Propene adsorption on gold particles on $TiO_2(110)$

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The adsorption of propene on rutile $TiO_2(110)$ and on gold islands dispersed on $TiO_2(110)$ [Au/$TiO_2(110)$], both at 120 K, has been studied using temperature programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS) and He^+ low energy ion scattering spectroscopy (LEIS). Propene adsorbs on both $TiO_2(110)$ and Au/$TiO_2(110)$, with desorption peak temperatures at low coverage of ~190 and ~240 K, respectively. When only 16% of the $TiO_2(110)$ surface is covered by gold islands [16% Au/$TiO_2(110)$], moderate propene doses populate both the 240 and 190 K TPD peaks, in that order. The 190 K peak, seen also without Au, is due to propene bound to bare Ti sites. The 240 K peak is attributed to propene adsorbed to Ti sites at the edges of gold islands. Tiny doses of propene to the 16% Au/$TiO_2(110)$ surface give this a 240 K TPD peak but no 190 K feature, showing that the propene is mobile on $TiO_2(110)$. A TPD feature at ~150 K, which is more prominent at higher Au coverages and higher propene doses, is due to propene bound only to metallic Au islands. Propene desorption shows additional intensity at 265–310 K when the gold islands are only one atom thick, due to propene adsorbed on 2D Au islands or at Ti sites near their edges.

KEY WORDS: gold; titania; propene; selective oxidation; nanoparticles; $TiO_2(110)$; chemisorption; ion scattering spectroscopy

1. Introduction

Propene epoxide (CH_3CHOCH_2) and its production are industrially relevant, with a market on the order of several billion dollars per year [1–3]. The two current industrial-scale methods for propene epoxidation, the chlorohydrin process and the hydroperoxide process, have their drawbacks, including the fact that both are indirect processes and the hydroperoxide process produces a co-product [1–3]. Consequently, a promising new catalyst, consisting of gold islands dispersed on titania, in various incarnations, was recently developed, which has resulted in several patents [4–9].

It has been found that propene epoxide can be produced in >99% selectivity and 1.1% yield from a gaseous mixture of propene, oxygen, and hydrogen over a catalyst consisting of small gold islands dispersed on titania [10]. One very interesting part of the work was the observation that the size of the gold islands changed the reactivity of the catalyst. For catalysts with gold islands with mean diameters of 1.5 and 1.7 nm, propane was produced instead of propene epoxide. This reactivity changed from partial oxidation to reduction, based on the size (diameter) of the gold islands. Other powder catalyst studies have been done which had similar results [10–12]. A kinetic isotope effect was found, indicating that hydrogen was involved in the rate-limiting step of propene epoxide production [12]. Additional studies in the condensed phase have further helped to elucidate the mechanism of propene epoxide production [13,14]. It has been proposed that the oxidant, which is some sort of peroxide species, is created on the gold islands, spills over to the titania surface and reacts with the propene adsorbed on the titania surface [11–15].

Only recently has work on propene ($CH_3CH{=}CH_2$) adsorption in ultrahigh vacuum (UHV) on Au(100) and Au(111) been published [16]. Propene adsorbed at 120 K desorbs molecularly at 140 K and 150 K, respectively, with an activation barrier for desorption (E_a^d) of ~38 kJ/mole. Propene was found to react with adsorbed oxygen adatoms on these gold surfaces, as one might expect from the relationship established by Madix and coworkers [17] between the gas-phase acidity of the adsorbate and its reactivity with oxygen adatoms adsorbed on the (110) faces of the noble metals. For 1.0 ML of oxygen adatoms, the result is a shoulder at 200 K in the propene desorption and complete oxidation products: H_2O, CO, and CO_2. However, at 0.4 ML oxygen adatom coverage, masses 56 and 58 were seen, consistent with several possible products, propene epoxide amongst them. The authors did not further identify these products.

The growth of gold islands on $TiO_2(110)$ has been extensively studied by our group [18], as well as by others [19,20]. Gold vapor deposited on $TiO_2(110)$ initially grows islands that are one atom thick until ~9% of the surface is covered by islands (0.09 ML) [18].

Here we study propene adsorption and desorption on a model support, $TiO_2(110)$, and then on a model catalyst, gold islands dispersed on $TiO_2(110)$. We assign a number of TPD features with the aid of LEIS and XPS, and find E_a^d for molecularly adsorbed propene

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on $TiO_2(110)$, on $Au/TiO_2(110)$ and at the $Au–TiO_2$ interface. We also show that propene is mobile on the model support, $TiO_2(110)$. This compliments our previous study of adsorbed oxygen adatoms on this same model catalyst [21].

2. Experimental

The UHV apparatus used, previously described in [18], consists of an analysis chamber and a sample preparation chamber with base pressures of 2×10^{-10} mbar and 5×10^{-9} mbar respectively. The analysis chamber is equipped for X-ray photoelectron spectroscopy (XPS), Auger spectroscopy, low energy ion scattering spectroscopy (LEIS), and temperature programmed desorption (TPD). XPS was performed with Al Kα radiation with an energy of 1486.6 eV. LEIS was performed at a helium ion energy of 1275 eV, by leaking He directly into the ion source of an LK Technologies ion gun, until a partial pressure of helium of 8×10^{-8} mbar was established in the main UHV chamber. All pressures reported are uncorrected for ion gauge sensitivity. LEIS spectra were usually taken over an energy window of 800–1250 eV, which enabled measurement of both the Ti peak, which was centered at about 915 eV, and the Au peak, which was centered at about 1145 eV. LEIS peak areas were determined after subtraction of a small, energy-independent background.

The polished $TiO_2(110)$ crystal (Commercial Crystal Laboratories) is mounted on a tantalum sample holder, which is cooled with liquid nitrogen or resistively heated. The temperature of the crystal is monitored by a chromel-alumel thermocouple attached to the edge of the crystal by high-temperature cement.

Routine $TiO_2(110)$ surface preparation was as follows: 1.0 keV argon ion sputtering (to remove Au and other impurities from the previous experiments) at a partial pressure of argon of 1.8×10^{-5} mbar for the equivalent of 130 min at room temperature, followed by a 10 min annealing in a partial pressure of $O_2(g)$ of 3×10^{-6} mbar at 873 K. While holding the oxygen pressure at 3×10^{-6} mbar, the sample was allowed to cool to 373 K, at which point the oxygen-leak valve was closed and the sample allowed to cool to room temperature. This recipe has been shown to result in a well-ordered LEED pattern [22], which we verified. Although an STM study has shown that such cooling in O_2 results in a $TiO_2(110)$ surface that is not perfect (1×1), and a more perfect (1×1) structure when cooled in UHV instead of O_2 [23], XPS showed near perfect stoichiometry (only Ti^{4+} and no Ti^{3+} signal) for this surface preparation, whereas cooling in UHV (instead of O_2) gave more Ti^{3+} in XPS. The $TiO_2(110)$ crystal resulting from the procedure used was transparent, colorless and sufficiently conductive at room temperature to eliminate charging at 300 K. However, significant charging (seen in XPS) occurred at 120 K.

Gold was vapor deposited using a tantalum crucible coated with a gold-nonwetting (auruphobic) material (Ceramabond 503 from AREMCO Products, Inc., a high temperature ceramic glue [18]). A combined LEIS/XPS method was used to determine gold island thickness and coverage. The total amount of gold deposited on the surface was determined from the ratios of XPS Au(4f) and Ti(2p) peak areas, and calibrated following ref. [18]. The LEIS Ti peak areas before and after gold deposition determined the amount of the $TiO_2(110)$ surface covered by the gold, as described in [18]. Together, these measurements provided the fractional coverage of the $TiO_2(110)$ surface by gold islands and the average gold island thickness. The latter is reported in terms of monolayers (ML), where 1 ML is defined as the Au(111) packing density (1.39×10^{15} gold atoms/cm^2) or a 2.34 Å thick layer (at the bulk Au density).

Reagent-grade propene of 99.6% purity from Scott Specialty Gas was used as received. The mass spectrum from this propene matched the published NIST mass spectrum [24]. Propene was dosed with a directed doser, using an ion gauge to determine the background pressure rise. The nominal (uncorrected for directed dosing) exposure, in Langmuirs (10^{-6} Torr s), was determined used the dosing time and the background pressure rise measured by an ion gauge. As mentioned previously, ion gauge sensitivities were not taken into account nor was the doser enhancement factor, which was calculated to be between 10–100 fold [25], depending on sample to doser distance, which we do not know exactly.

The propene dosing and TPD spectra here were taken after two previous TPD heatings up to as high as 420 K (without dosing propene) to make certain the gold islands would not appreciably thicken during the actual TPD. The islands were characterized with XPS and LEIS before these cycles and with LEIS after these cycles. The initial XPS was used to determine the total Au coverage, and the fractional coverage by islands was determined from the LEIS after these cycles. The corresponding average island thickness reported here is simply the ratio of these two values.

TPD spectra were taken with 5 K/s temperature ramps and for the TPD spectra shown, only mass 41 was followed, after using masses 17, 26, 27, 39 and 42 as well as the 0–200 mass range to verify that propene was the molecule being followed with mass 41. We saw no indication of other species contributing to the propene TPD peaks we report here. In addition, the experimentally observed mass spectrum of the desorbing species was consistent with the NIST mass spectrum for propene [24]. Control experiments verified that other masses in the cracking pattern for propene produced identical peak shapes. The TPD spectra are reported here after subtraction of a small, temperature-independent background due to outgassing from the sample holder.

3. Results

3.1. Gold-free $TiO_2(110)$

3.1.1. Saturation propene coverage on $TiO_2(110)$

The measured TPD peak areas versus propene dose to the Au-free $TiO_2(110)$ surface at 120 K (data not shown) appeared to saturate between 0.004 and 0.01 L (uncorrected for doser enhancement factor). The attenuation of the Ti LEIS peak also saturated by 0.01 L, showing that this dose is sufficient to saturate these surfaces. At saturation, the Ti LEIS peak area dropped to ~45% of its clean surface value. Assuming that each propene adsorbs with its carbon plane parallel to the surface and randomly masks an area in LEIS defined by the edge of the Van der Waals radii of its atoms (~24 Å^2), this attenuation gives a saturation coverage of propene of $\sim 2.4 \times 10^{14}$ propenes/cm^2.

From the ratio of C(1s) to Ti(2p) XPS peak intensities after a saturation dose of propene to $TiO_2(110)$, we are able to estimate the saturation coverage of propene on the $TiO_2(110)$ surface using the same method and parameter values as in [26] and the bulk density of propene (0.5193 g/cm^3 [27]) for the propene film. The resulting saturation coverage is 2.7×10^{14} propenes/cm^2. This estimate is probably only accurate to ~30% (which is about the error in the literature values for mean free paths of the electrons).

We also estimated the saturation coverage by using a space-filling model of adsorbed propene. Assuming that propene has its carbon plane parallel to the surface, its projected area onto the surface (using the edges of its atoms Van der Waals radii to define its size) is 24 Å^2. The area of one $TiO_2(110)$ unit cell is smaller than this (19 Å^2), so it is impossible to pack the propenes with one per unit cell in this orientation. A packing of one per two unit cells, however, is easily accomplished and allows each propene in a complete monolayer to bind to the same site (presumably with its π orbital of the C=C double bond donating into a Ti^{4+} site). This corresponds to a saturation coverage of 50% of the unit cells, or 2.7×10^{14} propenes/cm^2. The three different methods, LEIS, XPS, and space-filling model, agree on the propene saturation coverage of $2.4–2.7 \times 10^{14}$ propenes/cm^2. We define here as one monolayer (ML) of propene this last structure with one propene per two unit cells, or 2.7×10^{14} propenes/cm^2.

After a saturation dose of propene to a clean $TiO_2(110)$ surface, the LEED pattern still showed the spots characteristic of clean $TiO_2(110)$ and no new spots, but possibly with increased background intensity.

3.1.2. Propene TPD: $TiO_2(110)$

Figure 1 shows TPD measurements of propene adsorbed on gold-free $TiO_2(110)$ at 120 K for exposures ranging from 0.001 L to 0.01 L. Only molecular propene was observed to desorb from these surfaces, so we show here only the peaks for mass 41, whose intensity is proportional to the desorption rate of molecular propene. A broad background due to outgassing from the sample holder was subtracted from these TPD spectra. For the lowest dose, a single peak centered at 188 K appears. This peak increases in intensity and shifts to lower peak temperatures with increasing propene dose, with a peak temperature of 180 K for a dose of 0.01 L propene. Using first-order Redhead analysis [28], a prefactor (ν) of 10^{13} s^{-1}, and the heating rate of 5 K/s, activation energies for desorption (E_a^d) were calculated. This gives an E_a^d at zero coverage of 47.3 kJ/mole and a slope of −2.8 (kJ/mole)/ML, indicating repulsive interactions between the propene molecules. No residual carbon was observable on the surface by XPS or LEIS after repeated such TPDs.

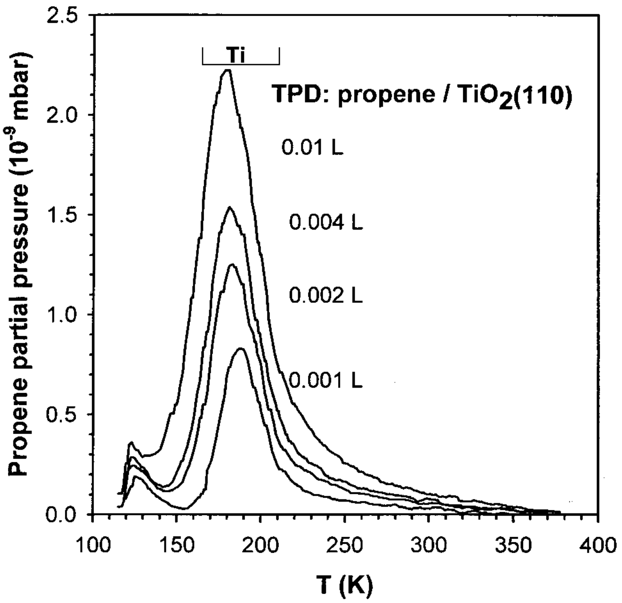

Figure 1. TPD spectra, with a heating rate of 5 K/s, after propene exposures to $TiO_2(110)$ at 120 K. Mass 41 is followed and transformed into propene partial pressure using mass spectrometer sensitivities. "Ti" is the identification label for peaks at 155–210 K, due to adsorption on the $TiO_2(110)$.

3.2. Au/$TiO_2(110)$

Upon vapor deposition of Au on TiO_2 at room temperature, two-dimensional islands one atom layer thick are formed, up to a critical coverage of 8.6% of the TiO_2 surface, then further Au deposition mainly adds to the tops of the two-dimensional islands, forming three-dimensional islands. Several STM and electron microscopy studies show the shapes of the Au islands formed [19,29,30]. The number density of islands formed under similar growth conditions is reported in [29]. Gold films are described here with the nomenclature: "Au(island thickness, fractional island coverage)/$TiO_2(110)$". For example, gold islands of average island thickness 1.5 ML and covering 16% of the $TiO_2(110)$ surface are reported as "Au(1.5 ML, 16%)/ $TiO_2(110)$". The total Au coverage for such a surface is only $1.5\,ML \times 0.16 = 0.23\,ML$.

3.2.1. Saturation coverage of propene

The Ti and Au LEIS peaks were attenuated upon dosing propene to $Au/TiO_2(110)$ at 120 K, reaching minima of ~46% and 26% of their initial values, respectively, at a dose of 0.01 L of propene for various gold island coverages (see Section 3.3, below). From this, we conclude that 0.01 L is sufficient to saturate these surfaces. Doses of propene to Au-free $TiO_2(110)$ and to gold-dosed $TiO_2(110)$ with total Au coverages up to 7 ML resulted in TPD areas that were the same, independent of Au coverage, for a given propene dose up to 0.01 L within the reproducibility of dosing (~16% standard deviation). We conclude that the sticking probability and saturation coverage of propene is nearly the same as on Au-free $TiO_2(110)$. That saturation coverage was $\sim 2.4-2.7 \times 10^{14}$ propenes/cm^2 (see above).

3.2.2. TPD: Au(1.5 ML, 16%)/$TiO_2(110)$

Gold islands on average 1.5 ML thick and covering 16% of the $TiO_2(110)$ surface were dosed with propene and TPD was performed. Figure 2 shows typical results. At the lowest dose, 0.001 L, there are two distinguishable peaks, one at 152 K and the other at 240 K. The 152 K peak is assigned to desorption of propene from the tops of the gold islands, based on a study by Davis and Goodman [16] of the desorption of propene from Au(111) and Au(100), as well as the LEIS measurements described below in Section 3.3. This state may not fully saturate here due to the close proximity of its desorption temperature to the dosing temperature. The broad 240 K peak is seen on neither pure Au nor pure TiO_2, so it is assigned to desorption of propene bonded to the edges of the gold islands, where the molecule interacts with both the gold islands and the $TiO_2(110)$ surface. (This assignment is also supported by the LEIS below.) By 0.002 L an additional peak appears at ~190 K and its intensity increases with increasing doses of propene, shifting to lower temperatures as the intensity of the peaks increases, until at a dose of 0.01 L, the peak saturates at 177 K. On the basis of the very similar peak seen for propene on Au-free $TiO_2(110)$ (see above), this peak is assigned to propene desorption from Au-free patches of $TiO_2(110)$.

At both this and the higher coverage of Au below, as well as for the Au-free $TiO_2(110)$ surface, some mass 28 and mass 44 desorption intensity was seen over a broad region (100–300 K), but the intensities did not correlate with the propene exposure, so these products are attributed to outgassing from the sample holder.

3.2.3. TPD: Au(9.0 ML, 84%)/$TiO_2(110)$

The $TiO_2(110)$ surface with gold islands of average thickness 9.0 ML covering 84% of the surface area was dosed with propene. Typical TPD results are shown in figure 3. At the lowest dose there are two peaks, one at 143 K and another at 230 K. As for Au(1.5 ML,

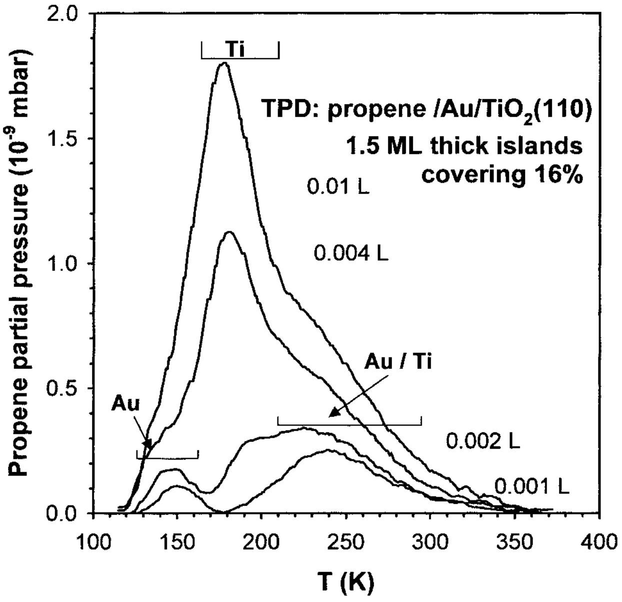

Figure 2. TPD spectra, at 5 K/s, after propene adsorption on $TiO_2(110)$ containing Au islands of 1.5 ML average thickness covering ~16% of the surface at 120 K. "Au": peaks at 125–155 K, due to propene adsorption on the tops of gold islands. "Ti": peaks at 155–210 K, due to adsorption on the $TiO_2(110)$. "Au/Ti": peaks at 210–295 K, due to propene adsorbed at the edges of gold islands.

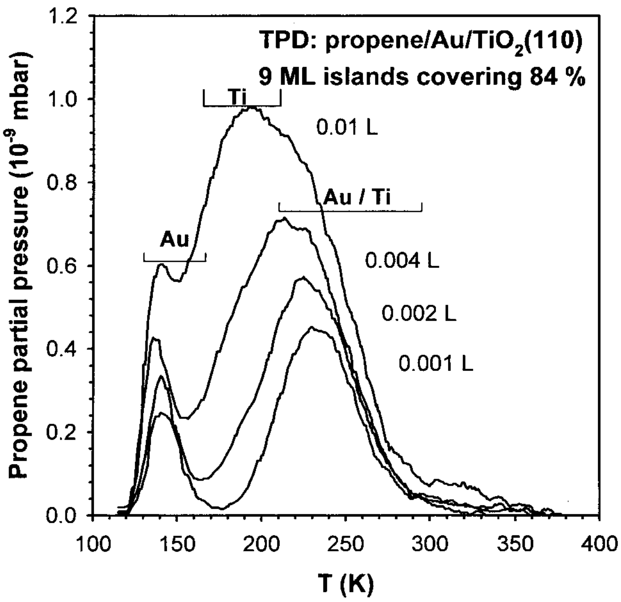

Figure 3. TPD spectra, at 5 K/s, of propene adsorbed on $TiO_2(110)$ with Au islands of average thickness 9 ML covering 84% of the surface at 120 K. "Au": peaks at 125–155 K, due to propene adsorption on the tops of gold islands. "Ti": peaks at 155–210 K, due to adsorption on the $TiO_2(110)$. "Au/Ti": peaks at 210–295 K, due to propene desorption from the edges of gold islands.

16%)/TiO_2(110), we assign the 143 K peak to propene on top of gold islands and the 230 K peak to propene at the edges of gold islands interacting with both gold and TiO_2. The low temperature peak may not saturate due to its close proximity to the dosing temperature. As the dose increases and these peaks grow, a new peak at ~190 K appears and grows until it dominates the spectrum. This is attributed to the increasing contribution from propene at Au-free TiO_2(110) patches, which gives a peak at 180 K in the absence of Au (figure 1).

In figures 2 and 3, one can see that the lowest dose of propene did not populate this TPD peak at 180–190 K associated with bare TiO_2(110) sites, even when those sites covered 84% of the surface (figure 2), but the 240 K peak readily populated. Thus, the propene molecules that adsorb on the bare TiO_2(110) patches must move to the more stable adsorption sites associated with gold island edges before desorbing. This indicates that the adsorbed propene molecules are freely mobile over the TiO_2(110), either while dosing at 120 K or during TPD below 180 K. In general, figures 2 and 3 seem to be a superposition of TPD peaks from: (1) bare TiO_2(110) patches; (2) the tops of Au islands; and (3) Ti sites at the edges of Au islands, with the relative intensities of these features depending on the amount of Au and the propene dose. On closer inspection, figures 2 and 3 (for both low and high doses) show that there is more desorption intensity at 265–310 K for the Au islands with average thickness 1.5 ML (figure 2) than for the 9 ML thick islands (figure 3). This is shown more clearly in figure 4, which compares TPD curves from TiO_2(110), Au(1.5 ML, 16%)/TiO_2(110), and Au(9.0 ML, 84%)/TiO_2(110) for roughly equal propene coverages (~0.3 ML). (The area under the TPD trace for a dose of 0.01 L to TiO_2(110) alone is defined as 1 ML propene.) This indicates that the propene binding sites which give rise to desorption in this region are strictly associated with Au islands that are only one or two ML thick. These propene sites may be on top of these very thin islands or at their edges. These are the most stable sites for propene seen in TPD here. Using a peak temperature of 240 K as representative of the 9.0 ML thick Au islands and a peak temperature of 288 K as representative of the one-atom-thick islands, the E_a^d increases from 59.9 kJ/mole to 72.3 kJ/mole due to the average thickness of the gold islands. The sites on late transition metal islands that are only one atom thick on oxide supports are generally seen to be considerably more stable for adsorbates than sites on thicker islands [21,31].

3.3. LEIS

Figure 5 shows the effect of dosing propene on the Ti and Au LEIS peak areas, normalized to the clean (propene-free) values for a small coverage of thin gold islands on TiO_2(110) at 120 K. Both Ti and Au atoms appear to be blocked by propene at small doses at 120 K and the attenuations increase at higher doses of propene. The LEIS peaks are attenuated to a minimum at a dose of 0.01 L. At saturation coverage, the minimum normalized LEIS signal is about 0.46 for Ti and about 0.26 for Au. This suggests that the packing density of propene is slightly higher on the Au islands than on bare TiO_2 patches, where the packing is about the same as in the

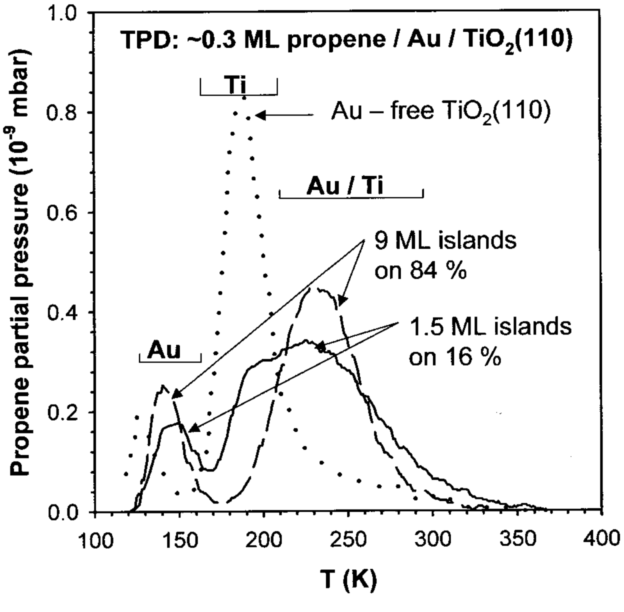

Figure 4. Comparison of TPD for equivalent propene coverage (~0.3 ML) on the clean TiO_2(110) surface and this surface with two different gold island coverages. "Au": peaks at 125–155 K, due to propene adsorption on the tops of gold islands. "Ti": peaks at 155–210 K, due to adsorption on the bare TiO_2(110) patches. "Au/Ti": peaks at 210–295 K, due to propene adsorbed at the edges of gold islands.

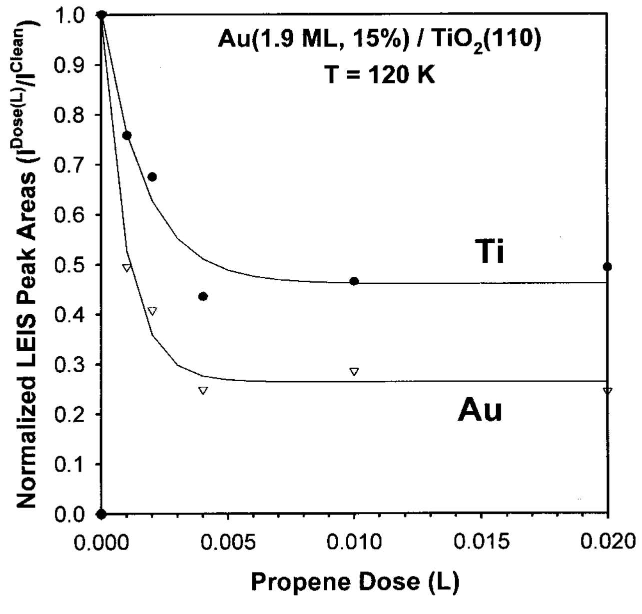

Figure 5. Normalized LEIS peak areas for Ti and Au versus propene exposure onto TiO_2(110) at 120 K containing Au islands of average thickness 1.5 ML covering 16% of the surface. The LEIS peaks are normalized to the value for the same surface before propene adsorption.

absence of Au. (The weaker oxygen LEIS signal was noisier than the Ti signal and gave no additional insight.)

To elucidate the thermal stability of the adsorbed propene species, LEIS spectra were collected for Au/$TiO_2(110)$ surfaces after dosing propene just as in the TPD experiments above, and then again after briefly heating the sample to incrementally increasing temperature. These temperature-dependent LEIS spectra were taken as soon as possible after the temperature ramp of 5 K/s was shut off. The sample cooled by ~5–15 K during LEIS signal acquisition, before it was heated again. The annealing temperature (T_{anneal}) reported below is the highest temperature to which the sample rose before that LEIS spectrum. The fractional coverage of propene adsorbed at Au sites was determined using the LEIS Au peak area. The fraction of Au sites occupied by adsorbed propene is assumed here to be proportional to the difference between the LEIS Au peak area for the surface without adsorbed propene minus the Au peak area with adsorbed propene ($I^{\text{Au:clean}} - I^{\text{Au}}$). The fraction of the initially adsorbed propene which remains after flashing to a particular temperature, T, is just this difference ($I^{\text{Au:clean}} - I^{\text{Au:}T}$) normalized by this difference for the same surface measured immediately after the initial saturation dose of propene at 120 K ($I^{\text{Au:clean}} - I^{\text{Au:120 K}}$):

$$\text{Fraction remaining} = \frac{(I^{\text{Au:clean}} - I^{\text{Au:}T})}{(I^{\text{Au:clean}} - I^{\text{Au:120 K}})}.$$

The results are shown in figure 6 *versus* annealing temperature (T_{anneal}). This figure includes Au islands with a thickness from 1.5 ML to 9.0 ML (total Au coverages from 0.23 to 7 ML) and propene doses from 0.002 to 0.02 L. The relative Au-bound propene coverage decreases with annealing temperature starting just above 120 K and drops to <10% of its initial value somewhere between ~300 and 380 K. It thus appears that propene molecules which bind to Au at sites (and therefore block Au signal in LEIS) desorb over a very broad temperature range, from ~130 K to ~300 K. This is consistent with our assignment of Au-bound species to two TPD peaks: one at ~140 K (propene bound solely to metallic Au sites) and one at ~240 K (propene simultaneously bound to Au atoms at the edges of islands and to Ti cations). The results also show that adsorbed propene does not migrate from the $TiO_2(110)$ sites to gold sites upon heating, since the fraction of propene adsorbed on Au sites would increase in the temperature range where this occurred. This suggests that the rapid propene migration from bare $TiO_2(110)$ patches to the edges of Au islands, mentioned above, is already occurring at 120 K. (In principle, it also could occur simultaneously with the desorption of some Au-bound propene here, thus masking observation of such migration.) The annealing temperatures in figure 6 are equivalent to TPD temperatures that are 25 K higher, due to the difference between the dynamic heating in a TPD *versus* the annealing experiment [32]. (A temperature of 175 K in figure 6 should be compared to 200 K in any of the TPD figures.)

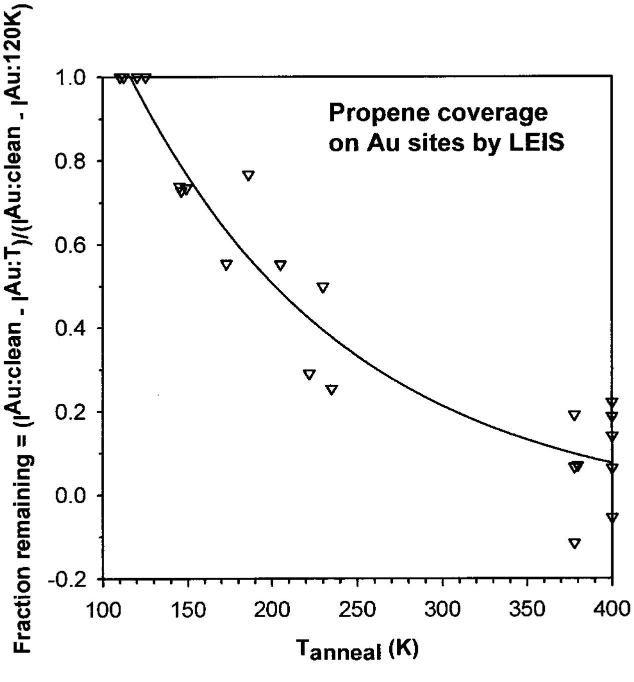

Figure 6. The fraction of the initially adsorbed propene bound to Au sites which remains following a brief anneal *versus* that annealing temperature, for various coverages of gold islands and doses of propene at 120 K (see text for details). The fractions were determined from the Au LEIS intensity (see text for details). The solid curve is just to guide the eye.

Figure 7 shows complementary data in which the LEIS peak areas for Au and Ti (normalized to the corresponding propene-free LEIS peak areas for the Au-covered surface) are reported as a function of annealing temperature. TPDs for propene desorption from the Au(1.5 ML, 16%)/$TiO_2(110)$ surface are shown also, for doses of 0.002 L and 0.01 L. Due to dosing errors of about 15%, the dose of 0.002 L in TPD does not exactly correspond to the 0.002 L dose in the LEIS experiment. Similarly, the 0.01 L dose of propene in TPD is expected to be representative of both the 0.01 L and 0.02 L doses of propene in the LEIS experiment. The TPDs for 0.002 L and 0.01 L have been reproduced exactly from figure 2. The x-axis is in terms of TPD equivalent temperature, which is 25 K higher than the annealing temperature (see above). If we look at the LEIS for the dose of 0.002 L to the surface at 120 K, we initially see an attenuation of the relative Au LEIS signal to ~60% and an attenuation of the Ti LEIS signal to about ~80%. As the surface is annealed to a temperature of ~225 K (~250 K in TPD), the Ti LEIS signal remains the same, while the Au LEIS signal recovers to ~85%. This corresponds well to our TPD peak assignments, since we see no propene desorption from Ti sites and no change in the Ti LEIS signal below ~250 K (~225 K in TPD), while we see a significant increase in the Au LEIS signal, corresponding to unmasking of Au sites by desorption of propene from the tops of the

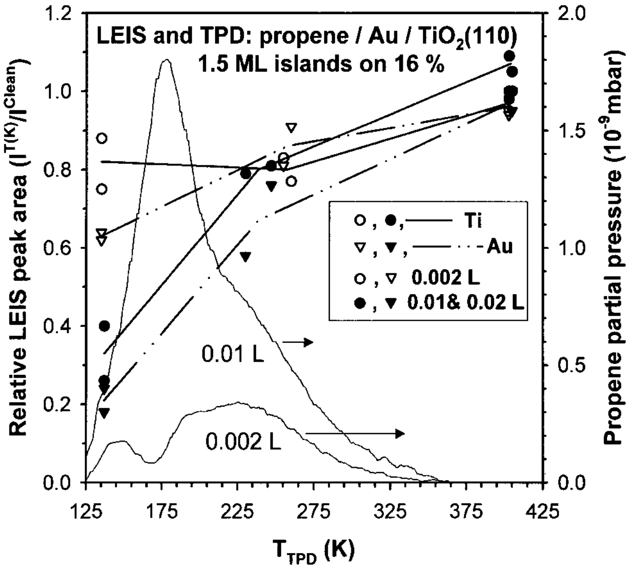

Figure 7. A comparison of LEIS annealing experiments with propene TPD for the Au(1.5 ML, 17%)/TiO$_2$(110) surface after propene exposures at 120 K. LEIS peak areas, normalized to clean Au/TiO$_2$(110), for both Ti and Au, versus annealing temperatures for Au(1.5 ML, 17%)/TiO$_2$(110) and Au(1.8 ML, 16%)/TiO$_2$(110). The lines connect averages of the points for identical doses of propene. The TPD traces for propene doses of 0.002 L and 0.01 L are the same as in figure 2. The annealing temperatures have been corrected to the TPD temperature scale by $T_{\mathrm{TPD}}(\mathrm{K}) = T_{\mathrm{anneal}}(\mathrm{K}) + 25\,\mathrm{K}$ (see text).

Au islands. Furthermore, at ~225 K (~250 K in TPD), *both* Au and Ti atoms are still partially masked by propene. This corresponds to propene adsorbed at a site which allows it to mask both Au and Ti atoms, giving rise to the single desorption peak above 250 K. We assign this species to adsorption of propene at the edges of gold islands (probably with its π bond at a Ti cation site and its methyl group associating with Au atom(s). As the surface is annealed from 225 to 380 K (250 to 405 K in TPD), the LEIS signal of both Au and Ti recovers to 100%, indicating that propene is removed completely from these sites that block both Ti and Au atoms in LEIS. Again, this is consistent with our assignment of the broad TPD peak extending from 230 to 350 K to Au bound at Ti sites at the edges of Au islands.

For the TPD corresponding to a dose of 0.01 L, the features previously mentioned for the dose of 0.002 L are present, but are obscured by the intense desorption peak corresponding to desorption of propene from TiO$_2$(110). This difference in the TPD spectra is reflected in the initial attenuation of the average LEIS signal (indicated by lines, see legend in figure 7) for doses of 0.01 and 0.02 L propene. For the initial doses at 120 K, one sees an average attenuation of the relative Ti LEIS signal to ~30%, a much stronger attenuation than for the 0.002 L dose. This corresponds to the markedly higher occupation of Ti sites by propene for the larger dose. The attenuation of the relative Au LEIS signal is also higher, to about ~20%. As the surface is annealed to ~225 K (~250 K in TPD), the Ti LEIS signal recovers to ~80%, almost the same signal as for the 0.002 L dose. At this point, according to TPD, the propene adsorbed on the gold-free TiO$_2$(110) patches has all desorbed, but there is still propene adsorbed on Ti sites at the gold island edges. The Au LEIS signal also recovers to about ~65% of its initial value, due to desorption of the 140 K TPD peak (propene bound to Au on Au islands). For this dose, the residual masking of Au and Ti signal in LEIS at 225 K means that at a temperature of ~225 K (~250 K in TPD), *both* Ti and Au atoms are masked by propene. This is consistent with our assignment of the TPD peak at ~200–300 K to propene bonded to *both* Ti sites and to Au at the edges of Au islands. Again, by 380 K (405 K in TPD), both the Au and Ti peak areas have almost completely recovered, indicating a clean surface.

4. Discussion

All our data seem to point to a fairly simple model for propene adsorbed on gold islands on TiO$_2$(110). Summarizing the TPD and LEIS results, there are three propene adsorption sites. The three sites are distinguished by three TPD peaks: (1) a small peak at 125–155 K; (2) a fairly large, sharp peak between 155 and 210 K, depending on coverage; and (3) a broad peak from 210 to 295 K whose maximum shifts from 250 to 190 K at higher coverages of gold and higher doses of propene.

The large, sharp peak at 155–210 K is easily identified as propene desorption from TiO$_2$(110) sites by comparison to clean TiO$_2$(110) (figure 1). The small peak at 125–155 K may be assigned with the help of the work done in [16], which found that propene molecularly adsorbed on Au(111) and Au(100) desorbed at peak temperatures of 140 K and 150 K, respectively. This data, combined with temperature-dependent LEIS data, which shows a continuous recovery of the gold signal through this temperature range, supports the assignment of this peak to propene desorbing from bulk-like Au sites on top of gold islands.

The broad high temperature peak at ~250 K is assigned to propene adsorbed on the Au island edges, where the propene interacts with both the TiO$_2$(110) and gold. The increase in this desorption peak's intensity with increasing Au coverage supports this assignment. The temperature-dependent LEIS measurements also support this assignment, by showing the simultaneous Ti and Au recovery between 280 and 380 K.

Figure 8 summarizes our model for propene adsorption and desorption from the gold islands dispersed on the TiO$_2$(110) system. Propene is mobile on the TiO$_2$(110) surface at the dosing temperature of 120 K, except at the edges of gold islands where they are tightly bound. These sites populate first. We consider three sites for

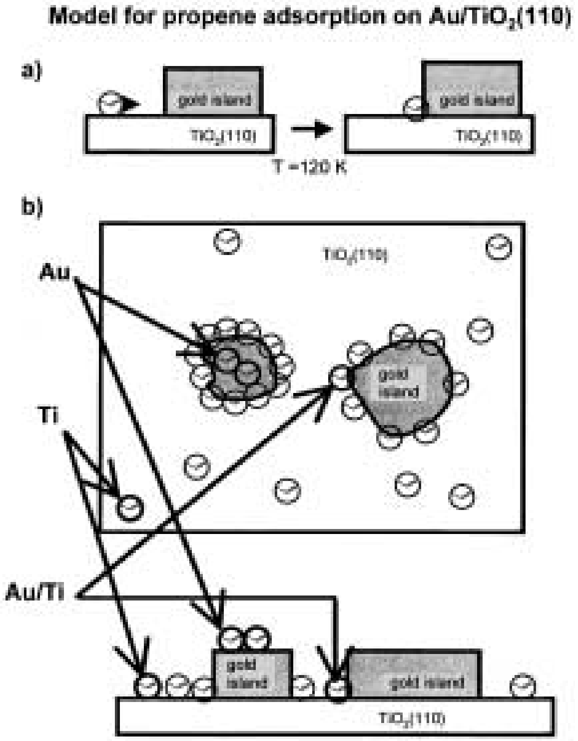

Figure 8. Schematic model for propene adsorption on Au/TiO$_2$(110) explaining the surface site origin of the various TPD peaks. The gold islands are mound-like in shape and not rectangular (as shown schematically in the figure). (a) Lowest propene coverage: Propene is mobile on the TiO$_2$(110) surface at the dosing temperature of 120 K, except at the edges of gold islands where they are tightly bound. These sites populate first. (b) Moderate propene exposures: "Au": TPD peak at 125–155 K, $E_a^d = 35.6$ kJ/mole, for propene molecules trapped (due to large barrier to diffusion) on top of the smallest gold islands by filled edge sites. "Ti": TPD peak at 155–210 K, $E_a^d = 46.1$ kJ/mole, for propene on Ti^{4+} sites of the TiO$_2$(110) surface, mobile at 120 K. "Au/Ti": TPD peak at 240 K, $E_a^d = 60.3$ kJ/mole, for propene bound at the edges of gold islands, where propene interacts with both the gold islands and the Ti^{4+} sites of the TiO$_2$(110) surface.

propene adsorption: on the tops of gold islands, on the TiO$_2$(110) surface and at the edges of the gold islands. The sites denoted as "Au", with a TPD peak temperatureof 125–155 K and E_a^d of 35.6 kJ/mole, indicate propene molecules on top of the gold islands. The sites denoted as "Ti", with a TPD peak temperature of 155–210 K and E_a^d of 46.1 kJ/mole, indicate propene adsorbed on the bare TiO$_2$(110) patches. The sites denoted as "Au/Ti", with a TPD peak temperature of ~240 K and E_a^d of 60.3 kJ/mole, indicate propene adsorbed at the edges of gold islands, where propene interacts with both the gold islands and the TiO$_2$(110) surface.

We now seek to answer the question of why less stable sites on the tops of gold islands populate before the more stable TiO$_2$(110) sites are filled. We attribute the population of these sites to the trapping of propene molecules on the tops of the gold islands by the propene molecules adsorbed at the perimeters of the gold islands. Since these perimeter states are populated first and are strongly bound, they will saturate these perimeter sites first and then prevent subsequent propene gas molecules, which hit the tops of the islands, from diffusing off the islands to the more stable bare TiO$_2$ patches.

Our model is that propene hits the surface and is mobile, ultimately ending up at the lowest energy sites, which are at the perimeter of gold islands. At the lowest doses of propene, all propenes landing on bare TiO$_2$(110) patches and on top of Au islands migrate to the energetically most favorable sites at the island edges. At higher doses of propene and with these perimeter sites filled, the propenes landing either on the TiO$_2$(110) surface or the Au island tops get trapped there.

The E_a^d of propene on clean TiO$_2$(110) runs from 44.8 to 46.9 kJ/mole, depending on coverage. This range is higher than observed on single-crystal gold surfaces, 35.2 kJ/mole [33] on Au(111) to 37.7 kJ/mole [16] on Au(100) and Au(111). This is in the same range as observed on Ag(110), which was found to be 45.2–52.8 kJ/mole [34], from peak temperatures of 150–175 K. However, the E_a^d of propene from gold islands on TiO$_2$(110) has two different values, depending on the site. We see an E_a^d of 48.6–58.2 kJ/mole for desorption from the edges of thicker gold islands. The highest E_a^d we see is from the edges (and/or tops) of very thin gold islands at low propene doses, giving ~72 kJ/mole (always assuming a prefactor of $10^{13}\ s^{-1}$). This is 34.8–37.7 kJ/mole higher than for single-crystal gold surfaces. Compared to oxygen adatoms, the E_a^d for propene on the Au/TiO$_2$(110) surface is very small, at most 72.4 kJ/mole, which corresponds to either physisorption or weak chemisorption. This is significantly smaller than even the smallest E_a^d for oxygen adatoms on the gold islands, which is 141 kJ/mole [21] and still even smaller than the strongest oxygen adatom E_a^d from gold that we saw, which is 193 kJ/mole [21]. (Calculations of E_a^d for oxygen adatoms were made using the following assumptions: ν is $10^{-13}\ s^{-1}$, the two peak temperatures were 545 and 741 K, respectively, and the heating rate was 4.5 K/s.) This brings up the interesting question of whether such a propene species is important in catalysis at higher temperatures. Of course, at the higher pressures of catalysis, such a species will be stable at significant concentrations to those higher temperatures. Moreover, a recently published article [35] presents evidence for a structure of propene adsorbed on TiO$_2$ (obtained at higher pressure and temperature) which involves interaction of the π-bond with Ti^{4+}, which is not inconsistent with our proposed structure.

Let us also consider the role of size in the reactivity of gold islands. The chemisorption energy of the oxygen adatom increases as the island thickness decreases [21]. The size effect on the propene adsorption is certainly smaller, as the propene E_a^d ranges from 58.2 kJ/mole on bulklike gold islands to 72.4 kJ/mole at one-atom-thick gold islands. Still, this 20% increase will likely be significant in global catalytic kinetics, just as the ~40% increase in oxygen adatom binding strength may be important [21]. Since the size of the gold islands does significantly affect the binding energy of propene to the gold islands, the particle size effect observed for propene epoxidation rates [15] may be at least partially due to the effect of island size on the propene binding energy. Oxygen adsorption experiments [21] have also shown stronger binding to smaller/thinner gold islands, so propene binding energy may not be the only effect contributing to the propene epoxidation size effect seen [10]. There may be a gold island thickness where both oxygen and propene are bound at the appropriate strengths to facilitate propene epoxidation.

The facile diffusion of propene on the surface to lowest energy sites, which happen to be at the edges of gold islands, is particularly interesting in light of the various reaction mechanisms that have been postulated [11–15], some of which suggest propene diffusion to different sites on the Au/TiO_2 surface. It has also been suggested that that the oxidant, some sort of peroxide species, is created on the gold islands, spills over to the titania surface, and reacts with the propene adsorbed on the titania surface [11–15]. Our study suggests that rather than spilling over to the titania, it is entirely possible that the oxidant, produced on the gold islands, reacts with propenes adsorbed at the perimeter of thin gold islands, since these are the most stable propene species and most likely to be fully populated.

5. Conclusions

In summary, on the Au island covered $TiO_2(110)$ system a new higher energy propene desorption site is found, different from the propene desorption sites seen with either $TiO_2(110)$ alone or with low-index single-crystal gold surfaces alone. It is attributed to desorption from the perimeter of gold islands on $TiO_2(110)$.

On clean $TiO_2(110)$, propene desorbs at 155 K–210 K, depending on propene coverage, and we assign that peak to propene interacting with $TiO_2(110)$. We estimate the saturation coverage of $TiO_2(110)$ to be 2.7×10^{14} propenes/cm^2 and the zero coverage E_a^d to be 47.3 kJ/mole, decreasing by 2.8 kJ/mole per ML.

When gold islands are added to the $TiO_2(110)$ surface, two new desorption peaks appear in the TPD spectra. The lower temperature peak (125–155 K) is assigned to desorption from the tops of the gold islands while the higher temperature peak (200–300 K) is assigned to propene molecules desorbing from the perimeter of the gold islands, where they are able to interact with both the gold islands and the $TiO_2(110)$ surface. Au islands that are only one atom thick have more propene desorption intensity in the higher end of this temperature range (265–310 K). We attribute this to the desorption of propene adsorbed on the tops or edges of one-atom-thick Au islands.

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