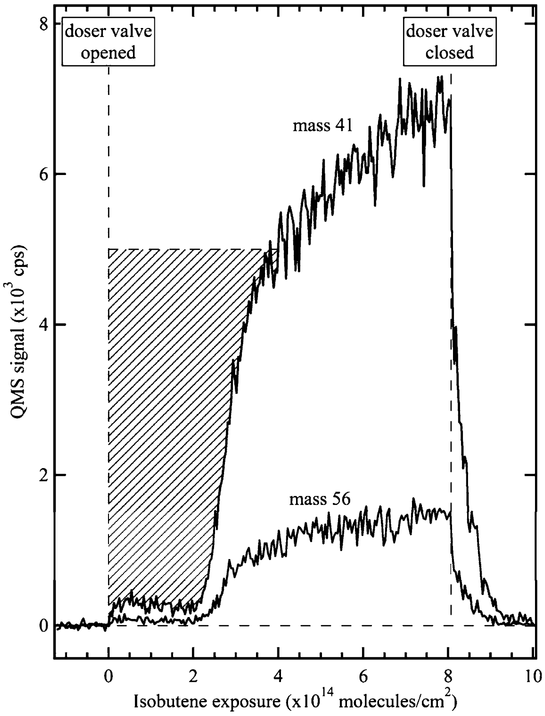

Fig. 2. King and Wells uptake spectra for isobutene on clean $TiO_2(110)$ at 140 K using masses 41 and 56. Details on the uptake experiment are in the text.

The King and Wells [29] uptake data in Fig. 2 suggest that the initial isobutene sticking probability on $TiO_2(110)$ at 140 K was near unity. A coverage of about 0.4 ML isobutene could be accumulated on the surface at 140 K before the sticking probability decreased and isobutene molecules not adsorbed on the crystal were exposed to other surfaces (e.g., the sample holder or chamber walls). This point coincides with the TPD spectrum in which the leading edge of the isobutene desorption trace shifted down to near the adsorption temperature (see the designated trace in Fig. 1). The departure from near-unity sticking was evidenced by the rise in chamber pressure during dosing for exposures above 2×10^{14} molecules/cm^2 (see Fig. 2). At 140 K, the first layer saturated with a coverage of about 4×10^{14} molecules/cm^2 (0.75 ML) based on both the TPD peak area (inset of Fig. 1) and the King and Wells uptake data (Fig. 2). The shaded area derived from the mass 41 signal depicted in Fig. 2 approximates the total uptake of isobutene by $TiO_2(110)$ at 140 K.

The key point in these data is that isobutene exposures at or below 2×10^{14} molecules/cm^2 (0.4 ML) resulted only in isobutene adsorption on the crystal face within the cross-sectional area defined by the doser. Under these conditions, there can be no significant adsorption of isobutene on other surfaces of the sample or sample holder that might otherwise account for partial oxidation events (discussed below) when the chamber is backfilled with O_2.

3.2. Isobutene and water

Because the presence of coadsorbed water is important in the partial oxidation of isobutene (as discussed later), Fig. 3

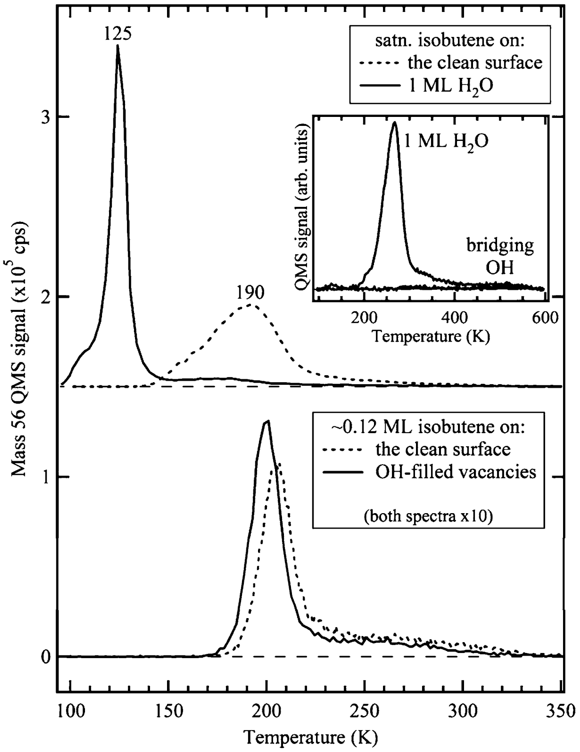

Fig. 3. Mass 56 TPD spectra from isobutene adsorbed at 140 K on clean $TiO_2(110)$ (- - -) and from an equivalent isobutene exposure at 95 K on preadsorbed water (—). The lower panel is for 0.12 ML isobutene on clean $TiO_2(110)$ and on OH-filled vacancies, and the upper panel is for saturation isobutene on the clean surface and on 1 ML of water. The inset shows the respective water (mass 18) TPD traces. Spectra are displaced vertically and provided with background lines for clarity.

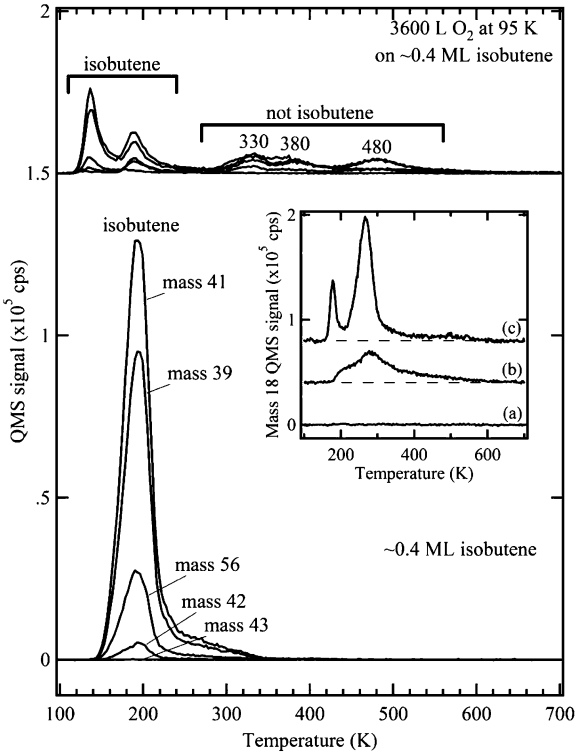

Fig. 4. TPD spectra using selected masses for 0.4 ML of isobutene on the clean $TiO_2(110)$ surface at 140 K (lower spectra), and for the same coverage followed by 3600 L O_2 at 95 K. The inset shows water TPD for the data in the lower portion (a), for the upper portion (b) and for 1.2 ML of water on the clean surface (c). Spectra are displaced vertically and provided with background lines for clarity.

examines the influence of water on isobutene TPD. The lower portion of the figure examines whether water dissociation in oxygen vacancies alters the TPD of a low coverage of isobutene (~0.12 ML) on the surface. The upper portion shows how a first layer saturated with water (1 ML) affects subsequent isobutene adsorption. In both cases, a multilayer of water was dosed at 95 K and preheated (to 400 and 200 K, respectively) to prepare the desired water coverage. The solid and dashed traces correspond to TPD of equivalent exposures of isobutene with and without coadsorbed water, respectively. For the TPD of the lower portion of Fig. 3, approximately 30% (0.04 ML) of the 0.12 ML isobutene adsorbed on the clean surface desorbed in the tail above 220 K. This amount, according to the previous discussion, reflects saturation of the surface states responsible for the tail. Preadsorption of a multilayer exposure of water on the surface, followed by annealing to 400 K, filled the 0.07 ML of vacancies on a clean surface generating twice the coverage of bridging OH groups (so designated because the oxygen atom binds to two Ti cations), but left little or no molecular water on the surface [28,30–32]. Under these conditions, the bridging OH groups were stable up to ~500 K, at which point they recombined as water and regenerated vacancies (see the inset to Fig. 3). In the solid trace, 0.12 ML of isobutene was adsorbed on the OH-filled vacancies. Although the isobutene TPD tail diminished slightly, the remaining intensity suggests that the tail may not be from desorption of isobutene associated with oxygen vacancies. Note also that filling the vacancies with OH groups shifted the main isobutene TPD feature to slightly lower temperature, indicating that bridging OH groups destabilized coadsorbed isobutene.

In the upper portion of Fig. 3, 1 ML of preadsorbed water (see inset) had a significant influence on subsequently adsorbed isobutene. Virtually all of what would have been first-layer isobutene on the clean surface was bound in a physisorbed (multilayer) state that desorbed at 125 K due to saturation of the first layer with water. A similar TPD spectra resulted from dosing water on isobutene-covered $TiO_2(110)$. Displacement of isobutene resulted from the much stronger binding of water than isobutene to $TiO_2(110)$. As a final note, no chemistry was observed between coadsorbed isobutene and water or OH. The TPD features associated with these molecules were not altered, suggesting that no reaction or reversible dissociation took place in the coadsorbed system.

3.3. *Isobutene and oxygen*

Isobutene adsorbed and desorbed from $TiO_2(110)$ intact without decomposition. However, TPD spectra of adsorbed isobutene after high oxygen exposures ($>10^2$ L) revealed significant partial oxidation. Fig. 4 shows an example of this chemistry. The lower portion of the figure shows mass 39, 41, 42, 43, and 56 TPD traces from 0.4 ML isobutene on clean $TiO_2(110)$. Keep in mind that dosing this coverage exposed only the $TiO_2(110)$ surface to isobutene. The relative intensities of the various features and their symmetry with respect to each other indicate that they all arose from mass spectrometer cracking of isobutene. In contrast, exposure of the same isobutene coverage to 3.6×10^3 L O_2 at 95 K had a significant influence on the subsequent TPD experiment. Aside from a splitting of the isobutene peak into two features at 135 and 190 K, new peaks were observed at 330, 380, and 480 K. Although not readily apparent in these data, the relative intensities of 39, 41, 42, 43, and 56 features in the 280–600 K range indicated that all three TPD peaks came from desorption of different species, and none of these species were isobutene. Additionally, AES analysis (not shown) indicated that no carbon remained on the surface after TPD. Thus, all products from the reaction of isobutene and O_2 desorbed from the surface below 600 K. The inset to Fig. 4 shows that whereas no water desorption was observed from isobutene on the clean surface (a), a significant amount (∼0.65 ML) was detected for the case involving postexposure of O_2 (b). The desorption profile of this water was significantly different from that of (1.2 ML) water adsorbed on the clean surface (c), suggesting that desorption states not found for water on the clean surface resulted from water on the partially oxidized isobutene adlayer. These new states may result from perturbation of molecularly adsorbed water by the C_4H_xO products or from reaction-limited processes associated with surface chemistry of these species.

Preoxidation of the surface alone was insufficient to initiate partial oxidation of subsequently adsorbed isobutene. In this case, isobutene TPD spectra were similar to those seen on the reduced surface (data not shown). TPD products in the 280–600 K range were detected only when O_2 was dosed on adsorbed isobutene. This suggests that chemisorbed forms of oxygen on $TiO_2(110)$, such as have been discussed in previous experimental [31,33–35] and theoretical [36–39] works, were not the forms of O_2 involved in the partial oxidation of isobutene. The more likely form of reactive oxygen was a physisorbed state that interacts with chemisorbed isobutene (discussed in more detail below).

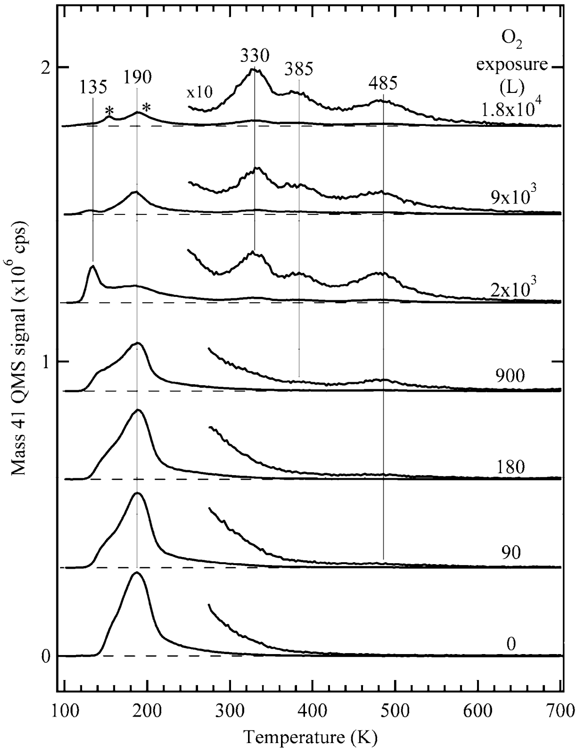

Fig. 5. Mass 41 TPD spectra from various post-exposures of O_2 at 95 K on saturation isobutene adsorbed at 140 K on clean $TiO_2(110)$. Spectra are displaced vertically and provided with background lines for clarity.

Fig. 5 shows the O_2 exposure dependence of the chemistry responsible for both the distortions in the isobutene TPD peak (at <220 K) and the new TPD features suggestive of a reaction between isobutene and O_2 (at 280–600 K). For these data, the mass 41 signal, which is intense for nearly all C_4 organics (isobutene included) was used, and a coverage of isobutene that saturated the surface at 140 K (0.75 ML) was used to maximize the TPD signals of the products. Low O_2 exposures (<900 L) showed a slight distortion on the isobutene TPD feature at 190 K and a slight enhancement in the mass 41 desorption signal above 350 K. A well-resolved feature at 485 K and a hint of another feature at 385 K (as well as more distortion in the isobutene state at 190 K) were detected with an O_2 exposure of 900 L. Exposures of $O_2 > 10^3$ caused all three high-temperature features to be clearly resolved in TPD. Interestingly, most of the isobutene signal below 200 K was absent, presumably due to a combination of reaction to form products and displacement from the first layer by adsorbed water. As discussed above, the onset of desorption from isobutene multilayers was below the apparatus base temperature. The weak feature at 135 K in the trace corresponding to an O_2 exposure of 2000 L was due to multilayer isobutene (compare with the TPD in Figs. 1 and 3), but the two features labeled with asterisks in the mass 41 spectrum from exposure of 1.8×10^4 L O_2 were not due to isobutene, as will be shown.

Artifacts may arise in TPD from backfilling exposures. Dosing by backfilling in a UHV chamber can result in adsorption of species desorbed from the walls, emitted from a pump, or formed on hot filaments. Interpretation of TPD experiments from backfilling exposures of any gas can be confused by desorption events from nonsample surfaces (e.g., holder, heating leads). Having already established that isobutene can be exclusively adsorbed on the crystal face by the use of a pinhole doser, we explored whether the mass 41 signals in Fig. 5 arose from inadvertent exposure of the crystal to a gas or gases arising from background sources during backfilling the chamber with O_2. Fig. 6a shows the mass 41 TPD trace from exposure of 0.75 ML isobutene to 2×10^3 L O_2 at 95 K (data from Fig. 5). Similarly, the TPD of 0.75 ML isobutene on the clean surface (shown in Fig. 6b) was as expected based on the preceding work. In contrast, no hint of a mass 41 signal was detected when the clean surface was exposed to 2×10^3 L O_2 at 95 K (Fig. 6c). Although not shown, desorption of molecular O_2 (mass 32) was detected at 410 K, as reported previously [34]. Comparison between the intensities of the three new mass 41 TPD features in the 280–600 K range (Fig. 6a) with the flat background in the control experiment (Fig. 6c) clearly indicates that the former features did not arise from adsorption of some C-containing background

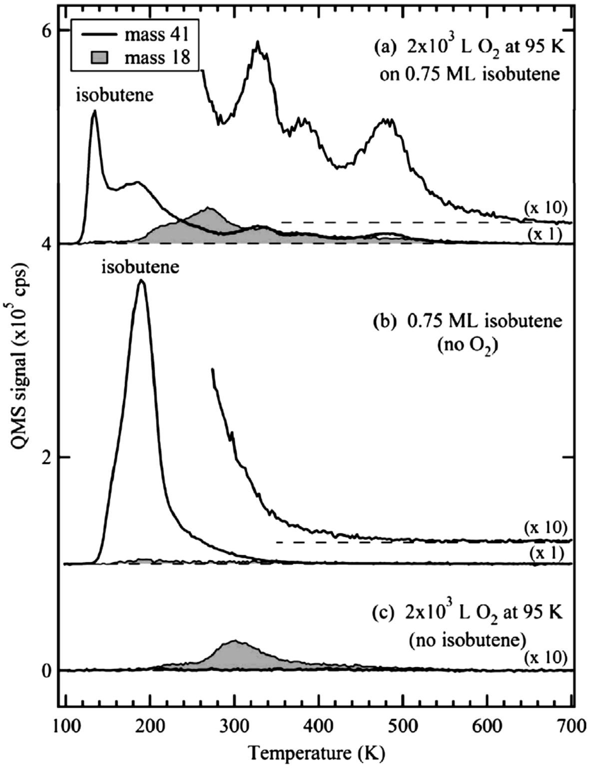

Fig. 6. Mass 18 and 41 TPD spectra from: (a) 2000 L O_2 exposure at 95 K on 0.75 ML isobutene adsorbed at 140 K on clean $TiO_2(110)$, (b) 0.75 ML isobutene adsorbed at 140 K on clean $TiO_2(110)$, and (c) 2000 L O_2 exposure at 95 K on clean $TiO_2(110)$. Spectra are displaced vertically and provided with background lines for clarity.

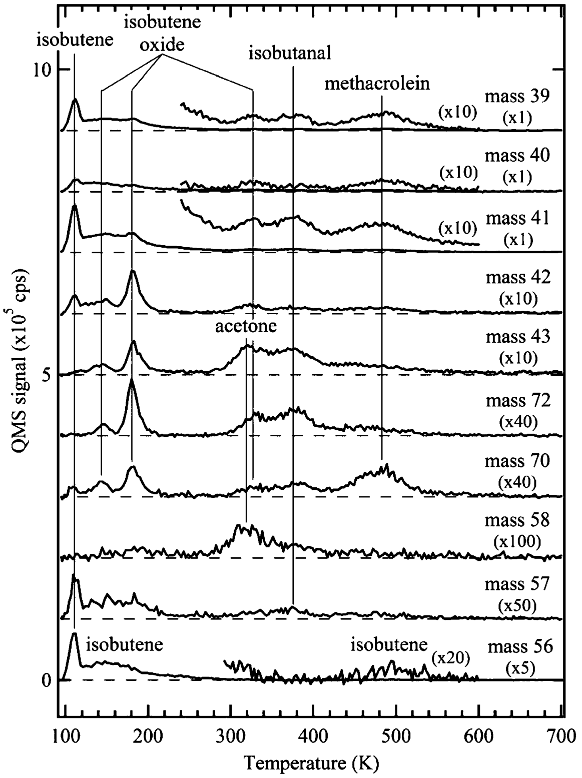

Fig. 7. TPD spectra using various masses from exposure of $\geqslant 9000$ L O_2 at 95 K on 0.75 ML of isobutene on the clean $TiO_2(110)$ surface at 140 K. Spectra are displaced vertically and provided with background lines for clarity.

gas or gases spuriously produced during O_2 backfilling of the chamber.

Nonetheless, examination of the three mass 18 TPD spectra (filled traces) in Fig. 6 shows that although no water was dosed with the isobutene (Fig. 6b), a significant amount adsorbed on the crystal during the 2×10^3 L O_2 exposures (Figs. 6a and 6c). Comparison of the amount of water desorbed from the surface after the isobutene oxidation reaction (Fig. 6a) with the control experiment (Fig. 6c) indicates that about 0.6 ML of the 1.7 ML of water seen from the reaction resulted from background adsorption. Most of this water should desorb below room temperature if only molecularly adsorbed, based on previous studies of water on $TiO_2(110)$ [40]. Water desorbing above room temperature was likely associated with the isobutene partial oxidation reaction, suggestive of a reaction-limited process. Although water appeared in TPD spectra as a reaction product and as a spectator, as discussed below, water was also necessary as a reactant for the partial oxidation of isobutene under these conditions.

A TPD survey of masses of 15–80 was conducted in an effort to identify the partial oxidation products of isobutene. Fig. 7 shows the results of this analysis for the case in which 0.75 ML isobutene was exposed to $\geqslant 9 \times 10^3$ L O_2 at 95 K. For simplicity, only those masses providing insight into the identities of species responsible for the new desorption features are shown. Where appropriate, mention is made of the absence of signal at certain mass values to exclude various candidate products. The most obvious species to hunt for are products in the C_4H_8O family (addition of an oxygen atom to isobutene),

$$C_4H_8 + (1/2)O_2 \rightarrow C_4H_8O, \tag{1}$$

and the C_4H_6O family (addition of an oxygen and removal of 2 H atoms),

$$C_4H_8 + O_2 \rightarrow C_4H_6O + H_2O. \tag{2}$$

A product in the latter family would be consistent with reaction-limited water desorption. Products with the formula C_4H_8O have a parent mass of 72, and products with formula C_4H_6O have a parent mass of 70.

Mass 70 and 72 TPD traces in Fig. 7 indicate that the desorption states at 145, 180, 330, 385, and 485 K were likely C_4H_8O or C_4H_6O products. Identification of these species was undertaken using the NIST library of mass spectra [41] as a reference point. The highest-temperature feature (485 K) had little mass 72 signal and thus was likely a C_4H_6O species. Two likely candidates are dimethyl ketene ($(CH_3)_2C{=}C{=}O$) and methacrolein (2-methylprop-2-enal; $CH_2{=}C(CH_3)CHO$). The mass spectra of these two molecules are similar, but subtle differences in the relative mass 39–43 signals, as well as the ratio of mass 69 (not shown) to mass 70, point to the 485 K TPD peak being methacrolein. A mass spectrum of methacrolein dosed into the chamber (data not shown) concurred with this assignment. TPD of methacrolein dosed on $TiO_2(110)$ (also not shown) gave a multilayer state at 145 K and a monolayer state at ~200 K, with little evidence for strong adsorption or thermal chemistry. Based on these observations, it can be concluded that the methacrolein feature at 485 K resulted from a reaction-limited process involving a surface intermediate between isobutene + O_2 and methacrolein,

$$C_4H_8 + O_2 \rightarrow \text{surface intermediate} \rightarrow C_4H_6O + H_2O. \qquad (3)$$

It is not clear whether the C=C bond in this methacrolein product was that same one as in the isobutene reactant, in which case one of the latter's methyl groups was oxidized. More likely, the aldehyde functionality formed at the 1 position of isobutene (CH_2=) and one of the methyl groups dehydrogenated to form a C=C bond.

The feature at 385 K is assigned to isobutanal (2-methylpropanal; $CH_3CH(CH_3)CHO$), which is distinguished by the parent signal at 72, by intense signals at 43 and 41, and weaker signals at 40, 42, and 57. Generation of this species requires formation of a new C–H bond at the 2 position of isobutene on an intermediate that has undergone oxidation at the 1 position. The hydride source may be internal, transferring from the 1 to 2 position, or external, resulting from the addition of an H atom from another source (e.g., HOO or water).

The 145, 180, and 330 K features all exhibited the same relative intensities for the masses 39–43, 70 and 72, although contributions at mass 43 from an additional species at 320 K (discussed below) made determination of the 43 contribution at 330 K difficult. Similarly, contributions at mass 39–42 in the temperature range of 130–220 K from unreacted isobutene posed difficulty for the 145 and 180 K features. Deconvolution of isobutene contributions using the mass 56 signal as a standard was helpful. Taking these considerations into account, it can be concluded that desorption in the 145, 180, and 330 K peaks arose from the same species, presumably evolving from physisorbed (145 K), weakly chemisorbed (180 K), and reaction-limited (330 K) states. Because the mass 72 signal in each feature was reasonably intense, it can be assumed that the responsible species was not a C_4H_6O species (mass 70). Nonetheless, assigning these features entails some difficulties, because no C_4H_8O species having a 72:70 fragmentation ratio of 2:1 was found in the NIST database [41]. Expanding the search to C_5, C_6, C_7, and C_8 hydrocarbons or oxygenates was also unsuccessful because of this 72:70 ratio, as well as for other reasons discussed below. However, certain C_4H_8O molecules could be excluded as candidates. Retaining the branching structure of the isobutene reactant limits the possibilities to three reasonable candidates: two enols and an oxirane. The absence of a significant mass 57 signal at 145, 180, and 330 K precludes 2-methyl-2-propen-1-ol ($HOCH_2C(CH_3)$=CH_2, which differs from isobutene by the insertion of an O atom into a C–H bond of one of the latter's methyl groups) and 2-methyl-1-propen-1-ol [42] ($(CH_3)_2C$=C(H)OH, which differs from isobutene by the insertion of an O atom into a C–H bond of the methylene end of the molecule), both of which have mass 57 as the most intense fragment in their mass spectrum. The ratios of the masses at 39–43 match well with the spectrum of isobutene oxide (2,2-dimethyloxirane; $(CH_3)_2\overline{C\text{–}CH_2\text{–}O}$), which has only a weak mass 57 signal according to the NIST database, although the mass 72:70 ratio seen in TPD was inconsistent with the mass spectrum of isobutene oxide. However, no more reasonable matches were found by extending the search to other isomers of the C_4H_8O structure, including ethers (from O insertion into C–C bonds), straight-chain molecules (which would require a methyl shift), or ring structures (which should be considerably less stable than the molecules identified thus far).

Abandoning the C_4H_8O formula also was not helpful. Higher molecular weight species generally have one or more intense fragments at 45–80 (other than 70 and 72), but the three TPD peaks at 145, 180, and 330 K did not have significant signals at any other mass in this range other than 70 and 72. Absence of appreciable signals at mass 31, 59, or 74 precludes formation of C_4 alcohols such as t-butanol (2-methylpropan-2-ol) or 2-methylpropan-1-ol. Based on these arguments, we tentatively assign the 145, 180, and 330 K TPD states to desorption of isobutene oxide. Formation of this species, both as a product of oxygen attack on the C=C of isobutene and as an intermediate leading to isobutanal and methacrolein, is reasonable. The fact that only isobutene oxide was observed at low temperature (<200 K) is also consistent with this species being formed at 95 K in a reaction between isobutene and an oxygen-containing species.

A fourth product was detected in TPD by the mass 43 and 58 signals at 320 K. The ratio of these features, as well as the peak temperature, point to desorption of acetone from the $TiO_2(110)$ surface [43]. Formation of acetone suggests that attack of oxygen on the C=C bond of isobutene leads to complete insertion of O between these two atoms according to the reaction

$$C_4H_8 + O_2 \rightarrow (CH_3)_2C{=}O + [H_2CO]. \qquad (4)$$

Broad, nondescript desorption features in the mass 29 and 30 signals at 100–250 K may be partially attributable to a formaldehyde product, but these features are typically result from backfilling exposures of O_2 and thus more likely result from background adsorption on the heating leads and sample holder. Nevertheless, observation of a C_3 product indicates that an O_2 attack on isobutene is able to cleave C–C bonds. Also note that a trace amount of isobutene was detected at 500 K, presumably from a back-reaction involving an intermediate that led to the methacrolein product at 480 K.

3.4. *Oxygen pressure or exposure?*

The results discussed above clearly demonstrate that a reaction occurs between isobutene and gas phase O_2 when the latter is exposed to isobutene adsorbed on $TiO_2(110)$ at 95 K. The extremely large O_2 exposures needed to build up detectable amounts of partial oxidation products suggest that (a) the reaction between O_2 and isobutene is a low-probability process at 95 K and/or (b) only a limited amount of O_2 can be sustained transiently on the surface at 95 K. Results in Fig. 8 suggest that the effect is not O_2 pressure-dependent, or at least that O_2 pressure is not the primary factor in dictating the extent of partial oxidation. In this figure, three O_2 pressures (1×10^{-6}, 5×10^{-6}, and 1×10^{-5} Torr) were used to dose 9×10^3 L

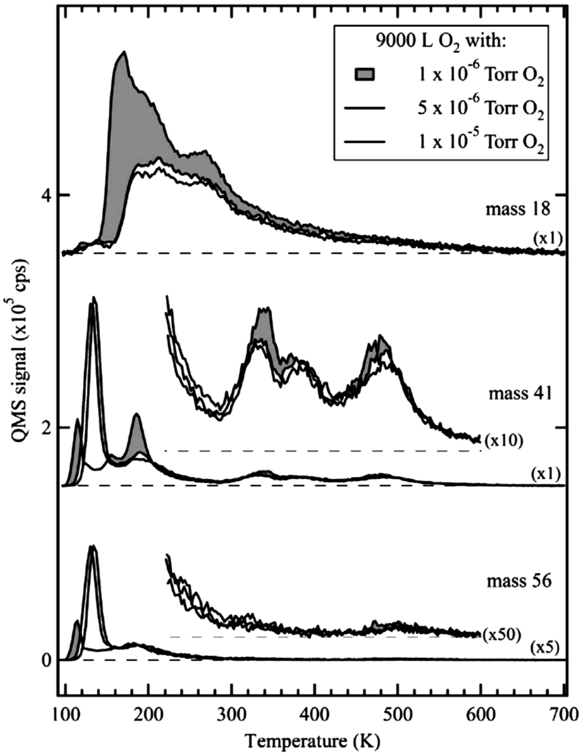

Fig. 8. Mass 18, 41, and 56 TPD spectra from three 9000 L O_2 exposures at 95 K on 0.75 ML isobutene adsorbed at 140 K on clean TiO_2(110). Two exposures are with 5×10^{-6} and 1×10^{-5} Torr O_2 (solid lines) and one is with 1×10^{-6} Torr O_2 (filled traces). Spectra are displaced vertically and provided with background lines for clarity.

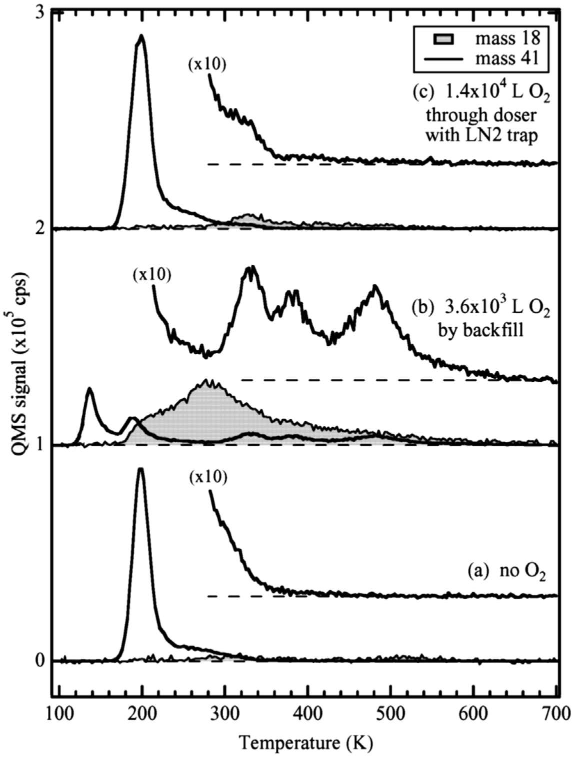

Fig. 9. Mass 18 and 41 TPD spectra from: (a) 0.75 ML isobutene adsorbed at 140 K on clean TiO_2(110), (b) 3600 L O_2 exposure (dosed by backfilling) at 95 K on 0.75 ML isobutene adsorbed at 140 K on clean TiO_2(110), and (c) 14000 L O_2 exposure (dosed through a LN2 trap and directional doser; see text for details) at 95 K on 0.75 ML isobutene adsorbed at 140 K on clean TiO_2(110). Spectra are displaced vertically and provided with background lines for clarity.

of O_2 on 0.75 ML isobutene at 95 K. (The time periods for these exposures were 150, 30, and 15 min, respectively.) The lower, middle, and upper traces are the resulting mass 56, 41, and 18 sets of TPD spectra, respectively, for these three pressures. Although only 1 decade of pressure was sampled, it is clear from the mass 41 data that the greatest amount of partial oxidation was with the lowest pressure of O_2 (filled traces). The spectra for all three masses were essentially the same for the two higher pressures (solid traces), but more isobutene oxide (at both <200 and 330 K) and more methacrolein were formed in the lower-pressure experiment. The key difference between the low-pressure exposure and the two higher-pressure exposures was the amount of water that built up on the surface during the O_2 exposure period. Almost twice as much water was adsorbed in the low-pressure exposure compared with both higher-pressure cases. The impact of this higher water coverage during the longer exposure in the lower O_2 pressure experiment suggests that the residence time of O_2 on the surface at 95 K is not as important as the reaction probability between isobutene and an oxidant that involves adsorbed O_2 and water.

3.5. *Role of water in isobutene partial oxidation*

Results in the previous section suggest that water plays a role in the partial oxidation of isobutene on TiO_2(110). Fig. 9 examines this issue in more detail using an O_2-dosing method that precludes generation of significant amounts of background H_2O normally experienced during O_2 backfilling. For comparison, Fig. 9a shows mass 41 (solid trace) and 18 (filled-in trace) data for TPD of 0.4 ML isobutene on clean TiO_2(110). No partial oxidation products were detected, and <0.1 ML of water was adsorbed from the background. Fig. 9b shows TPD of the same masses after exposure of 0.4 ML isobutene to 3.6×10^3 L O_2 at 95 K. As discussed above, the spectra show both production of partial oxidation products and the presence of water (from both background adsorption and the reaction). The question is whether background water was important in the partial oxidation of isobutene. To answer this question, O_2 was dosed through the directional doser on to 0.4 ML isobutene at 95 K (Fig. 9c). The O_2 gas line was passed through an LN2 trap near the pinhole to remove condensable impurities (e.g., water) before dosing. Because of the design of the directional doser, the O_2 flux emerging from the doser and impinging on the crystal was about a factor of 10^2 times that of the resulting rise in chamber pressure. For the experiment in Fig. 9c, 7.5 Torr O_2 was exposed to the pinhole doser, which yielded an O_2 flux at the crystal equivalent to an O_2 pressure of 8.4×10^{-6} Torr. However, the chamber pressure rose to only $\sim 3 \times 10^{-8}$ Torr during dosing. By excluding water from the O_2 gas line (with the LN2 trap) and minimizing the overall exposure of O_2 to the chamber walls and pump, approximately 1.4×10^4 L O_2 was dosed with accumulation of <0.2 ML of background wa-

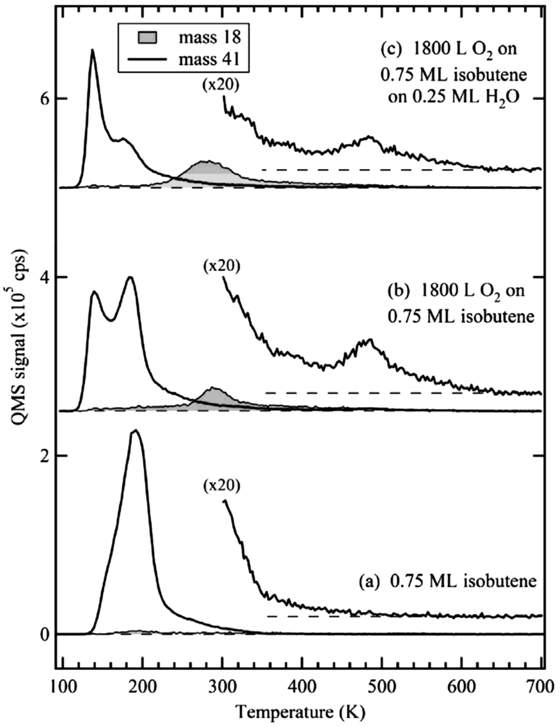

Fig. 10. Mass 18 and 41 TPD spectra from: (a) 0.75 ML isobutene adsorbed at 140 K on clean $TiO_2(110)$, (b) 1800 L O_2 exposure at 95 K on 0.75 ML isobutene adsorbed at 140 K on clean $TiO_2(110)$, and (c) 1800 L O_2 exposure at 95 K on 0.75 ML isobutene adsorbed at 140 K on 0.25 ML H_2O on clean $TiO_2(110)$. Spectra are displaced vertically and provided with background lines for clarity.

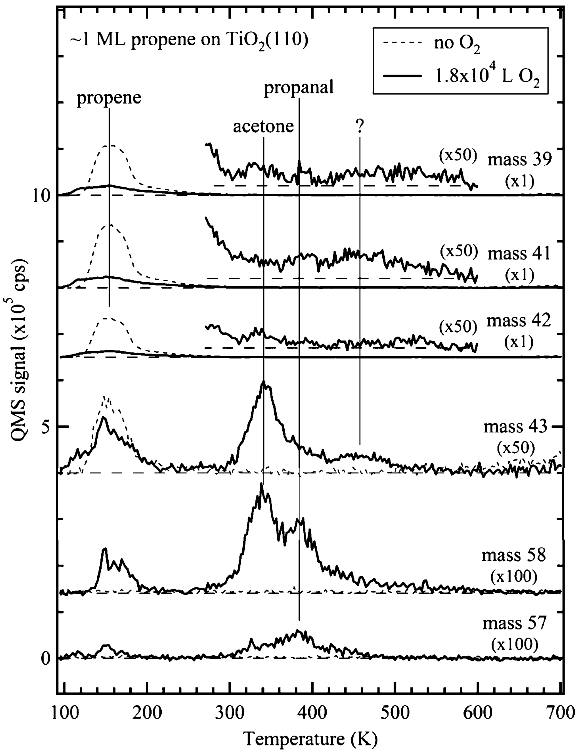

Fig. 11. TPD spectra using various masses from a saturation exposure of propene on the clean $TiO_2(110)$ surface at 95 K (- - -) and from exposure of 18000 L O_2 at 95 K a saturation exposure of propene on the clean $TiO_2(110)$ surface at 95 K (—). Spectra are displaced vertically and provided with background lines for clarity.

ter during the duration of the dose (30 min). As the data in Fig. 9c show, there is little or no evidence for partial oxidation of isobutene under conditions in which water was excluded from the O_2 exposure. These data strongly suggest that water is needed to promote the O_2 partial oxidation of isobutene on $TiO_2(110)$.

Although water was necessary to promote partial oxidation of isobutene, it is unclear what adsorption state of water (e.g., physisorbed or chemisorbed) was involved. Fig. 10 explores this issue. As was discussed with regard to Fig. 3, water binds more strongly to $TiO_2(110)$ than does isobutene; isobutene dosed at 95 K does not displace water molecules bound to Ti^{4+} surface sites on $TiO_2(110)$. Results discussed earlier also show that water dosed at 95 K (in this case from background) can displace first layer isobutene if the water exposure is sufficient. Figs. 10a and 10b show data previously discussed for TPD (masses 18 and 41) of 0.75 ML isobutene and partial oxidation (with 1.8×10^3 L O_2) of the same coverage, respectively. In Fig. 10c, a precoverage of 0.25 ML of water was adsorbed before isobutene and the partial oxidation treatment. More isobutene was displaced from the first layer as a result of the preadsorbed water, and the amount of partial oxidation products decreased by about 50% from the case without preadsorbed water. There are two possible reasons for this: (1) Isobutene molecules that were unable to interact directly with the $TiO_2(110)$ surface (in this case, because of preadsorbed water-blocking sites) were unreactive to the subsequent oxidation treatment, or (2) preadsorbed water inhibited O_2 adsorption and activation. This latter point has already been demonstrated in model studies on $TiO_2(110)$ [31]. In this case, water molecules hydrogen-bonded to bridging O/OH sites blocked access of O_2 to the surface. To whatever extent either of these possibilities is valid for the present system, the data in Figs. 9 and 10 demonstrate that water is both a necessary reactant and an unfortunate site-blocker in the partial oxidation of alkenes on TiO_2.

3.6. *Propene partial oxidation*

A preliminary experiment was performed with propene (C_3H_6) to test whether the partial oxidation effect on $TiO_2(110)$ extended to other alkenes. Fig. 11 shows TPD spectra from various masses for saturation coverage of propene dosed at 95 K (dashed traces), and also for the same coverage subsequently exposed to 1.8×10^4 L O_2 at 95 K. In the absence of O_2 exposure, propene was desorbed from $TiO_2(110)$ in a broad feature at about 160 K. The relative intensities of the masses sampled fit with the mass spectrum of the parent molecule, and no signs of thermal decomposition on the clean surface were detected. These conclusions are consistent with earlier work on propene adsorption on $TiO_2(110)$ by Ajo et al. [44]. In contrast with results on the clean surface, new features appeared in TPD at 340, 380, and 460 K after exposure to O_2. The 340 and 380 K features were preliminarily assigned to acetone and propanal, consistent with the NIST database [41], whereas the

460 K peak was not assigned. This latter species is not acrolein (2-propenal; $CH_2{=}CH\text{–}C(H){=}O$), allyl alcohol (2-propen-1-ol; $CH_2{=}CH\text{–}CH_2\text{–}OH$), or propene oxide (methyloxirane; $CH_3\text{–}\overline{C\text{–}CH_2\text{–}O}$), because of significant mismatches between the relative signals in TPD and those for these molecules in the NIST database. (Other possibilities include methyl ketene and 1-propen-2-ol; however, mass spectra for these molecules were not in the NIST database.) Additional work, including a more detailed survey of other masses, is needed to confirm and extend these assignments. Nevertheless, results in Fig. 11 clearly show that the same type of partial oxidation processes that were active for isobutene on $TiO_2(110)$ are also active for propene.

3.7. *Implications for alkene epoxidation on TiO_2-supported Au catalysts*

The reaction mechanisms and energy landscape for the conversion of an adsorbed alkene and O_2 to partially oxidized products are not simple. Greater understanding of the heterogeneous-phase reaction may be obtained by considering its gas-phase counterpart, which is of interest in combustion research. Chen and Bozzelli [45–47] reviewed the gas-phase literature of isobutene oxidation and extensively examined the partial oxidation of isobutene from a theoretical perspective. They found that an attack of HOO on the 2 position of isobutene leads to isobutane oxide (2,2-dimethyloxirane), but not in a single-step process. Reactions involving isobutene and an OH radical or between isobutene-related radicals and O_2 lead to oxygenates other than isobutane oxide. These gas-phase data provide an energetic and mechanistic basis for considering the role of the HOO radical in selective partial oxidation of alkenes to epoxides. In fact, H_2O_2 is used to selectively oxidize alkenes over TiO_2-based catalysts [8,18–20].

Similarities between the results discussed in this study on the model $TiO_2(110)$ surface and those in the literature for alkene epoxidation on TiO_2-supported Au catalysts [6,7,10,15–17,22] indicate that both processes involve similar reaction processes. In the latter studies, partial oxidation of alkenes by O_2 was facilitated by the presence of H_2 in the reaction stream. (To date, there are no studies exploring the role of water.) The current model in the literature for the role of H_2 is that it reacts with O_2 on the Au nanoparticles to generate an HOO species, which is a stronger oxidant than O_2. As mentioned in the Introduction, at least two groups [15,22] have provided strong evidence for the $H_2 + O_2$ reaction to HOO on Au nanoparticles. Once formed, the HOO species may diffuse onto the oxide where oxidation of the adsorbed alkene occurs. Observations in this study showed that partial oxidation of isobutene and propene by $O_2 + H_2O$ mixtures occurred on the model $TiO_2(110)$ surface in the absence of Au. This suggests that a reaction between adsorbed O_2 and H_2O may form HOO on $TiO_2(110)$. Oxygen vacancy sites need not (and likely do not) play a role in this reaction, because the extent of the isobutene $+ O_2 + H_2O$ reaction was not affected by preoxidation of the vacancies. In additionally, surface O_x species formed from preadsorption of O_2 at vacancies before alkene adsorption were inactive for the partial oxidation reaction. We propose that instead, charge transfer from finite electron density in a shallow, partially filled conduction band level of reduced rutile [48] to physisorbed O_2 led to an $O_2{}^{\delta-}$ species that can react with physisorbed water to generate HOO. This shallow conduction band state is essentially the source of the semiconducting properties of reduced rutile TiO_2. Adsorbed $O_2{}^{\delta-}$ species also formed from direct interaction of O_2 with reduced surface cation sites [34,36–39], but these species appear to be too strongly bound to the surface to participate in the initial step of alkene activation. Alternatively, HOO may form from reaction of physisorbed O_2 molecules and OH groups residing at oxygen vacancies on $TiO_2(110)$ [31].

4. Conclusion

We have demonstrated that alkenes (isobutene and propene) can be partially oxidized with O_2 on rutile $TiO_2(110)$ under UHV conditions in the absence of Au nanoparticles. The reaction requires the cooperative effect of coadsorbed water, although water and the resulting partial oxidation products both displaced the alkenes from the surface and thus inhibited the extent of the overall reaction. Based on comparisons with the literature, we propose that charge transfer from the reduced $TiO_2(110)$ surface to physisorbed O_2 facilitated formation of a hydrogen peroxo (HOO) species via reaction with coadsorbed water. Results presented here confirm speculation in the literature that partial oxidation of alkenes occurs on TiO_2 in the absence of Au, and that strongly bound intermediates and products on the oxide may be responsible for the low conversion numbers typically observed with these catalysts [10,13,17]. Our TPD results show that the various products of isobutene and propene partial oxidation were considerably more stable on $TiO_2(110)$ than were the parent molecules themselves. Also, water present either as a side-product of the partial oxidation process or as a spectator blocked alkene adsorption sites and limited the extent of the partial oxidation reaction.

Acknowledgments

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