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Structure sensitivity of alcohol reactions on (110) and (111) palladium surfaces

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A temperature programmed reaction/desorption (TPD) study of decomposition pathways of methanol, ethanol, 1-propanol and 2-propanol was conducted on the clean Pd(110) surface under ultra-high vacuum conditions. No alcohol underwent C–O scission. Alcohols appear to react on this clean surface via the same dehydrogenation and decarbonylation steps observed on the Pd(111) surface. In contrast to previous reports noting substantial differences in methanol chemistry on the Pt(110) and (111) surfaces, the reactions of methanol and ethanol were found to be the same on the Pd(110) and (111) surfaces, giving rise to H_2 plus CO from methanol, and H_2, CO, and CH_4 from ethanol. The C_3 alcohols, 1- and 2-propanol, did produce somewhat different products on the Pd(110) and (111) surfaces, but these differences can be accounted for by differences in the chemistry of intermediate reaction products, rather than different reaction pathways of the parent alcohols.

Keywords: temperature programmed desorption: Pd(110); primary and secondary alcohols

1. Introduction

Although the chemistry of alcohols on transition metal surfaces has been the subject of numerous investigations, only recently has the issue of structure sensitivity arisen in these studies. Among clean group VIII metals, methanol alone has been studied on Fe(100) [1], Fe(110) [2], Ru(001) [3], Ni(111) [4], Ni(110) [5], Ni(100) [6], Rh(111) [7,8], Rh(100) [9], Pd(111) [10–13], Pd(110) [14], Pd(100) [15], Pt(111) [16,17], Pt(110) [18–21], and Pt(100) [22] surfaces. Surface studies of higher carbon number reagents are less ubiquitous than those of C_1 reagents. Ethanol has been examined on Fe(100) [1], Pt(111) [16], Ni(111) [23], Ni(100) [24], Pd(111) [10], and Rh(111) [25] surfaces; 1-propanol and 2-propanol only on Fe(100) [1], Pt(111) [16], Pd(111) [10,11], and Rh(111) [26,27] surfaces. At least on the platinum-group metals, these studies have led to the formulation of what had been presumed to be

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generally applicable sequences of bond activation. Works by Gates et al. on Ni(111) [23], Sexton et al. on Pt(111) [16], Davis and Barteau on Pd(111) [10,11], etc., suggested that alcohols, after being adsorbed molecularly, undergo O–H scission to form alkoxide adspecies which continue to dehydrogenate further to form aldehyde and acyl intermediates on the surface; acyls then decarbonylate to produce CO, along with volatile and/or adsorbed hydrocarbons in the case of higher alcohols. Methanol dehydrogenates cleanly to CO plus hydrogen. In the case of secondary alcohols, the alkoxide decomposes via a ketone intermediate which either desorbs or reacts further possibly via the acyl pathway as outlined above [10,11]. The relative stabilities of these intermediates are different on different metals and can be altered significantly on oxygen-precovered metal surfaces [7,28,29], however the basic reaction network is unchanged on these metals.

In recent reports concerning methanol decomposition on the metastable (1 × 1)-Pt(110) surface, Wang and Masel [18–20] observed C–O bond scission with 30% selectivity for methane formation. Unlike methanol decomposition chemistry on the (1 × 2)-Pt(110) surface, where adsorbed methanol decomposed unselectively to produce CO and hydrogen via methoxy intermediates, methanol on the clean (1 × 1)-Pt(110) surface reacted via two independent decomposition pathways: methanolic C–O bond activation led to methyl and hydroxyl adspecies on the surface producing methane and water as desorption products, whereas methanolic O–H scission led to the formation of stable methoxy intermediates which later decomposed unselectively to CO and hydrogen. The authors explained this observation in terms of a critical ensemble of atoms as active centers, rather than steps, kinks or defects on the Pt(110) surface. Spectroscopic evidence from HREELS studies [19] has confirmed the structure-sensitivity of methanol C–O scission on Pt metal surfaces. A similar structure sensitivity for C=C scission in ethylene on different Pt surfaces has also been reported [30]. Several other groups [13,17,31–33] have suggested that C–O scission in methanol, leading to the production of methane, can also occur on Pt(111) and Pd(111) surfaces, although these claims have been disputed [34–36] and the low methane yields even in the most optimistic cases suggest that defect chemistry cannot be ruled out. As a result of these recent observations on platinum-group metals under UHV conditions, there is a renewed interest in understanding the structure-sensitivity of bond activation processes during oxygenate decomposition on transition metal surfaces.

Since Pd(110) has the same structure as the unreconstructed Pt(110) surface responsible for C–O scission during methanol decomposition according to Wang and Masel [18], we have conducted experiments on this surface using temperature programmed reaction/desorption (TPD) with C_1–C_3 primary alcohols, as well as other oxygenates, to look for any unusual bond activation. However, none of the alcohols examined – methanol, ethanol, 1-propanol, 2-propanol, or allyl alcohol – underwent C–O scission on the Pd(110) surface. Results of allyl alcohol experiments have been presented elsewhere [37]. The present report considers results from TPD studies of C_1–C_3 alcohol reactions on the clean Pd(110) surface. These are compared with previous results from Pd(111) to assess the potential structural dependence of alcohol chemistry on palladium.

2. Experimental

All experiments were carried out in a stainless steel ultra high vacuum chamber [38] equipped with a quadrupole mass spectrometer (UTI 100C) multiplexed with an IBM XT for TPD experiments. A double pass cylindrical mirror analyzer with integral electron gun (PHI 25–260AR) allowed the collection of AES spectra. Also, an ion gun was available for noble gas (Ar) ion-sputtering. The Pd(110) single crystal (5N purity), Metal Crystals and Oxides Ltd.), was polished using standard metallographic techniques and then mounted on the probe. The heating ramp of 3.7 ± 0.1 K/s was used throughout the experiments. The chamber base pressure was 2×10^{-10} Torr. The Pd(110) single crystal was cleaned by repeated cycles of Ar^+-ion based bombardment (2 keV, 0.5 mA) and annealing to ca. 1200 K for 0.5 to 1 h. The experimental procedure has been described in detail elsewhere [37].

The highly pure (Aldrich, 99+%) alcohol samples used in this work were stored in glass tubes connected to a stainless steel dosing line and purified prior to use by repeated freeze–pump–thaw cycles. Research-grade hydrogen and deuterium (Matheson) were also used. The TPD spectra presented and the yield calculations reported have been corrected for mass spectrometer sensitivity using the procedure of Ko et al. [39]. Surface exposures, however, have not been corrected for the ionization gauge sensitivity. The calibrations of hydrogen and CO coverages have been discussed in detail in a earlier paper [37]. The absolute yields of various products in this paper are indicated in units of monolayers (ML), representative of the number of palladium atoms on the top layer of the surface, 9.3×10^{14} cm^{-2}. Exposure is expressed in terms of langmuirs (L), equivalent to 10^{-6} Torr s.

3. Results

3.1. METHANOL

TPD spectra following a saturation exposure of methanol on an initially clean Pd(110) surface at 120 K are depicted in fig. 1. Methanol desorbed from a chemisorbed state at 225 K and from a multilayer state at 157 K. Adsorbed methanol decomposed cleanly to CO and hydrogen. There was no evidence of C–O scission products such as methane or water in methanol TPD; as can be seen from the accompanying spectrum for $m/e = 15$ in fig. 1, there was no contribution from any CH_3-containing product other than the parent molecule itself. Also, no partial dehydrogenation product, e.g., formaldehyde, was observed. The peak temperatures and the peak shapes of the H_2 and CO products were consistent with the de-

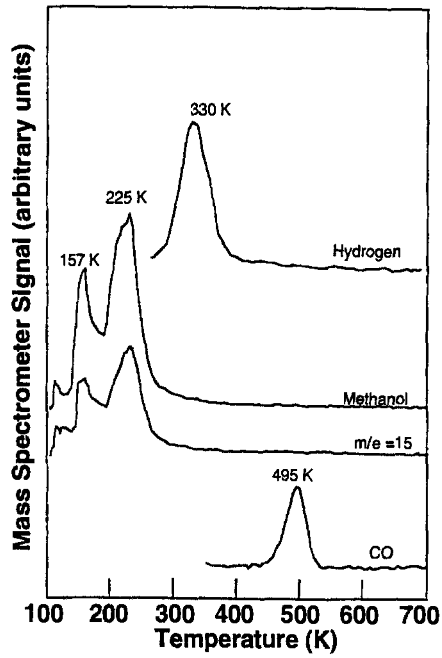

Fig. 1. TPD spectra following a saturation exposure of methanol onto an initially clean Pd(110) surface at 120 K.

sorption-limited evolution of these species [40,41]. Thus methanol decomposition must be complete before the onset (250 K) of the H_2 desorption peak on Pd(110) as on Pd(111) [10]. However, it is interesting to follow the development of the methanol desorption states on the Pd(110) surface. Fig. 2 depicts a series of $m/e = 31$ spectra (a–i) for methanol TPD at increasing exposures. Methanol desorption at ca. 245 K was observed for the lowest exposure (~ 0.1 L) of methanol onto an initially clean Pd(110) surface. For higher exposures, this methanol desorption peak shifted to lower temperature, however, it became submerged in a sharp peak at ca. 225 K (which did not shift further) for exposures greater than 0.6 L. This sharp peak may represent molecular methanol desorption from the submonolayer state which was finally saturated by an exposure of 1.3 L of methanol. A similar observation has been reported by Parmeter et al. [9] for methanol adsorption on the Rh(100) surface. These workers suggested that methanol desorbed at low coverages via recombination of methoxy with hydrogen adspecies and later this reaction was overshadowed by methanol desorption from the molecular state at higher coverages. Methanol desorption from a condensed layer at ~ 147 K was observed from Pd(110) once the desorption state at ~ 225 K was completely saturated. However, this observation differs from methanol desorption from the Rh(100) surface [9] in the sense that the condensed phase methanol appeared before the chemisorbed states were completely saturated on Rh(100). The peak for methanol desorption at ca. 147 K from Pd(110) shifted to higher temperature with increasing

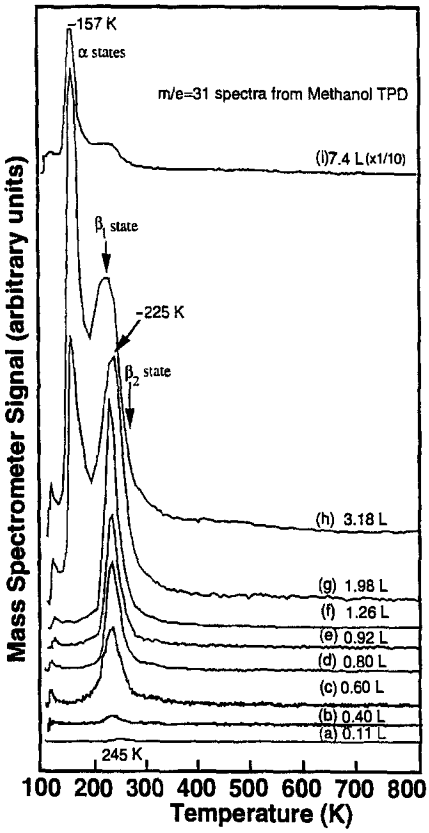

Fig. 2. Series of $m/e = 31$ spectra following different exposures of methanol on the Pd(110) surface at 120 K.

exposures as expected for zeroth-order desorption from a multilayer. The overall shift for the coverage range illustrated in fig. 2 was ca. 10–12 K. The relative yields for methanol decomposition products are listed in table 1. Following a saturation exposure, approximately 0.08 ML of methanol ultimately decomposed to CO and hydrogen, which is comparable to the levels reported for Rh(100) [9], Pd(111) [10], Pt(111) [15] and Pt(100) [20] following methanol adsorption below 170 K. As shown in table 1, nearly 30% of the adsorbed methanol in the first layer reacted on this surface.

Table 1
TPD yields following a saturation exposure of methanol on an initially clean Pd(110) surface at 120 K

Products	Yield (ML)
CH_3OH (225 K)	0.19
H_2 (330 K)	0.16
CO (495 K)	0.08

Low temperature adsorption studies [1–16], utilizing HREELS and TPD, have shown that adsorbed methanol molecules undergo O–H scission at low coverages to produce methoxy species in the temperature range 150–200 K on a number of transition metal surfaces. Studies on Ni(110) [5], Rh(111) [8], Rh(100) [9], Pd(100) [15], and Pt(110) [21] surfaces have indicated that methanol desorption can occur either from the molecularly adsorbed state or by recombination of methoxy and hydrogen adspecies in the vicinity of 180–250 K. On Pd(110) methanol initially desorbed from a 245 K peak which shifted to lower temperature with increasing methanol exposures. This state may correspond to the β_2 state (see fig. 2), identified first on Pd(100) by Christmann and Demuth [14]. However, development of the massive β_1 state $\sim$ 225 K quickly engulfed the β_2 desorption state, although skewedness in the high temperature side of the peak at 225 K may indicate the persistence of a small amount of the β_2 state. Similar studies on Rh(111) and Rh(100) [7–9] have shown that molecularly adsorbed methanol undergoes competing desorption and dissociation to methoxy species in the 180–220 K temperature range, and methanol desorption from these surfaces between 220 and 250 K is due to recombining methoxy species with hydrogen adatoms. In order to determine whether any of the methanol desorption peaks were due to methoxy recombination with adsorbed hydrogen atoms, or all originated from molecular methanol desorption, a few experiments with methanol on deuterium-precovered Pd(110) surfaces were performed. The clean Pd(110) surface at 200 K was exposed to deuterium up to saturation coverage ($\sim$ 1.5 ML) and then methanol was adsorbed on the D-precovered surface at 120 K. However, there was no sign of a $m/e = 33$ peak (corresponding to CH_3OD) in any experiment. This finding is similar to the study of methanol decomposition on Rh(111) by Houtman and Barteau [7] where methanol TPD experiments on a D-precovered Rh(111) surface found no evidence for deuterium recombination with the adsorbed methoxy species observed spectroscopically.

Further experiments with methanol on hydrogen-precovered Pd(110) did not produce significantly different results from those obtained on the clean surface, other than increased desorption of methanol from the state at 220 K, relative to that from the clean surface for similar exposures. The surface coverage which decomposed (i.e., the CO yield) remained the same. No formaldehyde was observed during any of the methanol TPDs. It is to be noted that the hydrogen precoverage used was sufficient to populate the sub-surface hydrogen sites on Pd(110) [40].

3.2. ETHANOL

Similar to results obtained on the Pd(111) single crystal surface [10], adsorbed ethanol on Pd(110) decomposed to methane, CO and hydrogen. No evidence of other products resulting from ethanol decomposition on Pd(110), including acetaldehyde, formaldehyde or any C_2 hydrocarbon, was found. Fig. 3 depicts TPD spec-

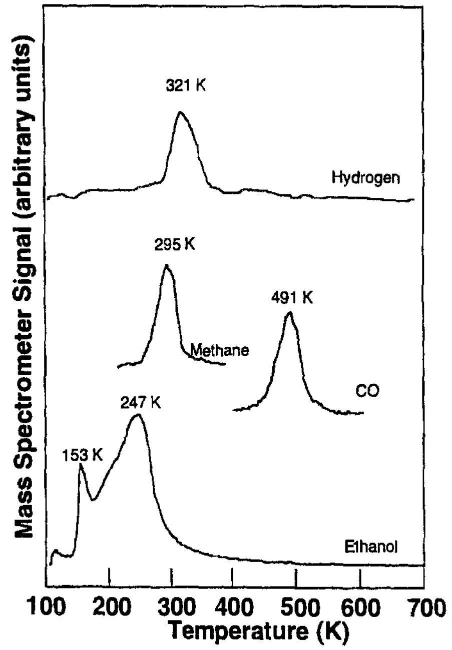

Fig. 3. TPD spectra following a saturation exposure of ethanol onto an initially clean Pd(110) surface at 120 K.

tra following a saturation exposure (~ 2 L) of ethanol on an initially clean Pd(110) surface at 120 K. No ethanol desorption took place at the lowest exposure. For exposures higher than 0.25 L (see fig. 4), ethanol desorption at 273 K was observed; this peak shifted to lower temperature with increasing exposures, finally reaching ca. 247 K at saturation of the chemisorbed state. At still higher exposures, a second ethanol desorption peak was observed at 160 K which could not be saturated even for very high ethanol exposures. This peak is attributed to ethanol desorption from a multi-layer state. The separation of the trailing edge of the 160 K peak and the leading edge of the 247 K peak was less distinct than that for methanol, suggesting that the desorption signal in this temperature range could arise from another desorption state of ethanol at ~ 210 K. The coverage-dependent ethanol ($m/e = 31$) desorption spectra from Pd(110) surface are presented in fig. 4. The first desorption peak shifted from ca. 273 to 247 K with increasing coverage and then a second desorption state at ca. 210 K began to develop at an ethanol exposure of 0.9 L. This state grew further, accompanied by filling of the third ethanol peak. The fraction of ethanol which ultimately decomposed decreased with increasing exposure from unity to one-third of the total chemisorbed ethanol coverage on the Pd(110) surface.

After ethanol desorption from the surface, the remaining adsorbed species decomposed to give CH_4 (294 K), H_2 (330 K), and CO (495 K). The desorption temperatures and the peak shapes suggest desorption-limited evolution of H_2 and

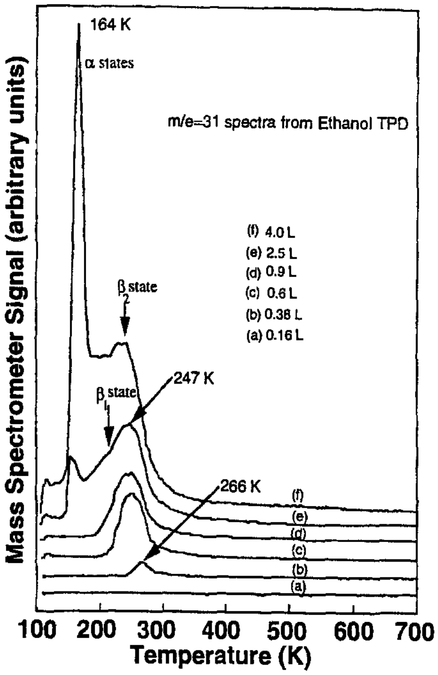

Fig. 4. Series of $m/e = 31$ spectra following different exposures of ethanol on the Pd(110) surface at 120 K.

CO [40,41]. The relative yield analysis is presented in table 2. Approximately 80% of the methyl groups of the ethanol molecules consumed reacted to form methane; 20% were dehydrogenated to deposit carbon on the surface which was quantified by subsequent oxygen adsorption and TPD. The presence of small, high temperature (>400 K) hydrogen desorption peaks is also consistent with further dehydrogenation of the adsorbed hydrocarbon species. Similar examples of the deposition of surface carbon accompanied by high temperature, reaction-limited, hydrogen desorption have been noted during ethanol decomposition on other group VIII metal surfaces [10,16,23–25]. All of the C–O bonds remained intact for ethanol decomposition on Pd(110), thus the sum of the methane and carbon yields was equal to the CO yield as shown in table 2. Also, the high coverage experiments dis-

Table 2
TPD yields following a saturation exposure of ethanol on the clean Pd(110) surface at 120 K

Products	Yield (ML)
CH_3CH_2OH (247 K)	0.20
CH_4 (295 K)	0.08
CO (491 K)	0.10
H_2 (250–600 K)	0.13
$C_{(ad.)}$	0.02

played almost indistinguishable coverage dependences for CH_4 and CO production. This observation is consistent with other studies of ethanol decomposition on Ni(111) [23], Pt(111) [16], and Pd(111) [10] surfaces.

In order to determine whether the presence of hydrogen atoms on Pd(110) would have any effect on the decomposition chemistry of the adsorbed ethanol, a series of ethanol TPD experiments on sub-monolayer and greater-than-monolayer hydrogen-precovered Pd(110) surfaces were performed. The clean Pd(110) surface was exposed to hydrogen at 200 K and subsequently ethanol was dosed at 120 K. The presence of hydrogen enhanced the amount of ethanol adsorbed, but the saturation ethanol decomposition products, i.e., CO and CH_4, showed no change from their corresponding yields from clean Pd(110), reported in table 2. Ethanol desorption from the chemisorbed state shifted to lower temperature by 20 K on the H-precovered surface and finally the desorption state seen at 247 K on the clean Pd(110) surface shifted to 220 K on the H-precovered Pd(110) surface. Saturation coverages of ethanol on the H-precovered surface were achieved for comparatively smaller doses. Although the fraction of the adsorbed ethanol decomposed was more or less unchanged by hydrogen precoverage, the methane selectivity increased for very small ethanol doses on the H-precovered surface.

3.3. 1-PROPANOL

TPD spectra following 1-propanol adsorption at 120 K on the clean Pd(110) surface are depicted in fig. 5. Approximately 50–60% of the 1-propanol adsorbed at monolayer coverage desorbed intact from both Pd(110) and Pd(111) surfaces [10]. 1-propanol desorption at sub-monolayer coverages took place first at ca. 265 K and progressed to lower temperature with increasing coverages. The multilayer continued to grow at 173 K, as this desorption state could not be saturated. It was not possible to resolve in 1-propanol TPD studies on Pd(110) the three different desorption states identified so far for methanol and ethanol. Adsorbed 1-propanol on Pd(110) decomposed unselectively to CO, hydrogen, and surface carbon which could be burned off by subsequent oxygen TPD. The absence of volatile hydrocarbons from 1-propanol decomposition on Rh(111) [26] and Pt(111) [16] surfaces has been reported previously, whereas 1-propanol decomposed on the Pd(111) surface to produce volatile ethylene and to deposit hydrocarbons on the surface which ultimately dehydrogenated to deposit surface carbon [10]. CO desorption from 1-propanol decomposition on Pd(110) took place at 488 K, whereas hydrogen desorbed over the 260–600 K temperature range. The hydrogen desorption at 304 K was desorption-limited [40] but the higher temperature peaks, at 460 K and >500 K, were reaction-limited. For the lowest exposure of 1-propanol on Pd(110), hydrogen desorption at three different temperatures, 320, 460 and 540 K, was observed. The reaction-limited hydrogen desorption peak positions at 460 and 540 K did not shift, whereas the desorption-limited peak shifted to 305 K with increasing coverage. The hydrogen desorption spectrum from 1-propanol is the

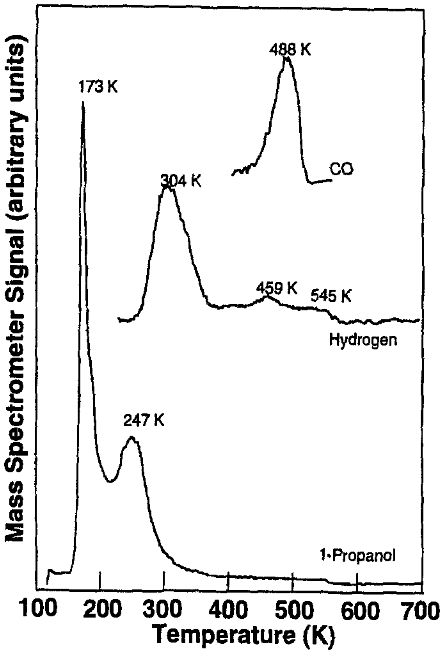

Fig. 5. TPD spectra following a saturation exposure of 1-propanol onto an initially clean Pd(110) surface at 120 K.

only example in the present study showing a prominent H_2 peak at temperatures higher than 500 K, indicative of the decomposition of higher hydrocarbon species on the surface. The product yields are listed in table 3. The saturation coverage was comparable to that of methanol.

Previous studies of primary alcohol decomposition on Pd(111) [11] have shown that net C–C scission at the α-carbon of the alkoxide deposits hydrocarbon ligands on the surface. Methane and ethylene, formed by decarbonylation of ethanol and 1-propanol, respectively, desorb from Pd(111) [10]. The absence of any hydrocarbon in the 1-propanol TPD spectra from Pd(110) is intriguing, as other C_3 oxygenates such as allyl alcohol, acrolein and propionaldehyde reacted on the Pd(110) surface to release volatile as well as adsorbed hydrocarbons [37,42]. However, the extents of decomposition (i.e., the CO yield) of those molecules were five times higher than that of 1-propanol reported above. Also, the fate of chemisorbed ethy-

Table 3
TPD yields following saturation exposure of 1-propanol on the Pd(110) surface at 120 K

Products	Yield (ML)
$CH_3CH_2CH_2OH$ (247 K)	0.12
CO (488 K)	0.07
H_2 (250–650 K)	0.29
$C_{(ad.)}$	0.13

lene on the clean Pd(110) surface has been shown to be coverage dependent [44]; chemisorbed ethylene on Pd(110), according to Nishijima et al. [44], decomposes unselectively to produce hydrogen and surface carbon for coverages less than 0.17 ML. It is to be noted that, at the saturation coverage for 1-propanol on Pd(110), the maximum yield of decomposition products was less than half of this threshold coverage for ethylene desorption from the clean Pd(110) surface [44].

3.4. 2-PROPANOL

Fig. 6 depicts the TPD spectrum following a saturation exposure of 2-propanol (1.6 L) onto an initially clean Pd(110) surface at 120 K. 2-propanol decomposed on Pd(110) to produce CO, methane, hydrogen and surface carbon. For comparison, the TPD spectrum following acetone decomposition on the clean Pd(110) surface is presented in fig. 7. The absolute yields corresponding to the TPD spectra for 2-propanol shown in fig. 6 are listed in table 4. Clearly, the coverage of 2-propanol decomposed was the lowest among the alcohols studied here. A comparable extent of decomposition for saturation coverages of acetone on Pd(110) was also observed. A similar decrease in saturation decomposition yield for the C_3 secondary alcohol relative to the primary alcohol has been noted in previous studies on Pt(111) [15] and Fe(100) [1]. The methane selectivity with respect to the amount of

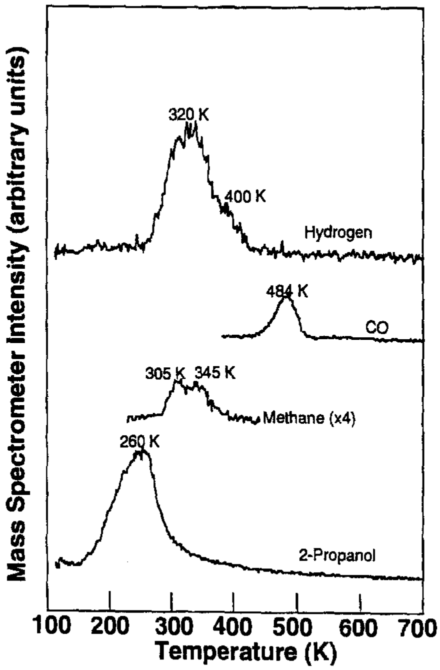

Fig. 6. TPD spectra following a saturation exposure of 2-propanol onto an initially clean Pd(110) surface at 120 K.

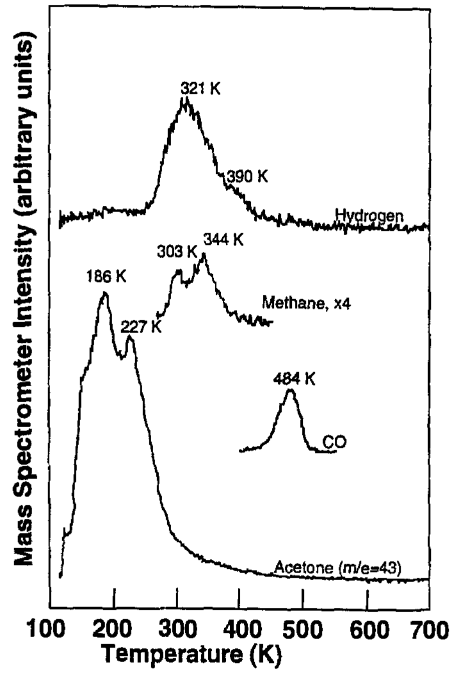

Fig. 7. TPD spectra following a near-saturation exposure of acetone on the clean Pd(110) surface at 120 K.

2-propanol decomposed (equated with the CO yield) was 25%. In fig. 8, TPD spectra for 2-propanol ($m/e = 45$), CO ($m/e = 28$), methane ($m/e = 16$) and hydrogen ($m/e = 2$) following exposure of the clean Pd(110) surface to increasing amounts of 2-propanol at 120 K are presented. For exposures between 0.48 and 1.6 L, $m/e = 45, 43, 58$, etc. peaks were observed at 265 K which continued to increase in intensity, along with a low temperature shoulder. By comparing the peak areas at 265 K with the cracking patterns of 2-propanol and acetone in our vacuum chamber, the peak at 265 K was assigned solely to 2-propanol desorption from a chemisorbed state. For higher exposures, the desorption channel at ~ 265 K was saturated and a sharp narrow peak at 160 K was observed which can be assigned to desorption of 2-propanol from the condensed multi-layer state. The series of $m/e = 45$ spectra for 2-propanol desorption illustrates the different desorption

Table 4
TPD yields following saturation exposure of 2-propanol on the Pd(110) surface at 120 K

Products	Yield (ML)
$CH_3CHOHCH_3$ (260 K)	0.32
CO (484 K)	0.04
CH_4 (305 K, 345 K)	0.02
H_2 (250–500 K)	0.10
$C_{(ad.)}$	0.06

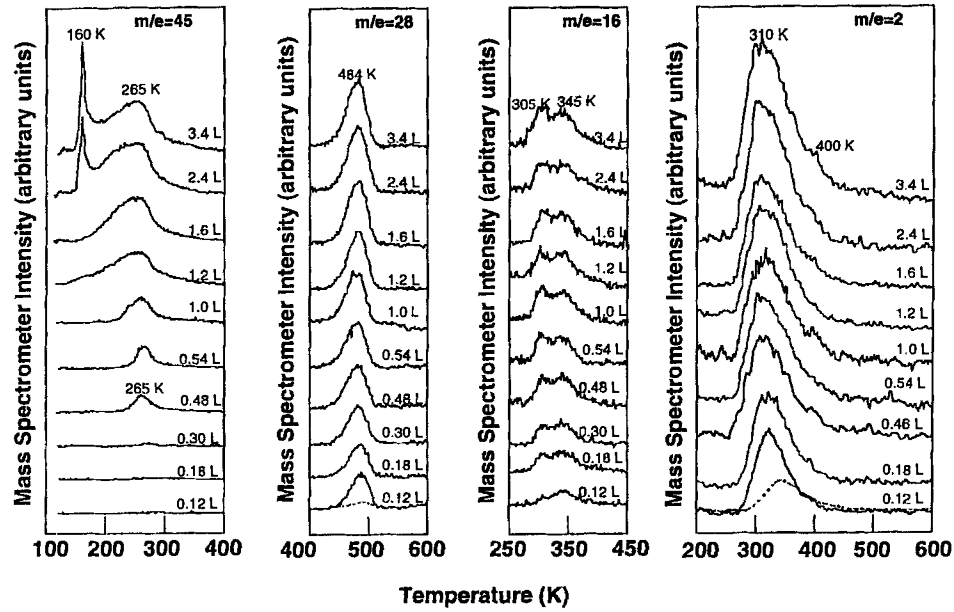

Fig. 8. Series of $m/e = 45, 28, 16$, and 2 spectra following different exposures of 2-propanol onto an initially clean Pd(110) surface (dashed curves for $m/e = 28$ and $m/e = 2$ indicate corresponding species desorption due to adsorption from the background).

states. In a recent study [27], 2-propanol on the clean Rh(111) surface was observed to decompose unselectively to yield hydrogen, CO and surface carbon, while molecular 2-propanol desorbed at 245 K. Further, the authors [27] noted that 2-propanol on the Rh(111)-p(2 × 1)O surface reacted to desorb acetone with 80% selectivity. Interestingly, 2-propanol chemisorbed on the Rh(111)-p(2 × 1)O desorbed at 180, 220 and 260 K [27], in a similar fashion to the different desorption states of 2-propanol from the Pd(110) surface. The chemisorbed 2-propanol on Pd(110) decomposed to produce CO, methane and hydrogen at the lowest exposure (0.12 L) examined in this study. Methane desorption first took place at 345 K, nearly 50 K higher than methane desorption during ethanol decomposition presented earlier, suggesting that C–C bond scission in the secondary alcohol (or intermediate ketone) exhibits a higher activation barrier than that for a primary alcohol or aldehyde.

The series of hydrogen spectra in fig. 8 following adsorption of various amounts of 2-propanol onto an initially clean Pd(110) surface at 120 K primarily indicates two different desorption states. Hydrogen desorption took place at 310 K with a shoulder at ca. 400 K. Similar hydrogen spectra were obtained during acetone decomposition on Pd(110) (see fig. 7) and Rh(111) [28]. Although no acetone desorbed from the surface during 2-propanol decomposition on Pd(110), the remarkable similarity between acetone and 2-propanol decomposition products and peak temperatures suggests that reaction on Pd(110) must proceed through a common acetone intermediate. On Pd(110), this species decomposes to produce CO, methane, and hydrogen. In contrast, on Pd(111), acetone formed by selective dehydrogenation desorbed at 310 K after 2-propanol adsorption at 170 K [10]. A few TPD experiments for 2-propanol on Pd(110) were performed at 170 K also, in order to duplicate the reaction conditions for a similar previous study on the Pd(111) surface. Still, no acetone desorption took place on the (110) surface, and methane was produced as it was following adsorption at lower temperatures.

4. Discussion

The primary goal of this work was to investigate the structure-sensitivity of C–O scission on group VIII metals by comparing the behavior of the Pd(110) and (111) surfaces. As discovered by Wang and Masel, methanol decomposition on the unreconstructed Pt(110) surface can also occur by C–O scission [18]. However, we have found no examples of C–O scission on the Pd(110) surface. Methanol, ethanol and 1-propanol underwent stoichiometric decarbonylation on Pd(110), as they did on Pd(111) [10,11]. No evidence was found for any reaction channel, e.g., CO_2 or H_2O formation, involving oxygen adatoms released by C–O scission. The peak positions and the slate of products following methanol and ethanol decomposition were indicative of decomposition pathways similar to those observed on the Pd(111) surface [10] and many other group VIII metal surfaces as well. In the case of methanol, only O–H and C–H bonds are activated sequentially to form CO and hydrogen atoms on the surface. Similar product spectra following ethanol and acetaldehyde [42] decomposition on Pd(110) surface suggest that the alcohol decomposes via an aldehyde intermediate, as concluded previously by Davis and Barteau [10,11] for Pd(111). However, there was evidence for structure-sensitivity of some of the reactions observed in the course of higher alcohol decarbonylation on the Pd(110) and (111) surfaces.

Previous studies on Pd(111) [10,11] have indicated that 1-propanol reacted via selective α C–C bond scission to produce ethylene, CO and hydrogen. However, there was no evidence of any volatile hydrocarbon in our present study of 1-propanol on Pd(110) surface. The absence of volatile hydrocarbons in 1-propanol TPD spectra from Pd(110) and not from Pd(111) [10] surface raises the issue of possible structure-sensitivity of alcohol decomposition pathways on palladium surfaces. Other C_3 oxygenates studied on Pd(110) surface (allyl alcohol, acrolein and propionaldehyde) produced reaction-limited hydrogen at ca. 460 K via dehydrogenation of ethynyl adspecies [37,42,44]. The evolution of ethylene following decarbonylation of allyl alcohol, acrolein and propionaldehyde has been observed for product surface coverages higher than 0.15 ML which is consistent with an earlier study of ethylene on the clean Pd(110) surface [44]. The saturation decomposition yield of 1-propanol noted here is much lower. At similar coverages on clean Pd(110), propionaldehyde also decomposes to produce CO, hydrogen and hydrocarbon adspecies which dehydrogenate to deposit surface carbon without production of volatile hydrocarbons. Thus the apparent selectivity difference for 1-propanol decomposition on the Pd(110) and (111) surfaces simply reflects the greater tendency of the (110) surface to decompose ethylene at low coverages, rather than any intrinsic difference in the interaction of alcohol or alkoxide species with these two surfaces.

2-propanol on the Pd(111) surface [11] reacted via an alkoxide to produce acetone, CO, hydrogen and methane. The selective dehydrogenation product, η^2-acetone, desorbed during TPD of 2-propanol on Pd(111), as decomposition of η^2-ketones was found to be less favorable than that of η^2-aldehydes [11]. A similar example of desorption of η^2-propionaldehyde produced by a surface reaction (acrolein hydrogenation) was observed on Pd(111) [43]. In contrast, acrolein on the Pd(110) surface [37] did not desorb from the η^2-state, and propionaldehyde desorption during acrolein TPD was observed at much lower temperatures, i.e., from the η^1-state. In the present study, there was no desorption of acetone in the 2-propanol TPD spectra, consistent with suppression of desorption from the η^2-state on Pd(110) and Pd(111) surfaces [37,43]. Davis and Barteau [29] noted reversible acetone adsorption on the clean Pd(111) surface. However, instead of permitting small amounts of acetone and acrolein to desorb from the η^2-state on the surface, Pd(110) decomposes carbonyl compounds adsorbed in the η^2-state. The absence of the selective dehydrogenation product, acetone, in 2-propanol TPD reflects this difference. The growth of two different desorption states for methane (nearly 40 K apart) of approximately equal magnitude at saturation may be indicative of sequential scission of the two C–C bonds of the adsorbed acetone intermediates on Pd(110). At the lowest coverage in fig. 8 methane desorption takes place only at 345 K; this peak continues to grow with development of the second methane peak at ca. 305 K.

The TPD results for the alcohol examined on the Pd(110) surface do not reflect any significant differences with respect to the corresponding alcohol reactivities observed previously for the Pd(111) surface [10]. The absence of volatile C_2 hydrocarbons in 1-propanol TPD spectra can be accounted for by the different coverage-dependent reactivity of the hydrocarbon species produced by alcohol decarbonylation, as observed for ethylene on Pd(110) [44] and Pd(111) [45,46] surfaces, where the surface coverage of ethylene required on the clean Pd(110) surface before the onset of ethylene desorption was approximately twice that on the clean Pd(111) surface. The absence of acetone in 2-propanol TPD on Pd(110) results from the facile dehydrogenation/decarbonylation of acetone bound in the η^2-state, in contrast to the previous observation of acetone desorption from the clean Pd(111) surface [11]. Therefore, the differences observed in the present TPD study can be accounted for by the fate of intermediates formed after alkoxide dehydrogenation, and not because the chemisorbed alcohols exhibit multiple reaction channels (O–H versus C–O scission) proposed to account for structure-sensitive methanol decomposition pathways on Pt surfaces [16–22].

5. Conclusions

None of the alcohols examined exhibited any evidence for C–O scission in the course of their reactions on an initially clean Pd(110) surface. The sole reaction pathways observed for surface alkoxides formed by initial O–H scission was sequential dehydrogenation and decarbonylation, in congruence with the earlier results on the Pd(111) metal surfaces. Decomposition of both C_3 alcohols studied here indicates that alcohol decomposition on palladium surfaces is structure-insensitive. The differences observed between the two palladium surfaces arise later in the reaction sequence, i.e., for reactions of aldehyde, ketone, and hydrocarbon species produced via common alcohol reaction pathways.

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